Designation: D 4326 – 97

Standard Test Method for
Major and Minor Elements in Coal and Coke Ash By X-Ray Fluorescence[1]

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 D 1757 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 the standard. The values given in parentheses are for information only.

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 1757 Test Methods for Sulfur in Ash from Coal and Coke[2]

D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal[2]

E 2 Methods of Preparation of Micrographs of Metals and Alloys (Including Recommended Practice for Photography as Applied to Metallography)[3]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[4]

3. Summary of Test Method

3.1 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 ($Li_2B_4O_7$) 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.

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

3.3 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.

4. Significance and Use

4.1 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.

4.2 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.

5. Apparatus

5.1 *Ashing Furnace*, with air circulation as specified in Test Method D 3174 and capable of having its temperature regulated between 700 and 750°C.

5.2 *Fusion Furnace or Fluxing Device*, with an operating temperature of at least 1000°C.

5.3 *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.

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

5.5 *Sieves*, 250-µm (No. 60) and 75-µm (No. 200) U.S.A standard sieve as specified in Specification E 11.

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

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[1] This test method is under the jurisdiction of ASTM Committee D-5 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. 10, 1997. Published May 1998. Originally published as D 4326 – 84. Last previous edition D 4326 – 94.

[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] Discontinued, see *1982 Annual Book of ASTM Standards*, Part 11.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

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

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

5.8.1 *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.

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

6. Reagents

6.1 *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.[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.

6.2 *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.

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

6.4 *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.

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

7. Preparation of Coal Ash and Coke Ash

7.1 Prepare the ash from a thoroughly mixed representative analysis sample of air-dried coal or coke that has been ground to pass a 250-μm (No. 60) U.S.A standard sieve. Spread the coal or coke in a layer not over 6 mm (¼ in.) in depth in a fireclay, porcelain, or platinum roasting dish. Place the ash 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 to constant weight, cool, grind to pass a 74-μm (No. 200) U.S.A standard sieve, and reignite at 750°C for 1 h. Immediately, prepare the analysis sample or store the dry ash in a vacuum desiccator. If samples are stored under atmospheric conditions, they must be reheated at 750°C and brought to constant weight before further use.

7.2 Materials previously ashed, fly ash, or bottom ash must be ignited to constant weight at 750°C and cooled in a desiccator before analysis sample preparation, or alternatively, weight loss or gain must be determined on a second sample at 750°C taken at the same time as the analysis sample so that analysis determined on an as-received basis can be reported on an ignited ash basis.

8. Preparation of Analytical Sample

8.1 Mix the powdered sample, weigh a portion of the sample, and mix with a suitable amount of flux (2 to 10 g of flux per gram of sample) (Note 3). When a heavy absorber is used (Note 4), 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.

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. All fluxes and other additives should be added in an appropriate manner at the time of sample preparation.

8.1.1 Fluxing materials commonly available are not consistent and can vary in volatile losses upon fusing. In order to eliminate errors caused by this loss, one of three methods must be employed. First, the entire bottle of flux may be heated to the fused state, then cooled, reground, and stored in a desiccator. Second, a weighed sample from each bottle is fused and a loss on fusion is determined, which is then applied as a correction for each sample prepared from that bottle. Third, the entire mass of each sample prepared (flux, sample, and heavy absorber, if used) may be weighed and an independent fusion loss calculated.

NOTE 4—Use of a heavy absorber has the advantage of allowing the use of a much smaller sample weight to reach infinite thickness and allows for calculation of concentrations 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.

8.2 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.

8.3 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 (25 000-lbs/in^2) pressure with a suitable backing as added support.

8.4 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.

8.5 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.

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

8.6 It is essential that the entire sample preparation procedure (including sample weight, flux weight 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 weighings to be made to the nearest 1 mg.

9. Preparation of XRF Spectrometer

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

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

10. Excitation and Exposure

10.1 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.

11. Safety Precautions

11.1 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.

12. Calculations and Calibration

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

12.2 Calculation of elemental concentrations may be accomplished by empirical fundamental parameter or linear regression in accordance with Practice E 2.

13. Precision and Bias [6]

13.1 *Precision*—The relative precision of this test method for the determination of major and minor elements in coal and coke ash was calculated from data obtained from ashes with the concentration ranges shown in Table 1.

NOTE 5—Data were also collected for MnO_2, SO_3, SrO, and BaO in the round robin used to generate the data for calculating the repeatability and reproducibility intervals or limits for the first nine elemental oxides in Table 1. These data were used to calculate the repeatability and reproducibility intervals or limits for the last four elemental oxides in the table. The analyses of MnO_2, SO_3, SrO, and BaO were not included in the original scope and responsibility of the Task Group and are listed for informational purposes only.

13.2 *Repeatability*—The difference in absolute value between two consecutive tests results, carried out on the same analysis sample, in the same laboratory, by the same operator, using the same apparatus, should not exceed the repeatability interval *I* (*r*) or limit more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval or limit, there is reason to question one, or both, of the test results. The repeatability intervals or limits for the elements determined by this test method are described in Table 1.

TABLE 1 Concentration Ranges and Intervals or Limits for Repeatability and Reproducibility for Major and Minor Elemental Oxides in Coal and Coke Ash

Elemental Oxide	Percent, by Weight, of Moisture-Free Ash		
	Concentration Range	Repeatability, $I(r)^A$	Reproducibility, $I(R)^A$
SiO_2	33.2–57.5	1.26	4.39
Al_2O_3	11.6–33.1	0.83	0.51 + 0.10(*x*)
Fe_2O_3	3.1–41.8	0.21 + 0.005(*x*)	0.99 + 0.035(*x*)
CaO	1.5–25.2	0.16 + 0.01(*x*)	0.22 + 0.07(*x*)
MgO	0.4–4.5	0.09 + 0.04(*x*)	0.14 + 0.09(*x*)
Na_2O	0.2–7.41	0.20	0.42
K_2O	0.3–3.1	0.14	0.16
P_2O_5	0.1–3.4	0.05 + 0.04(*x*)	0.23
TiO_2	0.5–1.5	0.06	0.24
MnO_2	0.008–0.26	0.01 + 0.18(*x*)	0.02 + 0.045(*x*)
SrO	0.02–0.95	0.04	0.14
BaO	0.05–2.84	0.02 + 0.03(*x*)	0.06 + 0.20(*x*)
— The following value is offered for information only (Note 5) —			
SO_3	0.41–14.72	0.20 + 0.09(*x*)	0.52 + 0.3(*x*)

^{A} The value of *x* is the average of two test results.

13.2.1 *Example*—Duplicate analysis for iron (Fe_2O_3) showed values of 5.83 and 5.76 %. The absolute difference between the two tests is 0.07 %, since this value does not exceed the *I* (*r*) value of 0.24 %, therefore, these duplicate analyses are acceptable at the 95 % confidence level.

13.3 *Reproducibility*—The difference in absolute value of replicate determinations carried out in different laboratories, on representative samples prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval *I* (*R*) or limit more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval or limit, there is reason to question one, or both, of the test results. The reproducibility intervals or limits for the elements determined by this test method are described in Table 1.

13.3.1 *Example*—Duplicate analysis for iron in one laboratory showed an average value of 5.79 %, and a value of 4.93 % was obtained in a different laboratory. The difference between the different laboratory values is 0.86 %. The reproducibility interval, *I* (*R*) from Table 1, is given as 1.18 %. Since the laboratory difference is less than the *I* (*R*), the two laboratory results are acceptable at the 95 % confidence level.

13.4 *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 (12.1) and compliance to this test method. No other statement on bias can be made for this test method.

14. Keywords

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

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[6] Supporting data are available from ASTM Headquarters. Request RR:D05-1006.

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