



Designation: ~~D3682~~—~~13~~ D3682 – 21

Standard Test Method for Major and Minor Elements in Combustion Residues from Coal Utilization Processes by Atomic Spectrometry¹

This standard is issued under the fixed designation D3682; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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 Method ~~D5016~~ shall be used for determination of sulfur.

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. ~~No other units of measurement are included in this~~ 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~~ safety, health, and ~~health~~ 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.* ~~8829-b596ce0ea434c/astm-d3682-21~~

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](#)

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.

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~~750 °C to a constant ~~weight~~mass. 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~~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~~500 °C and ~~750°C~~750 °C.

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

6.3 *Platinum Dish, Vessels (Dish or Crucible)*, ~~35- to 85 mL capacity~~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~~200 °C.

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

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.

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-ppm~~ 1000 µg/mL aluminum).

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

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

7.6 *Lanthanum Chloride Solution* (~~175-g/L~~ 175 g/L lanthanum chloride (LaCl₃) or equivalent 10 % mass concentration lanthanum).

7.7 *Fluxing Agent - Lithium Tetraborate*—~~Tetraborate—(Li₂B₄O₇), powder, or mixtures of lithium tetraborate (Li₂B₄O₇) and anhydrous lithium metaborate (LiBO₂).~~

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

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

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

7.11 *Sodium Stock Solution* (1000-ppm sodium):

7.12 *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:

7.10 *TitaniumSilicon Stock Solution* (~~1000-ppm~~ 200 µg titanium)/mL silicon) (**Note 2**).

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~~ 0.1070 g of reignited spectrographic grade silica (SiO₂) with ~~1-g~~ 1 g of lithium tetraborate, dissolving in solvent acid, and diluting to ~~250 mL~~ 250 mL as described for sample preparation in 9.3.1 and 9.3.2. This solution is ~~200-ppm~~ 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.

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.

7.13.2 *Nitric Acid (HNO₃)*—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)~~ 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~~500 °C ± ~~10~~10 °C at the end of ~~1 h~~ 1 h. Continue the gradual heating until the temperature rises from ~~500~~500 °C ± ~~10~~10 °C to ~~750~~750 °C ± ~~15~~15 °C at the end of ~~1 h~~ 1 h. Maintain the ~~750~~750 °C temperature until the test specimen reaches a constant mass or for an additional ~~two hours~~ 2 h. Allow the dish to cool, transfer to an agate mortar, and grind to pass a ~~75 μm (No. 200)~~ 75 μm (No. 200) U.S.A. standard sieve. Reignite the ash at ~~750~~750 °C for ~~1 h~~ 1 h, cool rapidly, and weigh—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~~107 °C ± ~~3~~3 °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 ~~75 μm (No. 200)~~ 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~~ 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~~500 °C ± ~~10~~10 °C at the end of ~~1 h~~ 1 h. Continue the gradual heating until the temperature rises from ~~500~~500 °C ± ~~10~~10 °C to ~~750~~750 °C ± ~~15~~15 °C at the end of ~~1 h~~ 1 h. Maintain the ~~750~~750 °C temperature until the combustion residue reaches a constant mass or for an additional ~~two hours~~ 2 h. Cool ~~2 h~~ 2 h. Allow the test specimen, specimen to cool, grind to pass a ~~75 μm (No. 200)~~ 75 μm (No. 200) U.S.A standard sieve, and reignite at ~~750~~750 °C for ~~1 h~~ 1 h.

8.5 If previously ignited samples are stored and the absorption of moisture or CO₂, or both, is in question, reignite the ash at ~~750~~750 °C before use. Alternatively, determine loss on ignition using Test Method **D7348** on a separate sample weighed 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 ~~percents~~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 ~~percent concentration~~mass fraction 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.

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, $\mu\text{g/mL}$,
 M = mass concentration of the test portion mass in solution, for example, 200 $\mu\text{g/mL}$ from 9.4.1 or 50 $\mu\text{g/mL}$ from 9.4.2,
 F = conversion factor from element to oxide, dimensionless, and
 100 = conversion factor from a mass fraction to a percentage, %.

NOTE 3—Percent mass fractions in the ash may be converted to the dry coal basis using the following expression:

$$C = (A \times B / 100 \%)$$

where:

C = elemental oxide (dry basis) in coal, %;
 A = elemental oxide in ash, %; and
 B = ash (dry basis) as determined in Test Method D3174 or Test Method D7582, %, and calculated using Practice D3180.
 See Practice D3180 for procedures to convert values to other bases.

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

$$w_C = w_A w_B / 100 \tag{2}$$

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 platinumware-platinum ware, if used, must be prepared by boiling in solvent acid (for example, HCl or HNO₃ (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 platinumware-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—Weigh 0.1 ± 0.0002 g of the sample as prepared in 8.2 – 8.5 into a platinum dish/vessel (6.3) (Note 43) and add 0.5 g of Li₂B₄O₇. Mix the ash and lithium tetraborate well, then add an additional 0.5 g of Li₂B₄O₇ to cover the mixture. Place the dish-platinum vessel in a clean silica or refractory tray and place in a muffle furnace preheated to 1000°C; 15 min at 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-vessel with the solvent acid (7.13.3) to remove possible contamination, then place it in a clean 250/250 mL 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.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, wash the platinum dish and 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 500500 µg ppm/mL with respect to the total sample mass and contains 55 g-g/L/L of Li₂B₄O₇ solution.

9.3.3 *Solution 1*—Pipet 20 mL of the sample solution prepared in 9.3.2 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 Li₂B₄O₇ solution.

9.3.4 *Solution 2*—Pipet 10 mL of the sample solution prepared in 9.3.2 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 ppm with respect to the total sample and contains 0.5 g/L of Li₂B₄O₇ 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.

9.4 *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 Li₂B₄O₇.

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 Li₂B₄O₇.

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 (SiO₂)

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 SiO₂ mass concentrations in the samples.

Silicon, Stock Solution (7.10), mL	Silicon, ppm	Equivalent SiO ₂ , %
25	50	53.5
20	40	42.8
15	30	32.1
10	20	21.4

solutions.

10.2 *Blank Solution*—Prepare a solution of 22 g-g/L/L of Li₂B₄O₇ solution in solvent acid.

TABLE 1 SiO₂ 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

10.3 *Sample Solution—Dilution Solution 1*—Use the ~~200~~200 ~~µg/ppm sample/mL sample mass dilution solution~~ as prepared in ~~9.3.39.4.1~~.

10.4 *Atomic Absorption Operating Conditions*—Use a silicon hollow-cathode lamp and set the monochromator at ~~251.6 nm~~. 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 concentration” “percent” directly. Determine ~~percent~~ w_{SiO_2} , the mass fraction of SiO_2 , %, as follows:

$$\text{SiO}_2, \% = [(C - B)/(A - B)] \times N \times 1.07 \quad (3)$$

$$w_{\text{SiO}_2} = \left[\frac{C - B}{A - B} \right] \left(\frac{N}{M} \right) (F) 100 \quad (3)$$

where:

A = absorbance of standard nearest C ,
 B = ~~absorbance of blank,~~
 C = ~~absorbance of sample, and~~
 N = ~~silicon in standard, ppm.~~

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~~10 ~~µg/mL to 30 ppm~~30 µg/mL aluminum and dilute with blank solution (10.2).

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

11.3 *Sample Solution—Dilution Solution 1*—Use ~~Solution 1~~ the 200 µg/mL sample mass dilution as prepared in 9.3.39.4.1.

11.4 *Atomic Absorption Operating Conditions*—Use an aluminum hollow-cathode lamp and set the monochromator at ~~309.2 nm~~. 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 ~~percent~~ $w_{\text{Al}_2\text{O}_3}$, the mass fraction of Al_2O_3 , %, as follows:

$$\text{Al}_2\text{O}_3, \% = [(C - B)/(A - B)] \times N \times 0.94 \quad (4)$$

$$w_{\text{Al}_2\text{O}_3} = \left[\frac{C - B}{A - B} \right] \left(\frac{N}{M} \right) (F) 100 \quad (4)$$

where:

A = absorbance of standard nearest C ,
 B = absorbance of blank,
 C = ~~absorbance of sample, and~~
 N = ~~aluminum in standard, ppm.~~
 N = aluminum in standard solution, µg/mL,
 M = mass concentration of the test portion mass in solution, µg/mL, for example, 200 µg/mL,