



Designation: D8247 – 19

Standard Test Method for Determination of Total Fluorine and Total Chlorine in Coal by Oxidative Pyrohydrolytic Combustion Followed by Ion Chromatography Detection¹

This standard is issued under the fixed designation D8247; 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 determination of total fluorine and total chlorine in coal. Samples containing 200 mg/kg to 4000 mg/kg of chlorine and 20 mg/kg to 100 mg/kg of fluorine can be analyzed directly.

1.1.1 It is possible for this method to be used for the determination of total bromine in coal. No precision and bias statement will be given for the determination of total bromine.

1.2 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 In determining the conformation of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method from Practice E29.

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, health, and 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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

[D121 Terminology of Coal and Coke](#)

[D1193 Specification for Reagent Water](#)

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.

[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](#)
[D7582 Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis](#)
[E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications](#)
[E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

2.2 *ISO Standard:*³

[ISO 5725-6:1994 Accuracy \(Trueness and Precision\) of Measurement Methods and Results – Part 6: Use in Practice of Accuracy Values](#)

3. Terminology

3.1 *Definitions*—Definitions applicable to this test method are listed in Terminology [D121](#).

3.2 *Abbreviations:*

3.2.1 *IC*—ion chromatograph

3.2.2 *CIC*—combustion ion chromatography

4. Summary of Test Method

4.1 A 50 mg to 100 mg sample is weighed into a sample boat and is introduced at a controlled rate into a high temperature combustion tube where the sample is combusted in a humidified oxygen pyrohydrolytic environment. The gaseous by-products of the combusted sample are trapped in an absorption solution where the hydrogen halides (HX) formed during combustion disassociate into their respective ions (X⁻). An aliquot of known volume of the absorbing solution is then injected into an ion chromatograph (IC). The halide anions are separated by the anion separation column of the IC. The conductivity of the eluent is reduced with an anion suppression device prior to detection of the chloride and fluoride ions with

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>.

a conductivity detector. Quantification of the fluoride and chloride is achieved by first calibrating the ion chromatograph with a series of aqueous standards containing known amounts of fluoride and chloride.

5. Significance and Use

5.1 This test method covers the measurement of the chlorine and fluorine contents in coal. These halides can contribute to emissions with some undesirable environmental consequences.

6. Interferences

6.1 Substances that co-elute with the anions of interest may interfere. A high mass concentration of one element can interfere with other constituents if their retention times are close enough to affect the resolution of their peaks.

7. Apparatus

7.1 *Pyrohydrolytic Combustion Unit*, which can maintain a temperature of 950 °C to 1100 °C consisting of:

7.1.1 *Furnace*, an electric furnace which can maintain a minimum temperature of 950 °C to 1100 °C.

7.1.2 *Gas Flow Control*—The apparatus shall be equipped with flow controllers capable of maintaining a constant flow of oxygen and inert carrier gas (argon or helium).

7.1.3 *Humidifier Delivery System*, capable of delivering Type 1 reagent water (8.2) to the combustion tube at a controlled rate sufficient to provide a pyrohydrolytic environment.

7.1.4 *Pyrohydrolytic Combustion Tube*, made of quartz or other suitable material and capable of withstanding temperatures up to 1100 °C. The combustion tube shall be of ample volume and may include quartz wool (or other suitable medium) to provide sufficient mixing and surface area to ensure complete combustion of the sample.

7.1.5 *Boat Inlet System*—The system provides a sampling port for the introduction of samples into the sample boat and is connected to the inlet of the combustion tube. The system is swept by a humidified inert carrier gas and shall be capable of allowing the quantitative delivery of the material to be analyzed into the oxidation zone at a controlled rate.

7.1.6 *Quartz or Ceramic Sample Boats*, sufficient in size to hold 50 mg to 100 mg of sample.

7.2 *Gas Absorption Unit*, having an absorption tube, with sufficient capacity to hold a minimum of 5 mL, which is automatically filled with a known volume of absorption solution by a built-in burette or other similar device. The gas absorption unit may be interfaced to the IC so that an aliquot of the absorption solution can be injected into the IC after the sample is combusted and the by-products of combustion are absorbed.

7.3 *Ion Chromatograph (IC)*, an analytical system with all required accessories including columns, suppressor, and detector.

7.3.1 *Injection System*, capable of delivering 20 μL to 3000 μL with a precision better than 1 %, or as recommended by the manufacturer for this determination. It is recommended to use an IC configured for pre-concentration or matrix elimination for injection volumes greater than 500 μL . Follow

manufacturer's instructions regarding the set-up of pre-concentration or matrix elimination.

7.3.2 *Pumping System*, capable of delivering mobile phase flows between 0.2 mL/min and 2.5 mL/min with a precision better than 2 %, or as recommended for this determination by the manufacturer.

7.3.3 *Continuous Eluent Generation (Optional)*, to automatically prepare and purify the eluent used in the ion chromatography. Electrolytic eluent generation and auto-buret preparation of eluent via in-line dilution of a stock solution have been found satisfactory for this method. Other continuous eluent generation devices may be used if the precision, bias, recovery, and accuracy of this method are met.

7.3.4 *Volumetric Flasks Class A*, at the volume specified to use in this method to prepare standards, reagents, and solutions.

7.3.5 *Guard Column*, for protection of the analytical column from strongly retained constituents. Improved separation is obtained with additional theoretical plates.

7.3.6 *Anion Separator Column*, capable of producing satisfactory baseline separations of the anion peaks of interest as shown in Fig. 1.

7.3.7 *Anion Suppressor Device*, reduces the background conductivity of the eluent after separation by the anion separator column. Both chemical and continuous electrolytic suppressors have been found satisfactory for this method. Other anion suppressor devices may be used as long as the precision and accuracy of the method are not degraded.

7.3.8 *Conductivity Detector*, temperature controlled to ± 0.01 °C, capable of at least 0 $\mu\text{S}/\text{cm}$ to 1000 $\mu\text{S}/\text{cm}$ on a linear scale.

7.3.9 *Data Acquisition System*, an integrator or computer data handling system capable of integrating the peak areas of an ion chromatograph.

7.4 *Balance*, analytical, with sensitivity to 0.0001 g used for preparation of standards and reagents.

7.5 *Balance (Optional)*, 5 place analytical, with sensitivity to 0.00001 g used to weigh specimens.

7.6 *Gas Regulators*—Two-stage gas regulators capable of regulating the pressures to 300 kPa to 400 kPa (40 psi to 60 psi) shall be used for the carrier and combustion gases. Follow instrument manufacturer's recommendations for pressure regulation.

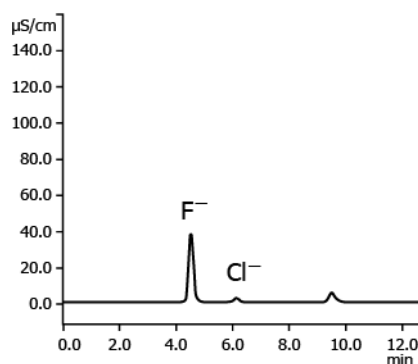


FIG. 1 Typical Chromatogram Containing Fluoride and Chloride Anion

7.7 *Purification Scrubbers or Filters*—Molecular sieve for moisture and activated charcoal (or equivalent) for hydrocarbons are recommended to ensure the removal of contaminants.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade or higher purity chemicals shall be used for the preparation of all samples, standards, eluent, and regenerator solutions. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ 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 Type I having a minimum value of 18 MΩ·cm resistance and conforming to Specification D1193 Type I reagent water. Comply with all ion chromatograph instrument and column vendor requirements for eluent preparation and handling (for example, filtering and degassing). The quality of the reagent water is critical to the performance, repeatability, reproducibility, and accuracy of the method. A chart of critical specification parameters for Type I reagent water per Specification D1193 is listed below in Table 1.

8.3 *Quartz Wool* (fine grade) or other suitable absorbent material that is stable and capable of withstanding temperatures inside the furnace may be used.

8.4 *Oxygen*, combustion gas, minimum 99.75 % purity.

8.5 *Argon or Helium*, inert carrier gas, minimum 99.98 % purity.

8.6 *Calibration Standards*, certified calibration standards from commercial sources or calibration standards prepared in the laboratory containing the elements of interest at the mass concentrations of interest. Other calibration standard sources and diluents may be used if precision and accuracy are not degraded.

8.7 *Sodium Fluoride*, FW 41.99 g/mol, 45.25 % fluoride.

8.8 *Sodium Chloride*, FW 58.44 g/mol, 60.66 % chloride.

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.

TABLE 1 Reagent Water Key Specifications

Measurement (unit)	Specification D1193 Standards for Reagent Water		
	Type I	Type II	Type III
Resistivity (MΩ·cm) at 25 °C	≥18	≥1	≥4
Total Organic Carbon (µg/kg)	≤50	≤50	≤200
Sodium (µg/kg)	≤1	≤5	≤10
Chloride (µg/kg)	≤1	≤5	≤10
Total Silica (µg/kg)	≤3	≤3	≤500

8.9 *Eluent Solution*—Follow the specific guidelines for the preparation and use of the eluent solution from the manufacturer of the columns used.

8.10 *Optional Phosphate Stock Solution (1000 mg/L)*—Dissolve 1.433 g of potassium dihydrogen phosphate (KH₂PO₄) in water and dilute to 1 L with water in a Class A volumetric flask and mix well.

8.11 *Optional Phosphate Absorbing Solution*—Dilute the phosphate stock solution with water (1+399) in a Class A volumetric flask to a final mass concentration of 2.50 mg/L. The mass concentration of phosphate in the absorbing solutions is used as an internal standard by the ion chromatograph.

8.12 *Optional Hydrogen Peroxide Absorbing Solution*—Typically, Type I water is used as absorber solution for fluoride and chloride analysis. If desired, a solution of 500 mg/L hydrogen peroxide may be used to improve recovery in bromide and sulfate determinations. Hydrogen peroxide is not required if the measurement of bromide and sulfur is not being determined.

8.13 *Suppressor (Chemical and Electrolytic)*:

8.13.1 *Chemical Suppressor Regenerant Solution*—Follow the specific manufacturer guidelines for the preparation and use of the suppressor solution. The manufacturer’s recommended solutions may be purchased from qualified vendors as long as the performance, precision, and accuracy are not degraded.

8.13.2 *Electrolytic Suppressor Current Setting*—Follow the specific manufacturer guidelines for the current setting of the suppressor being used based upon the flow rate and eluent concentration being used for the analysis.

9. Hazards

9.1 Consult the current version of OSHA regulations, supplier’s Material Safety Data Sheets, and local regulations for all materials used in this test method.

10. Sampling, Test Specimens, and Test Units

10.1 The coal analysis sample shall be prepared in accordance with Practice D2013.

10.2 Analyze separate test portions of the analysis sample for moisture content in accordance with Test Methods D3173 or D7582 so that calculations to other bases can be made.

11. Preparation of Apparatus

11.1 Assemble and check the apparatus for leaks in accordance with the manufacturer(s) instructions. A typical block diagram of a combustion IC system for analysis of a sample is shown in Fig. 2.

12. Calibration and Standardization

12.1 *Instrument Calibration*:

12.1.1 It is recommended to use five aqueous calibration standards curves to cover the scope of this method. Recommended mass concentrations of aqueous IC calibration standards are listed in Table 2. Other mass concentrations of calibration standards can be used as long as the accuracy and precision of the method is not degraded.