

FLUORINE DETERMINATION IN MINERALS AND ROCKS

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ABSTRACT

A 50-mg sample is fused with a flux mixture of 2.5 g of Na_2CO_3 and 0.5 g of ZnO , followed by digestion with distilled water on a hotplate. The fluoride is removed from the melt, taken up in water and transferred to a distillation flask, by steam distillation, and determined by the zirconium eriochrome cyanine R method. Recovery of F from minerals such as hornblende and apatite was within ± 1 to 3 percent of the total F present or added as standard NaF.

INTRODUCTION

For fluorine analysis in minerals and rocks, fluoride must be brought into a solution that is free from ionic interferences, particularly those of aluminum and silicon (Boltz, 1958). With samples containing more than 20 mg of aluminum oxide and above 50 mg of silicon oxide, difficulty of satisfactory recovery of fluorine arises (Reynolds and Hill, 1939; Shell and Craig, 1954; Willard and Winter, 1933). The purpose of the present study was to combine the fusion and HClO_4 distillation methods with the sensitivity of the colorimetric zirconium eriochrome cyanine R method for fluoride (Megregian, 1954) not hitherto used for the analysis of fluoride of soils and rocks. The interference by aluminum is eliminated by use of a small sample size (50 mg) instead of the time-consuming double distillation used by Willard and Winter, (1933) or a perchloric-phosphoric acid mixture as the distillation acid (Grimaldi *et al.*, 1955). The sample size recommended in the present method is applicable to the general range of fluorine content, an average of 700 g per ton of crustal rocks (Berry and Mason, 1959).

EXPERIMENTAL

Apparatus. Fluoride distillation apparatus (Fig. 1). Colorimeter (Bausch & Lomb, Spectronic 20) set at 527.5 mu. Absorption cell of 1-cm light path. Platinum crucibles, 30-ml. Glass beads. Meker burner.

Reagents. Standard sodium fluoride solution: 0.221 g of reagent grade NaF is dissolved in 1 liter of water (1 ml = 0.1 mg F). This solution is diluted 100-fold to provide a working solution. A sodium carbonate washing solution consists of 2 percent Na_2CO_3 aqueous solution. Sodium carbonate (reagent grade) and zinc oxide (reagent grade) are used for the fusion.

Perchloric acid: Reagent grade HClO_4 (60%) is added to 3 to 4 volumes of distilled water and boiled down to the original volume. This process is repeated and, after cooling, the acid is stored in a Pyrex bottle.

Reagent A: 1.800 g of eriochrome cyanine R is dissolved in distilled water and diluted to 1 liter.

Reagent B: 0.265 g of zirconyl chloride octahydrate is dissolved in 50 ml of water and

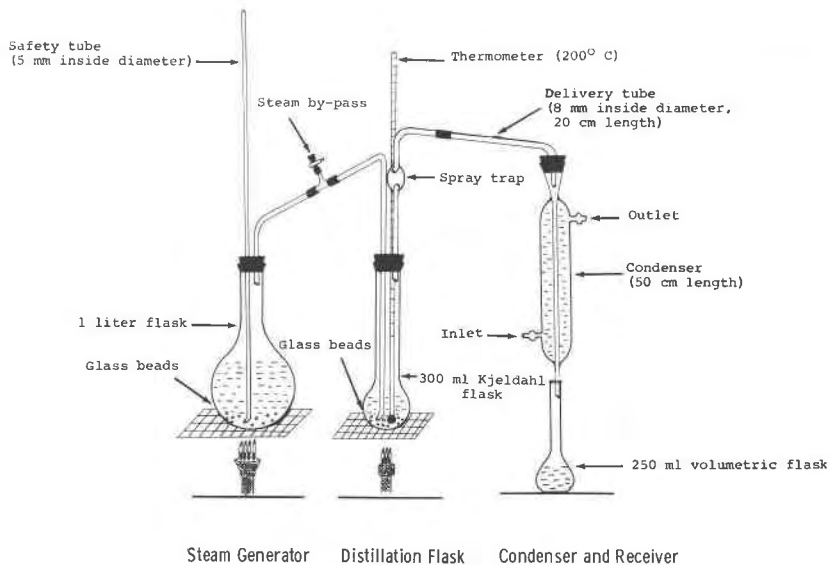


FIG. 1. Fluoride distillation apparatus.

700 ml of concentrated HCl (reagent grade, sp. gr. 1.19) is added to the zirconyl solution. The mixture is diluted to 1 liter with distilled water and cooled to room temperature before use.

Reference solution: 10 ml of reagent A is added to 100 ml of distilled water. To this solution is added 10 ml of a hydrochloric acid solution prepared by dilution of 7 ml of the concentrated acid (sp. gr. 1.19) to 10 ml with distilled water. The reference solution must be used because of the high absorbance arising from unreacted eriochrome cyanine R dye in the sample solution.

Decomposition of sample. A 50-mg sample is added to 2.0 g of Na_2CO_3 and 0.5 g of ZnO in a platinum crucible. The sample is thoroughly mixed with the Na_2CO_3 and ZnO by rotation of the crucible with fingers. Approximately 0.5 g of Na_2CO_3 is added on top of the mixture. The crucible is placed in a slanting position on a silica-covered triangle with the lid covering about seven-tenths of the top and then a low flame of a Meker burner is applied. The heat is gradually increased until the melt is liquefied. The fusion is completed in 30 minutes.

Isolation of fluoride. The crucible and contents are cooled and placed in a 100-ml beaker, and 25 ml of water is added. The beaker is covered and heated on a steamplate until the cake has softened. The crucible and lid are washed and removed. The volume of solution at this point should be around 50 ml. Any lumps are broken up with a stirring rod flattened at one end and then the solution is brought to boiling for several minutes, over a burner, with stirring continuously to prevent bumping. The digested cake suspension is allowed to cool and then transferred¹ quantitatively to the distillation flask. Fifteen to 20 ml of distilled water is used to make the transfer. The total volume at this point should be about 70 ml.

¹ As an alternative for layer silicates, the digested cake suspension is allowed to settle and as much as possible of the supernatant solution is decanted into the flask. The residue

Twenty ml of 60 percent perchloric acid is added slowly to the flask, the flask being kept cool by immersion in cold water. Eight to 10 glass beads are added. The distillation flask is connected to the condenser (Fig. 1) and the steam generator, and then the contents of the flask are mixed by gentle swirling. Heat is applied to the steam generator and the flask with the bypass open. When the temperature of the liquid in the flask reaches 135°C, steam is introduced by closing the bypass. The temperature is increased to 140°C and 150 ml of distillate is collected at a rate of about 5 ml per minute.

Caution. The flask temperature must be maintained between 130 and 140°C by adjusting the flame under the flask; particularly the upper limit should not be exceeded. The flame under the distillation flask should not touch any part of the flask which is not in contact with the liquid inside. Local superheating causes the decomposition of the distilling acid and thus results in the contamination of the distillate. The thermometer bulb and the steam inlet tube should remain immersed in the boiling liquid all through the distillation.

Upon the completion of distillation, the flames are removed and the steam bypass is opened. The distillate is diluted to 250 ml with distilled water and mixed thoroughly.

After each run, the flask and the attachments are thoroughly rinsed with distilled water, treated with 10 percent NaOH and finally once again rinsed thoroughly with distilled water. The apparatus should be free from contamination and all connections must be leakproof. This can be assured by checking the apparatus from time to time by determinations on standard fluoride solution.

Determination of fluorine. An aliquot of distillate, containing no more than 50 μg of fluorine¹ is diluted to 50 ml. Then 5 ml of reagent *A* followed by 5 ml of reagent *B* are added to the sample and mixed well. The colorimeter is set at zero absorbance (at 527.5 $\text{m}\mu$) with the reference solution and the absorbance of the sample solution is recorded. The fluorine value of the sample aliquot is determined from a curve prepared by subjecting standard solutions of fluoride to the above procedure and linearly plotting the absorbance values against *F* standards in the range of 0 to 50 μg of fluorine in 50 ml. The resultant plot is a straight line of negative slope, since zirconyl ions are withdrawn from the colored complex in proportion to *F* present, forming ZrOF_2 . Because the color reaction reaches equilibrium rapidly and is stable at ordinary temperature, the colorimeter reading can be taken immediately after mixing with the reagents. A new calibration curve is prepared at the same time that each set of samples is analyzed. A blank is carried with all reagents used on the procedure.

RESULTS AND DISCUSSION

The standard quantities of fluorine added to the sample were successfully isolated by steam distillation, in the presence of HClO_4 , of the aqueous Na_2CO_3 extract of the fused cake of silicates but not of phosphate rock (Table 1). Concordantly, the amounts of fluorine in hectorite determined by steam distillation of the aqueous Na_2CO_3 extract were in good agreement with those obtained for the whole melt (Table 2). Fluorine

is washed with three portions of hot 2% Na_2CO_3 solution, transferred to a filter paper and again washed with another three portions of the same solution. The solution collected from the washings is poured into the flask and the residue is discarded. As will be seen in the results (Tables 1 and 2), recovery of *F* in silicates was complete by this procedure, but that from apatite was not.

TABLE 1. RECOVERY OF FLUORINE ADDED TO SILICATES AND PHOSPHATE ROCKS

Sample ¹	Micrograms of fluorine			Recovered of F added	Error in recovery, %
	Native	Added	Observed ²		
Commercial vermiculite	0	200	205	205	+ 2.5
Montmorillonite (Wyoming)	0	200	203	203	+ 1.5
Kaolinite (Georgia)	0	200	198	198	- 1.0
Halloysite (Indiana)	0	200	198	198	- 1.0
Actinolite (Massachusetts)	0	200	205	205	+ 2.5
Hornblende (Ontario)	265	200	472	207	+ 3.5
Hectorite No. 34 (California)	850	1000	1875, 1875 ³	1025, 1025 ³	+ 2.5, + 2.5 ³
Phosphate rock I (Florida)	1890	1000	2042, 2890 ³	742, 1000 ³	- 25.8, 0 ³
Phosphate rock II (Florida)	1525	1000	2542 ³	1017 ³	+ 1.7 ³

¹ To 50 mg of sample, standard fluorine was added as NaF and the mixture was fused in Na₂CO₃ plus ZnO.

² In the aqueous Na₂CO₃ extract, except as indicated.

³ In the whole melt.

rine, not completely extracted from the fused melt of NBS standard phosphate rock in the usual hot aqueous Na₂CO₃ filtrate, was recovered by the modified method proposed (Tables 1 and 2). Retention of fluoride in the curd from which the Na₂CO₃ solution was decanted was attributed to precipitation of calcium fluorophosphate in the curd. Therefore, the general procedure adopted for determination of fluorine in minerals and rocks, particularly in phosphate rocks, calls for transfer of the whole melt into the distillation flask for the isolation of fluorine.

The results (Tables 1 and 2) show that the ionic interferences on the isolation of fluorine from silicate and phosphate minerals were eliminated by the proposed distillation and analytical procedure for semimicroquantities of F in earthy samples. Moreover, the deviation among the different runs and different analysts is small. The inaccuracy of the recovery of added standard fluorine to samples, which should measure the overall accuracy, is on the order of 1 to 3 percent, which is satisfactory for semimicrochemical analysis.

TABLE 2. CONTENTS OF FLUORINE IN SOME SILICATES AND PHOSPHATE ROCKS

Sample ¹	Per cent fluorine			
	In extract	In whole melt		NBS reported ³
Hectorite No. 34 (whole sample)	1.67	1.70		
Hectorite No. 34 ($<2\mu$)	2.35	2.25		
Hornblende	0.53	—		
Actinolite	0	—		
Phosphate rock I (NBS phosphate rock 120, Florida)	a 2.65 b 2.75 c 2.60 Av 2.67	a 3.75 b 3.83 c 3.75 Av 3.78	a 3.75 ² b 3.66 ² Av 3.71	a 3.74 b 3.71 c 3.82 Av 3.76
Phosphate rock II (Florida)	2.48	3.05		
Phosphate rock III (San Francisco)	3.50	3.45		

Av = Average.

¹ The source of sample was the same as stated in Table 1.

² Independently analyzed by Amin Hamad Al-Rawi, University of Wisconsin.

³ Report of the U. S. National Bureau of Standards.

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REFERENCES

BERRY, L. G. AND B. MASON (1959) *Mineralogy*. W. H. Freeman and Co., San Francisco, p. 211-218.

BOLTZ, D. F. (1958) *Colorimetric Determination of Nonmetals*. Interscience Publishers, Inc., New York, p. 231-259.

GRIMALDI, F. S., B. INGRAM, AND F. CUTTITTA (1955) Determination of small and large amounts of fluorine in rocks, *Anal. Chem.* **27**, 918-921.

MEGREGIAN, S. (1954) Rapid spectrophotometric determination of fluoride with zirconium-eriochrome cyanine R lake. *Anal. Chem.* **26**, 1161-1166.

REYNOLDS, D. S. AND W. L. HILL (1939) Determination of fluorine, *Ind. Eng. Chem., Anal. Ed.* **11**, 21-27.

SHELL, H. R. AND R. L. CRAIG (1954) Determination of silica and fluorine in fluorsilicates. *Anal. Chem.* **26**, 996-1001.

WILLARD, H. H. AND O. B. WINTER (1933) Volumetric method for determination of fluorine. *Ind. Eng. Chem., Anal. Ed.* **5**, 7-10.

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