



Microchemistry

Microdetermination of Fluorine by Thorium Nitrate Titration

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THE Willard and Winter method for determining fluorine (11) with the use of sodium alizarin sulfonate indicator as proposed by Armstrong (2) has been modified recently as follows: by Hoskins and Ferris (8) who introduced the use of a buffer of monochloroacetic acid; by Armstrong (1) who titrated fluoride in an aqueous solution rather than in an alcoholic solution, and used silver perchlorate to remove interfering chlorides; and by Churchill, Bridges, and Rowley (3) who eliminated the effect of phosphate by a double distillation. Rowley and Churchill (10) applied the aqueous titration to the determination of quantities of 1 to 50 mg. of fluorine. Eberz, Lamb, and Lachele (6) studied the titration in alcoholic solution of quantities of 100 to 150 micrograms of fluorine. [Dahle and associates (5) have recently studied a "back-titration procedure" as suggested to them by W. S. Allen.]

The microdetermination of fluorine according to Armstrong gave an average error of -2.0 per cent in the recovery of 2.0 micrograms of fluorine (1) and "the lower limit seems to be in the vicinity of 0.4 gamma." The method (1) appears particularly advantageous also in that the quantities of reagents and the analytical sample may be reduced to a minimum. The results presented herein, however, show that the titration is less sensitive than Armstrong reports. One of the most disturbing features is an appreciable blank titration which tends to fix the minimum quantity of total determinable fluorine appreciably higher than Armstrong suggests. The minimum quantity actually titrated in aliquots, with reasonable accuracy, was found to equal about 5.0 micrograms.

Limit of Accuracy of the Titration

Titration results with pure fluoride solutions using Armstrong's method, with the use of the Hoskins and Ferris buffer, are given in Table I. The determination of the end point was found to be difficult and frequently uncertain. For best results the color of the unknown and standard was judged with the vial resting on a dull white surface, in light produced by a monochromatic daylight bulb. The end point was scarcely sensitive to a variation of less than 0.030 to 0.050 cc. of the thorium nitrate, equivalent to 0.15 to 0.25 microgram of fluorine. In order to obtain the high recovery which Armstrong reports, it is necessary to titrate much closer than this—i. e., with an error equal to about 0.04 microgram of total fluorine (1) or even less, since aliquots of the total are titrated.

As shown in Table I there is an average blank titration of 0.355 cc. which represents thorium nitrate required to produce the pink colored lake formed following the fluorine-thorium nitrate reaction and used as the end point. It was not thought desirable to have this titration blank equal to more than a third of the total actual titration figure. This in itself restricts the method to the determination of a minimum of about 10.0 micrograms of total fluorine under the conditions that the aliquot titrated is not less than $\frac{1}{5}$ —i. e., at least 2 micrograms are taken for the actual titration, and 3 or 4 aliquots are titrated to obtain an average titration figure.

TABLE I. TITRATION OF AQUEOUS FLUORIDE SOLUTIONS WITH THORIUM NITRATE

Fluorine Added Gamma	Th(NO ₃) ₄ Required for 1/10 Aliquot ^a Cc.	Total Fluorine Titrated Gamma	Total Fluorine Found Gamma	Error in Fluorine Found Gamma	Recovery %
10.0	0.200	1.04	10.4	+0.4	104.0
10.0	0.247	1.28	12.8	+2.8	128.0
11.3	0.232	1.21	12.1	+0.8	107.1
11.3	0.216	1.13	11.3	0.0	100.0
20.0	0.369	1.92	19.2	-0.8	96.0
20.0	0.408	2.12	21.2	+1.2	106.0
50.0	1.038	5.40	54.0	+4.0	108.0
50.0	1.000	5.20	52.0	+2.0	104.0
68.0	1.354	7.04	70.4	+2.4	103.5
68.0	1.342	6.98	69.8	+1.8	102.6
100.0	1.940	10.09	100.9	+0.9	100.9
100.0	1.831	9.52	95.2	-4.8	95.2
100.0	1.873	9.74	97.4	-2.6	97.4

^a Net titration after subtracting blank. Titration figures for five blanks equalled 0.303, 0.363, 0.313, 0.358, and 0.360 cc.; av., 0.355 cc. 1 cc. of Th(NO₃)₄ = 5.2 gamma of fluorine.

For best results the actual titration was carried out on at least 5 to 10 micrograms of fluorine, requiring from 1.5 to 3.0 cc. of the thorium nitrate. These limits are more in keeping with the limits of accuracy found in the actual titration and with the size of the blank titration figure.

Effects of Evaporation in Glass or Porcelain

Table II gives results obtained from evaporation on a water bath of pure fluoride solutions, using glass, porcelain, and platinum containers. The recoveries are generally low with evaporation in glass and porcelain. The addition of the buffer did not give the characteristic bright yellow color to these solutions. On adding thorium nitrate the pink color of the end point appeared quite as usual but the fluoride-thorium nitrate reaction apparently was interfered with in view of the low titration figures. These results show the need of avoiding the use of porcelain and glass containers for the

TABLE II. COMPARISON OF GLASS, PORCELAIN, AND PLATINUM CONTAINERS FOR EVAPORATION OF ALKALINE SOLUTIONS OF SODIUM FLUORIDE

Fluorine Added Gamma	Glass (150-cc. volumes evaporated, made to 10 cc., 1/10 aliquot titrated)			Porcelain			Platinum		
	Th(NO ₃) ₄ required for 1/10 aliquot Cc.	Error in total fluorine Gamma	Recovery %	Th(NO ₃) ₄ required for 1/10 aliquot Cc.	Error in total fluorine Gamma	Recovery %	Th(NO ₃) ₄ required for 1/10 aliquot Cc.	Error in total fluorine Gamma	Recovery %
0.0	0.340	0.319	0.385
0.0	0.319	0.335	0.356
0.0	0.358	0.329	0.413
10.0	0.470	-5.4	54.0	0.531	+0.2	102.0	0.626	+1.9	119.0
10.0	0.413	-6.3	37.0	0.486	-2.1	79.9	0.572	-0.7	93.0
50.0	1.125	-10.7	78.6	1.239	-4.5	91.0	1.309	-3.7	92.6
50.0	1.098	-12.0	76.0	1.138	-9.5	81.0	1.450	+2.3	104.6
100.0	2.226	-5.7	94.3	1.728	-29.9	70.1	2.416	+1.7	101.7
100.0	2.188	-12.6	87.4	2.114	-10.7	89.3	2.410	+1.3	101.3
150.0	3.300	-2.0	98.6	2.992	-16.8	88.8	3.377	-0.3	99.8
150.0	3.110	-10.6	92.9	3.084	-12.2	91.8	3.441	+2.9	101.9

evaporation of the alkaline fluoride distillates. The cause of this interference was not determined. It indicates strikingly the extreme sensitivity of this titration to slightly modified conditions.

Addition of Silver Sulfate to Distilling Flask

Hoskins and Ferris (8) reported an effect of chloride on the alcoholic titration; Armstrong (1) found chloride to interfere in both aqueous and alcoholic titration of fluorine. The author's data show a similar interference beginning at about 4.0 mg. of chlorine per cc.

Armstrong (1) eliminated chloride from the distillate by a rather involved procedure requiring precipitation with silver perchlorate, filtering, redistilling the filtrate, and evaporating the second distillate which is treated with activated charcoal and filtered again before making up to volume. Eberz, Lamb, and Lachele (6) add silver perchlorate solution to a solution of the ash to be distilled, carefully avoiding any excess of silver salt. This ash mixture is dried and transferred to the distilling flask. They found distillation in the presence of silver chloride precipitate "entirely satisfactory, not giving trouble by bumping, holding back fluorine, or releasing the chloride which it is desired to eliminate" (6).

The precipitation of chloride in the distilling flask as the silver salt recommends itself as a simple and effective procedure and had been studied prior to the appearance of the article by Eberz *et al.* (6). The recovery of fluorine was satisfactory (Table III). Although bumping at first proved troublesome, this was partially overcome by the use of solid silver sulfate added directly to the ash solution or to a first distillation concentrate. A less flocculent precipitate was formed under these conditions than when the silver salt was added in a solution. Bumping is eliminated to some extent also in the steam-distillation procedure where the precipitate is kept continuously agitated by steam entering the mixture. It does not appear necessary to avoid a slight excess of silver sulfate. If a second distillation is to be made the required silver sulfate is added for the second distillation.

Application of Method to Biological Materials

As has been pointed out by Dahle and Wichmann (4) and by Hoffman and Lundell (7), considerable uncertainty may still surround the method of separation of fluorine by volatilization in the presence of perchloric or sulfuric acid. It is desirable, therefore, to report satisfactory results (average error about =3.0 micrograms) using perchloric acid and the general technique of Armstrong (1) and of Hoskins and Ferris (8), in the recovery of fluoride added to the distilling flask. The distilling blank titration equals 0.400 to 0.500 cc. (these figures include titration blank of 0.20 to 0.30 cc. previously discussed), owing perhaps to fluorine in the reagents or to

volatilized perchloric acid. It was not found possible to change this blank appreciably by collecting several volumes of distillate from the same sample of perchloric acid or by heating the acid to 170° C. and then collecting 150-cc. samples of distillate at 140° C. Perchlorate ion was found to affect the titration when equal to about 2.0 to 4.0 mg. per cc.

As applied to the determination of the fluorine in biological material, the total body of experimental test rats, for example (9), the procedure was as follows:

The animal body was autoclaved at 120° C. (15 pounds) for about 0.5 hour, dried first in a warm air bath and then in an oven at 100°, moistened with 5 per cent magnesium acetate (12), and ashed in a muffle furnace at 500° C. An aliquot of the ash, equaling approximately 0.50 gram or less, was taken for the fluorine determination.

TABLE III. ELIMINATION OF EFFECT OF CHLORIDE BY ADDITION OF SILVER SULFATE

(Sodium chloride and silver sulfate added to distilling flask, 150-cc. distillate collected, evaporated, made to 5 cc., 1/5 aliquot titrated)

Fluorine Added Gamma	NaCl Added Gram	Ag ₂ SO ₄ Added Grams	Th(NO ₃) ₄ Required for 1/5 Aliquot Cc.	Total Fluorine Found Gamma	Error in Fluorine Found Gamma	Recovery %
20.0	0.0	0.0	1.228	20.7	+0.7	103.5
20.0	0.0	0.0	1.341	24.0	+4.0	120.0
20.0	0.0	0.0	1.499	21.0	+1.0	105.0
20.0	0.0	0.0	1.396	19.1	-0.8	95.5
20.0	0.1	0.0	1.660	25.0	+5.0	125.0
20.0	0.1	0.0	1.680	25.4	+5.4	127.0
20.0	0.2	0.0	1.725	26.5	+6.5	127.5
20.0	0.2	0.0	1.718	26.3	+6.3	126.5
40.0	0.4	0.0	2.324	46.5	+6.5	116.2
40.0	0.4	0.0	2.456	49.8	+9.8	124.5
20.0	0.1	0.3	1.358	23.3	+3.3	116.5
20.0	0.2	0.6	1.343	21.2	+1.2	106.0
25.0	0.2	0.6	1.364	22.5	+2.5	110.0
50.0	0.2	0.6	2.405	48.6	-1.4	97.2
50.0	0.2	0.6	2.525	51.6	+1.6	103.2
100.0	0.4	1.2	2.421	97.8	-2.2	97.8
100.0	0.4	1.2	2.529	103.3	+3.3	103.3

TABLE IV. ANALYSIS OF BONE ASH

Sample Weight Gram	Fluorine Added Gamma	Th(NO ₃) ₄ Required for Aliquot Cc.	Total Fluorine Found Gamma	Recovery of Added Fluorine Gamma	Fluorine in Sample %
0.500	0.0	1.729	59.5	..	0.0119
0.500	0.0	1.695	60.6	..	0.0121
0.500	50.0	2.632	108.4	48.4	0.0120
0.500	50.0	2.596	106.6	46.6	0.0120
0.500	50.0	2.661	109.9	49.9	0.0120
0.040	0.0	2.108	77.3	..	0.0192
0.040	0.0	2.181	80.7	..	0.0207
0.040	0.0	2.735	92.5	..	0.0212
0.040	0.0	2.552	98.1	..	0.02452
0.020	0.0	2.915	100.0	..	0.05000
0.020	0.0	2.674	103.8	..	0.05190
0.020	0.0	3.215	112.7	..	0.05635
0.020	0.0	3.246	114.0	..	0.05200

The ash sample was placed in a 50-cc. Claissen flask together with 5 cc. of 60 per cent perchloric acid, 0.1 gram of pure silica, 10 cc. of distilled water, and two glass beads. The mixture was steam-distilled at a temperature of 138° to 142° C. receiving the distillate in a solution kept definitely alkaline to phenolphthalein, and continuing the distillation until 150 cc. were collected. The distillation should be completed in about 30 minutes. The alkaline distillate was placed in a platinum dish, evaporated on the water bath to about 5 cc., neutralized with dilute hydrochloric acid, and made up to 10 cc. Four or five 1-cc. aliquots were titrated in a manner essentially as described by Armstrong (1). Some results obtained in applying the above procedure to bone and body ash are given in Table IV.

50 to 100 micrograms of added fluorine varied from 80.0 to 125.0 per cent. Doubtless the quantity of fluorine dealt with is too small, but a larger analytical sample would require increased quantities of reagents, a larger flask, and perhaps other modifications, which may affect the distillation (5) and alter the titration conditions.

No attempt has been made to introduce such modifications as appear to be necessary from the above results, in order to apply the method successfully to substances such as milk powders.

TABLE V. ANALYSIS OF SKIM-MILK POWDER

Sample Weight Grams	Mg(Ac) ₂ Gram	Ag ₂ SO ₄ Grams	Fluorine Added Gamma	Aliquot Titrated	Th(NO ₃) ₄ Required for Aliquot Cc.	Total Fluorine Found Gamma	Recovery of Added Fluorine Gamma	Fluorine in Sample Gamma P. p. m.
0.0	0.0	0.0	0.0	1/5	0.453
0.0	0.0	0.0	0.0	1/5	0.403
0.0	0.0	0.0	0.0	1/5	0.383
0.0	0.0	0.0	0.0	1/5	0.471
0.0	0.5	2.0	0.0	1/5	0.643	8.9
0.0	0.5	2.0	0.0	1/5	0.623	8.2
0.0	0.5	2.0	100.0	1/10	2.614	108.6	100.1
0.0	0.5	2.0	100.0	1/10	2.586	107.2	98.7
0.0	0.5	2.0	50.0	1/5	2.405	57.1	48.6
0.0	0.5	2.0	50.0	1/5	2.525	60.1	51.6
50.0	0.5	2.0	...	1/5	2.256	45.4	...	36.9 0.73
50.0	0.5	2.0	...	1/5	1.668	30.6	...	22.1 0.44
50.0	0.5	2.0	...	1/5	1.929	37.1	...	28.6 0.57
50.0	0.5	2.0	100.0	1/10	3.694	162.6	124.9	(29.2) ..
50.0	0.5	2.0	100.0	1/10	2.840	111.0	81.3	(29.2) ..
50.0	0.5	2.0	50.0	1/10	2.453	100.6	62.9	(29.2) ..
50.0	0.5	2.0	50.0	1/10	2.146	85.2	47.5	(29.2) ..

In the majority of these determinations 50.0 to 100.0 micrograms were adopted as the range of determinable fluorine and 0.50 gram or less of ash constituted the analytical sample. It was intended to keep the size of the analytical sample as small as possible to avoid interfering elements. The recovery of fluorine in the presence of these small quantities of ash was within the limits of error found for pure fluoride solutions added to the distilling flask. Duplicate determinations agreed within 2.0 to 6.0 micrograms of fluorine. In bone and tooth ash or total body ash the only interfering substance would appear to be phosphate. Its effect was eliminated by a double distillation, as proposed by Churchill *et al.* (3) when the sample exceeded 0.1 gram. [An interference of phosphate (PO₄) on the titration was noted at a concentration of about 1.0 microgram per cc.]

In the determination of fluorine in foods and biological materials where the quantities of fluorine present may be 10 p. p. m. or less, more serious difficulties are encountered. The size of sample which will yield a determinable quantity of total fluorine may be extremely large and may include a large yield of ash containing large quantities of interfering chlorides and phosphates, and perhaps other interfering agents. An effort was made to apply the method outlined to dried milk powder which is extremely low in fluorine and high in total ash containing considerable phosphate and chloride. In limiting the determinable fluorine to a minimum of 50 micrograms, at least 100 grams of a material containing 0.5 to 1.0 p. p. m. of fluorine must constitute the analytical sample. Total ash from 100 grams of milk powder is excessive for a 50-cc. flask and 5 cc. of perchloric acid are not enough to keep the ash in solution for distilling. Even on reducing the sample to 50 grams as was done for the data reported in Table V, 10 cc. of perchloric acid, instead of the recommended 5 cc., were required. Under these modified conditions 50-gram duplicate samples varied as much as 14 micrograms of fluorine in an average of approximately 30 micrograms of total fluorine determined. The results for the same sample showed 0.44 to 0.73 p. p. m. of fluorine present. Recovery of

Summary

The microdetermination of fluorine by titration in aqueous solution with thorium nitrate according to Armstrong's latest technique did not give the high degree of accuracy obtained by Armstrong. The recovery of fluoride added to bone ash in 50.0- to 100.0-microgram quantities varied about =5.0 micrograms from the total added. Duplicate samples of bone and tooth ash agreed within 2.0 to 6.0 micrograms of total fluorine, where a total of 50.0 to 100.0 micrograms of fluorine were determined, the size sample equaling not more than 0.5 gram of ash. An attempt to apply the method to the analysis of a material such as milk powder containing less than 1.0 p. p. m. of fluorine was not successful.

The necessity of avoiding glass or porcelain containers in evaporation of alkaline fluoride distillates, previous to titration with thorium nitrate, is indicated. A method for the prevention of volatilization of chloride, by precipitation with silver sulfate added to the distilling flask, was found satisfactory.

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