



Designation: E 815 – 99

Standard Test Method for Determination of Calcium Fluoride in Fluorspar by Complexometric Titration¹

This standard is issued under the fixed designation E 815; 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 *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.*

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals³

E 276 Test Methods for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal-Bearing Ores and Related Materials³

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁴

3. Summary of Test Method

3.1 The sample is decomposed by digesting with nitric and perchloric acids and the fluorine is expelled by fuming. The residue is dissolved in dilute hydrochloric acid, 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 CaF₂ content is then calculated.

4. Significance and Use

4.1 Fluorspar is used as a flux in steelmaking, glass industry, and manufacture of hydrofluoric acid.

4.2 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 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 E 882.

5. Interferences

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

6. Apparatus

6.1 *Fluoride Ion-Selective Electrode.*⁵

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

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

6.4 *Polyethylene Beakers*, 100-mL.

6.5 *Single Junction Ag/AgCl Reference Electrode.*⁶

7. Reagents and Materials

7.1 *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.⁷ Other grades may be used,

¹ This test method is under the jurisdiction of ASTM Committee E-1 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 *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 03.05.

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

⁵ Orion model 94-91 has been found suitable for this purpose.

⁶ Orion model 90-01-00 has been found suitable for this purpose.

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.

provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

7.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D 1193.

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

7.4 Calcium Carbonate, high purity (minimum 99.95 % CaCO_3).

7.5 Ethylenediaminetetraacetic Acid Disodium Salt (EDTA)— $\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$ 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.

7.6 Hydrochloric Acid (2 + 98)—Mix 2 volumes of concentrated hydrochloric acid (HCl) with 98 volumes of water.

7.7 Hydrochloric Acid (1 + 10)—Mix 1 volume of concentrated hydrochloric acid (HCl) with 10 volumes of water.

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

7.9 Potassium Acetate Buffer—Dilute 283 mL of glacial acetic acid (CH_3COOH) to 1200 mL with water. While cooling and stirring, add 50 % (W/V) potassium hydroxide solution (KOH) to adjust the pH to 5.0 (approximately 350 mL of KOH solution are required).

7.10 Potassium Hydroxide Solution (22.5 %) (W/V)—Dissolve 225 g of potassium hydroxide (KOH) in water and dilute to 1 L with water. Store in a plastic bottle.

7.11 Potassium Hydroxide Solution (50 %) (W/V)—Dissolve 500 g of potassium hydroxide (KOH) in water and dilute to 1 L. Store in a plastic bottle.

7.12 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.

7.13 Triethanolamine Solution (1 + 1)—Mix 50 mL of triethanolamine ($\text{NC}_6\text{H}_{15}\text{O}_3$) with 50 mL of water.

8. Sampling, Test Specimens, and Test Units

8.1 Pulverize the test units so that 95 % passes a No. 100 mesh sieve (150- μm) in accordance with Test Methods E 276.

9. Calibration and Standardization

9.1 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. While covered, cautiously add 75 mL of HCl (7.7) 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.

9.1.1 Titration—

9.1.1.1 Transfer a 50.00-mL aliquot of this solution to a 400-mL beaker, add 5 mL of triethanolamine (7.13), dilute to 200 mL, make just alkaline with potassium hydroxide solution (7.10), using a strip of litmus paper, and then add an additional 15 mL of potassium hydroxide solution (7.10).

9.1.1.2 Add 0.2 g of hydroxynaphthol blue indicator and titrate immediately with 0.025 M EDTA solution (7.5). At the equivalence point, the color changes from pink to blue. Determine the calcium equivalent of the EDTA solution as follows:

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

where:

V = millilitres 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.

9.2 Calibration—Transfer 10 mL of acetic acid (1 + 10) (7.3) into a series of seven 100-mL polyethylene beakers and add 20 mL of potassium acetate buffer (7.9) (Note 2). Add standard fluoride solution (7.12) and water according to the following:

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 (6.1 and 6.5) and wait for 3 to 5 min for potential to reach equilibrium. Record the potential in millivolts. Plot millivolts (linear scale) versus F^- concentration in milligrams (log scale) on a semilog paper.

NOTE 2—Potential measurements in calibration standards and sample should be carried out concurrently.

10. Procedure

10.1 Determination of Total Calcium:

10.1.1 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 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 weight loss. Transfer the sample to a 400-mL beaker and reweigh the capped bottle to the nearest 0.1 mg. The difference between the two weights is the weight of the sample taken for analysis.

10.1.2 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 3—If an insoluble residue remains, filter through a fine-textured paper, and wash the paper thoroughly with hot HCl (7.6), ignite the paper and residue in a platinum crucible, and 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 it to about 80 mL and cool.

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