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THE DETERMINATION OF SMALL AND LARGE AMOUNTS OF FLUORINE IN ROCKS*

By

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	67

CONTENTS

TABLES

THE DETERMINATION OF SMALL AND LARGE AMOUNTS OF FLUORINE IN ROCKS

By F. S. Grimaldi, Blanche Ingram, and Frank Cuttitta

ABSTRACT

Gelatinous silica and aluminum ions retard the distillation of fluorine in the Willard and Winter distillation method. Because large samples must be processed in the determination of small amounts of fluorine, this effect is especially serious with rocks containing aluminum or silicon, or both, as major constituents. Generally such samples require the separation of fluorine from aluminum and silicon prior to the distillation. These separation procedures are time consuming, and large intractable precipitates are obtained with the added danger of possible loss of fluorine by occlusion. The present work was undertaken to develop a generally applicable simple method for the determination of both small or large amounts of fluorine in materials high in aluminum or silicon, or both.

The sample is fused with a mixture of sodium carbonate and zinc oxide, leached with water, and filtered. The residue is granular and retains nearly all of the silica. The fluorine in the filtrate is distilled directly from a perchloric acid-phosphoric acid mixture. Phosphoric acid permits the quantitative distillation of fluorine in the presence of much aluminum at the usual distillation temperature and without the collection of large volumes of distillate. The fluorine is determined either by microtitration with thorium nitrate or colorimetrically with thorin. The procedure has been applied with excellent

results to the determination of small and large amounts of fluorine in silicate rocks and in samples from the aluminum phosphate (leached) zone of the Florida phosphate deposits.

INTRODUCTION

In the determination of fluorine it is common practice to isolate fluorine as fluosilicic acid by some modification or adaptation of the Willard and Winter distillation method (10). It is known that gelatinous silica or large amounts of aluminum, or both, as well as other elements of the ammonium hydroxide group retard the distillation of fluorine. For example, with the usual distillation temperature of 135° to 140° C and with the collection of about 150 ml of distillate, fluorine is not completely recovered in the presence of more than about 50 mg of silicon dioxide in the gelatinous form (6,8,10) and about 20 mg of aluminum oxide. The interference from these sources is especially serious for silicate rocks, because silicon and aluminum are major constituents, and large samples are required for determination of small quantities of fluorine, about 0.03 percent. The analyst is confronted with these same difficulties in the determination of fluorine in samples from the aluminum phosphate (leached) zone of the Florida phosphate deposits.

It has been reported (1,10) that better recovery of fluorine is obtained by distilling at higher temperatures (160° to 165° C) and by collecting larger volumes of distillate. It is our experience, however, that such procedures fail to give quantitative recovery of fluorine on such samples as described above.

Up to the present time the best approach has been to separate fluorine from silica and from the elements of the R_2O_3 group before the distillation step. Some adaptation of the Berzelius method is usually used for this separation, silica and aluminum being precipitated by zinc oxide from a nearly neutral or slightly ammoniacal solution (3,10). This procedure is time consuming, and there is always danger of loss of fluorine by coprecipitation on the large gelatinous precipitates obtained.

Recently Shell and Craig (8) have recommended a flux mixture of sodium carbonate and zinc oxide for decomposing silicate samples. The melt is digested in water and ammoniacal zinc oxide is added directly without a preliminary filtration of the water leach. After filtration the fluorine is determined both in the residue and in the filtrate. This method represents an important advance, because when the melt is leached with water a granular precipitate retaining most of the silica is obtained.

Our investigation was undertaken to develop a generally applicable simple method for the determination of both small and large amounts of fluorine in rocks, especially those containing aluminum and silicon as major constituents. Independently of Shell and Craig we arrived at a similar flux mixture for the decomposition of silicate rocks, and this feature of our procedure is the same as that of Shell and Craig. The major difference is the elimination of the ammoniacal zinc oxide separation of aluminum. After the sample is fused, leached with water, and filtered, the fluorine in the filtrate is distilled directly from a perchloric acid-phosphoric acid mixture. Phosphoric acid permits the quantitative distillation of fluorine in the presence of much aluminum at the usual distillation temperature and without the collection of large volumes of distillate. The fluorine in the distillate may be determined either by microtitration with thorium nitrate or colorimetrically by a modification of the thorin method of Horton and others (4). Although phosphoric acid has been used for the distillation of fluorine (2,5,6), it has not been generally adopted in the past because of the possibility of entraining sufficient phosphate with fluorine during the distillation to interfere subsequently with the determination of fluorine. We have found that this difficulty is of little consequence.

This work was completed as part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

EXPERIMENTAL DATA

Preliminary experiments sought to establish the following:

1. The amount of silica that may be expected in the filtrate from a water leach of a zinc oxide-sodium carbonate fusion of a sample.
2. The maximum amount of soluble aluminum that can be tolerated in the distillation of fluorine from a perchloric acid medium.
3. The effect of at least 200 mg of soluble aluminum in the distillation of fluorine from a perchloric-phosphoric acid medium.
4. The amount of phosphate that can be tolerated in the microtitration and colorimetric method for determining fluorine.
5. The amount of phosphate that accompanies fluorine in the distillation from a perchloric-phosphoric acid medium.

6. The minimum amount of distillate from the phosphoric-perchloric acid medium required for quantitative recovery of fluorine.

In the experiments 6 g of a (1 + 5) zinc oxide-sodium carbonate mixture was used in the silica studies; aluminum was added as a solution of aluminum perchlorate, and fluoride as a standard solution of pure sodium fluoride. Either 20 ml of perchloric acid alone or mixed with 2 ml of phosphoric acid was used in the distillation experiments. A standard phosphate solution made by dissolving pure potassium dihydrogen phosphate was used where required. The techniques used in the experiments are given in the section on procedure.

The following results were obtained:

1. Using pure silica in amounts varying from 0.01 to 0.70 g, from 1 to 16 mg of silica were found in the water leach of the sodium carbonate-zinc oxide melt; the greatest amount of silica was obtained from the test on 0.70 g of silica. No greater amounts of silica were found in the filtrates from the silicate samples analyzed. These amounts do not retard the distillation of fluorine.

2. Table 1 gives data on the recovery of fluorine in the presence of various quantities of aluminum when perchloric acid alone is used for the distillation. About 20 mg of aluminum oxide can be tolerated at the distillation temperature of $140^\circ \pm 3^\circ$ C.

3. Distillation experiments at $140^\circ \pm 3^\circ$ C from perchloric-phosphoric acid medium at three levels of fluorine (0.4, 5, and 15 mg F) and six levels of aluminum (20, 50, 75, 100, 150, and 200 mg Al_2O_3) for each level of fluorine showed that quantitative recoveries of fluorine were obtained in each instance. Thus, at least 200 mg of Al_2O_3 can be tolerated in the distillation.

Table 1.--The retarding effect of aluminum on the distillation of fluorine (150 ml of distillate at prescribed temperature).

F taken (mg)	Al_2O_3 taken (mg)	Distillation temperature (°C)	F recovered (mg)
5.00	20	140 ± 3	4.92
5.00	50	140 ± 3	4.76
5.00	75	140 ± 3	4.51
5.00	100	140 ± 3	3.82
5.00	150	140 ± 3	3.64
5.00	200	140 ± 3	3.15
5.00	20	148 ± 3	4.99
5.00	50	148 ± 3	4.90
5.00	75	148 ± 3	4.72

4. With mixtures containing varying quantities of phosphate and 1 mg of fluorine, it was found that no more than 50 γ P_2O_5 could be tolerated in the microtitration with thorium nitrate (50 γ P_2O_5 corresponds to 20 γ of fluorine). At least 200 γ P_2O_5 could be tolerated in the thorium-thorin method in the range from 0 to 100 γ of fluorine. The data on the effect of phosphate in the thorium-thorin procedure are given in table 2.

5. To determine the amount of phosphorus carried over in the distillation with perchloric-phosphoric acid, separate 25-ml portions of water were distilled with the mixed acids, and 150-ml distillates were collected. The phosphate in the distillates were determined by the

Table 2.--Effect of phosphate on the spectrophotometric determination of fluorine with thorin.

P_2O_5 (mg)	Absorbance			
	20 γ F	40 γ F	60 γ F	80 γ F
None	0.453	0.417	0.370	0.336
0.050	0.453	0.419	0.372	0.336
0.100	0.454	0.417	0.371	0.334
0.200	0.455	0.415	0.369	0.335
0.400	0.447	0.412	0.366	0.332
0.800	0.442	0.407	0.361	0.328
1.60	0.443	0.398	0.354	0.323

molybdenum-blue method. The distillates contained from 0.2 γ to 0.4 γ of P_2O_5 per milliliter. These correspond to from 30 γ to 60 γ P_2O_5 in the total distillates. As only an aliquot portion of the distillate is used for the determination of fluorine, no interference should be expected from this source. This is confirmed by the excellent results obtained with the procedure on samples containing known amounts of fluorine (tables 4 and 5). In several experiments the distillation temperature was raised to 150° C and no greater amounts of phosphate were found in the distillates. As the amount of phosphate carried over into the distillate may depend on the type of still used, it is recommended that each analyst test this for himself. Although we found that no trap was necessary in the still, some other design may require a trap to prevent the entrainment of phosphate.

6. The data in table 3 indicate that essentially quantitative recoveries of fluorine are obtained with the collection of less than 150 ml of distillate at 140° ± 3° C.

Table 3.--Completeness of recovery of fluorine with distillation at 140° ± 3° C.

	Fluorine recovered (mg)	
	Sample 1	Sample 2
1st 50 ml of distillate	1.89	14.30
2d 50 ml of distillate	0.11	0.64
3d 50 ml of distillate	0.02	0.06
Total found	2.02	15.00
Total taken	2.00	15.00

REAGENTS AND APPARATUS

The procedure for the titration of fluoride is well known, and except where specific instructions are desirable only a brief listing of the reagents will be made. Reagent-grade chemicals were used in all experiments.

Sodium fluoride: The primary-standard sodium fluoride was prepared by treating sodium bicarbonate solution with an excess of hydrofluoric acid in a platinum dish, evaporating the excess acid, and heating the residue at 600° C in air. (Reagent-grade sodium fluoride is not a dependable primary standard).

Standard fluoride solution for microtitrimetry, 1 ml contains 1 mg of fluoride.

Standard fluoride solution for spectrophotometry, 1 ml contains 5 γ of fluoride.

Thorium nitrate solution for microtitrimetry, 0.02 N. The method of standardization is given in the procedure.

Thorium nitrate solution for spectrophotometry, 1 ml contains 50 γ of thorium dioxide.

Sodium alizarin sulfonate, 0.1 percent aqueous solution.

Phenolphthalein, 0.1 percent alcoholic solution.

Chloracetate buffer, 0.2 M in monochloroacetic acid and 0.2 M in its sodium salt.

Sodium carbonate wash solution, a 2 percent aqueous solution.

Sodium hydroxide, a 2 percent aqueous solution.

Hydroxylamine hydrochloride, a 10 percent aqueous solution.

Thorin, 1-(o-arsenophenylazo-2 naphthol-3, 6 disulfonic acid), a 0.10 percent aqueous solution.

Hydrochloric acid (1 + 99), phosphoric acid (85 percent), perchloric acid (70 percent), anhydrous sodium carbonate, zinc oxide.

Fluorine still: Capacity 125 ml. The still we used is one manufactured by Ace Glass, Inc., Vineland, N. J., (no. 6431 in catalog 50) in which we substituted a steam delivery tube for the dropping funnel.

Beckman DU spectrophotometer supplied with 2-cm corex cells.

PROCEDURE

Isolation of fluoride

1. Fuse a 1.000-g sample with a mixture of 1.2 g of zinc oxide and 6 g of sodium carbonate in a platinum or nickel crucible. The fusion

should be made under oxidizing conditions to prevent attack on platinum when this container is used. Cool.

2. Place the crucible and contents in a 100-ml beaker and add 30 ml of water. Cover and heat on the steam bath until the cake has softened. Remove the crucible, police and wash it. The volume of solution at this point should be about 50 ml.

3. Break up any lumps with a stirring rod flattened at one end, and then bring the solution to boil, stirring to prevent bumping. Boil for several minutes, remove from the heat, and allow the residue to settle.

4. Filter the solution directly into the distillation flask, decanting as much of the liquid as possible. Wash the residue by decantation with several small portions of hot sodium carbonate wash solution. Transfer the residue to the filter paper and wash several more times. Reject residue. The total volume of solution at this point should be about 70 ml.

5. Add slowly 20 ml of perchloric acid and 2 ml of phosphoric acid to the flask, keeping the flask cool by immersing it in cold water.

6. Begin the distillation, collecting the distillate in a 250-ml volumetric flask. When the temperature reaches about 135° C, pass in steam from an auxiliary flask. Increase the temperature to 140° C and collect 150 ml of distillate at this temperature. The distillate should be collected at a rate of about 4 ml per minute. Dilute the distillate to 250 ml with water and mix.

Determination of fluoride by microtitration

7. Transfer a 50-ml aliquot to a 125-ml Erlenmeyer flask. Add 12 drops of sodium alizarin sulfonate, and then titrate with sodium hydroxide until the indicator becomes pink. Discharge the pink color by careful addition of (1 + 99) hydrochloric acid. Add 2.5 ml of buffer, and then titrate with 0.02 N thorium nitrate solution. For a more detailed description the reader is referred to the paper by Reynolds and Hill (6). The thorium nitrate is standardized against solutions of sodium fluoride, titrating aliquots of 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, and 3 mg of fluorine. A curve is drawn, plotting milliliters of thorium nitrate against milligrams of fluorine. Each sodium fluoride solution used in the standardization is obtained by taking a water leach from a blank fusion, adding fluoride equal to five times each amount of fluorine to be titrated, and distilling according to the procedure. The usual 50-ml aliquot from 250 ml of final solution is taken for the titration. The working curve is a straight line above 1 mg of fluorine, but is slightly curved below this amount necessitating several points in the lower region. A slightly lower fluorine equivalent is obtained for the thorium nitrate if standardized against pure sodium fluoride solutions which have not been distilled. This is inherent in the distillation-titration method and is not due to the inclusion of phosphoric acid in the distillation medium.

Determination of fluoride spectrophotometrically with thorin

8. Transfer a 5-to-15-ml aliquot to a 25-ml volumetric flask. Add a drop of phenolphthalein and neutralize with sodium hydroxide to a

faint pink color of the indicator. Add, by means of pipets, 0.2 ml of perchloric acid (70 percent), 1 ml of hydroxylamine hydrochloride, 2 ml of standard thorium nitrate solution (equivalent to 100 γ ThO_2), and 2 ml of thorin reagent. Adjust the volume to 25 ml with distilled water and mix. Measure the absorbance of the solution after 15 minutes on a Beckman DU spectrophotometer at 545 mμ, using a 2-cm corex cell and a slit width of 0.05 mm. The reference cell should be a blank containing perchloric acid, hydroxylamine hydrochloride, and thorin at the same concentrations as in the sample. The standard curve, absorbance versus concentration of fluoride, is obtained by plotting the absorbances for colors developed with known amounts of fluoride in the range of zero to 100 γ of fluoride. A straight line is obtained. The standard fluoride solution is prepared directly; previous distillation is unnecessary. One microgram of fluoride in 25 ml decreases the absorbance of the thorium-thorin color by about 0.002. Although a pH of 1 is used in the above thorin procedure, the thorium-thorin system is fairly stable in the range of pH 0.65 to 1.7.

TEST OF PROCEDURE

The procedure was applied to the determination of microgram and milligram amounts of fluorine. For the small amounts of fluorine, 1-g portions of two silicate rocks, granite G-1, and diabase W-1 (7), were used to which various amounts of a standard sample such as fluorspar, phosphate rock, or opal glass were added. The fluorine contributed by the spikes varied from 0.05 mg to 0.2 mg. In several tests the residues obtained from the fusion and water leach were re-fused to determine the amount of fluorine remaining in the residue. The fluorine contents of the granite and diabase were established by replicate analyses, the granite containing 0.061 percent fluorine and the diabase 0.016 percent fluorine. After distillation the fluorine was determined by microtitration and colorimetrically by the thorin procedure and by Talvitie's alizarin method (9) on aliquots of the same distillates. Talvitie's procedure was included for comparison purposes. The results given by the various methods, table 4, are in good agreement. The results indicate that the residue from the first fusion and leach need not be reworked, as the amount of fluorine retained is negligible for all practical purposes. The slightly greater amount of fluorine retained when phosphate rock was used as the spike is to be expected because of the presence of calcium and phosphate ions in the rock.

Standard samples of phosphate rock, fluorspar, and opal glass were used in testing the procedure on milligram amounts of fluorine. Both the phosphate rock and fluorspar were directly distilled from the perchloric-phosphoric-acid medium without preliminary treatment. A 0.25-g sample was taken for the phosphate-rock test, and 25 mg was used for the fluorspar. The fusion procedure cannot be used on phosphate concentrates because of the retention of much fluorine by the residue obtained after leaching the melt. A 0.5-g sample for the opal glass was fused, leached with water, and half of filtrate was taken for distillation. For all samples, the fluorine was determined by titration. The results obtained are compared to the National Bureau of Standards certificate values in table 5 and show good agreement. The retention of fluorine in the residue after leaching is again negligible for the opal glass.

Table 4.--Test of procedure in determining small amounts of fluorine.

Sample	Spike with 1/	In residue 2/	Fluorine (percent)						
			Microtitration		Thorium-alizarin (colorimetric)		Thorium-thorin (colorimetric)		Present 3/
			In filtrate	Total 4/	In filtrate	Total 4/	In filtrate	Total 4/	
Granite G-1 5/ (0.061% F)	Fluorspar 79	0.01	0.25	0.26	0.25	0.26	0.25	0.26	0.26
Do.	Opal glass 91	0.005	0.25	0.26	0.25	0.26	0.26	0.27	0.26
Do.	do.	--	0.16	--	0.16	--	0.15	--	0.16
Do.	do.	--	0.11	--	0.11	--	0.10	--	0.11
Do.	Phosphate rock 120	0.03	0.23	0.26	0.23	0.26	0.23	0.26	0.26
Do.	do.	--	0.17	--	0.15	--	0.15	--	0.16
Do.	do.	--	0.11	--	0.12	--	0.11	--	0.11
Diabase W-1 5/ (0.016% F)	Opal glass 91	0.01	0.23	0.24	0.25	0.26	0.20	0.21	0.22
Do.	do.	--	0.07	--	0.08	--	0.07	--	0.07

1/ National Bureau of Standards, standard samples.
2/ Based on original sample.
3/ Calculated from the fluorine contents of sample and spike.
4/ Sum of fluorine in residue and in filtrate.
5/ See Schlecht (7).

Table 5.--Test of procedure in determining larger amounts of fluorine by titration.

Sample 1/	Percent fluorine			Percent fluorine, Nat. Bur. Standards certificate values
	In filtrate	In residue 2/	Total	
Opal glass 91	5.72	0.03	5.75	5.72
Do.	5.73	--	--	
Phosphate rock 120	--	--	3.80	3.76
Do.	--	--	3.76	
Fluorspar 79	--	--	46.07	46.15
Do.	--	--	46.07	

1/ National Bureau of Standards, standard samples.
2/ Based on original sample.

The direct distillation procedure was applied also to samples from the aluminum phosphate (leached) zone of the Florida phosphate deposits, and again excellent results were obtained.

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