



Designation: D4326 – 21

Standard Test Method for Major and Minor Elements in Coal Ash By X-Ray Fluorescence¹

This standard is issued under the fixed designation D4326; 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 covers the analysis of the commonly determined major and minor elements in ash from coal using X-ray fluorescence (XRF) techniques.

NOTE 1—Test Method D5016 is used for determination of sulfur.

NOTE 2—Although not included in the present method, the determination of barium, strontium, and manganese may be required to yield adequate totals.

1.2 *Units*—The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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

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

D5016 Test Method for Total Sulfur in Coal and Coke

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.

Current edition approved Sept. 1, 2021. Published October 2021. Originally approved in 1984. Last previous edition approved 2013 as D4326 – 13. DOI: 10.1520/D4326-21.

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.

- 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
- D8146 Guide for Evaluating Test Method Capability and Fitness for Use
- E2 Methods of Preparation of Micrographs of Metals and Alloys (Including Recommended Practice for Photography As Applied to Metallography); Replaced by E 883 (Withdrawn 1983)³
- E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—Definitions applicable to this test method are listed in D121, Terminology of Coal and Coke.

4. Summary of Test Method

4.1 The coal to be analyzed is ashed under standard conditions and ignited to constant mass. Previously ashed materials are ignited to constant mass under standard conditions. The ash is fused with lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) or other suitable flux and either ground and pressed into a pellet or cast into a glass disk. The pellet or disk is then irradiated by an X-ray beam of short wavelength (high energy). The characteristic X-rays of the atom that are emitted or fluoresced upon absorption of the primary or incident X-rays are dispersed and intensities at selected wavelengths are measured by sensitive detectors. Detector output is related to mass fraction by calibration curves or by computerized data-handling equipment.

4.2 The K spectral lines are used for all of the elements determined by this procedure.

4.3 All elements are determined as the element and reported as the oxide and include Si, Al, Fe, Ca, Mg, Na, K, P, Ti, Mn, Sr, and Ba.

³ The last approved version of this historical standard is referenced on www.astm.org.

5. Significance and Use

5.1 A compositional analysis of ash is used in describing the quality of coal for its complete characterization. Ash composition is useful in predicting slagging and fouling characteristics of combusted materials as well as the potential utilization of ash by-products.

5.2 The chemical composition of laboratory prepared coal ash is rarely, if ever, representative of the composition of the mineral matter in the coal because the ashing process can alter some minerals. However, it can approximate the composition of the fly ash and slag resulting from commercial combustion of 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 or Fluxing Device*, with an operating temperature of at least 1000 °C.

6.3 *Fusion Crucibles*, either high-purity graphite (22 mm high and 19 mm wide, inside diameter) or platinum-gold alloy of a similar or larger capacity.

6.4 *Pulverizers*, including agate, mullite or tungsten carbide mortar, and pestle, minimum capacity 25 mL.

6.5 *Sieves*, 250 µm (No. 60) and 75 µm (No. 200) U.S.A. standard sieve as specified in Specification E11.

6.6 *Compactor*—A press equipped with a gauge enabling reproducible pressures (exceeding 1.72×10^8 Pa (25 000 psi)) if pressed pellets are utilized.

6.7 *Excitation Source*, with a stable electrical power supply ($\pm 1\%$) and a high-intensity, short-wavelength X-ray capability.

6.8 *Spectrometer*—A wavelength or energy dispersive system equipped with a vacuum sample chamber.

6.8.1 *Analyzing Crystal (Wavelength Units)*—The choice of the analyzing crystal is made on the basis of the element to be determined. An attempt should be made to use the crystal that yields the maximum sensitivity with minimum interferences. The same crystal must be used for standards and unknowns.

6.8.2 *Detectors*—Scintillation and gas-flow counters are used with wavelength systems while lithium-drifted diodes are used for energy dispersive systems.

7. Reagents

7.1 *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.⁴ Other grades may be

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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

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.

7.2 *Detector Gas*—The usual gas composition of the gas used in the flow-proportional counters is 90 % argon, 10 % methane, although other compositions may be used.

7.3 *Heavy Absorber*—Where heavy absorbers, such as lanthanum oxide or barium oxide, are used they shall be a minimum of 99.99 % purity.

7.4 *Fluxes*—Lithium or sodium borates or carbonates, or combination thereof, are often used for sample fusion. Lithium or ammonium iodide used as a nonwetting agent and potassium or ammonium nitrate used as an oxidizing agent may be used provided they do not contribute to spectral interference.

7.5 *Binders*—Where pressed pellets are used for analysis, the binder used shall contribute no spectral interferences during the determination.

8. Sample Preparation

8.1 *Coal*—Prepare the analysis sample in accordance with Practice D2013 for coal 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 Analysis Sample*—Prepare the ash from a thoroughly mixed analysis sample of coal (see 7.1). Spread the coal in a layer not over 6 mm (¼ in.) in depth in a porcelain, quartz, or fused silica roasting dish. Place the dish in a muffle furnace that is at ambient temperature and heat gradually so that the temperature reaches 500 °C \pm 10 °C at the end of 1 h. Continue the gradual heating until the temperature rises from 500 °C \pm 10 °C to 750 °C \pm 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 to room temperature, transfer the ash to an agate mortar, and grind it to pass a 75 µm (No. 200) U. S. A. standard sieve. Reignite the ash at 750 °C for 1 h, allow to cool rapidly to room temperature, 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 \pm 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) 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 muffle furnace that is at ambient temperature and heat gradually so that the temperature reaches 500 °C \pm 10 °C at the end of 1 h. Continue the gradual heating until the temperature rises from 500 °C \pm 10 °C to 750 °C \pm 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 to room temperature, grind it to pass

a 75 μm (No. 200) U. S. A. standard sieve, and reignite it at 750 °C for 1 h and allow to cool to room temperature.

8.5 If previously ignited samples are stored and the absorption of moisture of CO₂, 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 at the same time as the test portion and make the necessary corrections. Thoroughly mix each sample before determining its mass.

9. Preparation of Analytical Sample

9.1 Mix the powdered sample, determine the mass of a portion of the sample, and mix with a suitable amount of flux (2 g to 10 g of flux per gram of sample) (Note 3). When a heavy absorber is used (Note 5), it is added at this point in an amount equal to the amount of sample and thoroughly blended with the mix. A portion of the flux used as a cap on the mix ensures washing down any of the material from the sides of the crucible. Add all fluxes and other additives in an appropriate manner at the time of sample preparation.

NOTE 3—The amount of sample and flux used are determined by the necessity of forming a disk or pellet of 2 mm thickness to fit the sample holder of the spectrometer used.

NOTE 4—Beads thinner than 5 mm might not be infinitely thick for Sr K-L_{2,3} radiation. If the specimen (in this case the bead) is not infinitely thick for one or more analytes, then the intensity of those analytes depends not only on the composition but also on the thickness. Unless the thickness is taken into account explicitly, determination of the mass fractions is then much more difficult. In this case, it is important that the mass of sample and flux is strictly controlled and that loss of ignition (LOI) during fusion is kept to a minimum. An alternative is to use thicker beads by increasing the masses of sample and flux.

9.1.1 Fluxing materials commonly available are not consistent and can vary in volatile losses upon fusing. In order to eliminate errors caused by this loss, use one of the following two methods. First, a sample of known mass from each lot of flux is fused and a loss on fusion is determined, which is then applied as a correction for each sample prepared from that lot of flux. Or, alternatively, the entire mass of each sample prepared (flux, sample, and heavy absorber, if used) may be determined and an independent fusion loss calculated.

NOTE 5—Use of a heavy absorber has the advantage of allowing the use of a much smaller sample mass to reach infinite thickness and allows for calculation of mass fractions using a simple linear regression coefficient. It does, however, prevent determination of a number of trace elements and may be impractical for energy dispersive systems where its addition may cause increased detector dead time and complicate correction procedures. The use of a heavy absorber is recommended only when its absence is impractical or inconvenient.

9.2 The sample mix is fused at approximately 1000 °C, in a fusion furnace of fluxing device, for a length of time sufficient to guarantee complete dissolution of the sample. Some type of agitation of the crucible, such as swirling or shaking, must be used in order to ensure a uniform melt.

9.3 The fusion melt will then be made into a suitable mount by casting the liquid into a mold and forming a glass disk or by allowing the pellet to cool, grinding to a fine powder with 2 % of a plasticizer or binder, and pressing into a pellet at a minimum of 1.72×10^8 Pa pressure with a suitable backing as added support.

9.4 The glass disk must be cooled at a rate that is fast enough to prevent any segregation occurring and, at the same time, slowly enough to prevent stresses that will crack the glass. Cracked glass disks may be refused and recast without loss of precision.

9.5 Whichever method of preparation of the analytical mount is used, it is essential that a smooth, uniform, and flat surface is exposed to the exciting radiation.

9.6 It is essential that the entire sample preparation procedure (including sample mass, flux mass and ratio, grinding, casting, and so forth) be followed precisely for all analytical mounts and standards. Even a small change in the selected procedures will require remaking of all standards to match the changed procedure. All calibration standards and the unknowns to be used with them must be prepared in exactly the same manner with all mass determinations to be made to the nearest 1 mg.

10. Preparation of XRF Spectrometer

10.1 Follow the manufacturer's instruction for the initial assembly, conditioning, and preparation of the XRF unit.

10.2 Follow the manufacturer's instructions with respect to control setting and operation.

11. Excitation and Exposure

11.1 Position the sample in the chamber provided for this purpose. Avoid touching or otherwise contaminating the sample surface. Produce and record the spectrum at the settings recommended for the instrument. Prepare and analyze duplicate mounts for all samples with duplicate readings on each mount. For in-house laboratories, single determinations may be performed as long as the precision and bias limits are met.

12. Safety Precautions

12.1 It is necessary to obtain training before using X-ray fluorescence equipment and important to understand completely the operation of the instrument to ensure that the provisions of 1.3 are met.

13. Calculations and Calibration

13.1 Standards for calibration may be prepared from standard reference materials or synthetically blended pure compounds. It is required that the range of mass fractions represented by the standards exceeds that of any unknown.

13.2 Calculation of elemental mass fractions may be accomplished by empirical fundamental parameter or linear regression in accordance with Practice E2.

14. Precision and Bias⁵

14.1 *Precision*—The relative precision of this test method for the determination of major and minor elements in coal combustion residues was calculated from data obtained from ashes with the mass fraction ranges shown in Table 1.

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-2003. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Mass Fraction Range and Limits for Repeatability and Reproducibility for Major and Minor Elemental Oxides in Ash (Dry Basis) from Combustion Residues^{A,B}

Parameter	Mass Fraction Range, %	Repeatability Limit, <i>r</i>	Reproducibility Limit, <i>R</i>
SiO ₂	30.12 to 63.95	0.818	1.736
Al ₂ O ₃	11.87 to 33.76	0.020 \bar{x} + 0.173	0.049 \bar{x} + 0.577
Fe ₂ O ₃	3.09 to 42.26	0.009 \bar{x} + 0.137	0.041 \bar{x} + 0.416
TiO ₂	0.50 to 3.66	0.017 \bar{x} + 0.038	0.091 \bar{x} + 0.092
CaO	1.50 to 25.77	0.016 \bar{x} + 0.083	0.056 \bar{x} + 0.076
MgO	0.75 to 7.27	0.014 \bar{x} + 0.095	0.056 \bar{x} + 0.242
Na ₂ O	1.16 to 7.31	0.008 \bar{x} + 0.152	0.108 \bar{x} + 0.282
K ₂ O	0.28 to 3.08	0.075 \bar{x} - 0.015	0.102 \bar{x} + 0.020
BaO	0.38 to 2.84	0.006 \bar{x} + 0.052	0.206 \bar{x} + 0.078
SrO	0.13 to 0.58	0.020 \bar{x} + 0.016	0.206 \bar{x} + 0.032
P ₂ O ₅	0.25 to 3.40	0.043 \bar{x} + 0.024	0.130 \bar{x} + 0.098
The values presented below are for information only.			
MnO ₂		0.135 \bar{x} + 0.014	0.351 \bar{x} + 0.017
SO ₃		0.045 \bar{x} + 0.161	0.135 \bar{x} + 0.660

^A Where \bar{x} is the average of two single test results.

^B Where the lower scope limit is the larger of the following: the lowest sample mean tested in the Interlaboratory Study (ILS) or the test level where the ratio of the test level to the within laboratory standard deviation (*S*) is ten. The latter is calculated from the relationship expressing the repeatability limit for the test method as $r_{\text{intercept}} / (0.28 - r_{\text{slope}})$, see Guide **D8146**.

NOTE 6—**Table 1** indicates that the precision for SO₃ and MnO₂ is for information only. For SO₃, this is explained by observed inconsistencies in the results within and between labs, likely caused by the fusion process. For MnO₂, this is explained by the observed mass fraction of this oxide being low enough on most of the ILS samples such that trace analysis would be required.

14.1.1 *Repeatability*—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 %.

NOTE 7—The interlaboratory studies used to determine the precision of this method in **Table 1** defined separate test determinations as “two fused glass disks prepared from separate test portions of coal derived ash.”

14.1.2 *Reproducibility*—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 %.

14.2 *Bias*—Analysis of ash by X-ray fluorescence is empirical and its approach to accuracy is dependent upon the

accuracy of the reference materials to be used for calibration (**13.1**) and compliance to this test method. No other statement on bias can be made for this test method.

14.3 Interlaboratory studies, designed consistent with Practice **E691**, were conducted in 1984, 1989 and 1995 for major and minor elemental oxides in ash from combustion residues; however, data from the 1984 ILS was not used for derivation of the precision information in **Table 1** because of inconsistencies in the number of replicates reported for that study. The total number of participating laboratories between the 1989 and 1995 studies was twenty-three (23); however, some laboratories' results were excluded for some materials, and the average number of participating laboratories for a given element and material was seven (7). The details of the study and supporting data are given in ASTM Research Report RR:D05-2003.⁵

15. Keywords

15.1 coal; coal ash; major elements; minor elements; X-ray fluorescence

ANNEX

(Mandatory Information)

A1. PRECISION STATISTICS

A1.1 See **Table A1.1**.

A1.1.1 *Repeatability Standard Deviation (S_r)*—The standard deviation of test results obtained under repeatability conditions.

A1.1.2 *Reproducibility Standard Deviation (S_R)*—The standard deviation of test results obtained under reproducibility conditions.

A1.1.3 *Analytical Performance Value (APV_r)*—The ratio of the repeatability to the average test level expressed as a percent.

A1.1.4 *Performance Ratio (PR)*—The ratio between reproducibility and repeatability.

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