

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 180

High-Grade Fluorspar

This Standard Reference Material (SRM) is a high-grade fluorspar certified for its calcium fluoride content. SRM 180 is intended primarily for use in geological and geochemical analyses. This SRM is not recommended as a substitute for SRM 79a, Customs Grade Fluorspar, which is used in the assay of fluorspar imported for industrial use.

The certified fluorspar content is the mean of eight determinations using the method given on the reverse side of this certificate. The method requires the use of hydrogen sulfide which is both an irritant and an asphyxiant. Users of the method should follow all safety procedures for using hydrogen sulfide.

<u>Constituent</u>	<u>Percent. by weight</u>
CaF ₂	98.80 ± 0.03 ^a

^aThe uncertainty is expressed as the standard deviation of a single determination.

The following values, obtained by qualitative spectrochemical analysis, are provided for information only and are not certified: Fe, 0.1 - 1.0%; Al, Ba, Mg, Pb, Si, and Sr, 0.01 - 0.1%; Cu, K, Mn, Na, Ti, and V, 0.001 - 0.01%; Ag and Li, less than 0.001%. The spectrochemical analyses were performed by E.K. Hubbard, Analytical Chemistry Division, Institute for Materials Research, National Bureau of Standards.

The analytical work leading to certification was performed by K.M. Sappenfield, Analytical Chemistry Division, Institute for Materials Research, National Bureau of Standards.

This material was supplied by Minera Frisco of San Francisco Del Oro, Chih, Mexico.

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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Stanley D. Rasberry, Chief
Office of Standard Reference Materials

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METHOD FOR THE DETERMINATION OF CaF_2 FLUORSPAR

*Transfer 0.50 g of fluorspar, previously dried at 100 to 105 °C, to a tared, ignited platinum crucible. Add 15 mL of acetic acid (1:9) containing 0.667 g of CaCO_3 per liter. Digest on a steam bath for 30 minutes and stir at five minute intervals. Add about 0.04 g of ashless filter pulp and stir for an additional minute. Filter through a double 12.5 cm extra dense filter paper (S & S No. 589 Red Ribbon) to which has been added about 0.04 g ashless filter pulp. Thoroughly wash the crucible, paper, and stirring rod with 5 mL portions of hot water (40 to 60 °C), using a total of about 35 mL. After washing, wipe the stirring rod with a small piece of wet filter paper and add the paper to the filter. Transfer the paper and residue to the crucible, dry in an oven at 80 °C, char slowly under an infrared lamp, and ignite in a muffle furnace at 600 °C.

**Add 3 mL of HF to the residue in the crucible and evaporate to dryness. Add 1 to 2 mL of HClO_4 and evaporate to dryness under the hood. Cool, wash the inside of the crucible with 1 mL more of HClO_4 (to catch any undecomposed particles of calcium fluoride), and again evaporate to dryness. Cool the crucible and immerse in a beaker containing 150 mL of dilute HCl (5:95). Warm the beaker gently and remove the platinum crucible, being sure to remove adhering particles of $\text{Ca}(\text{ClO}_4)_2$.

Boil the contents of the beaker for 10 minutes. If any insoluble matter remains; filter, wash, and ignite it in platinum. Treat the ignited residue with a few drops of HF and HClO_4 and heat to expel the acids. Add 1 to 2 mL of HCl and digest on a steam bath. Transfer the contents to the main filtrate.

Pass H_2S into the clear filtrate for several minutes and then make the solution ammoniacal. Continue with H_2S for 10 minutes and allow the precipitate to settle for 20 to 30 minutes. Filter and wash with $\text{NH}_4\text{Cl}-(\text{NH}_4)_2\text{S}$ solution. (Prepare by passing a moderate stream of H_2S for 5 minutes through a solution containing 5 mL of NH_4OH and 10 g of NH_4Cl per liter.)

Neutralize the filtrate and washings with HCl, and add an additional 20 mL of HCL. Boil for 2 to 3 minutes to expel most of the H_2S . Add KBr- Br_2 solution (20% solution of KBr saturated with Br_2) until the solution remains yellow. Boil until the finely divided sulfur has been oxidized and the bromine has been expelled. If the sulfur or sulfides are not removed by the bromine treatment, filter, wash the paper well and discard the residue. Dilute the filtrate to about 200 mL. Precipitate the calcium by adding 2 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and, while stirring, slowly add NH_4OH until the solution is slightly ammoniacal. Heat on a steam bath for one-half to one hour, stirring occasionally. Cool to room temperature. Filter on a close textured paper. Wash with a cold 0.1 percent solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. Ignite to constant weight. Calculate the percent CaF_2 from the weight of the CaO.

References:

*Removal of soluble calcium in acetic acid. Interlaboratory study of soluble calcium.

**Method: Calcium in fluorspar

The Analysis of Fluorspar by G. E. F. Lundell and J. I. Hoffman, J. Res. Nat. Bur. Stand. (U.S.), 2 (1929) R.P. 51.