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

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SUMMARY

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

2. The conditions for the accurate estimation of fluorine are described. The permissible concentration of different interfering ions is given. The limitations and accuracy of the method are discussed, and the use of other indicators is suggested.

INTRODUCTION

In the First Part, it has been shown that the reaction between hydrofluosilicic acid and thorium nitrate, though is different from that taking place between sodium fluoride and thorium nitrate, is not always the same, and is determined by the manner in which hydrofluosilicic acid is distilled. The reaction has been further investigated, and the details for the correct estimation of fluorine are presented in this communication.

Reagents Required

(1) *Sodium fluoride solution.*—Solution of sodium fluoride containing 1 mgm. of fluorine per c.c. is prepared by dissolving 2·210 gm. of pure sodium fluoride in a litre of water. The solution should be stored in paraffined bottles.

(2) *Thorium Nitrate.*—M/1000 thorium nitrate solution is prepared from a more concentrated solution of thorium nitrate whose thorium concentration is determined by precipitating thorium as oxalate, converting it into dioxide and weighing it as such.

(3) *Buffers.*—0·02 M monochloro acetic acid and 0·02 M sodium hydroxide; pH of the buffers should be verified potentiometrically.

(4) 50 *per cent. sulphuric acid.*—The acid should be boiled to make it free from sulphur dioxide.

(5) *Pumice or Glass Pieces and Silicon Carbide.*—These should be boiled with 50 per cent. sulphuric acid for a sufficient length of time to render them free from fluorine, and finally should be washed with distilled water prior to using for the distillation.

(6) *Ashing Agent.*—This is prepared by mixing 1 gm. of calcium oxide, 1 gm. of magnesium oxide and 7 gm. of magnesium acetate with 100 c.c. of water.

(7) *Indicators.*—Sodium alizarin sulfonate 0·05 per cent.; bromophenol blue 0·04 per cent.

Details of the Method

The method for the determination of fluorine, when it is associated with organic or interfering material, consists of the following steps: (i) destruction of the organic matter by ashing; (ii) separation of fluorine as hydrofluosilicic acid from the ashed material by distilling it with suitable acid; (iii) making up the distillate to a suitable volume, and determination of its pH; (iv) buffering the suitable aliquot of the distillate with monochloroacetic acid and sodium hydroxide buffer, and titrating it with thorium nitrate solution in the presence of sodium alizarin sulfonate to the appearance of a pink colour.

When the sample is free from organic and other interfering material, fluorine is directly distilled as hydrofluosilicic acid.

(i) *Ashing of the Sample.*—The accuracy in the estimation of fluorine in materials, which are to be ashed, is determined by the nature of the ashing agent employed and the temperature at which the material to be analysed is ashed. The most suitable ashing agent is that obtained by mixing 1 gm. of calcium oxide, 1 gm. of magnesium oxide and 7 gm. of magnesium acetate with 100 c.c. of water. The reagents employed are of high purity. The fluorine content of the ashing agent is determined. The material to be ashed is minced or ground to fine particles, macerated with a known volume of the ashing agent, first dried on a water-bath, later at 100° C. in an oven, gently ignited over a bunsen burner, and finally ashed in a muffle furnace at 500° C. Very consistent results have been obtained by ashing the material in this procedure with the above ashing agent.

(ii) *Distillation of Fluorine as Hydrofluosilicic Acid.*—In the distillation of fluorine as hydrofluosilicic acid, using sulphuric acid or perchloric acid, two factors have to be rigidly controlled: (i) bumping and (ii) rise in temperature over and above that required for the complete distillation of hydrofluosilicic acid. As a result of bumping and high temperature, acids are carried over in the distillate in amounts which severely impair the sensitivity of the reaction between thorium nitrate and hydrofluosilicic acid. The solution in that case is either rejected or redistilled. Various devices have been contrived to prevent bumping and the excessive rise in temperature

(Scott and Henne, 1935; Lockwood, 1937, Rempel, 1939; Clifford. 1941; Huckaby, *et al.*, 1947; and Willard, *et al.*, 1947). Some of these devices, though reported to be efficient, cannot be easily employed under ordinary conditions, owing to their elaborate nature. The problem has been satisfactorily solved by carrying out the distillation in the following manner. The ashed material is dissolved in 40 c.c. of previously boiled and cooled 50 per cent. sulphuric acid, and transferred quantitatively to a distillation flask of 125 c.c. capacity, containing 2 or 3 pieces of fluorine-free pumice stone and 0·5 gm. of fluorine-free silicon-carbide. The distillation flask is fitted with a three-holed rubber cork, carrying a 200° C. thermometer. 50 c.c. separating funnel and an inverted U-tube, 9″ long and 6″ wide. Boththe thermometer and the end of the funnel extend to with in ½″ of the bottom of the flask. The inverted U-tube, just above its end inside the distillation flask, carries a trap of the type shown in Fig. 1. The other end of the tube is attached through a rubber cork to the condenser. Enough water is placed in the receiver to permit complete immersion of the condenser tip during the first few minutes of the distillation. The distillation flask is clamped ½″ above the wire-gauze which is heated with a bunsen burner. In this position, the flask is not heated directly but by means of hot air. It is heated on an air-bath, and is heated uniformly. The distillation is carried out between 135–45° C. The temperature is maintained within these limits by slowly introducing water from the funnel into the distillation flask. Bumping has been completely eliminated, and by properly adjusting the

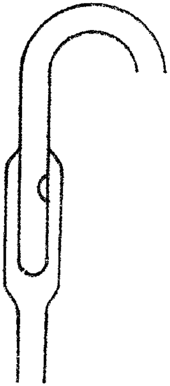

FIG. 1. The type of trap used in the distilation of fluorine as hydrofluosilicic acid

flow of water from the funnel into the flask, sometimes a complete distillation of fluorine has been carried out without experiencing the necessity of re-adjustment of flow of water to keep the temperature within prescribed limits, as any change in the heating capacity of the flame brings about a much smaller change in the heating of the flask which is not being heated directly. Ordinarily, employing small quantities of fluorine, complete distillation takes about 60 to 90 minutes. The recovery of fluorine in the distillate is affected, when the material either is not properly ashed or it carries with it sodium silicate, boric acid or aluminium salts. The effect of the presence of these susbtances in the samples on the recovery of fluorine is shown in Table I.

TABLE I

Effect of sodium silicate, boric acid, and aluminium salts on the recovery of fluorine

Substance	Fluorine present mg.	Fluorine recovered after distillation for			F. unaccountable mg.
		1st hr. mg.	2nd hr. mg.	3rd hr. mg,	
Sodium silicate (500 mg.) ..	3·184	2·604	0·3424	0·020	0·218
Boric acid (500 mg.) ..	3·184	2·11	0·9886	0·075	0·011
Aluminium sulphate (500 mg.)	3·184	2·604	0·5783	Trace	..

It is clear from the results presented in Table I that, even at the end of 3 hours of distillation, fluorine is not quantitatively recovered in the distillate when sodium silicate is present. Under conditions, when the presence of boric and aluminium salts is anticipated in the samples, distillation should be continued for longer periods to effect complete recovery, and to prevent the contamination of the subsequent samples with the fluorine left over in the flask from silicate bearing samples, the flask should be cleansed with hot sodium hydroxide solution.

Titration of Hydrofluosilicic Acid with Thorium Nitrate—Effect of pH.—By titrating known quantities of fluorine as hydrofluosilicic acid with thorium nitrate, different results have been obtained at different pH. Lower values have been obtained at higher pH, and high values, at lower pH. The results are presented in Table II.

The results clearly indicate that the reaction between thorium nitrate and hydrofluosilicic acid takes place in stoichiometric proportions at pH 3·0 only, and that a variation in the pH of the reaction mixture by 0·1 unit

TABLE II

Effect of pH on the titration of hydrofluosilicic acid with thorium nitrate

pH	Fluorine present	Fluorine found	pH at the end of reaction	pH	Fluorine present	Fluorine found	pH at the end of reaction
2·2	22·02 μ	39·08	2·15	3·0	22·02 μ	22·28	3·00
2·4	22·02 μ	36·20	2·25	3·1	22·02 μ	21·86	3·15
2·6	22·02 μ	32·70	2·45	3·2	22·02 μ	16·73	3·40
2·8	22·02 μ	29·50	2·70	3·4	22·02 μ	11·03	3·55
2·9	22·02 μ	23·57	2·80	3·6	22·02 μ	9·43	3·7

leads to erroneous results. In the titration of larger quantities of fluorine, requiring high titre of thorium nitrate solution, it was observed that significantly higher results were obtained (Table III).

TABLE III

Titration of larger quantities of fluorine at pH 3·0

Fluorine present μ	Fluorine found μ	pH at the end of the titration	Fluorine present μ	Fluorine found μ	pH at the end of the titration
20·70	20·94	3·0	60·00	62·12	2·90
32·70	33·52	3·0	70·00	73·70	2·85
51·10	52·2	2·95	80·00	87·60	2·80

As seen from the data in Table III, the higher results, obtained in the titration of larger quantities of fluorine, are due to the change in the pH of the reaction mixture, though initially the pH of the solution was adjusted to 3·0. The increase in acidity is due to the acidity of the thorium nitrate solution added, and also due to the acidity developed as a result of the reaction between thorium nitrate and hydrofluosilicic acid, as shown in the equation (3), *vide* Part I. To maintain the pH of the solution constant at 3·0, the monochloro-acetic acid-sodium hydroxide buffer was employed. The maximum volume of the buffer, which can be added without interfering with the accuracy of the method, was determined after a series of experiments (Table IV). The volume of the aliquot used in each case was 2 c.c., to which increasingly large volumes of buffer were added.

TABLE IV

Effect of the volume of buffer on the titration between hydrofluosilicic acid and thorium nitrate

Volume of buffer added in c.c.	Fluorine		Volume of buffer added in c.c.	Fluorine	
	Present	Found		Present	Found
0·20	16·42 μ	16·39 μ	0·40	16·42 μ	16·75 μ
0·25	16·42 μ	16·45 μ	0·50	16·42 μ	20·50 μ
0·30	16·42 μ	16·45 μ	0·75	16·42 μ	25·52 μ

It was found that the addition of buffer to the solution to the extent of 20 per cent. or more of the volume of the aliquot markedly affected the accuracy of the method. Larger volumes of buffer, when added to the aliquot, resulted in considerably higher values.

Thus, after the distillation of fluorine as hydrofluosilicic acid, the distillate is made up to volume. A suitable aliquot is taken, its pH is determined—it is usually acidic—the volume of N/50 alkali, required to bring its pH approximately to 3·0, is noted. A similar aliquot is taken, the noted volume of N/50 alkali is added, and to this is added the buffer solution not exceeding 20 per cent. of the volume of the aliquot and one drop of the indicator solution, and the titration is carried out with M/1000 or M/5000 thorium nitrate solution to the appearance of a pink colour. To facilitate the observation of the first appearance of the pink colour, it is viewed against a similarly treated aliquot.

Interference by other Ions.—In the titration of hydrofluosilicic acid with thorium nitrate, interference is caused by any cation or anion that can form an insoluble compound or a stable complex with thorium or fluorine; but, in the separation of fluorine as hydrofluosilicic acid with sulphuric acid or perchloric acid, the cations are entirely held back in the distillation mixture, unless the distillate is contaminated as a result of violet bumping during the process of distillation. In such cases, the solution should be either re-distilled or rejected. However, one encounters, in the estimation of fluorine in the biological materials, the presence, in the distillate, of halides, NO_3^-, ClO_4^-, SO_3^{--}, SO_4^{--}, AsO_3^{---}, AsO_4^{---}, PO_4^{---} and some organic anions in amounts sufficient to affect the results markedly. These anions are present in the distillate either as a result of contamination due to bumping or brought over from the salts present in the ashed material. The interference due to these anions is determined by the relative amounts of these anions and of hydrofluosilicic acid involved in the titration, and by the nature of the medium in which the titration is carried out. By titrating, in the presence of interfering anions, 50 μ of fluorine as hydrofluosilicic acid in 2 c.c. aliquot with thorium nitrate solution, the permissible concentration of some of the interfering anions has been determined. The results are given in Table V.

TABLE V

The permissible concentration of some anions in the titration of hydrofluosilicic acid with thorium nitrate solution

Anions	Permissible concentration	Anions	Permissible concenttation
Cl^-, Br^-	$10^{-3} \times 3 \cdot 8$ M	SO_3^{--}	$10^{-4} \times 1 \cdot 2$ M
NO_3^-	$10^{-3} \times 2 \cdot 2$ M	PO_4^{---}	$10^{-5} \times 6 \cdot 5$ M
ClO_4^-	$10^{-3} \times 3 \cdot 2$ M	AsO_3^{---}	$10^{-5} \times 5 \cdot 4$ M
SO_4^{--}	$10^{-4} \times 2 \cdot 5$ M	AsO_4^{---}	$10^{-5} \times 8 \cdot 6$ M

The amounts of sulfate, perchlorate and phosphate in the distillate can be reduced to non-interference level by carrying out the distillation in the manner indicated above, as their presence in the distillate is entirely due to the contamination of the distillate with the distilling mixture. The interference of halides can be eliminated by adopting the modification suggested by Armstrong (1936) who used silver perchlorate to remove chloride ion in the distillation of fluorine from a perchloric acid solution, or the one suggested by McClure (1939) who used silver sulfate with sulphuric acid for the same purpose. The interference due to SO_3^{--}, AsO_3^{---}, AsO_4^{---} and NO_3^-, however, cannot be eliminated by any of the methods outlined above nor it is feasible to make appropriate corrections in the calculation of fluorine, for that would involve a separate determination of each impurity and its corresponding interference effect. In this connection, much attention has recently been directed towards compensating titrimetric technique of Dahle, Wichmann and Bonners (1938). As it is, the modification is based on the following unproved assumptions: (i) The reaction between thorium nitrate and hydrofluosilicic acid is similar to the one taking place between thorium nitrate and sodium fluoride. (ii) Interference caused by halides, NO_3^-, SO_4^{--}, SO_3^{--}, PO_4^{---}, AsO_3^{---}, AsO_4^{---} is more or less the same. Back-titration of thorium nitrate with standard hydrofluosilicic acid has not given consistent and reproducible results, chiefly due to the difficulty in locating the end point. Even as it is, the method is applicable to cases where the interference is due to one anion. In such cases, better results are obtained if a balancing quantity of the corresponding salt is added to a solution containing known quantities of fluorine as hydrofluosilicic acid. Such a solution is then titrated with thorium nitrate solution, and the interference effect due to the impurity is determined, and appropriated correction is made in the calculation of fluorine.

Evaporation of Solution Containing Hydrofluosilicic Acid

In the estimation of fluorine as hydrofluosilicic acid, it is sometimes necessary, when extremely small quantities of fluorine are to be estimated, with a view to obtaining the maximum accuracy of the method, to concentrate the distillate to smaller volume, after it is made alkaline to phenolphthalein. The subsequent estimation of fluorine gives values which are low as much as by 30 per cent. The cause therefor has not so far been determined.

Accuracy of the Method.—Ashing the material, isolating fluorine as hydrofluosilicic acid, and titrating the evolved hydrofluosilicic acid according to the procedure outlined above, the method has given very accurate results. The accuracy of the method is markedly affected by NO_3^-, AsO_3^{---} AsO_4^{---}, SO_3^{--}, when these are present in the distillate in quantities more than permissible. For the estimation of very much smaller quantities of fluorine, the accuracy of the method is less than otherwise obtainable. To obviate this, the solution cannot be concentrated, as attempts to concentrate the distillate, after it is made alkaline to phenolphthalein, have yielded values much lower than the theoretical. The stoichiometric accuracy of the method is obtainable only between pH 2·9–3·10. A small change in the pH of the reaction mixture causes a remarkably wide variation in the results, which cannot be overcome by employing larger volumes of the buffer, as the addition of larger volumes of buffer to the reaction mixture affects the accuracy of the method.

Significance of the Dissociation of the Indicator in the Reaction between Fluorine and Thorium Salt

As the end point in the reaction between fluorine and thorium nitrate is marked by the appearance of pink colour due to the formation of lake between thorium nitrate and alizarin sulfonic acid, it is explicitly assumed that the reaction will first take place between thorium nitrate and fluorine, and that only at the end of this reaction, the thorium ions will react with alizarin sulfonic acid to form the lake, and that under these conditions only, will the reaction between hydrofluosilicic acid and thorium nitrate take place according to the laws of chemical proportions. Such conditions, in the first instance, will be determined by the concentration of hydrofluosilicic acid and alizarin sulfonic acid in the reaction mixture, and in the second, by the dissociation of alizarin sulfonic acid. That, the dissociation of hydrofluosilicic acid is not so much related to the stoichiometric relationship obtaining between thorium nitrate and hydrofluosilicic acid between pH 2·9–3·1, is evidenced by the following observations: (i) The reaction between sodium fluoride, a neutral salt, and thorium nitrate, in the presence of alizarin sulfonic acid, takes place according to the laws of chemical proportions, only between pH 2·9 and 3·1. (ii) The reaction between hydrofluosilicic acid and thorium nitrate takes place in stoichiometric proportions, not necessarily between pH 2·9 and 3·1, as is indicated by other chemical and physical methods. The governing factor, it follows, in the proper reaction between fluorine and thorium nitrate in the presence of alizarin sulfonic acid is the dissociation of sulfonic acid. By adjusting the pH of the reaction mixture between 2·9 and 3·1, the dissociation of sulfonic acid is lowered to the necessary minimum which would permit the reaction between fluorine and thorium nitrate to take place first. The relationship between pH, and consequently between the dissociation of the acid and the formation of the thorium lake has been studied in the following manner:

To 10 c.c. aliquots of potassium hydrogen phthalate-hydrochloric acid buffer and distilled water acidified with hydrochloric acid to give different pH were added 4 drops of 0·05 per cent. solution of alizarin sulfonic acid. The solutions were titrated with thorium nitrate to a purplish colour of definite intensity, and the titre value was noted in each case. The results are given in Table VI.

TABLE VI

Effect of pH on the formation of the thorium lake

pH	Thorium nitrate required to produce a purplish lake of definite intensity in the case of	
	pH produced by buffer	pH produced by HCl alone
	c.c. M/1000 $Th(NO_3)_4$ solution	c.c. M/5000 $Th(NO_3)_4$ solution
2·2	1·70	1·50
2·4	1·52	1·00
2·6	1·32	0·90
2·8	1·14	0·70
3·0	1·00	0·55
3·2	0·75	0·52
3·4	0·50	0·48
3·6	0·42	0·48
3·8	0·42	0·48

It is clear that, for the formation of the lake between thorium and alizarin sulfonic acid, much larger quantities of thorium are required at lower pH and in the presence of salts than at higher pH and in the absence of salts. At the same pH, the quantity of thorium required for the formation of lake in the presence of salts is nearly 5 times that found necessary in the absence of the salts. Thus, in the reaction between hydrofluosilicic acid and thorium nitrate in the presence of alizarin sulfonic acid, due to lower pH, and consequently due to reduced dissociation of alizarin sulfonic acid, the reaction between thorium nitrate and sulfonic acid is held in abeyance till the reaction between thorium nitrate and hydrofluosilicic acid is over. The dissociation constant of the sulfonic acid and its dissociation at different pH have been determined.

Dissociation Constant of the Indicator

The dissociation constant of the indicator was determined by the colorimetric method of Salm (1906), employing the equation, $Ka = (H^+)$, when $\alpha = \frac{1}{2}$, where Ka is the dissociation constant of the indicator and α is the degree of dissociation. The determination of the dissociation constant by this method was beset with peculiar difficulties. As the colour of the indicator is yellow-greenish from pH 1 to 3·6, red-brownish from pH 4·5 to 5·5, and red-lilac from pH 7 to 8, it was difficult to compare the resultant of yellow-greenish and lilac with any shade of red or pink. The alkaline colour of the indicator therefore employed was the maximum red obtainable at pH 6·8. The dissociation constant of the indicator determined in this way was found to be $10^{-6} \times 7{\cdot}07$, and its pK therefore, 5·15. Denoting the alizarin sulfonic acid by HIn, the colour changes at any pH in terms of equilibria are represented by HIn (Undissociated coloured) $\rightleftharpoons$ H + In (Differently coloured anion). Applying the law of mass action,

$$\mathrm{K\,HIN} = \frac{(\mathrm{H})\,(\mathrm{In})}{(\mathrm{HIn})}$$

Therefore, $$(\mathrm{H}) = \mathrm{K\,HIN}\,\frac{(\mathrm{HIn})}{(\mathrm{In})}$$

$$\text{Therefore pH} = \mathrm{pK_{HIN}} + \log\frac{(\mathrm{In})}{(\mathrm{HIn})} = \mathrm{pK} + \log\frac{\alpha}{1-\alpha}$$

where α is the fraction of the total indicator as ions. Thus, at any known pH, the fraction α of the indicator of known dissociation constant can be calculated with the help of this equation. The fraction α, at different pH, in the case of alizarin sulfonic acid has been calculated, and is given in Table VII.

TABLE VII

The percentage dissociation of alizarin sulfonic acid at different pH

pH	% dissociation of the indicator	pH	% dissociation of the indicator
5·0	41·49	2·9	0·5597
4·0	6·616	2·8	0·4449
3·6	2·743	2·6	0·2810
3·4	1·749	2·4	0·1775
3·2	1·11	2·2	0·1121
3·1	0·8845	2·0	0·0661
3·0	0·7033		

With the data given in Table VII, it is difficult to prescribe the maximum and minimum dissociation of the indicator which would permit the reaction between fluorine and thorium nitrate to take place to completion. At the same time, it cannot be explained as to why the reaction between fluorine as sodium fluoride or hydrofluosilicic acid and thorium nitrate takes place in chemical equivalence at the pH of 2·9 to 3·1 only. It can be comprehended that at higher pH, due to the greater dissociation of the indicator, there is a kind of competition between the fluoride ions and the indicator ions to react with thorium ions, and the indicator ions succeed in reacting with thorium ions, and in producing the pink colour of the lake even in the presence of fluoride ions. Such a situation would naturally yield results which are not in agreement with the theoretical values. What is required, it seems, for the stoichiometric reaction between thorium and fluorine, in the presence of alizarin sulfonic acid, is a certain degree of dissociation of the indicator, which is neither small nor large. It is difficult to explain as to how such a condition is fulfilled between pH 2·9 and 3·1. Nevertheless, it is obvious that accurate results cannot be obtained if the reaction between fluorine and thorium is carried out in a solution having acidity more than that prevails at pH 3, or if the solution contains more than the permissible quantity of salts. For such reasons, this method cannot be employed for the determination of large quantities of fluorine either as sodium fluoride or hydrofluosilicic acid, for in the first case [*vide* equation (1), Part I], large quantities of salts will be produced, and in the second [*vide* equation (4), Part I], acids in quantities which cannot be contained by the permissible concentration of buffer solutions. Both these conditions will severely affect the accuracy of the method.

DISCUSSION

For its determination, fluorine, under all circumstances, must be separated from its accompanying organic or other interfering material as hydrofluosilicic acid by the method outlined above. Even in the case of solutions of pure fluorides, it should be preferrred to convert fluorine into hydrofluosilicic acid, for in dilute solutions of fluorides containing a few μg per c.c., on adding the equivalent amount of thorium solution, owing to its solubility, thorium fluoride is not precipitated. The dissolved thorium fluoride dissociates.

$$ThF_4 \rightleftharpoons Th^{\cdot\cdot\cdot\cdot} + 4F'.$$

Thus, in the solution, there are $Th^{\cdot\cdot\cdot\cdot}$ ions and F' ions. On adding a slight excess of thorium solution, the pink colour of the thorium lake with alizarin sulfonic acid should appear;

$$HIn \rightleftharpoons \dot{H} + In'$$

$$Th^{\cdot\cdot\cdot\cdot} + 4\ In' + 4\ ThIn$$

but, owing to the dissociation of thorium fluoride, there are F' ions which compete with indicator In' ions for $Th^{\cdot\cdot\cdot\cdot}$ ions in the lake, causing the lake to dissociate into $Th^{\cdot\cdot\cdot\cdot}$ ions and indicator In' ions. Thus, at the end point of the reaction between sodium fluoride and thorium nitrate in the presence of alizarin sulfonic acid, there is an equilibrium between the following reactions:

$$ThF_4 \rightleftharpoons Th^{\cdot\cdot\cdot\cdot} + 4F'$$

$$HIn \rightleftharpoons \dot{H} + In'$$

$$Th^{\cdot\cdot\cdot\cdot} + 4In' \rightleftharpoons ThIn$$

$$ThIn + 4F' \rightleftharpoons ThF_4 + 4\ In'.$$

Thus, owing to the presence of free F' ions, which cause the thorium lake to dissociate, the end point, as marked by the appearance of pink lake, cannot be observed unless a larger excess of thorium ions is added to the reaction mixture, which will suppress the dissociation of dissolved thorium fluoride into $Th^{\cdot\cdot\cdot\cdot}$ and F' ions. This will naturally yield very high values for fluorine. From this view-point, it is obvious that the interference in the estimation of fluorine due to F' ions will be relatively less as more and more concentrated solution of fluorine is employed for titration with thorium nitrate in the presence of alizarin sulfonic acid, till, theoretically at least, a point will be reached, when the interference of free F' ions is minimum, and when further increments of $Th^{\cdot\cdot\cdot\cdot}$ and F' are nearly stoichiometric. To obviate the lack of equivalence between $Th^{\cdot\cdot\cdot\cdot}$ and F' in dilute solutions, Williams (1946) suggested that the dissociation of thorium fluoride should be kept at a minimum by adding an equal volume of alcohol, acetone or glycerol to the reaction mixture or at a maximum by using acids. Though by this modification, the dissociation of thorium fluoride is maintained at a definite degree, the dissociation of alizarin sulfonic acid, which has not been taken into account by him, will be altered. It will be lowest in the presence of acids, and in the case of acetone, alcohol or glycerine, much more than that is permissible by the data given in Table VII.

In the case of reaction between hydrofluosilicic acid and thorium nitrate, resulting in the formation of H_2ThF_6, the interference due to free F′ ions is less as the compound has nearly one seventeenth the sclubility of thorium fluoride in water, and is much less dissociable than thorium fluoride. On this basis, it is more accurate to determine fluorine, even in pure solutions, as hydrofluosilicic acid. As the formation of the thorium lake, which marks the end point of the reaction between thorium and hydrofluosilicic acid, is determined by the dissociation of alizarin sulfonic acid, which, in this case, is sharply governed by pH changes and salt concentration (Tables VI and VII), it will be useful to investigate, for the same purpose, the use of other indicators whose dissociation is not so sharply altered by the salt concentration and the pH of the reaction mixture. Such an indicator will increase the accuracy and convenience of the method.

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REFERENCES

1. Armstrong, W. D. .. *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 384.
2. Clifford, P. A. .. *J. Assoc. Official Agr. Chem.*, 1941, **24**, 350.
3. Dahle, D., Wichmann, H. J. and Bonner, R. H. *Ibid.*, 1938, **21**, 468.
4. Hauckaby, W. B., Welch, E. T. and Metler, A. V. *Ind. Eng. Chem., Anal. Ed.*, 1947, **19**, 154.
5. Lockwood, H. C. .. *Analyst*, 1937, **62**, 775.
6. McClure, F. J. .. *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 171.
7. Rempel, H. G. .. *Ibid.*, 1939, **11**, 376.
8. Salm, E. .. *Z. Physik. Chem.*, 1906, **57**, 471; [Quoted from Clark, W. M. (1928)—*The Determination of H⁺ Ions*, p. 101, Bailliere & Co.]
   .. *Z. Electrochem.*, 1906, **12**, 99.
9. Scott, E. W. and Henne, A. L. *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 297.
10. Willard, H. H., Toribara, T. Y. and Holland, L. N. *Ibid.*, 1947, **19**, 343.
11. Williams, H. A. .. *Analyst*, 1946, **71**, 175.