

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 79a

Fluorspar

This Standard Reference Material is an acid-grade fluorspar concentrate, to be used primarily for the assay of imported fluorspar for industrial applications. The assay value certified is dependent on the U.S. Customs Laboratory Method given in this Certificate; however, two options exist for the determination of soluble fluoride calculated as calcium fluoride in the acetic acid leach solution. Either the spectrophotometric procedure (Part B), which was used for the original certification of this material, or the ion electrode procedure (Part C), which is included on this Certificate, may be used. The results of the two procedures show excellent agreement.

<u>Constituent</u>	<u>Percent by weight</u>
CaF ₂	97.39 ^a ± 0.06 ^b

^aMean value based on 32 determinations using the U.S. Customs Laboratory Method of analysis (attached). The determinations were made by two analysts at each of three Customs laboratories and one NBS laboratory.

^bStandard deviation of a single determination.

The following values, obtained by quantitative spectrochemical analysis, *are given for information only and are not certified*: Fe, 0.05-0.1%; Al and Sr, 0.01-0.1%; Mg, 0.01-0.05%; Na, 0.001-0.01%; Ba, 0.001-0.005%; K, <0.005%; and Cu, Li, Mn, Pb, and Ti, <0.001%.

The chemically determined value for SiO₂ is 0.67%.

The analytical work leading to certification was performed in the Division of Technical Services, U.S. Customs Laboratories, and by J. R. Moody and K. M. Sappenfield of the NBS Center for Analytical Chemistry. The spectrochemical determinations were made by M. Darr of the NBS Center for Analytical Chemistry.

A comparison of the ion electrode procedure with the spectrophotometric procedure was performed by R. L. Zimmerman, Jr., and H. G. Bertrand of the U.S. Customs Laboratory, New Orleans, La., and by J. R. Moody of the NBS Center for Analytical Chemistry.

This material was supplied by the American Smelting and Refining Company of El Paso, Texas; it was ground to pass a 177 μm (80 mesh) screen.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague, R. E. Michaelis, and C. L. Stanley.

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George A. Uriano, Chief
Office of Standard Reference Materials

(over)

Method for the Determination of CaF_2 in Fluorspar

A. Calcium Fluoride Determination: Transfer a 0.5 ± 0.01 g sample, previously dried at 100 to 105 °C, to a 60 mL Pt dish. Add 15 mL acetic acid (1:9) and approximately 50 mg of dry, ashless filter pulp. Digest on a steam bath for 30 minutes and stir with a small glass rod at 5-minute intervals. Stir and filter through an 11-cm close-texture filter paper (S&S No. 589 Red Ribbon, or equal) to which has been added approximately 4 mL filter pulp slurry (1 g ash-free pulp in 100 mL of water). Thoroughly wash crucible, stir rod, and paper with small portions of hot water (approximately 35 mL). The filtrate and washings should be collected in a polyethylene bottle for the determination of dissolved fluoride by either the spectrophotometric method described in Part B or the ion-selective electrode method described in Part C. Transfer paper and residue to original crucible, wipe the funnel with a small piece of filter paper, and add the paper to the crucible to assure recovery of fine particles. Dry crucible and contents, ignite to a dull red heat (600 °C), and cool to room temperature.

Transfer the residue, as completely as possible, from the crucible to a 400-mL beaker by gently tapping the crucible. Add 5 to 10 mL HCl to the crucible and warm on a steam bath or a temperature-regulated sand bath. Transfer the HCl to the beaker containing the residue. Polish and wash the crucible with a minimum amount of hot water. Repeat adding HCl and washing 2 or 3 times using a total of 25 mL HCl. Add approximately 0.5 g of crystalline boric acid to beaker, cover with a watch glass, and digest on the steam bath for 15 minutes. Remove the beaker and cool to room temperature. Add 0.5 mL HNO_3 and slowly evaporate on the steam bath to approximately 10 mL. During evaporation, the cover glass should be gradually removed from the beaker. Wash down the sides of the beaker with a fine stream of water and adjust the volume to approximately 75 mL. Heat to 70 to 80 °C, remove from heat, and add 100 mL of precipitating solution [3.8 g ammonium oxalate, 1.1 g oxalic acid, and 0.05 g disodium ethylenediaminetetraacetate (EDTA) in 100 mL of water]. If a white precipitate forms at this point, add HCl dropwise until it dissolves.

Heat to boiling and slowly add NH_4OH (1:1) until a heavy white precipitate forms. Add 1 mL of bromocresol green solution (0.1 g soluble salt in 100 mL of water) and continue the addition until the color of the solution changes from yellowish-orange to grayish-green. Digest for 30 minutes on the steam bath, let stand for 60 minutes at room temperature, and filter by decantation through a prepared Gooch crucible (size 3, prepared with 2.1 cm glass-fiber filter paper, H. Reeve Angel No. X-934AH, or equivalent). Wash 3 or 4 times with a cold wash solution (0.2 g ammonium oxalate and 0.1 g oxalic acid in 100 mL of water) and finally with 3 or 4 10-mL portions of cold water. (The washed precipitate should be free of chloride, ammonium oxalate, or any other contaminant that might reduce the KMnO_4 solution.) Transfer the contents of the crucible to a 400-mL beaker, add 250 mL H_2SO_4 (1:19), and adjust the solution temperature to 27 ± 3 °C. While stirring, add approximately 90 percent of the 0.15 N KMnO_4 solution to be used for titration. This should be added at a rate of approximately 30 mL per minute from a buret. Allow to stand until the pink color disappears, e.g., approximately 45 seconds. (If pink color persists, too much KMnO_4 solution has been added and the determination must be repeated.) Heat to 57 ± 3 °C and complete the titration by slowly adding the last 0.5 to 1 mL KMnO_4 solution dropwise and allowing each drop to decolorize completely before adding the next drop. The end point is a pink color persisting for 30 seconds or more. See calculations.

B. Determination of Fluoride in Acetic Acid Leach Solution: Remove all ions from the solution that might cause interference in the spectrophotometric determination of dissolved fluoride, by using either the ion-exchange method, or the fluorine-distillation method described in 2 and 3. Prepare a reagent blank, by substituting 15 mL of acetic acid (1:9), diluted to approximately 55 mL with distilled water and analyze simultaneously with sample.

1. Preparation of calibration curve: Prepare a dilute fluoride standard (1 mL = 0.1 mg CaF_2) from a standard solution (1 mL = 1 mg CaF_2) of 1.0755 g NaF diluted to one liter in a polypropylene volumetric flask with distilled water. Take a series of aliquots of 1, 2, 4, 6, 8, 11, 16 mL, etc., from the diluted fluoride standard and transfer them to 60-mL polyethylene bottles. Add 15 mL of acetic acid (1:9) and sufficient distilled water to bring the final volume to approximately 55 mL. Proceed to the ion-exchange or fluorine-distillation method.

2. Ion-exchange method: Prepare an anion-exchange column by pouring a slurry of distilled water and Rexyn 201 (OH) resin, or equivalent, sufficient to give a total exchange capacity of 27 to 30 meq, into a 25 mL polystyrene buret plugged with washed absorbent cotton (not glass wool) and drain off the excess water without allowing the water level to fall below the top of the resin column at any time. Continue this procedure until the resin is within about 5 mL of the top of the buret. Wash the resin with 20 mL N NaOH, and finally with distilled water (approximately 100 mL), until the effluent is no longer alkaline. Adjust the stopcock to give a flow rate of approximately 100 drops per minute. The flow rate is an indicator of the state of the column. Backwash with distilled water whenever the flow rate falls below 100 drops per minute. Resin must be covered with liquid at all times.

Prepare a cation-exchange column in the same manner as the anion exchange column using a slurry of distilled water and Rexyn 101(H) resin, or equivalent, sufficient to give a total exchange capacity of 40 to 45 meq. Wash the resin with 50 mL of 1N HCl, and finally with distilled water (approximately 200 mL) until the effluent is free of chloride ion. Flow rate should be approximately 100 drops per minute.

Each of the diluted aliquots, as well as the blank, is run separately as follows: After completing both columns, pass the entire volume from the polyethylene bottle through the anion-exchange column, always maintaining the liquid level slightly above the top of resin. Wash the polyethylene bottle with distilled water and pass washings through the column using a total of approximately 60 mL for each sample. Discard the effluent and washings. Recover the fluoride, acetate, and other anions from the column by passing 20 mL of 1N NaOH through the column at a flow rate of approximately 100 drops per minute. Collect the effluent in the original polyethylene bottle. Wash the column with distilled water and collect washings in the same bottle to capacity (60 mL). Pour the contents of this bottle, and water used to rinse it, into the cation column and collect the effluent in a 100-mL volumetric flask. Wash the column with distilled water and collect just short of the mark in the same flask. Bring the liquid to the mark with distilled water. Proceed to the spectrophotometric determination.

3. Distillation method: Have water in a steam generator actively boiling, but do not connect to the fluoride distillation apparatus (Willard and Winter, or equivalent) at this time. Distill each of the diluted aliquots, as well as the blank, separately as follows: Transfer the entire volume from the polyethylene bottle to the 500-mL Claisen flask of the distillation apparatus using a minimum quantity of water for rinsing. Add 50 mL H₂SO₄ (1:1) and a few glass beads. Insert a stopper carrying the steam tube and thermometer, and heat the flask with a Bunsen burner or an electric heater. Connect the condenser at once and place a 200-mL polypropylene volumetric flask at the receiving end. Water soon begins to distill over and the temperature of the liquid rises as the H₂SO₄ concentration increases. When the temperature reaches 120 °C connect the flask to the steam generator by means of the rubber tube. The rate of steam generation and the rate at which the Claisen flask is being heated should be regulated so that the temperature of the liquid in the distilling flask is maintained at 135 to 145 °C. Distill until the total volume in the receiver is approximately 185 mL (Note 1). Disconnect the condenser and rinse with a small portion of water, catching the washings in the flask containing the distillate, and fill to mark with distilled water. Proceed to the spectrophotometric determination.

4. Spectrophotometric determination: Pipette about one-tenth of the volume of the solution from steps B-2 or B-3 containing approximately 0.1 to 0.2 mg CaF₂ (not more than 50 mL) into a 100-mL polypropylene volumetric flask and add 15 mL 0.1 N sodium acetate solution and 25 mL methyl cellosolve. Bring the solution level in the flask almost to mark with distilled water and allow to cool to room temperature (mixing reaction is slightly exothermic) before making a final volume adjustment. (Resulting solution should have a pH of 3 to 5; optimum color development occurs in this range.)

Pour the entire contents of the volumetric flask into a 125-mL stoppered erlenmeyer flask containing 0.1 g of thorium chloranilate (Note 2). Stopper the flask and place on a shaking apparatus. Shake for 55 minutes, remove, and allow the contents of the flask to settle for 5 minutes. Filter through a close-texture filter paper, discarding the first 5 to 10 mL of filtrate.

Read the absorbance of sample against the reagent blank using 1 cm absorption cells in a Beckman DU spectrophotometer, or its equivalent, at a wavelength of 330 nm and a slit width of about 0.2 mm. Plot absorbance vs mg of CaF₂. This should yield a straight line passing through the origin.

5. Analysis of acetic acid leach solution: Carry the entire filtrate from the acetic acid digestion through steps B-2 or B-3 and finally B-4. Determine mg of CaF_2 by using the calibration curve and proceed with calculation.

C. Determination of Fluoride in Acetic Acid Leach Solution with an Ion-Selective Electrode.

1. Apparatus, Reagents, and Solutions

a. Special Apparatus

- 1) Fluoride specific ion electrode
- 2) Single junction reference electrode
- 3) Expanded scale pH meter with millivolt capability

b. Reagents

ACS Reagent grades of sodium fluoride, glacial acetic acid, sodium chloride, and sodium hydroxide, must be used. For (1,2 Cyclohexylenedinitrilo)- tetraacetic acid (CDTA), a practical grade available from a commercial source may be used.

c. Solutions

1) TISAB II - (Total Ionic Strength Adjustment Buffer)

To 500 mL of distilled water in an 800 mL beaker, add 57 mL of glacial acetic acid, 58 g of sodium chloride, and 4 g of CDTA. Place the beaker in a cold water bath, on a magnetic stirrer. Stir the mixture, while adding concentrated sodium hydroxide, to provide a pH between 5.0 and 5.5. Transfer the contents of the beaker to a 1-liter flask, and dilute to the mark with distilled water. (TISAB II is used to provide a constant ionic strength background, decomplex the fluoride ions, and adjust and buffer the pH of the solution.)

2) Standards

- a) Stock Solution (1900 ppmF^-) - Dissolve 4.199 g of sodium fluoride in a 1-liter polypropylene volumetric flask and dilute to volume with distilled water.
- b) Working stock solution (19.00 ppmF^-) - Transfer 10 mL of stock solution (a) to a 1-liter polypropylene volumetric flask and dilute to the mark with distilled water.
- c) Working standards - Prepare standards according to Table 1.

TABLE I

F^- Conc. ($\mu\text{g}/\text{mL}$)	Working Stock (mL)	TISAB II (mL)	Distilled Water ¹ (mL)
9.50	50.0	50	--
4.75	25.0	50	25
2.85	15.0	50	35
1.90	10.0	50	40
0.95	5.00	50	45
0.38	2.00	50	48

¹If prepared in a 100 mL flask, dilute to mark with distilled water.

Store working standards in polyethylene bottles and refrigerate until use.

2. Procedure

Transfer the contents of the polyethylene bottles containing the acetic acid wash (Section A) to 200 mL polyethylene volumetric flasks and dilute to volume with distilled water. Transfer a 25 mL aliquot to a 50 mL polyethylene volumetric flask and dilute to volume with TISAB II. Place in refrigerator until ready for use. In a polyethylene bottle, prepare a reagent blank consisting of 15 mL of acetic acid (1:9) and approximately 55 mL of distilled water.

Transfer the working standards, test solutions, and the reagent blank to 150 mL polyethylene beakers and allow to come to room temperature. Stir all solutions with magnetic stirrers. Adjust the pH meter to -150 mV by use of the 19.00 ppm F^- working stock solution. Record the values of the solutions beginning with the least concentrated working standard. NOTE: For solutions containing low concentrations of fluoride, the pH meter may require approximately two minutes to stabilize (cessation of drift). Rinse and dry the electrodes with tissue paper between readings. Record the values of the test solutions and the reagent blank immediately following the working standards.

Plot a curve from the values obtained for the working standards, and determine the concentration of the test solutions from the curve. Proceed with calculations.

D. Calculations:

First, calculate the % CaF_2 found in Part A. Then calculate the % CaF_2 found in either Part B (spectrophotometric procedure) or Part C (electrode procedure). Add the value calculated for either Part B or C to that calculated for Part A, to determine the total % CaF_2 in the sample.

$$\text{For Part A: } \% CaF_2 = \frac{3.904 V_1 N}{W_s}$$

where: V_1 = Volume of $KMnO_4$ solution used (corrected for blank)

N = Normality of $KMnO_4$ solution

W_s = gram weight of sample

$$\text{For Part B: } \% CaF_2 = \frac{0.1 W_c F}{W_s}$$

where: W_c = milligram weight of CaF_2 in aliquot

F = aliquot factor; $\frac{\text{Total volume from B-2 or B-3}}{\text{volume used}}$

W_s = gram weight of sample

$$\text{For Part C: } \% CaF_2 = \frac{CV_2AG}{W_s} \times 10^{-4}$$

where: C = observed concentration in ppm F^- ($\mu g F^-/mL$)

V_2 = volume of test solution

A = aliquot factor; $\frac{\text{total volume}}{\text{volume used}}$

G = gravimetric factor; $\frac{CaF_2}{2F}$

W_s = gram weight of sample

For the conditions described in Part C, this formula may be simplified as follows:

1) The sample is diluted to 200 mL and a 25 mL aliquot is taken; thus the aliquot factor, A, is: $A = \frac{200}{25} = 8.00$

2) The volume of test solution V_2 is always 50 mL; $V_2 = 50.0$ mL

3) The gravimetric factor, G, is : $G = \frac{\text{CaF}_2}{2\text{F}} = \frac{78.0768}{37.9968} = 2.055$

by substitution:

$$\% \text{CaF}_2 = \frac{C \times 50.0 \times 8.00 \times 2.055}{W_s} \times 10^{-4} \text{ or}$$

$$\% \text{CaF}_2 = \frac{0.0822C}{W_s}$$

Note 1. The volume of distillate necessary for complete recovery of fluoride will vary with the capacity of the distillation apparatus. Calibrate the apparatus by distilling a known quantity of fluoride to various final volumes to determine the volume necessary for complete recovery.

Note 2. Chloranilates are supplied as dry powders of high stability. However, long storage may reduce activity. Drying at 105 °C for at least 4 hours restores activity. Keep bottles tightly capped to prevent moisture absorption, which reduces activity and hinders the color development.