Designation: D3761 – 10

Standard Test Method for Total Fluorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method[1]

This standard is issued under the fixed designation D3761; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers the analysis of total fluorine in coal.

1.2 This test method was successfully tested on coals containing 25 % ash or less.[2]

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 7.

1.5 All accountability and quality control aspects of Guide D4621 apply to this test method.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

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

D4621 Guide for Quality Management in an Organization That Samples or Tests Coal and Coke (Withdrawn 2010)[4]

D5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures (Withdrawn 2010)[4]

E144 Practice for Safe Use of Oxygen Combustion Bombs

3. Summary of Test Method

3.1 Total fluorine is determined in this test method by combusting a weighed sample in an oxygen bomb with a dilute base absorbing the fluorine vapors. The bomb is rinsed into a beaker with water and following the addition of a citrate buffer, the fluorine is determined by ion-selective electrode.

4. Significance and Use

4.1 This test method permits measurement of the fluorine content of coal for the evaluation of potential fluorine emission from coal combustion or conversion processes. When coal samples are combusted in accordance with this test method, the fluorine is quantitatively retained and is representative of the total fluorine concentration in whole coal.

5. Apparatus

5.1 *Combustion Bomb,* constructed of materials that are not affected by the combustion process or products. The bomb must be designed so that all liquid combustion products can be quantitatively recovered by washing the inner surfaces. There must be no gas leakage during the test. The bomb must be capable of withstanding a hydrostatic-pressure test to 20 MPa (approximately 3000 psig) at room temperature without stressing any part beyond its elastic limit.

5.2 *Water Bath*—A container large enough to hold the combustion bomb and enough cooling water to dissipate the heat generated during the combustion process. The container shall be designed to allow a constant flow of water around the combustion bomb.

5.3 *Sample Holder*—Samples shall be burned in an open crucible of platinum, quartz, or acceptable base metal alloy.

[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 Dec. 1, 2010. Published January 2010. Originally published as D3761 – 79. Last previous edition D3761 – 96(2002). DOI: 10.1520/D3761–10.

[2] This standard is based on a published report by Thomas, J., Jr., and Gluskoter, H. J., "Determination of Fluoride in Coal with the Fluoride Ion-Specific Electrode," *Analytical Chemistry*, Vol 46, 1974, pp. 1321–23.

[3] 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.

[4] The last approved version of this historical standard is referenced on www.astm.org.

Base-metal alloy crucibles are acceptable if after a few preliminary firings the weight does not change significantly between tests.

5.4 *Ignition Wire,* 100-mm, nickel-chromium alloy, No. 34 B & S gage, or platinum, No. 34 or No. 38 B & S gage.

5.5 *Ignition Circuit*—A6 to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A step-down transformer connected to an alternating-current lighting circuit or batteries may be used.

5.6 *Balance,* analytical, with a sensitivity of 0.1 mg. The balance shall be checked periodically to determine its accuracy.

5.7 *Specific-Ion Meter*—A pH meter with an expandable millivolt scale, specific-ion meter, sensitive to 0.1 mV, suitable for method of standard addition determinations.[5]

5.8 *Electrodes,* fluoride-sensing, with the appropriate reference-type electrode as recommended by the manufacturer.

5.9 *Laboratory Ware*—All laboratory ware, for example, beakers, bottles, and so forth, used for solutions containing fluoride ions must be made of polyethylene or a heat-resistant polymer such as polypropylene.

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.[6] 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 *Reagent Water*—Reagent water, conforming to Type IV of Specification D1193, shall be used for preparation of reagents and washing of the bomb interior. (**Warning—**Some reagents used in this test method are hazardous. Follow the precautions listed in the Material Safety Data Sheet of the manufacturer for each reagent.)

6.3 *Buffer Solution*—Dissolve 294 g of sodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$) and 20.2 g of potassium nitrate (KNO_3) in approximately 850 mL of water. Adjust the pH to 6.0 with crystalline citric acid ($C_6H_8O_7$) and dilute to 1 L with water.

6.4 *Standard Fluoride Stock Solution* (1000 Mg/g)—Dissolve 2.2101 ± 0.0002 g of Sodium Fluoride (NaF) in water and dilute to 1 L. Mix well. Dry the NaF for 1 h at 105°C and cool to room temperature in a desiccator before weighing.

6.5 *Standard Fluoride Stock Solution* (100 Mg/g)—Dilute 10.0 mL of fluoride stock solution (6.4) to 100 mL in a volumetric flask with water. Mix well.

6.6 *Oxygen,* free of combustible matter and guaranteed to be 99.5 % pure.

6.7 *Sodium Hydroxide, Standard Solution* (1.0 *N*)—Dissolve 40 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

6.8 *Sulfuric Acid, Standard* (5.0 *N*)—Cautiously dilute 142 mL of sulfuric acid (H_2SO_4, sp gr 1.834 to 1.836) to 1 L with water.

6.9 *Sulfuric Acid, Standard* (0.5 *N*)—Cautiously dilute 100 mL of 5.0 *N* H_2SO_4 (6.8) to 1 L with water.

7. Hazards

7.1 *Precautions*—The following precautions are recommended for safe operations in the use of the oxygen combustion bomb. Additional precautions are given in Practice E144, for use of oxygen combustion bombs. Consult the manufacturer's installation and operating manuals before using the calorimeter.

7.1.1 The mass of coal sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

7.1.2 Inspect the bomb parts carefully after each use. Frequently check the threads on the main closure for wear. Replace the cracked or significantly worn parts. Return the bomb to the manufacturer occasionally for inspection and possibly proof testing.

7.1.3 The oxygen supply cylinder should be equipped with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety code. Suitable reducing valves and adaptors for 3 to 5-MPa (approximately 400 to 600-psi) discharge pressure are obtainable from commercial sources of compressed-gas equipment. Check the pressure gage periodically for accuracy.

7.1.4 During ignition of a sample, the operator must not permit any portion of his body to extend over the calorimeter.

7.1.5 Exercise extreme caution when combustion aids are employed so as not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb. Do not fire loose fluffy material such as unpelleted benzoic acid, unless thoroughly mixed with the coal sample.

7.1.6 Do not fire the bomb if it has been filled to greater than 3-MPa (30-atm) pressure with oxygen, if the bomb has been dropped or turned over after loading, or if there is evidence of a gas leak when the bomb is submerged in the calorimeter water.

7.1.7 Hydrofluoric acid (HF) is very corrosive and may hasten corrosion problems with the combustion bomb.

7.1.8 For manually operated calorimeters, the ignition circuit switch shall be of the momentary double-contact type, normally open, except when held closed by the operator. The switch shall be depressed only long enough to fire the charge.

8. Sample

8.1 Prepare the analysis sample in accordance with Method D2013 to pass through a 250-µm (60-mesh) sieve. Pulverize the analysis sample to pass a 150-µm (100-mesh) sieve.

[5] Midgley, D., and Torrance, K., *Potentiometric Water Analysis*, John Wiley and Sons, Inc., New York, NY, 1978.

[6] *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.