Designation: D6722 – 11

Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis[1]

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 EPA and many state 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 or mercury-containing products, or both, in your state may be prohibited by state 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

D2013/D2013M 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

D4621 Guide for Quality Management in an Organization That Samples or Tests Coal and Coke (Withdrawn 2010)[3]

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

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

3. Terminology

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

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 and chemically decomposed. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace, where oxidation is completed and halogens as well as nitrogen and sulfur oxides are trapped. The remaining 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, the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance peak height or peak area, as a function of mercury concentration, is measured at 253.7 nm.

NOTE 1—Mercury and mercury salts can be volatized 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 this procedure, the total mercury is representative of concentrations in the sample.

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[1] This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is 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] The last approved version of this historical standard is referenced on www.astm.org.

6. Apparatus

6.1 There are several configurations of the instrumental components that can be used satisfactorily for this test method. Functionally, the instrument shall have the following components: drying compartment, decomposition tube, catalyst tube, gold amalgamator, amalgamator furnace, measuring cuvettes, mercury lamp, and detector. The following requirements are specified for all approved instruments. (Note 2).

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 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 800°C.

6.1.3 The catalyst in the catalytic tube 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 550°C.

6.1.4 The instrument shall contain a 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 a absorption cell with measuring cuvettes 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,* made of nickel and convenient size suitable for use in the instrument being used.

7. Sample

7.1 *Coal*—Prepare the analysis sample in accordance with Practice D2013/D2013M by pulverizing the material to pass a 250-μm (No. 60) sieve.

7.2 *Solid Combustion Residue*—Dry a representative portion of the solid residue to constant weight at 110 to 115°C. Determine the moisture loss during this drying step if it is desirable to calculate results to an as-received basis. Crush the dried portion of the sample to pass a No. 200 (75-μm) sieve. Use a mill that minimizes metal contamination. Use portions of the -200 mesh material for analysis.

7.3 *Activated Carbon Sorbent Material*—Activated carbon sorbent material is used in tubes for the absorption of mercury from stack gases. The absorbed mercury is unevenly dispersed in the tubes. The activated carbon material in smaller absorption tubes (100-200 mg) may be analyzed directly without further preparation. The activated carbon and absorbed mercury in larger sorbent tubes must be homogenized before any sample subdivision. The procedure given in Appendix A2 is recommended for the homogenization and subdivision of the activated carbon sorbent material.[4]

7.4 Analyze separate test portions for moisture content in accordance with Test Methods D3173 or D7582 so that calculation to other bases can be made.

8. Reagents

8.1 *Oxygen*—High purity oxygen, as specified by the instrument manufacturer, shall be used.

8.2 *Certified Reference Materials (CRMs)*—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.

8.3 All CRMs, reference coals, or calibrating agents must have precision values of less than or equal to method repeatability. Such CRMS, reference coals, or calibrating agents must be stable with respect to moisture and be pulverized to pass 100 % through a 250 μm (No. 60) USA Standard Sieve. CRMs, reference coals, or calibrating agents must be mixed thoroughly before each use.

9. Instrument Preparation

9.1 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.

9.2 *Adjustment of Response of Measurement System*—Weigh an appropriate test portion of certified reference material (CRM), calibrating agent, or reference coal. Analyze the test portion (see 9.1). Repeat this procedure. Adjust instrument response, as recommended by the manufacturer, until the absence of drift is indicated.

9.3 *Calibration*—Select coal CRMs or other calibrating agents and materials specified by the manufacturer that have certified mercury values in the range of samples to be analyzed. Three such CRMs or calibrating agents are recommended for each range of mercury values to be tested. When possible, two of the CRMs or calibrating agents shall bracket the range of mercury to be tested, with the third falling within the range.

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[4] This procedure was developed by the LECO Corporation in St. Joseph, MI. The procedure and results from an 11-laboratory interlaboratory study of four analytical methods for the analysis of mercury in Appendix K sorbent tubes can be found in the publication: Evaluation of Methods for Mercury Analysis of Appendix K Sorbent Tubes, EPRI, Palo Alto, CA, Tennessee Valley Authority (TVA), Chattanooga, TN, AEP, Columbus, OH, Consumer's Energy, Jackson, MI, First Energy, Cleveland, OH, LECO Corporation, St. Joseph, MI, Eon U.S., Lexington, KY, Southern Company, Birmingham, AL and TXU Power, Dallas, TX: 2007, 1014565, 110 p

9.3.1 All coal CRMs should be in accordance with 8.2 and shall be supplied by or have traceability to an internationally recognized certifying organization.**Warning—**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.

9.3.2 *Calibration Procedure*—Analyze, as samples, portions of a CRM, reference coal, or calibrating agent chosen to represent the level of mercury in the samples to be tested. Use the "as-determined" mercury values for calibration. These values must have been calculated previously from the certified "dry basis" mercury values and residual moisture determined using either Test Methods D3173 or D7582. Continue analyzing until the results from five consecutive determinations fall within the repeatability interval of these test methods. Calibrate the instrument according to the manufacturer's instructions using these values. Analyze, as samples, two CRM reference coals or calibrating agents that bracket the range of values to be tested. The results obtained for these samples much be within the stated precision limits of the CRM, reference coal, or calibrating agent or the calibration procedure must be repeated. Records for all calibrations must be in accordance with Guide D4621.

9.3.3 *Periodic Calibration Verification and Recalibration*—In accordance with Guide D4621, 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.

10. Procedure

10.1 Analyze a test specimen of the analysis sample in accordance with the manufacturer's instructions.

11. Calculation

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

$$A = \frac{(B \times C)}{D} \times 100 \qquad (1)$$

where:

A = mg/Kg of the analyte,
B = detector response for that analyte,
C = unit mass per detector response established for the analyte during calibration, and
D = mass of test specimen, g.

The calculations can be provided automatically by the instrumental system used for these methods.

12. Report

12.1 Report results from the mercury determination on any of the several common bases that differ solely with respect to moisture. Procedures for converting the as-determined concentrations to the other bases are specified in Practice D3180.

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

	Concentration Range, ppm	Repeatability Limit *r*	Reproducibility Limit *R*
Hg	0.017 – 0.586	0.008 + 0.06 $\bar{x}$	0.007 + 0.13 $\bar{x}$

13. Precision and Bias

13.1 *Precision*—The precision of this test method for the determination of mercury in coal, is 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.

13.1.1 *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 %.

13.1.2 *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 %.

13.2 *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.

NOTE 3—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.

13.3 An interlaboratory study, designed consistent with Practice E691, was conducted in 2000. Eight labs participated. The details of the study and supporting data are given in ASTM Research Report RR: RR:D05-1026 filed at ASTM headquarters[5].

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1026.

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 Level	RR Value, ppm	CRM Value, ppm	Bias, ppm	Significant (95% Confidence)
NIST 1630a	0.0912	0.0938	–0.0026	no
NIST 2692b	0.124	0.1333	–0.0093	yes
SARM 20	0.25	0.25	0	no

ANNEXES

(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
hvCb Arizona	0.017393	0.002358	0.002930	0.006602	0.008203
hvAb NIST 2692b	0.124464	0.003669	0.007333	0.010274	0.020533
hvCb SARM 20	0.249750	0.006167	0.015203	0.017268	0.042568
FGD A-1	0.585786	0.019241	0.031515	0.053875	0.088241
FGD A-2	0.318536	0.004404	0.014187	0.012330	0.039725
HvAb Pennsylvania	0.114357	0.004501	0.007793	0.012604	0.021821
hvBb Ohio	0.116679	0.004924	0.007548	0.013788	0.021135
hvBb Colorado	0.033107	0.005618	0.007377	0.015730	0.020655
sub A Wyoming	0.074857	0.006189	0.006189	0.017331	0.017331
lig A Texas	0.101214	0.008171	0.008171	0.022878	0.022878
hvAb NIST 1630a	0.091250	0.005386	0.005386	0.015082	0.015082

A2. SORBENT TUBE SAMPLE PREPARATION AND ANALYSIS FOR MERCURY EQUIPMENT

A2.1 Equipment

A2.1.1 Spex Mill 8000M[6] mixer/mill,

A2.1.2 Spex mixing vial, 2 ⅜ in. diameter × 3 in. vial body with screw on cap and O-ring,

A2.1.3 Spex mix/mill balls, three ¼ in. steel balls, and

A2.1.4 AMA254 Mercury Analyzer.

A2.2 Procedure

A2.2.1 The sorbent tube is opened and the total weight of the carbon in both sections is determined and recorded. Section A is the analytical portion of the tube and section B is used to check for analyte break-through.

A2.2.2 The front portion of section B is analyzed without grinding to check for analyte break-through. Only one analysis is made on this section unless the result is greater than five times the average blank measurement on the mercury analyzer, in which case, a second determination is performed to confirm

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[6] Spex Mill 8000M is a trademark of SPEX CertiPrep, 203 Norcross Ave., Metuchen, NJ 08840

the result. Such a result would be indicative of analyte break-through and any results from the analytical portion (section A) are suspect.

A2.2.3 Section A is divided into two relatively equal portions.

A2.2.4 Each portion of section A is ground separately in a ball mill. Place a portion of section A into the mixing vial with three ¼ in. steel balls and screw the mixing vial lid on securely.

NOTE A2.1—Section A is split to avoid overloading the mixer mill.

A2.2.5 Place the mixing vial into the vial holder within the mixing mill and tighten the vial restraint.

A2.2.6 Set the timer on the mill for two minutes. After the first two minutes of grinding allow the vial to sit for one minute. Then set the timer for an additional two minutes of grinding.

NOTE A2.2—The one minute delay is used to keep the mill and material cool to avoid the possibility of analyte loss.

A2.2.7 Remove the mixing vial, unscrew the cap and remove the ground sample and mixing balls.

A2.2.8 The other portion of Section A is also ground following steps A2.2.4-A2.2.7.

A2.2.9 The two ground portions of section A are then combined and thoroughly mixed by placing them together into the mixing vial with three ¼ in. steel balls and screw the mixing vial lid on securely.

A2.2.10 Place the mixing vial into the vial holder within the mixing mill and tighten the vial restraint.

A2.2.11 Set the timer on the mill for one minute.

A2.2.12 Remove the mixing vial, unscrew the cap and remove the ground sample and mixing balls.

NOTE A2.3—The mixing vial and balls are rinsed with Ethanol between analyses.

A2.2.13 The total ground section A is weighed and recorded and sample loss from grinding is determined.

NOTE A2.4—The sample loss observed for this sample handling and grinding step has been determined to be ~4% with a maximum loss of <8%.

A2.2.14 Three determinations are then made on this ground and mixed material from section A. If the deviation of these three replicates is high, additional runs are added.

NOTE A2.5—The calculated RSD of this procedure is 5%. In many cases it is better than 2%.