



Designation: D8214 – 18

Standard Test Method for Forms of Sulfur in Coal by Inductively Coupled Plasma Atomic Emission Spectrometry¹

This standard is issued under the fixed designation D8214; 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 applies to the determination of sulfate sulfur and pyritic sulfur in coal and calculates organic sulfur by difference. This test method is not applicable to coke or other carbonaceous materials.

1.2 The values stated in SI units are to be regarded as standard. Non-SI units, if provided, are considered informational and are contained within parentheses

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
- 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
- D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
- D4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion

¹ This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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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
- E832 Specification for Laboratory Filter Papers
- 2.2 *ISO Standards:*³
- ISO 5725-6 Accuracy (Trueness and Precision) of Measurement Methods and Results – Part 6: Use in Practice of Accuracy Values

3. Terminology

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

4. Summary of Test Method

4.1 *Sulfate Sulfur:*

4.1.1 Sulfate sulfur is extracted from the analysis sample with a dilute hydrochloric acid solution. The sulfate sulfur in the extract is determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Sulfates are soluble in hydrochloric acid, pyritic sulfur and organic sulfur are not soluble in hydrochloric acid.

4.2 *Pyritic Sulfur:*

4.2.1 Pyritic sulfur is extracted from the pretreated sample with a dilute nitric acid solution. The pyritic sulfur in the extract is determined by correlating extracted iron content, measured by ICP-AES, as pyritic sulfur content.

4.2.2 Monosulfides (pyrites and FeS₂ are disulfides) of iron and elements such as cadmium, lead, vanadium, and zinc can be present in coal. In mass fractions up to 100 $\mu\text{g/g}$, these monosulfides do not contribute significantly to the total inorganic sulfide content.⁴⁻⁶

³ Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <http://www.iso.org>.

⁴ Edwards, A. H., Daybell, G. N., and Pringle, W. J. S., "An Investigation into Methods for the Determination of Forms of Sulfur in Coal," *Fuel*, Vol 37, 1958, pp. 47-59.

⁵ Burns, M. S., "Determination of Pyritic Sulfur in Australian Coals," *Fuel*, Vol 49, 1970, pp. 126-133.

⁶ Shrimp, N. F., Helfinstine, R. J., and Kuhn, J. K., "Determination of Forms of Sulfur in Coal," *Symposium on Sulfur and Nitrogen in Coal and Oil Shale*, 1975, pp. 99-108.

5. Significance and Use

5.1 This test method provides for a separation of coal-associated sulfur into two commonly recognized forms: pyritic and sulfate. Organic sulfur is calculated by difference. Results obtained by the test method are used to serve a number of interests, including the evaluation of coal preparation and processing operations designed to reduce coal sulfur levels.

6. Analysis Sample

6.1 The analysis sample is that sample which has been pulverized to pass a 250 μm (No. 60) sieve as prepared in accordance with Practice **D2013**.

6.2 Determine the moisture in the analysis sample in accordance with Test Method **D3173** or Test Methods **D7582** to permit calculation to other bases.

7. Apparatus

7.1 *Balance*, sensitive to 0.1 mg.

7.2 *Hot Plate*, electric or gas-heated with capability for temperature control.

7.3 *Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES)*—Either a sequential or simultaneous spectrometer is suitable. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limits, precision, linear dynamic range, and interference effects shall be investigated and established for each analyte on that particular instrument. All measurements shall be within the instrument's linear range in which correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements of this test method. The analyst shall maintain quality control data confirming the instrument performance and analytical results.

8. Reagents and Materials

8.1 *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.⁷ Other grades may be used, provided that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification **D1193**, Type II.

8.3 *Ethanol*, reagent grade, denatured.

8.4 *Filter Paper*—Unless otherwise indicated, references to filter paper shall be understood to mean filter paper conforming to Specification **E832**.

8.5 *Hydrochloric Acid*, 4.8 N (2 + 3)—Mix two volumes of concentrated aqueous hydrochloric acid (HCl, 12 N) with three volumes of water.

8.6 *Nitric Acid*, 2 N (1 + 7)—Mix one volume of concentrated nitric acid (HNO₃, 15.8 N) with seven volumes of water.

8.7 *Standard Stock Solutions*—Stock solutions of 1000 $\mu\text{g}/\text{mL}$ for sulfur and iron are needed for preparation of dilute standards. Prepare stock solutions from 99.99 % purity metals or salts. Alternatively, one can use commercially available stock solutions specifically prepared for ICP-AES

8.8 *Internal Standard*—Solution of yttrium, 200 $\mu\text{g}/\text{mL}$ in nitric acid or other suitable element not found in significant mass fractions in the test samples.

9. Procedure for Sulfate Sulfur

9.1 *Extraction*—Weigh, to the nearest 1 mg, a 1 g test specimen and transfer it to a 200 mL beaker (tall-form/Berzelius). Add 50 mL of 4.8 N HCl and a few drops of ethanol to the coal sample. Ethanol facilitates the wetting process. Cover the sample with a watch glass, place it on a hotplate, and heat at 85 °C for 30 min while stirring it with a magnetic stir bar or periodically using a glass stir rod.

9.2 *Filtering*—Carefully filter the contents of the beaker into a 250 mL to 500 mL vacuum flask, using a Type II, Class F or G filter paper. Wash the filter paper and contents with sufficient small volume water washings to ensure the transfer of all the HCl extract to the vacuum flask. Save the filter paper with extracted residue for the subsequent extraction of pyritic sulfur content.

9.3 *Test Solution Preparation*—Transfer the filtrate to a 200 mL volumetric flask with a glass stir rod. Rinse the vacuum flask with small volume water washings and transfer to the volumetric flask. Add 10 mL of 200 $\mu\text{g}/\text{mL}$ yttrium solution or appropriate non-interfering internal standard and fill the flask to volume with water. Stopper the flask and mix well. Store the sample solution in washed plastic sample bottles.

9.4 *Sulfate Blank*—Prepare a sulfate blank following the same procedure and using the same amounts of all reagents as described above. Save this filter paper for determining the pyritic iron blank.

9.5 *Preparation of Calibration Solutions*—Prepare a set of sulfur calibration standards (2.5, 5, 10, 25, 50, 100) $\mu\text{g}/\text{mL}$.

9.5.1 *Spectrometric Conditions*—Suitable ICP-AES conditions for the determination of sulfur are as follows:

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|-----------------------|----------------------------|
| Wavelength | 180.731 nm |
| Wavelength | 182.624 nm |
| Wavelength | 182.034 nm |
| Single integration of | 300 s |
| RF Power: | 0.8 kW |
| Torch Gas: | Coolant 20 L./min |
| | Aux 0.5 L./min |
| | Nebulizer 200 kPa (30 psi) |

⁷ *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. Pharmacopeia Convention, Inc. (USPC), Rockville, MD.