Designation: E815 – 17

Standard Test Method for Determination of Calcium Fluoride in Fluorspar by Complexometric Titrimetry[1]

This standard is issued under the fixed designation E815; 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 calcium fluoride in acid-grade fluorspar and other types of fluorspar that can be rendered soluble by the procedure described in the test method.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 This test method has been evaluated in accordance with Practice E1601 and Guide E1763. Unless otherwise noted in the precision and bias section, the lower limit in the scope of each method specifies the lowest analyte content that may be analyzed with acceptable error (defined as a nominal 5 % risk of obtaining a 50 % or larger relative difference in results on the same test sample in two laboratories).

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.*

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]

D1193 Specification for Reagent Water
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E276 Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal-Bearing Ores and Related Materials
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method
E1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods (Withdrawn 2015)[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 The sample is decomposed by digesting with HNO_3 and $HCLO_4$ and the fluorine is expelled by fuming. The residue is dissolved in dilute HCL, the solution made alkaline, and the calcium titrated with standard EDTA solution. Calcium present as carbonate is determined in a separate sample with EDTA solution, after extracting the former with dilute acetic acid. A correction for calcium fluoride, solubilized by dilute acetic acid digestion, is applied by determining the fluoride in the acetic acid extract by fluoride ion-selective electrode. The CaF_2 content is then calculated.

5. Significance and Use

5.1 Fluorspar is used as a flux in the steelmaking and glass industry, and in the manufacture of HF.

5.2 This test method is intended to be used for compliance with compositional specifications for calcium fluoride content. It is assumed that all who use these procedures will be trained

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[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

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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.

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

analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory and that proper waste disposal procedures will be followed. Appropriate quality control practices must be followed such as those described in Guide E882.

6. Interferences

6.1 None of the elements normally found in fluorspar interfere with this test method.

7. Apparatus

7.1 *Fluoride Ion-Selective Electrode.* [4]

7.2 *Magnetic Stirrer and TFE-Fluorocarbon-Coated Spin Bar.*

7.3 *pH Meter with High Impedance*—Suitable for ion-selective electrode.

7.4 *Polyethylene Beakers,* 100-mL.

7.5 *Single Junction Ag/AgCl Reference Electrode.* [5]

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents 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 sufficient 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 reagent water conforming to Type I or II of Specification D1193. Type III or IV may be used if they effect no measurable change in the blank or sample.

8.3 *Acetic Acid Solution* (1 + 10) —Mix 1 volume of glacial acetic acid (CH_3COOH) with 10 volumes of water.

8.4 *Calcium Carbonate,* high purity (minimum 99.95 % $CaCO_3$).

8.5 *Ethylenediaminetetraacetic Acid Disodium Salt (EDTA)*-—$Na_2C_{10}H_{14}O_8N_2{\cdot}2H_2O$ *Solution* (0.025 mol/L)—Dissolve 9.3062 g of EDTA in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

8.6 *Hydroxynaphthol Blue Indicator*— Grind 0.2 g of the salt with 50 g sodium chloride (NaCl).

8.7 *Potassium Acetate Buffer*—Dilute 283 mL of glacial acetic acid (CH_3COOH) to 1200 mL with water. While cooling and stirring, add KOH solution B (8.9) to adjust the pH to 5.0 (approximately 350 mL of KOH solution B are required).

8.8 *Potassium Hydroxide Solution A*—Dissolve 225 g of KOH in water and dilute to 1 L with water. Store in a plastic bottle.

8.9 *Potassium Hydroxide Solution B*—Dissolve 500 g of KOH in water and dilute to 1 L. Store in a plastic bottle.

8.10 *Sodium Fluoride Solution*—Dissolve 0.2210 g sodium fluoride (NaF) in water in a polyethylene beaker and dilute to 1 L in a volumetric flask. Store in a stoppered polyethylene bottle. This solution has a concentration of 1 mL = 0.10 mg F^- and is stable for 6 months.

8.11 *Triethanolamine Solution* (1 + 1) —Mix 50 mL of triethanolamine ($NC_6H_{15}O_3$) with 50 mL of water.

9. Hazards

9.1 For precautions to be observed in this method, refer to Practice E50.

10. Sampling, Test Specimens, and Test Units

10.1 Pulverize the test units so that 95 % passes a No. 100 mesh sieve (150-µm) as directed in Test Methods E276.

11. Calibration and Standardization

11.1 *Standardization*—Weigh and transfer 2.4970 g of $CaCO_3$ (dried at 110 °C for 1 h and cooled in a desiccator) to a 600-mL beaker. Using a hood and appropriate personal protective equipment, cautiously add 75 mL of HCl and warm. Cool, transfer to a 1-L volumetric flask, dilute to volume with water, and mix. This solution has a concentration of 1 mL = 1.0000 mg of calcium.

11.1.1 *Titration:*

11.1.1.1 Transfer a 50.00-mL aliquot of this solution to a 400-mL beaker, add 5 mL of triethanolamine (8.11), dilute to 200 mL, make just alkaline with KOH solution A (8.8), using a strip of litmus paper, and then add an additional 15 mL of KOH solution A (8.8).

11.1.1.2 Add 0.2 g of hydroxynaphthol blue indicator and titrate immediately with 0.025 *M* EDTA solution (8.5). At the equivalence point, the color changes from pink to blue. Determine the calcium equivalent of the EDTA solution as follows:

$$1\text{ mL of EDTA solution} = (50.0/V) = C\text{ mg of calcium} \qquad (1)$$

where:

V = milliliters of EDTA used.

NOTE 1—If a sample with a known CaF_2 content is available, the standardization with $CaCO_3$ can be omitted. The "standard" CaF_2 sample should then be carried through all steps of the procedure.

11.2 *Calibration*—Transfer 10 mL of acetic acid (1 + 10) (8.3) into a series of seven 100-mL polyethylene beakers and add 20 mL of potassium acetate buffer (8.7). Potential measurements in calibration standards and sample should be carried out concurrently. Add standard fluoride solution (8.10) and water as follows:

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[4] Thermo Scientific Orion model 94-91 has been found suitable for this purpose.

[5] Thermo Scientific Orion model 90-01-00 Single Junction Reference Electrode has been found suitable for this purpose.

[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 the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

Test	Standard F^- mL	Solution mg	Water, mL
1	0	0	5
2	0.5	0.05	4.5
3	1.0	0.10	4.0
4	2.0	0.20	3.0
5	3.0	0.30	2.0
6	4.0	0.40	1.0
7	5.0	0.50	0

Stir the solution, immerse the electrodes (7.1 and 7.5) and wait for 3 min to 5 min for potential to reach equilibrium. Record the potential in millivolts. Plot millivolts (linear scale) versus F^- concentration in milligrams (log scale).

12. Procedure

12.1 *Determination of Total Calcium:*

12.1.1 Transfer approximately 0.50 g of the sample to a small weighing bottle, previously dried at about 105 °C. Dry the bottle and contents for 1 h at 105 °C to 110 °C. Cap the bottle and cool to room temperature in a desiccator. Momentarily release the cap to equalize the pressure and weigh the capped bottle to the nearest 0.1 mg. Repeat the drying and weighing until there is no further loss of mass. Transfer the sample to a 400-mL beaker and reweigh the capped bottle to the nearest 0.1 mg. The difference between the two masses is the mass of the sample taken for analysis.

12.1.2 *Decomposition of Sample*—Add 5 mL of HNO_3, cover with a watch glass, and digest on a hot plate. Cool somewhat, add 5 mL of $HClO_4$, and evaporate first to fumes of $HClO_4$. When decomposition appears to be complete, tilt the cover and evaporate carefully to complete dryness. Allow to cool, add 5 mL of HCl, dilute to approximately 50 mL with water, and heat until all the soluble salts have dissolved. This is the main solution.

NOTE 2—If an insoluble residue remains, filter through a fine-textured paper, wash the paper thoroughly with hot HCl, ignite the paper and residue in a platinum crucible, treat the insoluble residue again with HNO_3 and $HClO_4$ as in sample decomposition, and combine this solution with the main filtrate. If the volume exceeds 90 mL, evaporate the volume to about 80 mL and cool.

12.1.3 Transfer the solution to a 100-mL volumetric flask, dilute to volume, and mix.

12.1.4 Transfer an appropriate aliquot (20.00 mL in the range from 80 % to 100 % CaF_2 and 25.00 mL in the range from 40 % to 80 % CaF_2) to a 400-mL beaker. Add 5 mL of triethanolamine (8.11). Make the solution just alkaline with KOH solution A (8.8) and add 15 mL of additional KOH solution A (8.8). Titrate with EDTA solution as described in 11.1.1.

NOTE 3—As used in this test method (except as related to the term *relative standard deviation*), "percent or "%" refers to mass fraction (wt/wt) of the form g/100g.

12.2 *Determination of Soluble Calcium:*

12.2.1 Transfer 1.00 g of sample to a 250-mL beaker. Add 20 mL of acetic acid (1 + 10) (8.3) and digest at just below boiling point for 60 min. Cool, filter through a fine-textured filter paper, and wash five times with acetic acid (1 + 10) (8.3), collecting the filtrate and washings into a 50-mL volumetric flask. Dilute the contents to mark with water.

12.2.2 Pipet a 25-mL aliquot into a 400-mL beaker and evaporate to dryness. Redissolve the residue in 1 mL to 2 mL of HCL and dilute to 200 mL with water. Add 5 mL of triethanolamine (8.11) and proceed as in total calcium determination. Record the titration. Calculate milligrams of calcium in the 50-mL volume by multiplying the titration (in milliliters) by 2C (proceed as in 11.1).

12.2.3 Transfer a 10-mL aliquot into a 100-mL polyethylene beaker, add 20 mL of potassium acetate buffer (8.7) and 5 mL of water, and mix (pH should be 5.0). Measure the potential in millivolts using reference and fluoride ion-selective electrodes as described in 11.2. Obtain the milligrams of F^- by referring to the graph in 11.2.

13. Calculation

13.1 Calculate total calcium as follows:

$$\text{Total calcium, } \%\ T = \frac{10VC}{ab} \qquad (2)$$

where:

V = volume of titrant, mL,
C = calcium equivalent of EDTA solution, mg/mL,
a = milliliters of aliquot,
b = grams of sample used, and
T = total calcium present,% .

13.2 Calculate soluble calcium as follows:

$$\text{Soluble calcium, } \%\ S = \frac{(2)(V)(C) - (5.2737)(F^-)}{10} \qquad (3)$$

where:

V = volume of titrant, mL,
C = calcium equivalent of EDTA solution, mg/mL,
F^- = fluoride ion content, mg.

13.3 Calculate calcium fluoride as follows:

$$\text{Calcium fluoride, } \% = (T - S) \times 1.948 \qquad (4)$$

where:

T = total calcium percent found in 13.1, and
S = soluble calcium percent found in 13.2.

13.4 Rounding of test results obtained using this test method shall be performed in accordance with Practice E29, Rounding Method, unless an alternative rounding method is specified by the customer or applicable material specification.

14. Precision and Bias[7]

14.1 *Precision*—Table 1 indicates the precision of the test method between laboratories.

TABLE 1 Precision Data

Fluorspar Grade	Average Calcium Fluoride Content, %	Relative Standard Deviation, %	Number of Participating Laboratories
Spanish acid	97.63	0.195	14
African acid	96.78	0.257	14
Mexican ceramic	91.84	0.173	14
Mexican metallurgical	87.72	0.263	14

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[7] Supporting data giving the results of cooperative testing are available from ASTM International Headquarters. Request RR:E16-1003.

14.2 *Bias*—No information on the bias of this test method is known. Accepted reference materials may have not been included in the materials used in the interlaboratory study. Users of this test method are encouraged to employ accepted reference materials, if available, and to judge the bias of this test method from the difference between the accepted value for the calcium fluoride content and the mean value from interlaboratory testing of the reference material.

15. Keywords

15.1 calcium content; calcium fluoride content; complexometric titrimetry; fluorspar; soluble calcium content

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