



Designation: D 3682 – 01

Standard Test Method for Major and Minor Elements in Combustion Residues from Coal Utilization Processes¹

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1. Scope

1.1 This test method covers the analysis of the commonly determined major and minor elements in combustion residues from coal utilization processes.

NOTE 1—Test Methods D 1757 or D 5016 shall be used for determination of sulfur.

1.2 The values stated in SI units (IEEE/ASTM SI 10) shall to be 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 1193 Specification for Reagent Water²
- D 1757 Test Method for Sulfate Sulfur in Ash from Coal and Coke³
- D 2013 Method of Preparing Coal Samples for Analysis³
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke³
- D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal³
- D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases³
- D 5016 Test Method for Sulfur in Ash from Coal, Coke, and Residues from Coal Combustion Using High-Temperature Tube Furnace Combustion Method with Infrared Absorption³
- D 5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures³

¹ This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D 05.29 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.

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁴
IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System⁴

3. Summary of Test Method

3.1 The combustion residue to be analyzed is ignited in air at 750°C to a constant weight. The ash is fused within lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) followed by a final dissolution of the melt in either dilute hydrochloric acid (HCl) or dilute nitric acid (HNO_3). The solution is analyzed by atomic absorption/emission for applicable elements.

4. Significance and Use

4.1 A compositional analysis of the ash in coal is often useful in the total description of the quality of the coal. Knowledge of ash composition is also useful in predicting the behavior of ashes and slags in combustion chambers. Utilization of the ash by-products of coal combustion sometimes depends on the chemical composition of the ash.

4.2 Note that the chemical composition of laboratory-prepared coal ash may not exactly represent the composition of mineral matter in the coal or the composition of fly ash and slag resulting from commercial-scale burning of the coal.

5. Apparatus

5.1 *Ashing Furnace*, with an adequate air circulation and capable of having its temperature regulated between 700 and 750°C.

5.2 *Fusion Furnace*, with an operating temperature of 1000°C.

5.3 *Platinum Dish*, 35- to 85-mL capacity.

5.4 *Stirring Hotplate and Bars*, operating temperature of 200°C.

5.5 *Atomic Absorption Spectrometer*—Any dual-channel instrument using a deuterium (D_2) arc background corrector or other comparable simultaneous background correction system.

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

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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. The lithium tetraborate and lanthanum chloride reagents in particular should be examined for alkali and alkaline earth contamination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water as defined in Specification D 1193.

6.3 *Aluminum Stock Solution* (1000-ppm aluminum).

6.4 *Calcium Stock Solution* (1000-ppm calcium).

6.5 *Iron Stock Solution* (1000-ppm iron).

6.6 *Lanthanum Chloride Solution* (175-g/L lanthanum chloride (LaCl₃) or equivalent 10 % lanthanum).

6.7 *Lithium Tetraborate* —(Li₂B₄O₇), powder.

6.8 *Magnesium Stock Solution* (1000-ppm magnesium).

6.9 *Manganese Stock Solution* (1000-ppm manganese).

6.10 *Potassium Stock Solution* (1000-ppm potassium).

6.11 *Silicon Stock Solution* (200-ppm silicon) (Note 2).

6.12 *Sodium Stock Solution* (1000-ppm sodium).

6.13 *Solvent Acid*—Dilute 50 mL of concentrated hydrochloric acid (sp gr 1.19) or 50 mL of concentrated nitric acid (sp gr 1.42) to 1000 mL. Either acid solution may be used, but whichever is chosen should be used throughout the subsequent solution preparations.

6.14 *Titanium Stock Solution* (1000-ppm titanium).

NOTE 2—Commercial silicon standards prepared from sodium silicate have not proved satisfactory. A standard stock solution can be prepared by fusing 0.1070 g of reignited spectrographic grade silica (SiO₂) with 1 g of lithium tetraborate, dissolving in solvent acid, and diluting to 250 mL as described for sample preparation in 8.3.1 and 8.3.2. This solution is 200-ppm silicon. Preferable standard preparations for silica are made by fusion and dilution of ash sample(s) of known composition in accordance with 8.3.1 and 8.3.2. The standard sample(s) should have a composition(s) similar to the unknown.

7. Sample Preparation

7.1 The combustion residue to be analyzed must first be ignited in air at 750°C to a constant weight before analysis. Allow the ash to cool, transfer to an agate mortar, and grind to pass a 74-μm (No. 200) sieve. Reignite the ash at 750°C for 1 h, cool rapidly, and immediately weigh portions for analysis. If samples are stored, reignite the ash before weighing or determine the loss on ignition at 750°C on a separate sample weighted out at the same time as the analysis sample and make the necessary corrections. Thoroughly mix each sample before weighing.

7.2 If the ash is to be prepared from a coal, prepare the coal analysis sample in accordance with Method D 2013 by pulverizing the materials to pass a 250-μm (No. 60) sieve.

7.2.1 Analyze separate test portions of the coal for moisture and ash contents in accordance with Test Methods D 3173, D 3174, or D 5142 so that calculations to other bases can be made.

7.2.2 Prepare the ash from a thoroughly mixed analysis sample of coal. Spread the coal in a layer not over 6 mm (¼ in.) in depth in a fireclay or porcelain roasting dish. Place the dish in a cold muffle furnace and heat gradually so that the temperature reaches 500°C in 1 h and 750°C in 2 h. Ignite at 750°C until all carbonaceous matter is removed. Proceed with the preparation of the ash in accordance with 7.1. If samples are stored and the absorption of moisture or CO₂, or both, is in question, reignite the ash using the 500-750°C staged combustion before use. Alternatively, determine loss on ignition using the 500-750°C staged combustion on a separate sample weighed out at the same time as the test portion and make the necessary corrections. Thoroughly mix each sample before weighing.

8. Procedure

8.1 The solutions and proportions described below are for typical ash samples as represented by American coals of bituminous rank. Therefore, stronger or weaker dilutions may be required to establish suitable concentrations for those elements of varying percents outside the range of the typical sample. Each analyst must determine the sensitivity and linear range of calibration of their equipment and choose concentration ranges for standards compatible with the samples and instrument specific to their own work.

8.1.1 Calculations used in subsequent sections are developed from the following general formula for percent concentration of element oxide, *E*, in moisture-free coal ash:

$$E = [(C - B)/(A - B)] \times (N/M) \times F \times 100 \quad (1)$$

where:

A = absorbance of standard;

B = absorbance of blank;

C = absorbance of sample solution;

N = element in standard, ppm;

M = sample of solution, ppm; and

F = conversion from element to oxide.

NOTE 3—Concentrations in the ash may be converted to the air-dried coal basis using the following expression:

$$C = (AB/100)$$

where:

C = oxide in air-dried coal, %;

A = oxide in ash, %; and

B = ash as determined in Test Method D 3174 or Test Method D 5142, %.

See Practice D 3180 for procedures to convert values to other bases.

8.2 To minimize the potential of contamination, the platinumware must be prepared by boiling in solvent acid and rinsing thoroughly with reagent-grade water. After this initial cleaning, the platinumware must be handled with *clean* tongs

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.

and protected from further contamination from table tops, and so forth. All glassware used in analyses must be equally clean and equally protected.

8.3 Sample Fusion and Solution:

8.3.1 Weigh 0.1 ± 0.0002 g of the sample as prepared in 7.3 into a platinum dish (5.3) (Note 4) and add 0.5 g of $\text{Li}_2\text{B}_4\text{O}_7$. Mix the ash and lithium tetraborate well, then add an additional 0.5 g of $\text{Li}_2\text{B}_4\text{O}_7$ to cover the mixture. Place the dish in a clean silica or refractory tray and place in a muffle furnace preheated to 1000°C ; 15 min at 1000°C is sufficient to fuse the mixture completely. Remove the tray and dish and cool to room temperature. Carefully rinse the bottom and outside of the platinum dish to remove possible contamination, then place it in a clean 250- or 400-mL beaker. Place a clean TFE-fluorocarbon-coated stirring magnet inside the dish, add 150 mL of solvent acid to the beaker and dish, and place immediately on the stirring hotplate. Heat the solution to just below boiling temperature and maintain for not more than 30 min with constant stirring. This time and temperature are sufficient to completely dissolve the melt. If stirring is not maintained constantly, some of the ash constituents are apt to precipitate and the analysis must be repeated.

NOTE 4—The use of graphite crucibles and subsequent dissolution of fused beads from them was not investigated; however, their successful use in similar methods has been reported.⁶

8.3.2 Remove the beaker from the hotplate and permit to cool to room temperature. Quantitatively transfer the solution to a 200-mL volumetric flask, wash the platinum dish and beaker with small amounts of solvent acid and dilute to the 200-mL mark with the solvent acid. This solution is 500 ppm with respect to the total sample and contains 5 g/L of $\text{Li}_2\text{B}_4\text{O}_7$ solution.

8.3.3 *Solution 1*—Pipet 20 mL of the sample solution prepared in 8.3.2 into a 50-mL volumetric flask and dilute to volume with solvent acid. This solution is 200 ppm with respect to the total sample and contains 2 g/L of $\text{Li}_2\text{B}_4\text{O}_7$ solution.

8.3.4 *Solution 2*—Pipet 10 mL of the sample solution prepared in 8.3.2 into a 100-mL volumetric flask, add 10 mL of lanthanum solution (see 6.7), and dilute to volume with solvent acid. This solution is 50 ppm with respect to the total sample and contains 0.5 g/L of $\text{Li}_2\text{B}_4\text{O}_7$ solution.

NOTE 5—Lanthanum was included in the solution as a release agent in those determinations that may require it (for example, calcium). Alternative measures, such as the use of nitrous oxide flame, are permissible.

9. Silicon Dioxide (SiO_2)

9.1 *Preparation of Standards*—Prepare a series of standards by combining the following volumes of the silicon stock solution (see 6.11) with 1 mL of the aluminum stock solution (see 6.3) and diluting to 100 mL with the blank solution (see 9.2). Only those standards need be prepared that bracket the expected SiO_2 concentrations in the samples.

Silicon, Stock Solution (6.13), mL	Silicon, ppm	Equivalent SiO_2 , %
25	50	53.5
20	40	42.8
15	30	32.1
10	20	21.4

9.2 *Blank Solution*—Prepare a solution of 2 g/L of $\text{Li}_2\text{B}_4\text{O}_7$ solution in solvent acid.

9.3 *Sample Solution*—Use the 200-ppm sample solution as prepared in 8.3.3.

9.4 *Atomic Absorption Operating Conditions*—Use a silicon hollow-cathode lamp and set the monochromator at 251.6 nm. Use a nitrous oxide/acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

9.5 *Determination*—Read out absorbance values for the blank solution, standard solutions, and sample solution. In this and all subsequent determinations, those instruments so equipped may be calibrated to read out “percent concentration” directly. Determine percent SiO_2 as follows:

$$\text{SiO}_2, \% = [(C - B)/(A - B)] \times N \times 1.07 \quad (2)$$

where:

A = absorbance of standard nearest *C*,

B = absorbance of blank,

C = absorbance of sample, and

N = silicon in standard, ppm.

10. Aluminum Oxide (Al_2O_3)

10.1 *Preparation of Standards*—Prepare standard solutions containing from 10- to 30-ppm aluminum and dilute with blank solution 9.2.

10.2 *Blank Solution*—Use the blank as prepared in 9.2.

10.3 *Sample Solution*—Use Solution 1 as prepared in 8.3.3.

10.4 *Atomic Absorption Operating Conditions*—Use an aluminum hollow-cathode lamp and set the monochromator at 309.2 nm. Use a nitrous oxide-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

10.5 *Determination*—Read out absorbance values for the blank solution, standard solutions, and sample solution. Determine percent Al_2O_3 as follows:

$$\text{Al}_2\text{O}_3, \% = [(C - B)/(A - B)] \times N \times 0.94 \quad (3)$$

where:

A = absorbance of standard nearest *C*,

B = absorbance of blank,

C = absorbance of sample, and

N = aluminum in standard, ppm.

11. Iron Oxide (Fe_2O_3)

11.1 *Preparation of Standards*—Prepare standard solutions containing from 2- to 10-ppm iron and 10 mL of lanthanum solution per 100 mL. Dilute with blank solution (11.2).

11.2 *Blank Solution*—Prepare a solution of solvent acid containing 0.5-g/L $\text{Li}_2\text{B}_4\text{O}_7$.

11.3 *Sample Solution*—Use Solution 2 as prepared in 8.3.4.

11.4 *Atomic Absorption Operating Conditions*—Use an iron hollow-cathode lamp and set the monochromator at 248.3 nm.

⁶ Muter, R. B. and Nice, L. L., “Major and Minor Constituents in Siliceous Materials by Atomic Absorption Spectroscopy,” *Advances in Chemistry Series 141, Trace Elements in Fuels*, American Chemical Society, Washington, DC, 1975, pp. 57–65.