



Designation: D4326 – 13

Standard Test Method for Major and Minor Elements in Coal and Coke 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 or coke 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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:*²

D121 Terminology of Coal and Coke

D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis

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 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

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of Metals and Alloys (Including Recommended Practice for Photography As Applied to Metallography); Replaced by E 883 (Withdrawn 1983)³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

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 or coke to be analyzed is ashed under standard conditions and ignited to constant weight. Previously ashed materials are ignited to constant weight 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 concentration 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.

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.

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, 2013. Published September 2013. Originally approved in 1984. Last previous edition approved 2011 as D4326 – 11. DOI: 10.1520/D4326-13.

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.

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

5.2 The chemical composition of laboratory prepared coal or coke 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 or coke.

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 gage 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 (± 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 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 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 (see 7.1). Spread the coal and coke in a layer not over 6 mm (1/4 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 $500 \pm 10^\circ\text{C}$ at the end of 1 h. Continue the gradual heating until the temperature rises from $500 \pm 10^\circ\text{C}$ to $750 \pm 15^\circ\text{C}$ at the end of 1 h. Maintain the 750°C temperature until the test specimen reaches a constant mass or for an additional two hours. 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 weigh portions for analysis.

8.3 *Solid Combustion Residue*—Dry a representative portion of the solid residue to constant mass at $107 \pm 3^\circ\text{C}$. 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 $500 \pm 10^\circ\text{C}$ at the end of 1 h. Continue the gradual heating until the temperature rises from $500 \pm 10^\circ\text{C}$ to $750 \pm 15^\circ\text{C}$ at the end of 1 h. Maintain the 750°C temperature until the combustion residue reaches a constant mass or for an additional two h. Cool the test specimen, 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 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 weighed out at

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.