Designation: D 3684 – 01

Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method[1]

This standard is issued under the fixed designation D 3684; 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 describes a procedure for the analysis of total mercury in coal.

1.2 *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.* Specific precautionary statements are given in 8.3.1.

1.3 The values stated in SI units (IEEE/ASTM SI 10) shall be regarded as the standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 2013 Method of Preparing Coal Samples for Analysis[3]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[3]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[3]

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures[3]

E 144 Practice for Safe Use of Oxygen Combustion Bombs[4]

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

3. Summary of Test Method

3.1 Total mercury is determined in this test method by combusting a weighed sample in an oxygen bomb with dilute nitric acid absorbing the mercury vapors. The bomb is rinsed into a reduction vessel with dilute nitric acid, and the mercury is determined by the flameless cold vapor atomic absorption technique.

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

4. Significance and Use

4.1 The possible emission of mercury that may be found in coal from coal combustion is an environmental concern.

4.2 When test portions are burned according to this procedure, the total mercury is quantitatively retained and is representative of concentrations in the whole coal.

5. Apparatus

5.1 *Combustion Bomb*—The combustion bomb shall be constructed of materials that are not affected by the combustion process or products. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during the test. The bomb must be capable of withstanding a hydrostatic pressure test to gage pressure of 20 MPa (approximately 3000 psig) at room temperature without stressing any of the parts beyond the elastic limit.

5.2 *Water Bath*—A container shall be large enough to hold the combustion bomb, and enough cooling water shall be used to dissipate the heat generated during the combustion process. The container should be designed to allow a constant flow of water around the combustion bomb.

5.3 *Combustion Crucibles*—Samples shall be burned in an open crucible of platinum, quartz, or acceptable base-metal alloy.

5.4 *Firing Wire*, 100 mm of either No. 34 B&S (0.160-mm) nickel-chromium alloy, No. 34 B&S iron, or No. 38 B&S (0.101-mm) gage platinum wire.

5.5 *Firing Circuit*—A 6- to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A stepdown transformer connected to an alternating current lighting circuit or batteries may be used. The ignition circuit switch shall be of the momentary double-contact type, normally open, except when held closed by the operator. The switch should be depressed only long enough to fire the charge.

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

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

[3] *Annual Book of ASTM Standards*, Vol 05.06.

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

5.7 *Atomic Absorption Spectrophotometer,* with a flameless cold-vapor mercury analysis system comprised of either a closed recirculating system or an open one-pass system.

5.8 *Reduction Vessels*, biochemical oxygen demand (BOD) bottles, 300-mL capacity.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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 may 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.

6.2 *Reagent Water*—Reagent water, conforming to Type II of Specification D 1193, shall be used for preparation of reagents and washings of the bomb interior.

6.3 *Hydroxylamine Hydrochloride Solution (1.5 g/100 mL)*—Dissolve 1.5 g of hydroxylamine hydrochloride ($NH_2OH\cdot HCl$) in water and dilute to 100 mL.

6.4 *Mercury Standard Stock Solution* [*1000 ppm* (*1000 µg/mL*)]—Dissolve 1.080 g of mercury (II) oxide (HgO) in a minimum volume of HCl (1+1). Dilute to 1 L with water.

6.5 *Mercury Standard Solution* [*0.1 ppm* (*µg/mL*)]—Dilute 0.10 mL of mercury standard stock solution to 1 L with water. If micropipets are not available, this standard may be prepared by serial dilution of the mercury standard stock solution. Prepare the mercury standard solution daily.

6.6 *Nitric Acid* (*1+9*)—Dilute 100 mL of concentrated nitric acid (HNO_3, sp gr 1.42) to 1 L with water.

6.7 *Oxygen*—Oxygen shall be free of combustible matter. Only oxygen manufactured from liquid air, guaranteed to be greater than 99.5 % pure, will meet this requirement.

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

6.9 *Stannous Chloride Solution* (*10 g/100 mL*)—Dissolve 10 g of stannous chloride dihydrate ($SnCl_2\cdot 2H_2O$) in 45 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) and *cautiously* dilute to 100 mL with water.

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 Methods D 3173 or D 5142 so that calculation to other bases can be made.

8. Procedure for Bomb Combustion

8.1 Thoroughly mix the analysis sample of coal in the sample bottle. Weigh a test portion of about 1 g, to the nearest 0.0001 g, into a preignited crucible.

8.2 Transfer 10 mL of HNO_3(1+9) to the combustion bomb, attach the fuse wire to the bomb electrodes, place the crucible with sample into the electrode support of the bomb, and adjust the fuse wire to contact only the test portion.

8.3 Assemble the bomb in conformance with the manufacturer's directions and charge it with oxygen to a pressure between 2 to 3 MPa (20 and 30 atm). If the oxygen should exceed the specified pressure, stop, detach the filling connection, exhaust the bomb in the usual manner, and discard the test portion.

8.3.1 **Warning**—The following precautions are recommended for safe oxygen bomb operation. Additional precautions are given in Practice E 144.

8.3.1.1 The weight of the test portion and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

8.3.1.2 Inspect the bomb parts carefully after each use. Check the bomb for thread wear on any closures; if an inspection reveals any wear, replace the worn parts or return the bomb to the factory for testing or replacement of the defective parts. It is a good practice to replace the O-rings and seals, inspect screw cap threads, and hydrostatically test the bomb as per the manufacturer's recommendations.

8.3.1.3 Equip the oxygen supply cylinder with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety code. Suitable reducing valves and adaptors for 2.0- to 3.4-MPa (300- to 500-psi) discharge pressures are obtainable from commercial sources of compressed gas equipment. Check the pressure gage periodically for accuracy.

8.3.1.4 During ignition of a test portion, the operator must not permit any portion of his body to extend over the oxygen bomb.

8.3.1.5 Exercise extreme caution when combustion aids are used so as not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb. Do not fire loose fluffy material such as unpelleted benzoic acid, unless thoroughly mixed with the test portion.

8.3.1.6 Admit oxygen slowly into the bomb so as not to blow powdered material from the crucible.

8.3.1.7 Do not fire the bomb if it has been filled to greater than 3-MPa (30-atm) pressure with oxygen, or the bomb has been dropped or turned over after loading, or there is evidence of a gas leak when the bomb is submerged in the oxygen bomb water.

8.4 Place the bomb in the cooling water bath, with water flowing, attaching ignition wires from firing circuits, and ignite the test portion (**Warning**, 8.3.1). Allow the bomb to remain in the cooling water bath for 10 min to allow temperature equilibration and absorption of soluble vapors.

8.5 Remove the bomb and release the pressure at a uniform rate, such that the operation will require not less than 2 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.

Examine the bomb interior and discard the test results if unburned or sooty deposits are found.

8.6 Quantitatively rinse the bomb, electrodes, and crucible into the reduction vessel with several small portions of water. Dilute the contents of the reduction vessel with $HNO_3(1+9)$ to a total volume of 100 mL. Add $KMnO_4$ solution dropwise until the permanganate color persists for 60 s.

9. Procedure for Atomic Absorption Analysis

9.1 Align the optical cell in the beam path of the atomic absorption spectrophotometer and optimize the instrument using normal operating conditions as set forth by the instrument manufacturer.

9.2 Prepare standards of 0.10, 0.25, and 0.50 µg of mercury by diluting aliquots of the mercury standard solution to 100 ± 10 mL with $HNO_3(1+9)$ solution.

9.3 Add $KMnO_4$ solution dropwise to the standards until the permanganate color persists for 60 s.

9.4 Add 5 mL of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) solution. When the pink color fades, wait 30 s and add 5 mL of stannous chloride ($SnCl_2$) solution and immediately connect the reduction flask to the flameless mercury system and determine the absorbance.

9.5 Repeat this procedure (9.4) for unknown test portion solutions (8.6).

9.6 A reagent blank shall be prepared according to 9.2, 9.3, and 9.4, but omit the mercury standard solution in 9.2.

9.7 The absorbance signal is recorded by either a strip chart recorder or read directly from the instrument. An expanded scale can be used to increase the sensitivity.

10. Calculation

10.1 Calculate the concentration of mercury in ppm (µg/g) in the analysis sample as follows:

$$\text{Mercury, ppm } (\mu g/g) = \frac{\left(\frac{C}{A-B}\right)(A_1 - B)}{D} \tag{1}$$

where:

A = signal of standard sample nearest A;

A_1 = signal of analysis sample;

B = signal of blank sample;

C = total concentration of standard, µg; and

D = sample weight, g.

A standard curve may also be constructed by plotting peak height versus micrograms of mercury and the calculations performed as follows:

$$\text{Mercury, ppm } (\mu g/g) = W/S \tag{2}$$

where:

W = mercury in sample determined from calibration curve, µg, and

S = sample weight, g.

11. Report

11.1 The results of the mercury analysis may be reported on any number of bases, differing from each other in the manner in which moisture is treated, and the data must note the reporting base.

11.2 Use the percent moisture, as determined by Test Method D 3173 or Test Methods D 5142, in the analysis sample passing a 250-µm (No. 60) sieve to calculate the results of the analysis to a dry basis.

11.3 Procedures for converting the value obtained on the analysis sample to other basis are described in Practice D 3180.

12. Sensitivity

12.1 The detection limit of the test method described above is 0.01 µg assuming a 100 ± 10 mL volume in the reduction vessel.

13. Precision and Bias

13.1 *Precision*—The precision 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.

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 1630a, 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 2—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]

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

	Concentration Range, ppm	Repeatability Limit *r*	Reproducibility Limit *R*
Hg	0.042–0.192	0.036	0.054

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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.

TABLE 2 Comparison of Certified Values for Standard Reference Materials (SRM) 1630a and 2692b with Interlaboratory Study Values for Total Mercury in Coal

Reference CRM	RR Value, ppm	CRM Value, ppm	Bias, ppm	Significant (95 % Confidence Level)
SRM 1630a	0.1019	0.0938	0.0081	yes
SRM 2692b	0.1246	0.1333	–0.0087	yes
SARM 20	0.19	0.25	–0.06	yes

13.3 An interlaboratory study, designed consistent with Practice E 691, 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.

14. Keywords

14.1 coal; flameless cold vapor atomic absorption; mercury; oxygen bomb

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	0.124594	0.007694	0.01836	0.021543	0.051407
hvCb SARM 20	0.192406	0.018563	0.025913	0.051977	0.072557
hvAb Pennsylvania	0.11075	0.010897	0.021221	0.030512	0.05942
hvBb Ohio	0.113813	0.010804	0.014062	0.030252	0.039373
hvBb Colorado	0.042344	0.006456	0.010451	0.018076	0.029262
subA Wyoming	0.087938	0.011627	0.019424	0.032556	0.054388
ligA Texas	0.098625	0.018472	0.025239	0.051723	0.070668
hvAb NIST 1630a	0.101906	0.011817	0.015648	0.033087	0.043814