Designation: D3761 – 96 (Reapproved 2002)

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 [4]
D2013 Practice for Preparing Coal Samples for Analysis [4]
D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke [4]
D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases [4]
D4621 Guide for Quality Management in an Organization That Samples or Tests Coal and Coke [4]
D5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures [5]
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. 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

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[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] 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] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 05.06.

[5] *Annual Book of ASTM Standards*, Vol 14.04.

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.[6]

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.[7] 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.

8.2 Analyze a separate portion of the analysis sample for moisture content in accordance with Test Method D3173, if calculation to other than the as-determined basis is desired.

9. Procedure for Bomb Combustion

9.1 Thoroughly mix the analysis sample of coal. Carefully weigh approximately 1 g ± 0.1 mg into a previously ignited crucible in which it is to be combusted.

9.2 Transfer 5 mL of 1 *N* NaOH solution into the combustion bomb. Attach the fuse wire to the bomb electrodes. Place the crucible with the sample into the electrode support of the bomb, and insert the fuse wire into the coal sample.

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

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

9.3 Assemble the bomb in the normal manner and charge it with oxygen to a pressure between 2 to 3 MPa (20 to 30 atm). After (20 to 30 atm) insert—Admit the oxygen slowly into the bomb so as not to remove or displace any powdered material from the sample holder. If the oxygen should exceed the specified pressure, do not proceed with the combustion. In this case, detach the filling connection, exhaust the bomb in the usual manner, and discard the sample.

9.4 Place the bomb in a cooling water bath, with water flowing. Attach the ignition wires from the firing circuits, and ignite the sample (**Precaution**–See Section 7). Allow the bomb to remain in the cooling water for 15 min to allow cooling and absorption of soluble vapors.

9.5 Remove the bomb and release the pressure at a uniform rate, such that the operation will require not less than 2 min. Examine the bomb interior and discard the test if unburned or sooty deposits are found.

9.6 Thoroughly rinse the bomb, electrodes, and crucible into a 100-mL beaker with several small washings of water, keeping the volume below 45 mL.

10. Procedure for Ion-Selective Electrode Analysis

10.1 Adjust the pH of the sample to 6.0 with 5.0 N H_2SO_4 and finally to pH 5.0 to 5.2 with 0.5 N H_2SO_4, with constant stirring.

10.2 Heat the solution slightly on a steam bath for 10 min to drive off carbon dioxide (CO_2), and cool to room temperature.

10.3 Add 5.0 mL of the buffer solution (6.3) to the beaker.

10.4 Add 1.0 mL (100 µg) fluoride standard solution (6.5) and adjust the volume to 50 mL ± 5 % with water.

10.5 Prepare at least 5 standards with a concentration range from 50 to 600 µg fluoride by adding 0.5 to 6 mL of fluoride standard solution (6.5) into a 100-mL beaker.

10.6 Prepare a reagent blank by adding 1 mL of fluoride standard solution (6.5) into a 100-mL beaker.

10.7 Adjust the volumes of the standards and blank to 40 mL with water. Follow the same procedure as outlined for the samples in 10.1 and 10.2.

10.8 Add 5.0 mL of the buffer solution (6.3) and adjust the volume to 50 mL ± 5 % with water.

10.9 Repolish the electrode before analyzing the standards and samples (Note 1).

NOTE 1—Electrode response can be affected if the membrane is dirty or etched. Follow the manufacturer's recommended procedure.

10.10 For optimum results, measure electrode response at ambient temperature with constant stirring. Allow the response to stabilize for a period of not less than 3 min.

10.11 Determine the electrode potential of the blank and the standards.

10.12 Construct a calibration curve on semilogarithmic paper. Electrode potentials of standard solutions are plotted on the linear axis against their concentration on the log axis.

10.13 Determine the electrode potential of a fluoride standard, mid-range in concentration. Determine the concentration of the standard from the calibration curve. If the concentration does not differ from the standard value by more than 5 % relative, record the concentration as D1 and proceed with analysis of samples. Otherwise, the stability of the measurement system is suspect. Make necessary adjustments, recalibrate, and proceed with analysis.

10.14 Determine the electrode potential of a maximum of 4 sample solutions.

10.15 Determine the electrode potential of the fluoride standard measured in 10.13. Determine the concentration of the standard from the calibration curve. If the concentration does not differ from the standard value by more than 5 % relative, record the concentration as D2 and repeat 10.12 and 10.13 if further samples are to be analyzed. Otherwise, the stability of the measurement system is suspect. Reject all analyses made to this point. Make necessary adjustments, recalibrate, and proceed with analysis.

11. Calculation

11.1 From the curve, determine the concentration in solution of each sample and record as C_u. Calculate the concentration of fluorine in micrograms per gram (ppm) in the analysis sample, F, as follows:

$$C_s = C_u \times \{C_m/[(D1 + D2)/2]\} \tag{1}$$

where:

C_s = concentration of sample in solution corrected for drift, µg,

C_m = standard value of the mid range standard used to monitor drift

$$F = \frac{C_s - C_b}{W_s} \tag{2}$$

where:

C_s = concentration of sample in solution corrected for drift, µg,

C_b = concentration of blank in solution, µg,

W_s = mass of sample, g.

NOTE 2—Microprocessor pH/mV meters (ion meters) perform the necessary calculations and display the ion concentration directly.

11.1.1 Determine a reagent blank, concurrently with the test determination, using the same amounts of all reagents and following all steps of the procedure.

11.2 The electrode slope constant may be determined as follows:

11.2.1 Add by pipet, 50 mL of standard solution of concentration C_1 to a 150-mL plastic beaker.

11.2.2 Adjust the pH of the solution between 5.0 and 5.5 with H_2SO_4.

11.2.3 Add 5.0 mL of the buffer solution.

11.2.4 Stir the solution and when the electrodes give a steady reading, note the reading, E_1.

11.2.5 Repeat 11.2.1 with a second solution of concentration, C_2. Preferably $C_2 = 10C_1$ and should not be less than $2C_1$.

11.2.6 Repeat 11.2.2 through 11.2.4, noting the steady reading, E_2.

11.2.7 Calculate the slope constant S, which should be about – 58 mV/tenfold increase in concentration at 20°C, by the equation:

$$S = \frac{E_1 - E_2}{\log C_1 - \log C_2} \tag{3}$$

12. Report

12.1 The results of the fluorine analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

12.2 Use the percent moisture, as determined by Test Method D3173, in the analysis sample passing a 250-µm (No. 60) sieve, to calculate the results of the analysis to a dry basis.

12.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Practice D3180.

13. Precision and Bias [8]

13.1 *Precision*—The relative precision of this test method is being determined.

NOTE 3—Since the technical aspects of this test method have been altered, the prior repeatability and reproducibility statements must be re-examined. They are included in this note for indicative purposes only.

Repeatability—Results of two consecutive determinations carried out in the same laboratory by the same operator using the same apparatus should not differ by more than 15 µg/g (ppm).

Reproducibility—The means of results of duplicate determinations carried out by different laboratories on representative samples taken from the bulk sample after the last stage of reduction should not differ by more than 15 µg/g (ppm) (see 13.1).

13.2 *Bias*—The bias of this test method cannot be determined at this time.

14. Keywords

14.1 bomb combustion method; calorimeter; coal; coal products; fluorine content; ion-selective electrode

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[8] Supporting data are available from ASTM Headquarters. Request RR:D05-1004.