Designation: D3682 – 21

Standard Test Method for
Major and Minor Elements in Combustion Residues from Coal Utilization Processes by Atomic Spectrometry[1]

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.

1.2 Use Test Method D5016 for determination of sulfur.

1.3 *Units*—The values stated in SI units are to be regarded as standard. The values given in parentheses are provided for information only and are not considered standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D121 Terminology of Coal and Coke
D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis
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
D3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal

D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
D5016 Test Method for Total Sulfur in Coal and Coke Combustion Residues Using a High-Temperature Tube Furnace Combustion Method with Infrared Absorption
D7348 Test Methods for Loss on Ignition (LOI) of Solid Combustion Residues
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

3. Terminology

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

4. Summary of Test Method

4.1 The combustion residue to be analyzed is ignited in air at 750 °C to a constant mass. The ash is fused within lithium tetraborate ($Li_2B_4O_7$) 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 for applicable elements.

5. Significance and Use

5.1 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.

5.2 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.

6. Apparatus

6.1 *Ashing Furnace,* with an adequate air circulation and capable of having its temperature regulated at 500 °C and 750 °C.

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

6.3 *Platinum Vessels (Dish or Crucible),* 35 mL to 85 mL capacity. Graphite crucibles with 10 mL to 15 mL capacity may also be used (Note 1).

Note 1—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.[3]

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

6.5 *Flame Atomic Absorption Spectrophotometer*—Any dual-channel instrument using a deuterium (D_2) arc background corrector or other comparable simultaneous background correction system equipped with air/acetylene and nitrous oxide/acetylene burner heads.

6.6 *Hollow Cathode or Electrodeless Discharge Lamp,* for each element to be defined.

6.7 *Deuterium Continuum Lamp.*

6.8 *Compressed Air*—Appropriate pressure reducing regulator with base connections (see instrument manufacturer's instructions).

6.9 *Acetylene Gas and Regulator*—A cylinder of acetylene equipped with a two-gauge, two-stage pressure-reducing regulator (see instrument manufacturer's instructions).

6.10 *Nitrous Oxide Gas and Regulator*—A cylinder of nitrous oxide equipped with a two-gauge, two-stage pressure-reducing regulator (see instrument manufacturer's instructions).

7. Reagents

7.1 *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.[4] 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water as defined in Specification D1193.

7.3 *Aluminum Stock Solution* (1000 µg/mL aluminum).

7.4 *Calcium Stock Solution* (1000 µg/mL calcium).

7.5 *Iron Stock Solution* (1000 µg/mL iron).

7.6 *Lanthanum Chloride Solution* (175 g/L lanthanum chloride ($LaCl_3$) or equivalent 10 % mass concentration lanthanum).

7.7 *Fluxing Agent* - Lithium Tetraborate—($Li_2B_4O_7$), or mixtures of lithium tetraborate ($Li_2B_4O_7$) and anhydrous lithium metaborate ($LiBO_2$).

7.8 *Magnesium Stock Solution* (1000 µg/mL magnesium).

7.9 *Potassium Stock Solution* (1000 µg/mL potassium).

7.10 *Silicon Stock Solution* (200 µg/mL silicon) (Note 2).

Note 2—A standard stock solution can be prepared by fusing 0.1070 g of reignited spectrographic grade silica (SiO_2) with 1 g of lithium tetraborate, dissolving in solvent acid, and diluting to 250 mL as described for sample preparation in 9.3.1 and 9.3.2. This solution is 200 µg/mL silicon. Preferable standard preparations for silica are made by fusion and dilution of ash sample(s) of known composition in accordance with 9.3.1 and 9.3.2. The standard sample(s) should have a composition(s) similar to the unknown.

7.11 *Sodium Stock Solution* (1000 µg/mL sodium).

7.12 *Titanium Stock Solution* (1000 µg/mL titanium).

7.13 *Solvent Acid*

7.13.1 *Hydrochloric Acid (HCl)*—Concentrated hydrochloric acid, 12 N, specific gravity (sp) 1.19.

7.13.2 *Nitric Acid (HNO$_3$)*—Concentrated nitric acid, 16 N, sp 1.42.

7.13.3 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.

8. Sample Preparation

8.1 *Coal and Coke*—Prepare the analysis sample in accordance with Practice D2013 for coal or Practice D346 for coke by pulverizing the material to pass a 250 µm (No. 60) U.S.A. standard sieve.

8.1.1 Analyze separate test portions for moisture and ash contents in accordance with Test Methods D3173, D3174, or D7582, so that calculations to other bases can be made.

8.2 *Laboratory Ashing of Coal and Coke Analysis Sample*— Prepare the ash from a thoroughly mixed analysis sample of coal or coke (8.1). Spread the coal and coke in a layer not over 6 mm in depth in a porcelain, quartz, or fused silica roasting dish. Place the dish in a cold muffle furnace and heat gradually so that the temperature reaches 500 °C ± 10 °C at the end of 1 h. Continue the gradual heating until the temperature rises from 500 °C ± 10 °C to 750 °C ± 15 °C at the end of 1 h. Maintain the 750 °C temperature until the test specimen reaches a constant mass or for an additional 2 h. Allow the dish to cool, transfer to an agate mortar, and grind to pass a 75 µm (No. 200) U.S.A. standard sieve. Reignite the ash at 750 °C for 1 h, cool rapidly, and determine the mass of portions for analysis.

8.3 *Solid Combustion Residue*—Dry a representative portion of the solid residue to constant mass at 107 °C ± 3 °C. Determine the moisture loss during this drying step if it is desirable to calculate results to an as-received basis. Crush the

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[3] 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.

[4] *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.

dried portion of the sample to pass a 75 μm (No. 200) U.S.A. standard sieve. Use a mill that minimizes metal contamination.

8.4 *Ashing Solid Combustion Residue*—Spread an appropriate amount of the prepared sample in a layer not over 2 mm in a porcelain, quartz, or fused silica roasting dish. Place the dish in a cold muffle furnace and heat gradually so that the temperature reaches 500 °C ± 10 °C at the end of 1 h. Continue the gradual heating until the temperature rises from 500 °C ± 10 °C to 750 °C ± 15 °C at the end of 1 h. Maintain the 750 °C temperature until the combustion residue reaches a constant mass or for an additional 2 h. Allow the test specimen to cool, grind to pass a 75 μm (No. 200) U.S.A standard sieve, and reignite at 750 °C for 1 h.

8.5 If previously ignited samples are stored and the absorption of moisture or CO_2, or both, is in question, reignite the ash at 750 °C before use. Alternatively, determine loss on ignition using Test Method D7348 on a separate sample whose mass is determined out at the same time as the test portion and make the necessary corrections. Thoroughly mix each sample before weighing.

9. Procedure

9.1 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 mass concentrations for those elements of varying percentages outside the range of the typical sample. Each analyst must determine the sensitivity and linear range of calibration of their equipment and choose mass concentration ranges for standards compatible with the samples and instrument specific to their own work.

9.1.1 Calculations used in subsequent sections are developed from the following general formula for mass fraction of element oxide, E, %, in moisture-free coal ash:

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

where:

A = absorbance of standard solution,
B = absorbance of blank solution,
C = absorbance of sample solution,
N = mass concentration of the element in the standard solution, μg/mL,
M = mass concentration of the test portion mass in solution, for example, 200 μg/mL from 9.4.1 or 50 μg/mL from 9.4.2,
F = conversion factor from element to oxide, dimensionless, and
100 = conversion factor from a mass fraction to a percentage, %.

9.1.1.1 Percent mass fractions in the ash may be converted to the dry coal basis using the following expression:

$$w_C = w_A w_B/100 \qquad (2)$$

where:

w_C = elemental oxide (dry basis) mass fraction in coal, %,
w_A = elemental oxide mass fraction in ash, %,

w_B = ash (dry basis) mass fraction as determined in Test Method D3174 or Test Method D7582, %, and calculated using Practice D3180, and
100 = factor to correct the product of two percent values to a single percent value, %.

9.1.1.2 See Practice D3180 for procedures to convert values to other bases.

9.2 To minimize the potential of contamination, the platinum ware, if used, must be prepared by boiling in solvent acid (for example, HCl or HNO_3 (7.12), but never a mixture of both since the mixture would dissolve platinum) and rinsing thoroughly with reagent-grade water. After this initial cleaning, the platinum ware must be handled with *clean* tongs and protected from further contamination from table tops, and so forth. All glassware used in analyses must be equally clean and equally protected.

9.3 *Sample Fusion and Solution:*

9.3.1 *Sample Fusion*—Transfer 0.1 g ± 0.0002 g of the sample as prepared in 8.2 – 8.5 into a platinum vessel (6.3) (Note 3) and add 0.5 g of $Li_2B_4O_7$. Mix the ash and lithium tetraborate well, then add an additional 0.5 g of $Li_2B_4O_7$ to cover the mixture. Place the platinum vessel 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 vessel with the solvent acid (7.13.3) to remove possible contamination, then place it in a clean 250 mL or 400 mL beaker.

NOTE 3—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.[3]

9.3.2 *Solution*—Place a clean polymer-coated stirring magnet inside the beaker, and immediately place the beaker 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.

9.3.3 Remove the beaker from the hotplate and permit it to cool to room temperature. Wash the platinum vessel, if used, with small amounts of solvent acid into the beaker. Quantitatively transfer the solution to a 200 mL volumetric flask. Rinse the beaker with small amounts of solvent acid, add the rinsings to the flask, and dilute to the 200 mL mark with the solvent acid. This solution is 500 μg/mL with respect to the total sample mass and contains 5 g/L of $Li_2B_4O_7$ solution.

9.4 *Sample Dilution*

9.4.1 *Solution 1*—Pipet 20 mL of the sample solution prepared in 9.3.3 into a 50 mL volumetric flask and dilute to volume with solvent acid. This solution is 200 μg/mL with respect to the total sample mass and contains 2 g/L of $Li_2B_4O_7$.

9.4.2 *Solution 2*—Pipet 10 mL of the sample solution prepared in 9.3.3 into a 100 mL volumetric flask, add 10 mL of lanthanum solution (see 7.6), and dilute to volume with solvent

acid. This solution is 50 µg/mL with respect to the total sample mass and contains 0.5 g/L of $Li_2B_4O_7$.

9.4.3 Include lanthanum in the solution as a release agent in those determinations that may require it (for example, calcium). If this solution is to be used solely for the analysis of sodium or potassium, or both, lanthanum is not needed. Alternative measures to using lanthanum, such as the use of nitrous oxide flame, are permissible.

10. Silicon Dioxide (SiO_2)

10.1 *Preparation of Standards*—Prepare a series of standards by combining the following volumes of the silicon (Si) stock solution (see 7.10) with 1 mL of the aluminum stock solution (see 7.3) and diluting to 100 mL with the blank solution (see 10.2) as outlined in Table 1. Only those standards need be prepared that bracket the expected SiO_2 mass concentrations in the sample solutions.

10.2 *Blank Solution*—Prepare a solution of 2 g/L of $Li_2B_4O_7$ solution in solvent acid.

10.3 *Sample Dilution Solution 1*—Use the 200 µg/mL sample mass dilution solution as prepared in 9.4.1.

10.4 *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.

10.5 *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" directly. Determine w_{SiO2}, the mass fraction of SiO_2, %, as follows:

$$w_{SiO2} = \left[\frac{C - B}{A - B}\right]\left(\frac{N}{M}\right)(F)\,100 \qquad (3)$$

where:

A = absorbance of standard solution nearest C,
B = absorbance of blank solution,
C = absorbance of sample solution,
N = silicon in standard solution, µg/mL,
M = mass concentration of the test portion mass in solution, µg/mL, for example, 200 µg/mL,
F = conversion from element to oxide, for example, 2.139 for SiO_2/Si, dimensionless, and
100 = factor to correct the product of two percent values to a single percent value, %.

11. Aluminum Oxide (Al_2O_3)

11.1 *Preparation of Standards*—Prepare standard solutions containing from 10 µg/mL to 30 µg/mL aluminum and dilute with blank solution (10.2).

TABLE 1 SiO_2 Standards

Silicon (Si), Stock Solution (7.10), mL	Silicon Standard Series, µg/mL	Equivalent w_{SiO2}, %
25	50	53.5
20	40	42.8
15	30	32.1
10	20	21.4

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

11.3 *Sample Dilution Solution 1*—Use the 200 µg/mL sample mass dilution as prepared in 9.4.1.

11.4 *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.

11.5 *Determination*—Read out absorbance values for the blank solution, standard solutions, and sample solution. Determine w_{Al2O3}, the mass fraction of Al_2O_3, %, as follows:

$$w_{Al2O3} = \left[\frac{C - B}{A - B}\right]\left(\frac{N}{M}\right)(F)\,100 \qquad (4)$$

where:

A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample,
N = aluminum in standard solution, µg/mL,
M = mass concentration of the test portion mass in solution, µg/mL, for example, 200 µg/mL,
F = conversion from element to oxide, for example, 1.889 for Al_2O_3/2Al, dimensionless, and
100 = factor to correct the product of two percent values to a single percent value, %.

12. Iron Oxide (Fe_2O_3)

12.1 *Preparation of Standards*—Prepare standard solutions containing from 2 µg/mL to 10 µg/mL iron and 10 mL of lanthanum solution per 100 mL. Dilute with blank solution (12.2).

12.2 *Blank Solution*—Prepare a solution of solvent acid containing 0.5 g/L $Li_2B_4O_7$.

12.3 *Sample Dilution Solution 2*—Use the 50 µg/mL sample mass dilution as prepared in 9.4.2.

12.4 *Atomic Absorption Operating Conditions*—Use an iron hollow-cathode lamp and set the monochromator at 248.3 nm. Use an air-acetylene flame of stoichiometric composition. Adjust other instrument parameters to optimum for the particular equipment used.

12.5 *Determination*—Read the absorbance values for the blank solution, the standard solutions, and the sample solution. Determine w_{Fe2O3}, the mass fraction of Fe_2O_3, %, as follows:

$$w_{Fe2O3} = \left[\frac{C - B}{A - B}\right]\left(\frac{N}{M}\right)(F)\,100 \qquad (5)$$

where:

A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample,
N = iron in standard solution, µg/mL,
M = mass concentration of the test portion mass in solution, µg/mL, for example, 50 µg/mL,
F = conversion from element to oxide, for example, 1.430 for Fe_2O_3/2Fe, dimensionless, and

100 = factor to correct the product of two percent values to a single percent value, %.

13. Calcium Oxide (CaO)

13.1 *Preparation of Standards*—Prepare standard solutions containing 1 µg∕mL to 10 µg∕mL calcium and 10 mL of lanthanum solution per 100 mL. Dilute with the blank solution as described in 12.2.

13.2 *Blank Solution*—Use blank solution as described in 12.2.

13.3 *Sample Dilution Solution 2*—Use the 50 µg∕mL sample mass dilution as described in 9.4.2.

13.4 *Atomic Absorption Operating Conditions*—Use a calcium hallow-cathode lamp and set the monochromator at 422.7 nm. Use an air-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

13.5 *Determination*—Read the absorbance values for the blank solution, the standard solutions, and the sample solution. Determine w_{CaO}, the mass fraction of CaO, %, as follows:

$$w_{CaO} = \left[\frac{C - B}{A - B} \right] \left(\frac{N}{M} \right) (F) \ 100 \qquad (6)$$

where:
A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample,
N = calcium in standard solution, µg/mL,
M = mass concentration of the test portion mass in solution, µg/mL, for example, 50 µg∕mL,
F = conversion from element to oxide, for example, 1.399 for CaO/Ca, dimensionless, and
100 = factor to correct the product of two percent values to a single percent value, %.

14. Magnesium Oxide (MgO)

14.1 *Preparation of Standards*—Prepare standard solutions containing 0.5 µg∕mL to 2 µg∕mL magnesium and 10 mL of lanthanum solution per 100 mL. Dilute with the blank solution as described in 12.2.

14.2 *Blank Solution*—Use blank solution as described in 12.2.

14.3 *Sample Dilution Solution 2*—Use the 50 µg∕mL sample mass dilution as described in 9.4.2.

14.4 *Atomic Absorption Operating Conditions*—Use a magnesium hollow-cathode lamp and set the monochromator at 285.1 nm. Use an air-acetylene flame of stoichiometric composition. Adjust other instrument parameters to optimum for the particular equipment used.

14.5 *Determination*—Read the absorbance values for the blank solution, the standard solutions, and the sample solution. Determine w_{MgO}, the mass fraction of MgO, %, as follows:

$$w_{MgO} = \left[\frac{C - B}{A - B} \right] \left(\frac{N}{M} \right) (F) \ 100 \qquad (7)$$

where:
A = absorbance of standard nearest C,

B = absorbance of blank,
C = absorbance of sample,
N = magnesium in standard solution, µg/mL,
M = mass concentration of the test portion mass in solution, µg/mL, for example, 50 µg∕mL,
F = conversion from element to oxide, for example, 1.658 for MgO/Mg, dimensionless, and
100 = factor to correct the product of two percent values to a single percent value, %.

15. Sodium Oxide (Na₂O)

15.1 *Preparation of Standards*—Prepare standard solutions containing 0.5 µg∕mL to 2 µg∕mL sodium and 10 mL of lanthanum[5] solution per 100 mL. Dilute with blank solution as described in 12.2.

15.2 *Blank Solution*—Use blank solution as described in 12.2.

15.3 *Sample Dilution Solution 2*—Use the 50 µg∕mL sample mass dilution as described in 9.4.2.

15.4 *Atomic Absorption Operating Conditions*—Use a sodium hollow-cathode lamp and set the monochromator at 589.0 nm. Use an air-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

15.5 *Determination*—Read the absorbance values for the blank solution, the standard solutions, and the sample solution. Determine w_{Na2O}, the mass fraction of Na₂O, %, as follows:

$$w_{Na2O} = \left[\frac{C - B}{A - B} \right] \left(\frac{N}{M} \right) (F) \ 100 \qquad (8)$$

where:
A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample,
N = sodium in standard solution, µg/mL,
M = mass concentration of the test portion mass in solution, µg/mL, for example, 50 µg∕mL,
F = conversion from element to oxide, for example, 1.348 for Na₂O/2Na, dimensionless, and
100 = factor to correct the product of two percent values to a single percent value, %.

NOTE 4—Alternatively, sodium may be determined by flame emission.

16. Potassium Oxide (K₂O)

16.1 *Standard Preparation*—Prepare standard solutions containing 0.5 µg∕mL to 2 µg∕mL potassium and 10 mL of lanthanum[5] solution per 100 mL. Dilute with blank solution as described in 12.2.

16.2 *Blank Solution*—Use blank solution as described in 12.2.

16.3 *Sample Dilution Solution 2*—Use the 50 µg∕mL sample mass dilution as described in 9.4.2.

16.4 *Atomic Absorption Operating Conditions*—Use a potassium hollow-cathode lamp and set the monochromator at