Designation: D8247 – 19

Standard Test Method for Determination of Total Fluorine and Total Chlorine in Coal by Oxidative Pyrohydrolytic Combustion Followed by Ion Chromatography Detection[1]

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

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

[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 Feb. 1, 2019. Published April 2019. DOI: 10.1520/D8247-19.

[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] 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 µS⁄cm to 1000 µS⁄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.

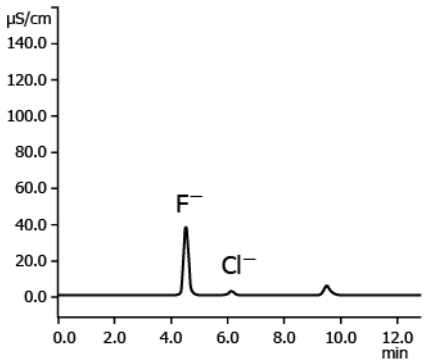

FIG. 1 Typical Chromatogram Containing Fluoride and Chloride Anion