DETERMINATION OF FLUORINE BY PRECIPITATION AS TRIPHENYLTIN FLUORIDE

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Introduction

Batchelder and Meloche[2] have recently given a survey of the gravimetric methods for fluorine in their paper on the determination of fluorine by titration with cerous nitrate. Treadwell and Köhl[3] have made critical studies of the various gravimetric procedures that have been proposed and other reviews have been published by Hawley, Adolph, and Wagner and Ross.[4] Hillebrand and Lundell treat the determination of fluorine extensively in their "Applied Inorganic Analysis."[5] The conclusion reached by these reviewers is that the gravimetric determination of fluorine is fraught with many difficulties and uncertainties. Especially is this true when small quantities of fluorine are being dealt with and in fact gravimetric methods are precluded in such cases and recourse must be had to the colorimetric methods of de Boer and Steiger-Merwin.[6] Such colorimetric methods cannot be expected to show a high degree of accuracy.

In 1920 Krause and Becker[7] reported the preparation of triphenyltin fluoride and recorded the observation that the substance "was so difficultly soluble in cold alcohol, ether and water that fluorine can be quantitatively precipitated with triphenyltin chloride." They prepared the fluoride by treating a boiling-hot water–alcohol solution of potassium fluoride with a hot dilute alcoholic solution of triphenyltin chloride. A search of the literature subsequent to the appearance of the above paper failed to reveal that any effort had been made to apply the formation of the triphenyltin fluoride to the determination of fluorine. In view of the reported low solubility of the substance and of the very small conversion factor to fluorine (0.05153) it was deemed worth while to make an exhaustive investigation of the possibilities of the compound in the gravimetric determination of fluorine.

[1] J. T. Baker Chemical Company Fellow in Analytical Chemistry for 1931–1932, Eastern Division.

[2] Batchelder and Meloche, THIS JOURNAL, 53, 2131 (1931).

[3] Treadwell and Köhl, Helv. Chim. Acta, 9, 470 (1926).

[4] Hawley, Ind. Eng. Chem., 18, 573 (1926); Adolph, THIS JOURNAL, 37, 2500 (1915); Wagner and Ross, J. Ind. Eng. Chem., 9, 1116 (1917).

[5] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929.

[6] De Boer, Chem. Weekblad, 21, 404 (1924); Steiger, THIS JOURNAL, 30, 219 (1908); Merwin, Am. J. Sci., 28, 119 (1909).

[7] Krause and Becker, Ber., 53, 183 (1920).

Experimental

Preparation of Materials.—Krause and Becker[7] used triphenyltin chloride as the precipitant in the preparation of the fluoride. This substance is not available commercially so it was prepared from tetraphenyltin. Two lots of the tetraphenyltin were prepared by Mr. R. E. Pflaumer of this Laboratory, using the zinc diphenyl method of Chambers and Scherer[8] for one lot, and the Grignard method proposed by Pfeiffer and Schnurmann for the other.[9] Mr. Pflaumer regards the latter method as the more satisfactory of the two, both in regard to the ease of execution and to the yield secured. A third lot of tetraphenyltin was procured from the Eastman Kodak Company. Identical results were secured with the three separate lots.

Krause prepared triphenyltin chloride by first making the bromide by treating tetraphenyltin in pyridine solution with bromine dissolved in pyridine while cooling with solid carbon dioxide.[10] The bromide was dissolved in ether, converted to the hydroxide and then to the chloride by shaking with 12 N hydrochloric acid. A less difficult method has been proposed by Chambers and Scherer[11] and this method was used in the present work. On account of a few minor changes, the procedure will be briefly outlined. Triphenyltin iodide is prepared by refluxing tetraphenyltin in chloroform solution with iodine, the chloroform and iodobenzene are distilled off, the iodide dissolved in ether and converted to the hydroxide by shaking with a cold 30% solution of sodium hydroxide. The hydroxide was found to be only slightly soluble in ether and it is liable to separate out at this stage as a pasty mass. The ether solution and any hydroxide that has separated are thoroughly washed with cold water by shaking in a separatory funnel. This point is not mentioned by Chambers and Scherer but is rather important because the sodium iodide if not removed is converted in part to hydriodic acid on treatment with hydrochloric acid and the former acid, being somewhat soluble in ether, is very difficult to remove from the crystals of triphenyltin chloride. The ether solution of the chloride is also washed with water to remove excess hydrochloric acid. It is then dried over anhydrous sodium sulfate, evaporated down to separate out the crystals of the chloride and the compound recrystallized from ether and dried in air at room temperature.

A few attempts were made to use the iodide as a precipitant but it was found to be less soluble in alcohol than the chloride and the solution showed some decomposition on standing, turning brown after a few days. Twenty grams of the pure chloride was weighed out and shaken vigorously with one liter of 95% ethyl alcohol and any small residue left undissolved was filtered off. Twenty grams of chloride per liter apparently represents the limit of solubility at room temperature; the solubility increases with rising temperature. This solution containing approximately 0.02 g. of triphenyltin chloride per ml. was used for all of the precipitations.

Various methods of preparing standard solutions of fluoride have been proposed. Batchelder and Meloche[12] prepared sodium fluoride from sodium bicarbonate and redistilled hydrofluoric acid; Clarke and Bradshaw[13] prepared the standard fluoride from solutions of potassium fluoride and sodium chloride; Kurtenacker and Jurenka[14] titrated hydrofluoric acid with standard carbonate-free sodium hydroxide and Hawley[15] used

[8] Chambers and Scherer, THIS JOURNAL, **48**, 1054 (1926).

[9] Pfeiffer and Schnurmann, *Ber.*, **37**, 319 (1904).

[10] Krause, *ibid.*, **51**, 913 (1918).

[11] Chambers and Scherer, Ref. 8, p. 1055.

[12] Batchelder and Meloche, Ref. 2, p. 2132.

[13] Clarke and Bradshaw, *Analyst*, **57**, 138 (1932).

[14] Kurtenacker and Jurenka, *Z. anal. Chem.*, **82**, 210 (1930).

[15] Hawley, Ref. 4, p. 574.

sodium carbonate and hydrofluoric acid. An adaptation of Hawley's method was used in this investigation. Sodium carbonate, C. P., was treated with an excess of C. P. hydrofluoric acid in a platinum dish and allowed to stand for several hours. The excess acid was then driven off by heating and after cooling, the mass was again treated with an excess of acid. After thorough mixing and stirring the dish was heated gently at first and then intensely until the sodium fluoride was entirely fused. The fused salt was cooled in a desiccator over calcium chloride and then pulverized in an agate mortar. The powder was dried in a platinum dish at 110° for three days and stored in platinum over calcium chloride. That this salt was relatively pure was shown by converting samples to sodium sulfate; the results are recorded in Table I.

TABLE I

Trial	NaF, g.	Calcd. wt. Na$_2$SO$_4$, g.	Found wt. Na$_2$SO$_4$, g.	Variation, %
1	0.5749	0.9723	0.9699	−0.25
2	.4932	.8341	.8330	− .13
3	.2199	.3719	.3709	− .27

For the preparation of a standard solution, enough salt for a 0.1 N solution was weighed out, dissolved in distilled water and diluted up to a known volume in an accurately calibrated flask. The solution was at once transferred to a paraffin-lined bottle and portions of this solution measured out by calibrated pipets as used. For the smaller amounts of fluorine a 0.005 N solution was prepared from the 0.1 N one by dilution as needed. It was found, however, that the dilute solution could be kept in glass without undergoing any change that could be detected.

Procedure for Precipitation.—Some thirty precipitations were made in order to find out the optimum conditions for a quantitative formation of pure triphenyltin fluoride. In the course of these experiments it was observed that the precipitant came down with the fluoride if the water content of the sodium fluoride solution was too high, this, of course, being due to the insolubility of triphenyltin chloride in water. On the other hand, a too high concentration of alcohol in the solution caused low results and it was found that the fluoride was relatively soluble in 95% ethyl alcohol. In a number of trials the precipitate was washed on a Jena sintered-glass crucible with 50 ml. of alcohol and approximately 2.5 mg. of the substance was dissolved. This points to a solubility of about 0.05 g. per liter; obviously then pure alcohol cannot be used for washing nor can water. By holding the alcohol concentration between 60 and 70% by volume and washing with 95% alcohol saturated with the triphenyltin fluoride, checking results were secured. No loss in weight of the fluoride was observed on washing with ether but any triphenyltin chloride precipitated with the fluoride could not be washed out with ether or with the alcohol wash solution. It appears that in the case of precipitant coming down with the fluoride there is co-precipitation of a type so often met with in gravimetric analysis where the impurity cannot be removed by washing. The fluoride is so insoluble in water that the precipitate is not even wetted by it. Triphenyltin chloride melts at 106° but the fluoride does not melt when heated in the open; it sublimes with partial decomposition around 300°. Krause reports that it melts in a sealed tube at 357°. The pure fluoride is stable at 110° and is quickly dried at that temperature. Precipitates dried in glass crucibles overnight at 110° changed their weight less than 0.2 mg., this being the maximum change observed for precipitates weighing about 0.4 g. If the precipitate is contaminated with chloride, heating at 110° produces a garlic-like odor but the loss in weight on continued heating is not appreciable.

The proper procedure for precipitation follows: 95% ethyl alcohol is added to the aqueous solution of the fluoride so that it comprises 60 to 70% of the final volume and the solution is heated to boiling. About twice the calculated amount of the triphenyltin

chloride solution containing 0.02 g. per ml. is diluted with an equal volume of 95% alcohol and also heated to boiling; this solution is then slowly run into the hot fluoride solution with rapid stirring and the whole again heated to boiling. The heat is then removed and the stirring continued until the solution has cooled down somewhat. The beaker is covered and allowed to stand overnight to complete precipitation as the reaction is a slow one. If the quantity of fluoride is large the precipitate begins to form in about a minute after the addition of the reagent as large white crystals, but with small amounts it does not appear until the solution has cooled down to room temperature and the crystals are much smaller. After standing overnight the beaker containing the precipitate is packed in ice and allowed to stand for about an hour to lower the solubility of the fluoride in the solution. If the amount of fluoride is large and the total volume of solution is small this step is not necessary as the solubility of the precipitate in the solution containing about 40% water and an excess of the precipitant is very slight. The precipitate is filtered off through a Jena sintered-glass crucible or other similar type crucible and washed with 95% ethyl alcohol saturated with triphenyltin fluoride, the washing solution being at room temperature and about 50 ml. being used. The precipitate is dried for 30 minutes at 110°, cooled in a desiccator and then weighed. Triphenyltin fluoride shows no tendency to take up moisture.

Using the above procedure the results listed in Table II were obtained. This table gives a summary of all of the determinations made in order to show the variations that were encountered. The low gravimetric factor justifies the calculation of the weight of fluorine to the fifth place. The volumes of sodium fluoride and of reagent used are shown in Table III.

TABLE II

DETERMINATION OF FLUORINE AS TRIPHENYLTIN FLUORIDE

Factor $(C_6H_5)_3$ SnF to F = 0.05153

Trials	F pres., mg.	Range wt. prec., mg.	Range wt. F found, mg.	Av. error, mg.
1– 2	47.46	920.4–917.7	47.43–47.29	0.10
3– 7	18.96	368.9–366.1	19.01–18.87	.03
8–11	9.48	186.1–183.5	9.59– 9.46	.035
12–17	3.84	76.5– 75.1	3.94– 3.87	.07
18–21	0.96	20.1– 19.9	1.04– 1.03	.075
22–26	.95	19.5– 18.1	1.00– 0.93	.02
27–34	.47	10.4– 8.3	0.54– .43	.03
35–40	.19	4.0– 3.2	.21– .16	.01

TABLE III

Trials	NaF, ml.	$\frac{N}{NaF}$	H_2O, ml.	Alcohol, ml.	Total vol., ml.	Reagent, ml.
1– 2	24.98	0.1000	5	60	90	60
3– 7	9.98	.1000	10	40	60	25
8–11	4.99	.1000	15	40	60	15
12–17	2.02	.1000	8	20	30	6
18–21	10.06	.00500	0	20	30	2
22–26	9.98	.00500	0	20	30	2
27–34	4.99	.00500	2	14	21	1
35–40	2.02	.00500	3	10	15	1

In Table IV are given results with very minute amounts of fluorine. In the first ten trials 1 ml. of 0.005 N sodium fluoride was measured from a

calibrated micro-buret and in the last five trials 0.5 ml. was used.   Enough water was added to bring the volume up to 5 ml. and then 10 ml. of 95% alcohol, making the solution about 63% alcohol by volume.   One ml. of the precipitant was used in each one of the trials.   No precipitate could be detected until after standing overnight and then it was quite evident. Blanks treated in exactly the same manner as the fluoride solutions showed no signs of precipitates even after standing for several days.   The weight of fluorine is calculated to the sixth place for the purpose of comparison; only the fifth place is justified by the data.

TABLE IV

DETERMINATION OF MINUTE QUANTITIES OF FLUORINE

Trials	Range wt. prec., mg.	Range wt. F found, mg.	F present, mg.	Av. error, mg.
1–10	2.0–1.4	0.103–0.072	0.095	0.0076
11–15	1.2–0.6	.062– .031	.048	.0081

If the last five trials in Table IV represent the limit of sensitivity of the method it is evident that the procedure may be successfully applied to quantities of fluorine down to 0.05 mg.   Since the volume of solution used in these trials was 15 ml., this is a concentration of fluoride of one part in 300,000.   On the other hand, the method does not lend itself so well to the determination of large quantities, both because of the large volume of reagent required and the bulk of the precipitate secured in such cases. With a weight of precipitate approaching one gram the results are erratic, hence the upper limit of fluorine that may be precipitated accurately is about 0.04 g.

Effect of Other Salts.—The solution of the fluoride to be precipitated should be at a P_H of 7 to 9; if acid some fluorine will be lost on heating to boiling and if too basic triphenyltin hydroxide will be precipitated along with the fluoride.   The hydroxide is readily soluble in the wash solution but if too much comes down with the fluoride it is difficult to wash out. Adolph[16] has pointed out that very little, if any, fluorine is lost on evaporating or boiling neutral or alkaline solutions of sodium fluoride.   A large number of inorganic salts are only slightly soluble in 60–70% alcohol and if present in high concentrations they will separate out when the solution cools down.   In some work on the application of the method to the determination of fluorine in rocks, the solution to be precipitated contained a very large amount of sodium and potassium nitrates which crystallized out on cooling.   It was found possible, however, to remove these salts by first washing the precipitate several times with the alcohol wash solution to remove the excess of precipitant and then with cold water to remove the salts.   It has already been pointed out that the triphenyltin fluoride is extremely insoluble in water.   A large amount of foreign salts appears to

[16] Adolph, *Z. anal. Chem.*, **55**, 395 (1916).

cause some of the chloride to come down with the precipitate, as the results tend to run high in such cases. If present in only moderate quantities nitrate, chloride, bromide, iodide and sulfate do not interfere. Carbonate should be removed by bringing to neutrality with dilute acid and boiling out the carbon dioxide. This is best done by neutralizing to phenolphthalein in the hot. Silicic acid and phosphate must be eliminated by prior treatment of the fluoride solution by the method of Berzelius or of Hoffman and Lundell.[17] These methods effect the complete removal of silicic acid through the use of ammoniacal zinc oxide.

A study of the influence of substances met with in the analysis of fluorspar and of rocks was made by preparing solutions of fluoride from the Bureau of Standards standard sample of fluorspar, No. 79. This sample contains 94.83% calcium fluoride or 46.20% fluorine.[18] Three samples of the fluorspar were treated by the method of Berzelius, all of the residues being fused a second time with sodium and potassium carbonates. The phosphate and a large part of the carbonate were removed by silver nitrate and the excess silver by potassium chloride; the carbonate was then completely removed by neutralizing with dilute nitric acid and boiling out the carbon dioxide. The resulting solutions were cooled and diluted up to 250 ml. in calibrated volumetric flasks; 10.06 ml. of each solution was pipetted out, 15 ml. of water and 50 ml. of 95% ethyl alcohol added and the fluoride precipitated in the regular manner. The results obtained appear in Table V.

TABLE V

RECOVERY OF FLUORINE FROM FLUORSPAR

Trials	Range wt. prec., mg.	Range wt. F found, mg.	F calcd., mg.	Av. error mg.
1–4	89.8– 89.0	4.63–4.59	4.51	0.10
5–8	113.5–110.8	5.85–5.71	5.75	.06
9–12	134.1–131.7	6.91–6.79	6.79	.08

The fluoride is recovered as triphenyltin fluoride to about 0.1 mg., but the accuracy is not as great as with solutions of pure fluoride and the variations are larger. The results run high as has been mentioned before. Further work on applications of the method to fluorspar and to rock analysis is now being carried out.

Disadvantages of the Method.—1. An uncommon and expensive reagent is used.

2. The sample must be of such a size that the amount of fluorine is below 0.04 g.

3. Care must be exercised to prevent precipitation of the reagent due to its insolubility in water.

[17] Hillebrand and Lundell, Ref. 5, pp. 800–807.

[18] Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, Inc., New York, 1931, pp. 562–572.

4. The precipitate is slightly soluble in alcohol and this necessitates washing with a saturated alcoholic solution of the precipitate.

5. Large amounts of foreign salts cause co-precipitation of the reagent and give high results.

Advantages of the Method.—1. It is particularly adapted to small amounts of fluorine due to the low conversion factor.

2. The precipitate is crystalline and is easily filtered and quickly washed.

3. The precipitate is stable and no ignitions have to be made.

4. Not counting the standing overnight, the time required for precipitation and further treatment of the precipitate to the final weighing is less than in any other gravimetric method for fluorine.

Summary

Fluorine may be quantitatively precipitated as triphenyltin fluoride as reported by Krause and Becker in 1920. The method is advantageous for small quantities of fluorine. The procedure for the precipitation and treatment of the fluoride is given.

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DIPOLE ROTATION IN CRYSTALLINE SOLIDS

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Another paper[1] has presented the results of a preliminary investigation of the possibility of contribution to the dielectric constant of a crystalline solid through the rotation of a polar group in a molecule fixed in the crystal lattice or through the rotation of the entire molecule in the lattice. It was found that heptyl bromide, hydroquinone dimethyl ether, and anisole showed no such contribution, while the apparent small contribution in phenol and benzoyl chloride was attributed to the effect of impurities. As it is the purpose of the present paper to extend this investigation with an improved apparatus, it is desirable to give some consideration of the factors involved.

It is evident that, if freezing fixes the molecules in the space lattice, dipoles fixed in the molecules cannot orient in an externally applied field and their contribution to the dielectric constant becomes zero. Accord-

[1] Kamerling and Smyth, unpublished.