THORIUM NITRATE TITRATION METHOD FOR THE ESTIMATION OF FLUORINE—PART I

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SUMMARY

1. The thorium nitrate titration method for fluorine estimation has been investigated.

2. It is shown that the reaction between fluorine as NaF and thorium nitrate is different from that taking place between fluorine as hydrofluosilicic acid and thorium nitrate. In the first case, ThF_4 is formed, and in the second, H_2ThF_6.

3. It is further shown that the reaction between thorium salt and hydrofluosilicic acid is not always the same and is determined by the manner in which hydrofluosilicic acid is distilled. Conditions have been indicated, which give rise to variations in the reaction between thorium salt and hydrofluosilicic acid.

INTRODUCTION

Numerous methods have been devised and employed for the determination of fluorine; but the one, which has received the widest acceptance amongst the workers on fluorine, is that developed by Willard and Winter (1933), requiring the titration of fluorine with thorium nitrate in the presence of zirconium alizarin sulfonate. The method subsequently has been modified by Armstrong (1936), who proposed the use of sodium alizarin sulfonate in place of zirconium alizarin sulfonate and carried out the titration with thorium nitrate in aqueous in place of 50 per cent. alcoholic solution, and by Hoskins and Ferris (1936), who introduced the use of monochloro acetic acid—sodium hydroxide buffer.

Despite the modifications proposed by these and other workers, there is a considerable element of unreliability and confusion in the method, as is indicated below. The method has been thoroughly investigated, has been modified in some parts, and some of the conflicting points have been clarified.

PRINCIPLE AND ACCURACY OF THE METHOD

From its associated matter, fluorine is first separated by distillation with 50 per cent. sulphuric acid or 60 per cent. perchloric acid as hydrofluosilicic acid. The evolved hydrofluosilicic acid is then titrated with

thorium nitrate of suitable strength in the presence of sodium alizarin sulfonate to indicate the end-point marked by the appearance of a pink colour formed as a result of the reaction between excess thorium and the indicator. Besides the variations in the results obtained, usually ascribed to the pH, concentration of the indicator and the interference by other ions, it has been observed that the reaction between thorium nitrate and hydrofluosilicic acid does not take place, even under the most strict conditions, according to the laws of chemical proportions. Even fixed equivalence has not been observed under certain conditions, usually owing to the interference by other ions. Armstrong (1936) noted that the results of titration of $1 \cdot 25$–$10 \cdot 0 \mu$ of fluorine in 48 per cent. alcohol fell on a straight line when plotted but the plotted data of the titration of $0 \cdot 5$–$1 \cdot 25 \mu$ of fluorine fell on another line. The smaller amounts of fluorine required more thorium nitrate than that which corresponded to the amounts predicted from the projection of the first mentioned line. It was Rowley and Churchill (1937) who showed that the titration between thorium nitrate and fluorine, when carried out at a pH of $2 \cdot 9$ to $3 \cdot 4$, gives results which are stoichiometrically correct. Such a titration gives correct results, when the interfering substances are not present, for example, they have employed it with satisfactory results in the determination of fluorine in lithium fluoride and in sodium fluoride without the previous separation of fluorine by distillation with sulfuric or perchloric acid. It should be noted in this case that, as distinguished from the normal procedure where thorium nitrate is titrated with hydrofluosilicic acid, the titration in this case has been carried out with sodium fluoride or lithium fluoride, and that no distinction has been made between titration of fluorine as sodium fluoride with thorium nitrate and the titration of fluorine as hydrofluosilicic acid with thorium nitrate. The full significance of this difference will be pointed out later.

ATTEMPTS MADE AT EXPLAINING AND OVERCOMING THE LACK OF PROPORTIONALITY IN THE REACTION BETWEEN THORIUM NITRATE AND FLUORINE

Attempts have been made to explain this lack of proportionality in the reaction between thorium nitrate and hydrofluosilicic acid or, failing that, to suggest methods to compensate for this anamoly or to standardise conditions wherein any fixed proportionality between thorium nitrate and hydrofluosilicic acid can be obtained. Armstrong (1936), with a view to correcting the lack of equivalence of the thorium nitrate solution for amounts of fluorine greater or less than $1 \cdot 25 \mu$, employed the following measures without any noteworthy success: (i) alteration of the amounts of hydrochloric acid of various dilutions added in excess of that required to adjust the colour

of the indicator to greenish yellow; (ii) use of nitric acid for the adjustment of the acidity of the solution for titration; (iii) use of mono-chloro acetic acid-sodium hydroxide buffer of Hoskins and Ferris (1936); (iv) the addition of one drop of 1N sodium chloride to the solution to produce approximately equal ionic concentration of all solutions; (v) the use of thorium nitrate solution in 48 per cent. alcohol; and (vi) various combinations of these measures.

Williams (1946) postulated that, during the reaction between thorium nitrate and fluoride, a simple compound ThF_4 is never formed in stoichiometric equivalence to the fluorine present, even when an excess of thorium nitrate solution is added, owing to the ionisation factors. When thorium and fluorine occur in correct stoichiometric proportions, F ions remain free, owing to the dissociation of ThF_4, and these compete with alizarin S for Th^{+++} ions in the lake, causing the latter to dissociate further and the yellow colour of acid alizarin S to predominate. For very small quantities of fluorine, a few μg in 50 ml. of water, more than twice the theoretical equivalent of thorium is necessary before the end point is reached but when the titration involves larger quantities of fluorine, the necessary excess is progressively diminished through reduction of the percentage dissociated, due to (i) the increase in pH owing to dilution, (ii) the decrease in the concentration of neutral salts originally present, and (iii) the limitation in the number of free ions owing to the approaching saturation. According to him, a point is indeed reached, when further increments of F and Th become stoichiometric. Based on such considerations, he has indicated the importance of ensuring a definite controlled degree of dissociation before any given Th : F equivalence can be relied upon at different fluorine concentrations. To achieve this, he has suggested that dissociation should be kept either at a minimum by adding an equal volume of alcohol, acetone or glycerol to the reaction mixture or at a maximum by using acids.

From the consideration of the above points, it would appear that there is lack of appreciation of the distinction between the reaction between fluorine as sodium fluoride and thorium nitrate and that between fluorine as hydrofluosilicic acid and thorium nitrate. It seems to have been assumed that the reaction between hydrofluosilicic acid and thorium nitrate and that between sodium fluoride and thorium nitrate are identical, and that, in both cases, a compound like ThF_4 tends to form, and that, by keeping the pH of the reaction mixture constant, and carrying out the titration in the absence of neutral salts, the equivalence between thorium nitrate and fluorine would depend upon the dissociation of ThF_4, which, in turn, keeping the other factors constant, would depend upon the concentration of fluorine

in the reaction mixture. In other words, the equivalence between thorium and fluorine will tend to increase with increasing dilution of solution of fluorine as NaF or hydrofluosilicic acid.

RESULTS OF THE PRESENT WORK

Numerous determinations of fluorine have been carried out with a view to assessing the validity of these assumptions and consequent conclusions. The determinations have been carried out under strictly controlled conditions presented in the Second Part. Some of the results obtained are presented below.

TABLE I

Titration of micro-quantities of fluorine as hydrofluosilicic acid with M/1000 Th (NO₃)₄ solution

The results are expressed in mgm.

Fluorine present	Fluorine found	Thorium required	Ratio, Thorium : Fluorine
0·654	0·652	1·327	2·028
0·981	0·990	2·016	2·054
1·308	1·320	2·687	2·055
1·500	1·539	3·133	2·088
2·000	2·012	4·097	2·048
2·500	2·546	5·132	2·049
		Average ..	2·053

Ratio, Thorium : Fluorine in thorium fluoride is 3·054.

From the data presented in Table I, it is clear that, during the reaction between hydrofluosilicic acid and thorium nitrate, a compound is formed, in which the ratio, thorium: fluorine, is 2·053, whereas, the ratio, thorium: fluorine, in thorium fluoride is 3·054. This is further clarified by the data presented in Table II and Fig. 1.

TABLE II

Volume of M/1000 Th(NO₃)₄ solution theoretically required for a given quantity of fluorine as NaF and experimentally required for the same quantity of fluorine as H₂SiF₆

Fluorine present (mgms.)	c.cs. of M/1000 Th(NO₃)₄ required for	
	NaF	H₂SiF₆
0·0342	0·45	0·30
0·0684	0·90	0·60
0·1026	1·35	0·90
0·1368	1·80	1·24
0·1710	2·25	1·56
0·2052	2·70	1·88

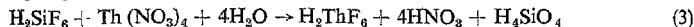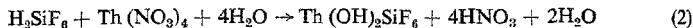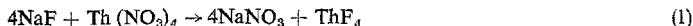Ratio, Thorium for NaF : Thorium for H₂SiF₆ = 3 : 2
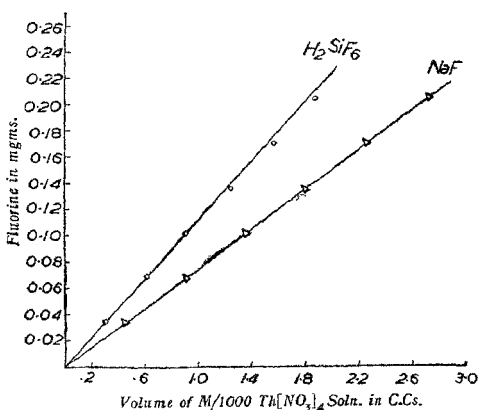
FIG. 1. Volume of M/1000 Th (NO 3)₄ solution theoretically required for a given quantity of fluorine as Na F and experimentally required for the same quantity of F as H₂ Si F₆.

The reaction between sodium fluoride and thorium nitrate is different from the one taking place between hydrofluosilicic acid and thorium nitrate,

The first one leads to the production of thorium fluoride and the second, to a compound in which the ratio, thorium : fluorine, is 2·053. The reactions between fluorine, as sodium fluoride and hydrofluosilicic acid, and thorium nitrate are shown by the following equations:

$$4NaF + Th (NO_3)_4 \rightarrow 4NaNO_3 + ThF_4 \tag{1}$$

$$H_2SiF_6 + Th (NO_3)_4 + 4H_2O \rightarrow Th (OH)_2SiF_6 + 4HNO_3 + 2H_2O \tag{2}$$

$$H_2SiF_6 + Th (NO_3)_4 + 4H_2O \rightarrow H_2ThF_6 + 4HNO_3 + H_4SiO_4 \tag{3}$$

$$2H_2SiF_6 + 3Th (NO_3)_4 + 2H_2O \rightarrow 3ThF_1 + 2H_4SiO_4 + 12HNO_3 + 4H_2O \tag{4}$$
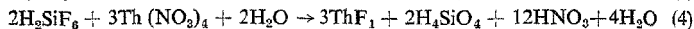
It is understandable that the reaction between sodium fluoride and thorium nitrate takes place as shown by the equation (1). That, the same reaction between hydrofluosilicic acid and thorium nitrate does not take place either according to the equation (1) or according to the equation (4), resulting in the production of thorium fluoride, has been amply demonstrated by the data present in Tables I and II and Fig. 1. This is further confirmed by the conductiometric titration of the same quantity of fluorine as sodium fluoride and hydrofluosilicic acid with thorium nitrate solution. The data are presented in Fig. 2. It is clearly shown that the reaction between
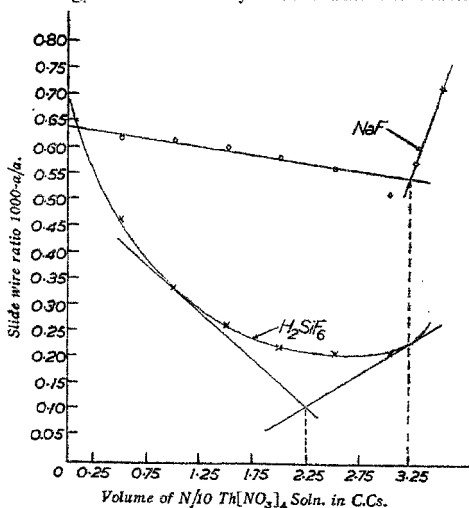

FIG. 2. Estimation of the same quantity of F as NaF and H_2SiF_6 by conductiometric titration with N/10 Th $[NO_3]_4$ solution.

Th $(NO_3)_4$ and hydrofluosilicic acid does not follow the course leading to the formation of thorium fluoride and that, for its completion, requires two-thirds of thorium necessary for the formation of thorium fluoride. That, the reaction between hydrofluosilicic acid and thorium nitrate does not take place as indicated in the equation (2) but takes place as shown by the equation (3) is supported by the following evidence.

(*a*) *Solubility*.—Th $(OH)_2SiF_6$ is relatively much more soluble than ThF_4 and H_2ThF_6. Silico-fluorides or fluo-silicates, with the exception of barium and potassium salts, which are sparingly soluble, are soluble in water (Vogel, 1946). 1000 c.c. of saturated solution of ThF_4 at 25° C. contain 0·17 gms. ThO_2 (Seidell, 1940) whereas, at the same temperature, one litre of saturated solution of H_2ThF_6 contains approximately 5 to 6 mgms. of the fluoride.

(*b*) *Production of acidity*.—In case the reaction between thorium nitrate and hydrofluosilicic acid were to take place, as shown in the equation (2), there would result, at the end of the reaction, for one mole of hydrofluosilicic acid, the production of 4 moles of nitric acid, and 4 moles of nitric acid and one mole of silicic acid and 6 moles of nitric and one mole of silicic acid if the reaction were to take place as represented by the equations (3) and (4) respectively. In other words, the acid, produced during and at the end of reaction, should be explicable on the basis of these equations. Experiments were carried out to determine the acidity at different stages of the reaction between thorium chloride and hydrofluosilicic acid. 20 c.c. of H_2SiF_6 solution of known strength were titrated with N/50 sodium hydroxide solution, using phenolphthalein as the indicator. The volume of the standard thorium chloride solution, of known acidity, required for complete reaction with fluorine, was calculated from the equations (2) and (3). Thorium chloride solution was next added in increasing volume to different 20 c.c. aliquots of hydrofluosilicic acid solution, and in no case was the thorium solution added, which was in excess of the calculated value, as it has been found that the precipitate is soluble in the excess of thorium salt. After shaking for few minutes, the solutions were centrifuged, and the acidity was determined in an aliquot of the clear supernatant. The necessary correction was made for volume changes due to the addition of thorium chloride solution. The results are presented in Table III.

It is seen that the total acidity, produced in the reaction mixture, is not explicable on the production of hydrochloric acid alone, if the reaction were to take place according to the equation (2), for the acid produced is more than that could be accounted for as due to hydrochloric acid and is less than that which would be produced if the reaction were to take place acccording

TABLE III

Determination of the acidity developed during the course of reaction between thorium chloride and hydrofluosilicic acid

20 c.cs. of H_2SiF_6 containing 7·6 mgms. of F will require 5·37 c.cs. of $ThCl_4$ solution containing 2·770 mgms. of thorium per c.c.

Acidity of 20 c.cs. of H_2SiF_6 solution corresponds to 19·66 c.cs. of N/50 sodium hydroxide.

Acidity is expressed in c.cs. of N/50 alkali.

Acidity of H_2SiF solution after the addition of n c.cs. of $ThCl_4$ solution (a)		Acidity due to $ThCl_4$ solution added (b)	Acidity due to unreacted H_2SiF_6 (c)	Acidity produced (a-b-c)	Acidity due to HCl produced	Remaining acidity
c.c.						
	19·54	0·77	16·00	2·77	2·3%	0·39
	19·29	1·54	12·33	5·42	4·77	0·65
	19·01	2·31	8·67	8·03	7·15	0·88
	18·68	3·08	5·01	10·59	9·54	1·05
5·05	18·21	3·89	1·17	13·15	11·92	1·23
5·37	18·10	4·13	0·00	13·97	12·80	1·17

to equation (4). The acidity in the reaction mixture is not due to hydrochloric acid alone but due to more than one acid. This can be easily explained on the basis of equation (3). According to this equation, as a result of the formation of H_2ThF_6, both silicic acid and hydrochloric acid are produced. In such low concentrations, as have been employed, silicic acid does not precipitate but remains in solution.

(c) *Thorium content of the precipitate.*—Thorium content of the precipitate, obtained as a result of reaction between thorium chloride and hydrofluosilicic acid in strong as well as in weak solutions, has been determined and has been found to be 66·54, 67·52, 66·92, 67·25 per cent.

From the percentage of thorium in different thorium and fluorine compounds given in Table IV, it is clear that the thorium fluorine compound,

TABLE IV

Percentage of thorium in different compounds of thorium and fluorine

Compound		Thorium percentage
ThF_4	..	75·34
$Th(OH)_2SiF_6$	..	56·87
H_2ThF_6	..	66·68

formed as a result of the reaction between hydrofluosilicic acid and thorium salt, has the composition as represented by H_2ThF_6 and not the one given by $Th(OH)_2SiF_6$ or ThF_4.

EFFECT OF DILUTION ON EQUIVALENCE BETWEEN THORIUM AND FLUORINE

A known quantity of fluorine as NaF and H_2SiF_6, contained in 1 c.c. of water, was titrated with thorium nitrate. Maintaining the quantity of fluorine constant, the solution was progressively diluted with water and titrated with thorium nitrate solution. The results are given in Table V.

TABLE V

Effect of dilution on equivalence between thorium and fluorine

Fluorine present 14·75 μ in		Fluorine found	
		H_2SiF_6	NaF
1 c.c.	..	14·79	15·12
2 c.c.	..	14·81	15·50
3 c.c.	..	14·81	16·12
4 c.c.	..	14·92	16·25
5 c.c.	..	14·92	16·95
10 c.c.	..	15·70	18·12

It is clear from the results presented that, despite the high dilution the solution has been carried to, the equivalence between thorium and fluorine in the case of hydrofluosilicic acid is relatively not so much altered as that between thorium and fluorine as sodium fluoride.

Thus it may be concluded from the data presented in the foregoing tables that (a) the reaction between sodium fluoride and thorium salt is different from the one between hydrofluosilicic acid and thorium salt in

strong as well as in weak solutions; in the course of the first reaction, ThF_4 is formed, and in the course of the second, H_2ThF_6; (b) under strictly controlled conditions, and within certain limits, the equivalence between thorium and fluorine in the case of hydrofluosilicic acid is not significantly influenced by dilution, indicating that the compound H_2ThF_6, under these conditions of dilution, does not dissociate on dilution to a degree to cause a pronounced variation in the results. The compound H_2ThF_6 is insoluble and less dissociable. The equivalence between thorium and fluorine in the case of sodium fluoride is markedly affected by dilution. This is due to relatively greater solubility and dissociation of thorium fluoride ThF_4.

The reaction between thorium salt and hydrofluosilicic acid is not always the same and is determined by the manner in which hydrofluosilicic acid is distilled off. The reaction between thorium salt and hydrofluosilicic acid described above is obtainable only under a particular set of conditions. Though at present no chemical explanation can be put forth to account for this variation in the reaction between thorium salt and hydrofluosilicic acid, by distilling, under different conditions. a known quantity of fluorine from sodium fluoride and calcium fluoride as hydrofluosilicic acid, and by reacting the evolved hydrofluosilicic acid with thorium salt, and by determining the total thorium and percentage of thorium in the precipitate, results have been obtained, which indicate the conditions which give rise to the variations in the reaction between thorium salt and hydrofluosilicic acid. The results are briefly given below.

(1) When fluorine is distilled from CaF_2 as hydrofluosilicic acid, anywhere between 135° to 145° C., in the manner that no fumes are formed either in the distillation flask or in the mouth of the condenser, on adding to the distillate two-thirds of thorium necessary for the formation of ThF_4, the precipitate is obtained, which has the composition as denoted by H_2ThF_6, and in which the ratio, Th : F, is about 2·036. When more thorium is added to the distillate, the precipitate takes up more thorium till it forms a compound in which the ratio, Th : F, is about 2·443, and which probably has the composition as represented by $HThF_5$; but when the total quantity of thorium, necessary for the formation of ThF_4, is added to the distillate, the precipitate is formed, which again has the ratio, Th : F, of about 2·036.

(2) When fluorine is distilled from CaF_2 as hydrofluosilicic acid, anywhere between 135° to 145° C., in the manner that fumes are formed either in the distillation flask or in the mouth of the condenser, on adding to the distillate two-thirds of thorium necessary for the formation of ThF_4, the precipitate is obtained in which the ratio, Th : F, is greater than 2·036, the

ratio necessary for the formation of H_2ThF_6, and smaller than $2\cdot443$, the ratio necessary for the formation of $HThF_5$. As more thorium is added to the distillate, the precipitate takes up more thorium till it forms a compound in which the ratio, $Th:F$, is about $2\cdot443$; but when the total quantity of thorium, necessary for the formation of ThF_4, is added to the distillate, the precipitate is formed, which again has the ratio, $Th:F$, of about $2\cdot036$.

(3) When fluorine is distilled from CaF_2 as hydrofluosilicic acid, anywhere between $130°$ to $145°$ C., whether gently or rapidly, whether with or without the formation of fumes in the distillation flask and the mouth of the condenser, on adding the thorium salt to the distillate, under no conditions is the precipitate obtained, which has the composition or the ratio, $Th:F$, of ThF_4.

(4) When fluorine is distilled rapidly at $140°$ to $145°$ C. from sodium fluoride as hydrofluosilicic acid, on adding the thorium salt to the distillate, the precipitate is obtained, which has the composition and ratio, $Th:F$, of ThF_4.

(5) When fluorine is distilled gently at $135°$ C. or below from sodium fluoride as hydrofluosilicic acid and without the formation of fumes in the distillation flask and the mouth of the condenser, on adding the thorium salt to the distillate, the precipitates are obtained, which are similar in composition to those obtained when fluorine is similarly distilled from CaF_2 as hydrofluosilicic acid.

(6) When fluorine is distilled as hydrofluosilicic acid from sodium fluoride mixed with calcium oxide, on adding the thorium salt to the distillate, the precipitates are obtained, which are similar in composition to those obtained when fluorine is distilled from CaF_2 as hydrofluosilicic acid.

REFERENCES

1. Armstrong, W. D.   ..   *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 384.
2. Hoskins, W. M. and   *Ibid.*, 1936, **8**, 6.
    Ferris, C. A.
3. Rowley, R. J. and   *Ibid.*, 1937, 9, 551.
    Churchill, H. V.
4. Vogel, A. I.   ..   *Text-Book of Qualitative Chemical Analysis*, Longmans, Green & Co., 1946.
5. Willard, H. H. and   *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 7.
    Winter, O. B.
6. Williams, H. A.   ..   *Analyst*, 1946, **71**, 175.