Designation: D 5987 – 96 (Reapproved 2002)

Standard Test Method for Total Fluorine in Coal and Coke by Pyrohydrolytic Extraction and Ion Selective Electrode or Ion Chromatograph Methods[1]

This standard is issued under the fixed designation D 5987; 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 analysis of total fluorine in coal and coke.

1.2 This analysis was successfully tested on coals containing 37 % ash or less (see AS 1038.10.4 and Conrad[2]).

1.3 The values stated in SI units shall be regarded as 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 Note 4.

1.5 All accountability and quality control aspects of Guide D 4621 apply to this test method.

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[3]

D 1193 Specification for Reagent Water[4]

D 2013 Practice for Preparing Coal Samples for Analysis[3]

D 2234 Practice for Collection of a Gross Sample of Coal[3]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[3]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[3]

D 4621 Guide for Quality Managment in an Organization that Samples or Tests Coal and Coke[3]

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal or Coke by Instrumental Procedures[3]

2.2 *Australian Standard:*[5]

AS 1038.10.4 Determination of Trace Elements—Coal, Coke and Fly-Ash-Determination of Fluorine Content—Pyrohydrolysis Method

3. Summary of Test Method

3.1 Total fluorine is determined in this test method by first subjecting the weighed test portion to pyrohydrolytic conditions which separate fluorine from the coal/coke matrix. The pyrohydrolysate is then gravimetrically processed and final determinations are made by either ion-selective electrode or ion chromatographic techniques.

4. Significance and Use

4.1 This test method permits measurement of the fluorine content of coal and coke 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 released from the coal and retained in the pyrohydrolysate so that it is representative of the total fluorine concentration in coal.

5. Apparatus

5.1 *Laboratory Ware*—Except as noted, all laboratory ware, for example, volumetric flasks, beakers, bottles, etc., used for solutions containing fluoride ions must be made of polyethylene, polystyrene, or a heat-resistant polymer such as polypropylene.

5.2 *Vials*—Glass or polystyrene, 10 to 30-mL capacity with tightly fitting snap-on plastic lids.

5.3 *Bottles*—Polypropylene, 125-mL capacity, wide-mouth, with liner-less leakproof polyethylene screw cap, for tube-furnace pyrohydrolysate processing.

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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] Conrad, V. B., and Brownlee, W. D., "Hydropyrolytic—Ion Chromatographic Determination of Fluoride in Coal and Geological Materials," *Analytical Chemistry*, Vol 60, No. 4, 1988, pp. 365–369.

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

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

[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

5.4 *Vials*—Polystyrene, 70-mL capacity, with liner-less leakproof polyethylene screw cap.

5.5 *Dispensing Bottles*—Polyethylene, 250-mL capacity, for the standard fluorine solution (6.3.1) and of 600-mL capacity for the absorption solution (6.3.3) and buffer (6.3.5).

5.6 *Micropipettes*—Polypropylene or other suitable polymer, variable volumes ranging from 0.1 mL to at least 2.0 mL. This is a satisfactory alternative to the 250-mL dispensing bottle (5.5), for the delivery of small volumes of the standard fluorine solution.

5.7 *Glass Dropper Bottle*—30-mL capacity for dispensing glacial acetic acid.

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

5.9 *Apparatus for Tube-Furnace Pyrohydrolysis* (see Fig. 1):

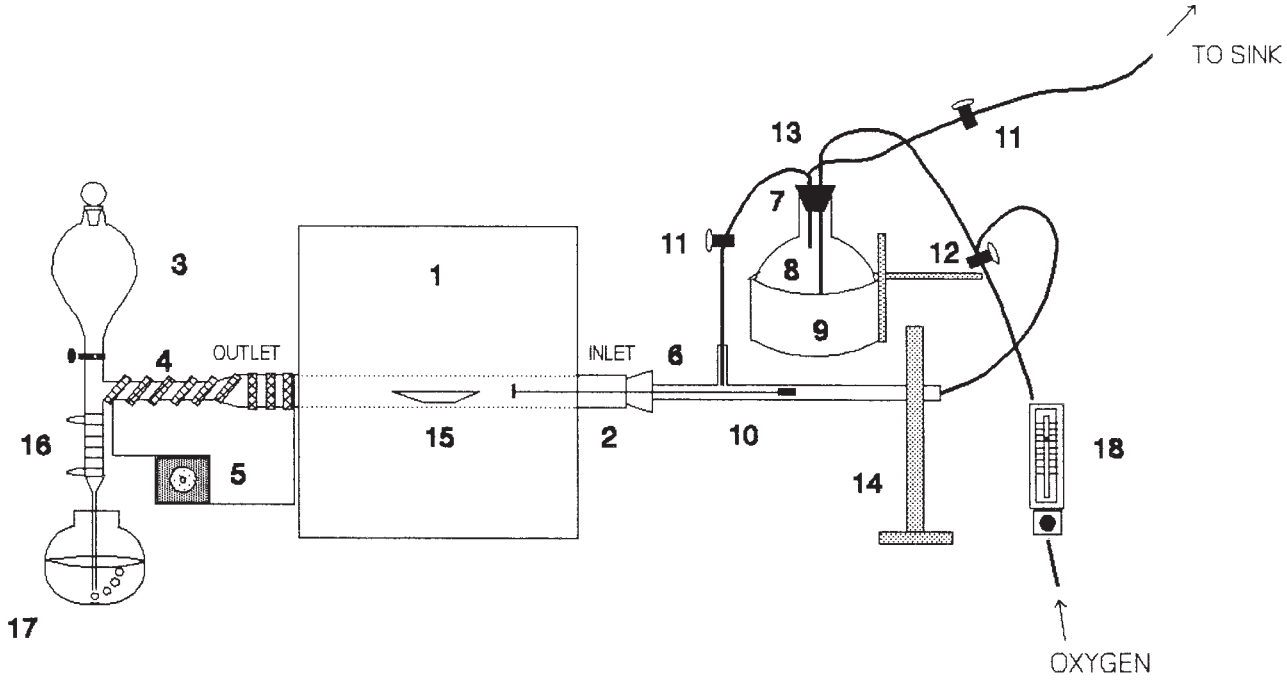
5.9.1 *Silica Tube-Furnace and Accessories*:

5.9.1.1 *Quartz Combustion Tube*—Translucent, pure silica (25-mm outside diameter, 20-mm inside diameter) of length appropriate to the particular furnace used. Preferably, the gas outlet end should be narrowed to a tubulure of approximately 7 mm in diameter.

NOTE 1—Combustion tubes of alternative refractory compositions do not have adequate thermal stress characteristics for operation with this test method.

5.9.1.2 *Silicone Stoppers*—20 mm in diameter, positioned at inlet end and outlet, if applicable, of silica combustion tube (5.9.1.1).

5.9.1.3 *Combustion Boats*—Unglazed porcelain, high alumina content, approximately 97 mm by 16 mm by 12 mm, preheated at 1000°C for 1 h.



1. FURNACE (5.9.1e)
2. SILICA TUBE (5.9.1a)
3. SEPARATORY FUNNEL (5.9.3a)
4. HEATING TAPE (5.9.1f)
5. POWER REGULATOR (5.9.1f)
6. SILICONE STOPPER (5.9.1b)
7. RUBBER STOPPER
8. ROUND BOTTOM FLASK (5.9.2a)
9. HEATING MANTLE (5.9.2b)
10. BOROSILICATE T-TUBE AND SILICA PUSHER (5.9.1d)
11. STOPCOCKS (5.9.2e)
12. THREE-WAY STOPCOCK (5.9.2e)
13. Y-PIECE (5.9.2c)
14. RETORT STAND AND CLAMP
15. COMBUSTION BOAT (5.9.1c)
16. GRAHAM CONDENSER (5.9.3b)
17. RECEIVING FLASK (5.9.3c)
18. FLOWMETER (5.9.2f)

FIG. 1 Pyrohydrolysis Furnace and Fluorine Absorption Assembly

5.9.1.4 *Silica Pusher and T-Tube*—A silica push rod of dimensions 5 mm in diameter by 50 cm long, fused at one end to provide a flat disk surface of 10 to 12 mm in diameter and having a piece of magnetic steel affixed to the other end by epoxy resin. The T-tube, 50 cm long, is composed of borosilicate glass and protrudes 10 mm into the silica tube (5.9.1.1) through a stopper (5.9.1.2). A magnet is used to move the pusher inside the T-tube.

5.9.1.5 *Combustion Furnace*—Capable of reaching a maximum temperature of at least 1100°C.

5.9.1.6 *Heating Tape and Power Regulator*—To prevent condensation from forming in the outlet end of the combustion train.

5.9.2 *Steam Generator (Fig. 1)*:

5.9.2.1 *Round Bottom Flask*—Glass, 2-L capacity.

5.9.2.2 *Heating Mantle*—Of size sufficient to heat the round bottom flask (5.9.1.1).

5.9.2.3 *Y-piece*—Glass, 10 mm in diameter.

5.9.2.4 *Gas Distribution Tube*—Zero porosity.

5.9.2.5 *Stopcocks*—One three-way and one two-way.

5.9.2.6 *Flowmeter*—Capable of regulating and delivering at least 1000 mL/min of the oxygen.

5.9.3 *Absorption Vessel Components*:

5.9.3.1 *Separatory Funnel*—Glass, 125-mL capacity for rinsing Graham Condenser into receiving flask, with stopcock and 24/40 joint with drip tip.

5.9.3.2 *Graham Condenser*—For condensing hydropyrolysate, with 24/40 outer joint at top. Water jacket length should be 300 mm.

5.9.3.3 *Receiving Flask*—250-mL capacity, flat bottom, wide neck, and tooled mouth, for collection of pyrohydrolysate.

5.10 *Ion-specific Electrode (ISE) Measurement Apparatus*:

5.10.1 *Specific Ion Meter*—A pH meter with an expandable millivolt scale sensitive to 0.1 mV, specific-ion meter or equivalent, suitable for method of standard addition determinations.[6]

5.10.2 *Electrodes*—Solid-state fluoride sensing, with the appropriate reference-type electrode as recommended by the manufacturer.

NOTE 2—The fluoride sensing element should be polished frequently and in accordance with the manufacturer's suggestions to prolong its optimal performance.

5.10.3 *Magnetic Stirrer*—Complete with polytetrafluoroethylene (PTFE) stirring bars and magnet for convenient removal of bars from vials.

5.11 *Ion-Chromatograph (IC)*—Equipped with three, 3 by 250-mm AS-3 anion separator columns and a fiber suppressor.[7]

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all chemicals shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8] 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 D 1193, shall be used in all cases unless otherwise indicated. (**Warning—**Some reagents used in this test method are hazardous. Follow the precautions listed in the Material Safety Data Sheets of the manufacturer for each reagent.)

6.3 *Solutions for ISE Test Method*:

6.3.1 *Standard Fluoride Solution* (1 g = 200 µg fluoride)—The following standard fluoride solutions are required:

6.3.1.1 *For Direct Comparison Method*—Dissolve 0.2210 ± 0.0002 g of dry (110°C for 1 h) sodium fluoride in approximately 400 mL of water in a 500-mL polypropylene beaker. Transfer by thorough rinsing with water to a 500-mL polypropylene volumetric flask. Dilute to mark with water and mix. Discard after one month.

NOTE 3—There will not be a classic meniscus in polypropylene volumetrics. The solution will correctly appear to have a flat surface.

6.3.1.2 *For Analyte-Addition Test Method*—Dissolve 0.2210 ± 0.0002 g of dry (110°C for 1 h) sodium fluoride in a 500-mL polypropylene beaker containing 150 mL of water and 250 mL of an unspiked buffered absorption solution (see 6.3.3). Transfer, by thorough rinsing with water, to a 500-mL polypropylene volumetric flask. Dilute with water to the mark and mix. Discard after one month (see Note 3).

6.3.2 *Absorption Solution* (0.025 *M* NaOH)—Dissolve 2.0 g of sodium hydroxide in about 500 mL of water. Transfer to a 2.0-L polypropylene flask, dilute to mark with water, and mix.

6.3.3 *Unspiked Buffered Absorption* (pH 6.5)—Dissolve 10.0 g of potassium nitrate, 2.0 g of sodium hydroxide, and 115 g of ammonium acetate in 1700 mL of water. Adjust pH to 6.5 with a small amount of glacial acetic acid. Transfer to a 2.0-L polypropylene flask, dilute to mark with water, and mix.

6.3.4 *Buffer Added After Tube-Furnace Hydrolysis* (pH 6.5)—Dissolve 10.0 g of potassium nitrate and 115 g of ammonium acetate in 350 mL of water. Adjust pH to 6.5 with a small amount of glacial acetic acid. Transfer to a 500-mL polypropylene volumetric flask, dilute to mark with water, and mix.

6.3.5 *Solution for Conditioning Fluoride ISE*—Using a pipette, transfer 20.0 mL of water, 20.0 mL of absorbing solution (6.3.2), and 10.0 mL of buffer (6.3.4) into a polystyrene vial (5.2). Add 200 µL of standard fluoride solution (6.3.1.1) and mix.

6.4 *Solutions for Ion-Chromatographic Measurement*:

6.4.1 *Standard Fluoride Solution* (1000 µg/mL fluoride)—Dissolve 2.2110 ± 0.0002 g of dry (105°C for 1 h) sodium

[6] Midgley, D., and Torrance, K., "Potentiometric Water Analysis," John Wiley and Sons, 1978.

[7] Rice, T. D., *Analytica Chimica Acta*, 1983, 151, pp. 383–389.

[8] *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.

fluoride in a 250-mL polypropylene beaker containing approximately 150 mL of water. Transfer with thorough rinses of water to a 1.0-L polypropylene volumetric flask. Dilute with water to the mark and mix (see Note 3).

6.4.2 *Standard Fluoride Solution* (1.0 µg/mL fluoride)—Transfer, by means of polypropylene pipette, 1.0 mL of standard fluoride solution (6.4.1) to a 1.0-L polypropylene volumetric flask; dilute to mark with water and mix (see Note 3). Prepare fresh solution daily.

6.4.3 *Sulfuric Acid, Standard* (2.5 *N*)—Cautiously dilute 71 mL of sulfuric acid (H_2SO_4, sp gr 1.834 to 1.836) to 1 L with water. Mix well.

6.4.4 *Sulfuric Acid, Standard* (0.025 *N*)—For use as suppressor regenerator. Using a pipette, cautiously dilute 10.0 mL of 2.5 *N* H_2SO_4(6.4.3) to 1 L with water. Mix well.

6.4.5 *Sodium Bicarbonate Solution* (0.0015 *M*)—Weak eluent, for use as the absorbing solution and the Graham condenser rinsing solution. Dissolve 0.2520 g of dry (105°C for 1 h) $NaHCO_3$ in water and dilute to 2.0 L. Mix well.

6.4.6 *Sodium Bicarbonate Solution* (0.02 *M*)—Strong eluent. Dissolve 1.6801 g of dry (105°C for 1 h) $NaHCO_3$ in water and dilute to 1.0-L. Mix well.

6.5 *Oxygen*—Free of combustible matter and guaranteed to be 99.5 % pure.

6.6 *Helium*—Refer to ion chromatograph manufacturer's recommendations for gas specifications.

7. Sample

7.1 Prepare the analysis sample in accordance with Method D 2013 or Practice D 346 to pass a 250-µm (60-mesh) sieve. Pulverize the analysis sample to pass a 75-µm (200-mesh) sieve.

7.2 Analyze a separate portion of the analysis sample for moisture content in accordance with Test Method D 3173 or Test Methods D 5142 if calculation to other than as-determined basis is desired. As an alternative, dry the analysis sample at 105 to 110°C for 2 h prior to weighing. Transfer the dried sample to a desiccator, and weigh for analysis promptly upon cooling, which will be approximately 10 min.

8. Procedure for Pyrohydrolysis

8.1 *Test Preparation*:

8.1.1 Thoroughly mix the analysis sample of coal or coke. Carefully weigh 1 g ± 0.1 mg into the combustion boat (5.9.1.1).

8.1.2 Program the reagent and apparatus blank tests (in duplicate) for the beginning, middle, and completion of the processing of the test samples.

8.2 *Tube-Furnace Pyrohydrolysis*:

8.2.1 *Apparatus Conditioning*—Add a few boiling chips and four sodium hydroxide pellets to the round-bottom flask (5.9.2.1) containing 1600 mL of water. Allow the steam generator to achieve a gentle boil. Place an empty receiving flask (5.9.3.3) under the Graham condenser. With the furnace set at an operational temperature of 1100°C, pass oxygen through the steam generator into the furnace at approximately 1000 mL/min for 15 min.

8.2.2 *Pyrohydrolysis*:

8.2.2.1 Add 50 ± 1 mL of the appropriate absorption solution (6.3.2) for ISE finish or 65 ± 1 mL of the absorption solution (6.4.5) for the IC finish to a clean receiving flask (5.9.3). Place the flask underneath the condenser. Ensure that cooling water is passing through the condenser.

8.2.2.2 Allow oxygen to flow, bypassing the steam generator, at 750 mL/min into the furnace. Place the analysis sample boat into a zone at which the temperature of the sample will not exceed 300°C. Redirect the oxygen flow through the steam generator and into the furnace. At subsequent intervals of approximately 30 s, push the analysis sample boat into hotter zones with the temperature not exceeding 400, 500, 750, and 1000°C, with a final push into the hottest zone.

8.2.2.3 Continue the pyrohydrolysis for a further 15 min, while monitoring the flow of oxygen and the level of water in the round bottom flask.

8.2.3 *Pyrohydrolysate Processing for ISE Finish*:

8.2.3.1 At the completion of the pyrohydrolysis time, redirect the oxygen flow around the steam generator and allow excess steam to escape.

NOTE 4—Caution should be exercised as to the direction in which the steam is vented. Preferably it should be allowed to escape into a sink or similar facility.

8.2.3.2 Rinse the condenser with two 5-mL aliquots of water through the separatory funnel (5.9.3.1).

8.2.3.3 Rinse the pyrohydrolysate into a tared polypropylene bottle (5.3) with a small amount of water and allow to cool to room temperature.

NOTE 5—With an oxygen flow of 750 mL/min, the correct heating rate on the steam generator and controlled washings, the total mass of pyrohydrolysate at this stage should be approximately 100 g.

8.2.3.4 Place the bottle containing the pyrohydrolysate on the balance and add approximately 0.75 g of standard fluoride solution (6.3.1.1) by means of a dispensing bottle or adjustable micropipette. The increase in mass allows calculation of the amount of fluorine added.

8.2.3.5 Dilute with water to 100 ± 0.1 g, if necessary and mix. Otherwise, record the mass of pyrohydrolysate and mix.

8.2.3.6 Using a polypropylene pipette, transfer 40.0 mL of pyrohydrolysate to a polystyrene vial (5.4). Transfer, by means of a pipette, 10.0 mL of buffer (6.3.4) needed to achieve a buffer concentration of 20 % (m/m). Seal vial and set aside for future measurement.

8.2.4 *Pyrohydrolysate Processing for IC Finish*:

8.2.4.1 At the completion of the pyrohydrolysis time, redirect the oxygen flow around the steam generator and allow excess steam to escape (see Note 4).

8.2.4.2 Rinse the condenser with a 50-mL aliquot of 0.0015 *M* $NaHCO_3$ (6.4.5) through the separatory funnel (5.9.3.1).

8.2.4.3 Transfer to a 200-mL polypropylene volumetric flask with rinsings of the 0.0015 *M* $NaHCO_3$(6.4.5).

8.2.4.4 Allow to cool to room temperature, dilute to the mark with the 0.0015 *M* $NaHCO_3$ (6.4.5), and mix (see Note 3).

9. Procedure for Ion-Selective Electrode Analysis

9.1 *Direct Comparison ISE Test Method*:

9.1.1 Add 50.0 ± 1 mL of absorption solution (6.3.2) to each of four tared 125-mL bottles (5.3).

9.1.2 Add approximately 500, 1000, 1500, and 2000 µL of standard fluorine solution (6.3.1.1) to each of the bottles, respectively. Weigh each addition to the nearest milligram. Dilute with water to 100.0 ± 0.05 g net and mix. Label the bottles S1, S2, S3, and S4. These solutions contain approximately 100, 200, 300, and 400 µg of fluorine in 100 g of solution. Add an exactly measured amount of buffer (6.3.4) to 40.0 mL of each of these solutions, in the same way as for the samples (see 8.2.3.5).

9.1.3 Insert the electrodes to a depth of approximately 20 mm into the conditioning solution (6.3.5).

9.1.4 Allow the measurement solution to reach ambient temperature before measurement. Place a stirring bar into the solution and a thermal mat between the vial and the magnetic stirrer. Remove electrodes (5.10.2) from the stirred conditioning solution (6.3.5) and stir the measurement solution for 5 to 10 s before inserting electrodes to a depth of approximately 20 mm and dislodging any air bubbles from the sensing element of the electrodes. During this 5 to 10-s period, gently shake into a waste beaker most of the adhering solution from the electrode tips. Record the potential to the nearest 0.1 mV after 2 to 3 min.

NOTE 6—This reading should not change by more than 0.1 mV during the next 2 min, provided that the sensing element has been polished and the reference electrode is functioning properly and contains fresh filling solution.

9.1.5 Remove electrodes from the measurement solution, briefly rinse with water into a waste beaker, and insert into the stirred conditioning solution (6.4.5) for at least 30 s before removing and inserting into the next measurement solution, as described in 9.1.4.

9.1.6 The electrodes are subject to minor drifting throughout the batch of measurements and some significant improvements in accuracy and precision are achieved by monitoring this drift. Proceed with readings by reading S2 before any other solution. Read S1, S3, S4, and then S2 again. Subsequently, read S2 after every four processed samples or blank solutions and finally against the completion of the batch. Linear adjustments of the bracketed sample/standard/blank solution's measurements are then possible, to achieve optimal data quality.

9.2 *Analyte-Addition ISE Test Method*:

9.2.1 Place the electrodes in the stirred conditioning solution (6.3.5).

9.2.2 Determine the slope of the electrode in accordance with the procedure given in 11.4.1.

9.2.3 Proceed as described in 9.1.3. Record the potential after 2 to 3 min, to the nearest 0.1 mV (E_1).

9.2.4 With the aid of a top-loading balance and a polyethylene dispensing bottle (5.5) or other suitable device, add between 0.5 and 3.0 g, measured to the nearest 0.1 mg, of standard fluoride solution (6.3.1.2) so that the meter reading falls by 20 to 30 mV. After 2 to 3 min, record the potential to the nearest 0.1 mV (E_2).

9.2.5 Remove electrodes from measurement solution, briefly rinse with water into a waste beaker and insert into stirred conditioning solution (6.3.5) for at least 30 s before removing and inserting into the next measurement solution as described in 9.1.3. Record the temperature of the measured solution to the nearest 0.2°C.

10. Ion-Chromatographic Procedure

10.1 Because of the differences between various makes and models of instruments, all instrumental operating instructions can not be provided. Instead, the analyst shall refer to the instructions provided by the manufacturer of the particular instrument.

10.1.1 Calibrate the selected instrument and analyze the pyrohydrolyzed samples according to the instrument manufacturer's instructions.

11. Calculations

11.1 *General*—Depending upon the particular procedure used to measure the amount of fluorine in the pyrohydrolysate, one of the equations outlined in subsequent clauses will be required. In each case, the mass of fluorine is calculated for each sample and blank test solution, and the concentration of fluorine in the sample is calculated from the following equation:

$$F_{ad} = \frac{m_f\,(\text{sample}) - m_f\,(\text{blank})}{m_s} \quad (1)$$

where:

F_{ad} = fluorine in the sample, mg/g,
m_f = mass of fluorine in sample or blank pyrohydrolysate, mg, and
m_s = mass of sample taken for pyrohydrolysis, g.

11.2 *Direct-Comparison ISE Test Method Following Tube-Furnace Pyrohydrolysis*—Normalize the concentrations of fluorine in the calibration solutions to micrograms per nominal buffered aliquot mass (50 g, that is, 40 g pyrohydrolysate + 10 g buffer; however, any convenient 4 to 1 dilution is admissible). Using the data obtained for the calibration solutions, graph the *logarithm* of fluorine concentration versus potential (mV). Then

$$m_f = \frac{c_2\,(m_a + m_b)}{m_n m_a}\,m_p - c_1 m_1 \quad (2)$$

where:

m_f = mass of fluorine in sample or blank test pyrohydrolysate, µg,
c_2 = mass of fluorine per nominal mass (m_n g) of buffered aliquot solution, from graph, µg,
m_a = mass of aliquot of pyrohydrolysate, g,
m_b = mass of buffer added to aliquot, g,
m_p = actual mass of sample or blank test pyrohydrolysate, g,
m_n = nominal mass of aliquot plus buffer, g + 50 g (from method),
c_1 = concentration of standard fluoride solution (6.3.1.1) µg/g,
= 200 µg/g (from method), and
m_1 = mass of standard fluoride addition (6.3.1.1) into pyrohydrolysate, g.

11.3 *Analyte Addition ISE Test Method Following Tube-Furnace Pyrohydrolysis*—Calculate the mass of fluorine from the following equation:

$$m_f = \frac{cm_p m_2}{m_a\left[\left(1+\frac{m_2}{(m_a+m_b)}\right)\left(\text{antilog}_{10}\frac{(E_1-E_2)298}{ST}-1\right)\right]} - cm_1 \quad (3)$$

where:

m_f = mass of fluorine in sample or blank test pyrohydrolysate, µg,
c = concentration of standard solution (6.3.1.2), µg/g,
m_p = mass of sample or blank test pyrohydrolysate, g,
m_2 = mass of standard solution (6.3.1.2) added to achieve potential E_2, g,
m_a = mass of aliquot of pyrohydrolysate, g,
m_b = mass of buffer added to aliquot, g,
E_1 = initial potential of buffered spiked pyrohydrolysate, mV,
E_2 = final potential of buffered spiked pyrohydrolysate after addition of standard fluoride solution (6.3.1.2), mV,
S = electrode slope constant. The 25°C slope of the electrode in millivolts per decade concentration (see section 11.4),
T = temperature of solution at time of measurement, °K, and
m_1 = mass of standard solution (6.3.1.2) added, g.

11.4 The electrode slope constant may be determined as follows:

11.4.1 Add by pipet, 50 mL of standard solution of concentration c_1 to a 150-mL plastic beaker.

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

11.4.3 Add 5.0 mL of the buffer solution.

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

11.4.5 Repeat 11.4.1 with a second solution of concentration, c_2. Preferably $c_2 = 10c_1$ and should not be less than $2c_1$.

11.4.6 Repeat 11.4.2-11.4.4, noting the steady reading, E_2.

11.4.7 Calculate the slope constant S, which should be about − 58 mV per tenfold increase in concentration at 20°C, by the equation

$$S = \frac{E_1 - E_2}{\log C_1 - \log C_2} \quad (4)$$

11.5 *IC Test Method*—Using the data obtained for the calibration solutions, graph concentration of fluorine in pyrohydrolysate versus IC instrument response (for example, recorder divisions or peak area). Note that all calibration solutions, sample and blank test pyrohydrolysate concentrations have to be normalized to µg/200 g for the tube-furnace. Then

$$m_f = \frac{c_2 m_p}{m_n} \quad (5)$$

where:

m_f = mass of fluorine in sample or blank test pyrohydrolysate, µg,
c_2 = normalized concentration of fluorine in sample or blank test pyrohydrolysate, in µg/200 g for tube-furnace pyrohydrolysis,
m_p = actual mass of sample or blank test pyrohydrolysate, g, and
m_n = nominal mass of sample or blank test pyrohydrolysate, in grams, − 200 g for tube-furnace pyrohydrolysis.

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 D 3173 or Test Methods D 5142, in the analysis sample passing a No. 60 (250-µm) sieve, to calculate the results of the analysis sample to a dry basis.

12.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Practice D 3180.

Reporting of Result

Magnitude of Result	Precision, µg/g
<100	Nearest 1
≥100 >500	Nearest 5
≥500	Nearest 10

13. Precision and Bias

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

NOTE 7—The precision of this test method for the concentration range of fluorine from 20 to 120 µg/g as established by a study conducted in Australia is as follows:

13.1.1 *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 10 µg/g at the 95 % level of confidence.[2]

13.1.2 *Reproducibility*—The means of results of duplicate determinations carried out by different laboratories on representative samples taken from the bulk sample after the last state of reduction should not differ by more than 20 µg/g at the 95 % level of confidence.[2]

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

14. Keywords

14.1 coal; coal products; coke; fluorine content; ion chromatograph; ion-selective electrode; pyrohydrolysis; tube-furnace