

THE FLUORIDES OF LANTHANUM, CERIUM AND THORIUM WITH SPECIAL REFERENCE TO THE DETERMINATION OF FLUORINE

> THESIS FOR THE DEGREE OF M. S. Cecil Chester Langham 1934





THE FLUORIDES OF LANTHANUM, CERIUM

AND THORIUM

WITH SPECIAL REFERENCE TO THE DETERMINATION OF FLUORINE

A THESIS

Submitted to the Faculty of Michigan State College of Agriculture and Applied Science in Partial Fulfillment of the Requirements for the Degree of Master of Science

ЪУ

Cecil Chester Langham

May 26, 1934.

T546 L279

e

- ACKNOWLEDGEMENT -

Grateful appreciation is expressed to Professor E. Leininger under whose kind, efficient direction this work was carried out.

Cecil C. Langham.

INTRODUCTION

Only within the last few years has fluorine assumed a place of sufficient importance in the scientific and economic world to warrant the general attention of investigators. Recently, however, a great deal of work has been done in connection with the detection and estimation of small amounts of fluorine in such materials as sprays, plant ash, sea water, etc. Yet, in spite of the numerous methods and modifications of methods proposed, there as yet remains to be found an accurate, rapid, and easily carried out method for the determination of fluorine.

This work comprises a series of observations and experiments conducted on the fluorides of lanthanum, cerium, and thorium in their relation to the fluorine determination.

HISTORICAL INTRODUCTION

Pisani (1) found that the addition of a solution of $Th(NO_3)_4$ to the solution of an alkali fluoride slightly acidified with AcOH or HNO_3

produces a heavy gelatinous precipitate of $\text{Th}F_44\text{H}_20$ which may be dried at 100° and weighed, or ignited and weighed as $\text{Th}O_2$. Adolph (2) reported unsatisfactory results from the method and advanced the idea that simple $\text{Th}F_4$ might not be precipitated from a solution of sodium fluoride without being accompanied at the same time by $\text{Na}_2\text{Th}F_6$. To prove this he treated a neutral solution of sodium fluoride with an excess of thorium nitrate, dissolved the washed precipitate with acid, precipitated the thorium with ammonia, and from the filtrate obtained a small amount of sodium chloride.

Gooch and Kobayashi (5) modified Pisani's method to include both a gravimetric and a volumetric method in which the gravimetric process serves as a preliminary step to the volumetric procedure. They precipitated the fluoride with a measured excess of $Th(NO_3)_4$ and ignited the $ThF_4 \cdot 4H_2O$ to ThO_2 . They then determined the excess thorium present in the filtrate by converting it to the oxalate and subsequent oxidation by $KMnO_4$.

Meyer and Schulz (4) carried out many experiments utilizing calcium, lanthanum, and thorium

- 2 -

salts as precipitants. They found that even in the case of the CaF2 method which is the oldest and best known method for the precipitation of fluorine, two opposing errors are involved. First, an unavoidable loss is suffered because of the considerable solubility of the fluoride, and second, a proportionate adsorption of calcium acetate on the fluoride molecule occurs. When they attempted the use of thorium salts as precipitating reagents, they found that an excess of the reagent caused the precipitate to apparently dissolve with the formation of a complex. However. they considered it questionable as to whether a complex formation actually took place or a peptization occured, but in either event, complete precipitation is not achieved. This led to the study of lanthanum salts as precipitants. The character of the precipitate is the same as that of thorium, but whereas, the fluoride dissolves in three times the equivalent amount of lanthanum nitrate or chloride, they found that it would not dissolve in an excess of lanthanum acetate. Upon the addition of the acetate ion, acetic acid or ammonium acetate, to the solution, the fluoride again separates as a gel. Other electrolytes cause only

- 3 -

incomplete flocculation. They found that LaF₃ adsorbs lanthanum acetate from solution, but not the nitrate or chloride, therefore, their method involved the precipitation of the fluoride and the use of a correction factor for the amount of adsorbed lanthanum acetate.

The above described work of Meyer and Schulz in which they used lanthanum acetate as a precipitant for fluoride ions suggested to Batchelder and Meloche (5) the possibility of the use of cerium. Their attempts to make a gravimetric separation of cerous fluoride were unsuccessful, however, because of the gelatinous character of the precipitate. The results obtained indicated a great amount of adsorption on the fluoride molecule. This difficulty led them to investigate a volumetric modification in the hopes that the error included in the gravimetric method due to adsorption might be eliminated. Accordingly. an attempt was made to precipitate the fluoride by adding an excess of cerous nitrate solution and titrate the excess cerium by means of potassium permanganate according to the method of Lenher and

- 4 -

C. Meloche (6). This method depends upon the equations $6Ce(NO_3)_3 + 2KMnO_4 + 4H_2O = 4Ce(NO_3)_4 + 2Ce(OH)_4 + 2KNO_3 + 2MnO_2$

and

 $Ce(NO_3)_4 + 4H_2O = Ce(OH)_4 + 4HNO_3$

Batchelder and Meloche were able to obtain results by this method with amounts of fluorine ranging from .1 to .001 g. with an accuracy of about .0003 g. They found the procedure rather cumbersome and difficult however, for one not accustomed to the method since it was necessary to filter off the precipitated MnO_2 , CeF_3 and $Ce(OH)_4$ at a point just before the equivalent point was reached. Filtration at this point was necessary to prevent an over-titration due to the adsorbed MnO_4^2 ion. Ions such as phosphate and oxalate which precipitate cerium interfere with the determination.

In an attempt to find a more suitable scheme of analysis they investigated the direct titration of fluorine with cercus nitrate using methyl red as the indicator after the method of Kurtenacker and Jurenka (7). Batchelder and Meloche obtained satisfactory results by this method with quantities of fluorine

amounting to less than a miligram. This was not consistent with the findings of Kurtenacker and Jurenka. however, who reported a deviation of results amounting to as much as 4% in some cases. Batchelder and Meloche explained the anomalous results obtained by Kurtenacker and Jurenka in the following manner: The color change of methyl red at the end point was attributed by them to be due to a change in pH caused by hydrolysis of the cerous nitrate. Batchelder and Meloche attempted to check this theory by running a blank determination to find out how much of the standard cerous nitrate solution was required to change the color of the indicator. They found that 2.5 cc. of the standard solution was required to change the color of an ageous solution of methyl red, whereas, if fluorine were present, the color change occured when an equivalent amount of cerous nitrate was added. They also found that when amounts of cerous nitrate which were insufficient to change the color of the indicator were titrated with sodium fluoride solution, the color changed gradually from yellow to red and at the equivalent point changed back to yellow. Now, if an excess of either the cerous nitrate or sodium fluoride were added the color change

- 6 -

was reversible. Hence, they concluded that in the presence of cerous cerium ions the precipitated cerous fluoride preferentially adsorbs indicator, while in the presence of fluoride ions, the cerous fluoride precipitate preferentially adsorbs fluoride.

They reported the interference of sulfate or, in general, any ions such as phosphates or oxalates which precipitate cerium.

Willard and Winter (8) have developed a volumetric method for the determination of fluorine based upon the decolorizing effect of the fluorine ion on zirconium-alizarine dye. The fluoride is titrated with a standard thorium nitrate solution, using a mixture of zirconium nitrate and sodium alizarine sulfonate as the indicator. In case interfering elements are present in the soluble fluoride solutions, the fluorine is separated by volatilizing it as hydrofluosilic acid and titration of the fluorine in the distillate. Armstrong (9) found that a dilute solution of sodium alizarine sulfonate alone could be used as the indicator. Shuey (10) found the method to be accurate for the direct titration of pure fluoride solutions, but he was able to recover only

- 8 -

about 90 per cent of the added fluorine from plant ash. This was attributed to loss of fluorine during ignition of the plant material.

Allen and Furman (11) titrated fluorine potentiometrically by the application of a ferriferrocyanide electrode. Good results are reported for amounts of fluorine ranging from 0.1 mg. to 50 mg. Large amounts of foreign salts mask the equivalent point, and ions which precipitate cerous cerium must be absent.

EXPERIMENTAL RESULTS

In attempting to find a suitable method for the volumetric determination of fluorine in plating solutions the Willard, Winter method was first tried out using thorium nitrate solution as the titrating reagent with a zirconium nitrate and alizarine dye mixture as indicator.

Before beginning this work, however, it was necessary to prepare some pure sodium fluoride. This was done in the following way:

Baker's C.P. sodium carbonate was treated with an excess of Baker's C.P. hydrofluoric acid in a large platinum dish. The product was allowed to stand several hours and then heated to drive off the excess acid. After cooling, an excess of hydrofluoric acid was again added and thoroughly mixed. The resulting product was then heated gently at first and then intensely until the sodium fluoride was entirely fused. After cooling the fused sodium fluoride in a dessicator and pulverizing it in an agate mortar, it was dried in a platinum dish at 110° for three days. The product was then stored in platinum over calcium chloride. The Willard, Winter method is promising inasmuch as neither sulfates nor borates apparently interfere, but from the writer's experience the fact that the endpoint of the titration is hard to determine because of the fading of the color, it seems evident that considerable experience would be necessary in order to consistently duplicate results.

An attempt was then made to apply the Kurtenacker and Jurenka method which consists of the determination of fluorine by means of cerous nitrate solution using methyl red as the indicator. This method, however, was not applicable because of the fact that sulfates in appreciable quantities and borates interfered. In the absence of sulfates and borates though, very satisfactory results were obtained as shown in Table I.

- 10 -

Trial	5 mg. Fluorine	10 mg. Fluorine	20 mg. Fluorine	50 mg. Fluorine
	Ce(NO3)3 (ec.)	Ce(NO3)3 (cc.)	Ce(NO3)3 (cc.)	Ce(NO ₃) ₃ (ec.)
г	2.58	5.25	10.40	26. 20
Q	2.63	5.88	10.55	26.18
1 2	8.57	5.87	10.45	26.10
•	8.60	5.15	10.40	
Ð	8.60	5.23	10.45	
ø		5.18	10.38	
47e.	2.59	5.21	10.40	86,16
46.00 F = 1 00. 08 (NO _B) ₅	1.950	1.919	1.925	119.1

TABLE I

.

(continued on next page)

- 11 -

TABLE I (Cont.)

In Presence of NagSO4

Trial	SO4 present (mg.)	Fluorine added (mg.)	Ce(NO ₃) ₃ (ec.)
T	50	10	5•65
61	20	10	5.65

In Presence of H₃BO₃

1al	BO _S present (mg.)	Fluorine added (mg.)	Ce(NO ₅) ₅ (cc.)
	20	10	No color change

The method works especially well with small amounts of fluorine present. In the case of the 50 mg. samples the color change was more gradual and the end-point hard to detect. With the smaller amounts of fluorine, however, the color change was very sharp and distinct.

Very unsatisfactory results were obtained in the presence of sulfates or borates. The sulfate ion caused high results, while no color change occured in the presence of borates.

It was attempted to substitute perchloric acid for sulfuric acid in the distillation of the fluorine, but the large amounts of acid carried over during the distillation rendered the end-point somewhat indistinct and harder to detect.

Lanthanum nitrate was also substituted for cerous nitrate, using methyl red as the indicator. The results of this are shown in Table II.

- 12 -

TABLE II

Trial	Fluorine present (mg.)	La(NO3)3(cc.)	mg. of $\mathbf{F} = 1cc. La(NO_3)$
1	5	4.60	•920
2	5	5 .13	1.026
5	5	5.13	1.026
4	10	9.85	•985
5	10	9.85	•985
6	10	9.80	•980
7	10	9.83	• 983
8	10	9.85	•985
9	10	9.87	•987
10	20	20,00	1.000
11	20	19.92	•996
12	20	20.85	1.045
13	20	20 .70	1.035
14	40	41.15	1,028
15	40	41.20	1.030
16	40	41.20	1.030

- 14 -

While some of the results obtained from this procedure seemed promising, the titrating itself was much less satisfactory than was the case with the cerous nitrate solution, due to the fact that the color change was so much more gradual and the endpoint harder to establish. This probably accounts for the wide variation of results in many cases.

It was next deemed advisable to try out a number of indicators selected more or less at random. Accordingly, a series of dyes and indicators was made up and tried both with lanthanum nitrate and thorium nitrate as titrating reagents. Those which were tried are listed below with their pH range.

(see next page)

TABLE OF INDICATORS

Indicator	pH Range	Indicator	pH Range
Congo Red	3.3 - 4.6	Methyl Orange	4.4 - 4.6
Phenol Red	7.0 - 7.4	Tropaeolin 00	1.4 - 2.0
Weutral Red	5.4 - 6.0	Lecnoid	4.4 - 6.8
Brom Thymol Blue	6 .4 - 7.0	Thymol Blue	8.4 - 9.2
Brom Cresol Purple	5.8 - 6.2	Malachite Green	
Ecsin		Rhodamine B.	
Fluorescein		Methyl Violet	0.4 - 1.0
Fuchsin		Alizarine Tellow	10.1 -12.1
Cresol Red	7.6 - 8. 2	Rosalic Acid	6.4 - 6.8
p-Nitro Phenol	5.0 - 5.8	Thymolphthalein	7.9 - 8.9
Cresolphthalein	8 . 8 - 9. 8	Brom Phenol Blue	5.8 - 4.0
Cochineal	4.8 - 6.2	Brom Cresol Green	3.8 - 5.4

- 15 -

٠

Both brom phenol blue and brom cresol green gave somewhat promising results when used as the indicator in the titration of fluorine with thorium nitrate solution. The color change seemed to be sharp, but upon standing a fading occured and further addition of the thorium nitrate solution caused a similar color change to take place. The point at which the change occured seemed to be dependent upon the rate at which the titration was carried out. It was thought that it should be possible to finally reach a point in the titration where no further fading would occur and subsequent addition of the thorium nitrate solution would only tend to cause a deepening of the color, but all attempts to consistently duplicate results were more or less unsatisfactory. The titration was carried out both in aqueous and alcoholic solution and in the presence of dextrine as a protective colloid, but even though some of the series run were in fairly close agreement, in the majority of cases there was such a wide variation in results that little reliance could be put in them. It has been shown later in

- 16 -

this work that in the titration of fluorine with cerous nitrate solution that there is an abrupt change in pH at practically the same point in the titration as where the end-point was determined with methyl red indicator, but whereas, the pH of the solution at that point was about 6.2. the pH range of methyl red is only from 4.8 - 5.4. Furthermore, some of the other indicators tried out such as lacmoid, p-nitro phenol, and cochineal which show color changes within the pH range of methyl red did not exhibit color changes in these titrations. Hence, it seems plausible that the change in color observed with brom phenol blue and brom cresol green is due largely, as suggested by Batchelder and Meloche, to preferential adsorption by the fluoride precipitate.

It was next decided to attempt some potentiometric titrations of the fluoride with the nitrate solutions of cerous cerium, thorium, and lanthanum. Batchelder and Meloche reported an unsuccessful attempt to carry out the titration potentiometrically with cerous nitrate. With a hydrogen electrode their results were corroborated, however, with the use of a quinhydrone electrode it was found possible to carry out the titration. For this purpose a small, commercial set of the type commonly used in making pH measurements was employed. The results obtained are graphically shown in figures 1, 2, and 3.

When the pH values were plotted against the volume of nitrate solution used during the titration the curves for both cerous nitrate and thorium nitrate exhibit a rather interesting phenomenon.

The first additions of the nitrate solution caused an increase in the pH values up to a certain point, whereupon, further addition of the reagent caused an abrupt drop in the pH of the resulting solution. The phenomenon was more pronounced in the case of the cerous nitrate solution, and was not observed at all with the lanthanum nitrate.

With the cerous nitrate the end-point of the titration occured at practically the same point as was observed by the use of methyl red

- 18 -







indicator but, whereas, the pH range of methyl red is from 4.8 - 5.4, the pH of the solution corresponding to the end-point of the titration was about 6.2. This, together with the previously described work with different dyes and indicators would tend to indicate that Batchelder and Meloche were right in their belief that the color change is not due simply to a change in pH of the solution, but rather, as previously stated, to preferential adsorption by the fluoride precipitate.

An attempt was also made to carry out the titration using a hydrogen electrode, but this proved to be entirely unsuccessful, due, perhaps, as suggested by Batchelder and Meloche, to poisoning of the electrode by the cerous fluoride precipitate.

It was then decided to make some distillations of fluorine by the Willard, Winter method using perchloric acid to evolve the fluorine, followed by titration of the distillate with standard cerous nitrate solution using methyl red as the indicator.

- 19 -

- 20 -

For this purpose cerous nitrate solution was prepared and standardized against the standard sodium fluoride solution. In order to have as nearly comparable conditions as possible in the standardization to those in the titration of the distillate the titrations were carried out in the presence of perchloric acid. The results of the standardization are given in Table III.

TABLE III

Trial	Fluorine (mg.)	Ce(NO3)3 (cc.)						
1	10	6.35						
2	10	6 .30						
3	10	6.31						
4	10	6.30						
5	10	6.35						
6	10	6 .34						
Averag	6.33							
l cc.	Ce(NO3)3 = 1.	579 mg. of Fluorine						

.

- 22 -

Since sulfates and borates interfere with the titration, little time was spent with this, but the results of the determinations made are given in Table IV. These results were obtained by distilling known fluoride samples and titration of the distillate with the standard cerous nitrate solution.

TABLE IV

	l cc. Ce(NG	03)3 = 1.579 mg	Fluorine
Trial	Ce(NO ₃) ₃	Fluorine Present	Fluorine Found
1	6.32 cc.	10 mg.	9.979 mg.
2	6.35	10	10.027
3	6 .29	10	9.932

In the absence of interferring substances this method gives theoretical results.

Since sulfates and borates interfere in the above procedure, it was decided to make some determinations by the Willard and Winter method using sulfuric acid to evolve the fluorine. Accordingly, a solution of $Th(NO_3)$ 4 was prepared and standardized against standard NaF solution using the zirconium alizarine mixture as indicator. The results of the standardization are given in Table V.

TABLE V

Standardization of Thorium

Trial Number	1	2	3	4	5	6
NaF added (cc.)	10	10	10	10	10	10
Fluorine added (mg.)	10	10	10	10	10	10
$m(NO_3)_4$ solution 10.05 10.05 10.00 10.05 10.07 10.04						
Average Th(NO3)4 used	:	10.0)4 cc.			
$1 \text{ cc. Th}(NO_3)_4 =$.996 m	lg. of	Fluori	.ne		

Nitrate Solution

When fluorine was evolved by sulfuric acid and the distillate titrated with the standard thorium nitrate solution, it was thought that the sulfuric acid carried over by the distillate tended to somewhat obscure the end-point. In order to determine to what extent, if any, the sulfate ion interferred, a series of titrations were run in the presence of varying amounts of sodium sulfate. The results of these determinations are shown in Table VI.

(see next page)

TABLE VI

ł

Trial Runber	-	থ	5		G	ø	6	8	0	10		5
Fluorine present (mg.)	2	10	סד	10	10	10	10	סד	στ	1		9
Nasflok present (z.)	-			5	3.	10	5	i) •	ii)	ų		
Th(RO3)4 used (ce.)	10.05	10.80	10.55	10.35	10.05	08°6	9-86	10-00	80.6	10.50	0	
Fluorine found (mg.)	10.00	10.16	10.50	10.28	6 6 °6	9.76	9.82	96 °6	16.6	10.25	01	
Error (mg.)	00	+.16		+.88	10 -	- 88	a	8	- 0	+ .25	+	9
												ī

- 26 -

These results do not show a consistent variation in either direction from the theoretical, but they would tend to indicate that the end-point is less distinct and harder to detect because of the presence of the sulfate ion. It was found that during a distillation the amount of sulfuric acid carried over with the distillate was equivalent to about .24 gram of Na_2SO_4 .

It was found in the direct titration that if the solution were filtered before the equivalent point was reached, the color change was much sharper, but the end-point depended on the point at which the filtration was made. This was shown by running a series of titrations in which the solution was filtered after the addition of definite amounts of the reagent. The results of these titrations are given in Table VII.

Error (mg.)	- 86	87	- 5t	74			19	17	10.+	08
Fluorine Found (mc.)	9.14	9.15	9.46	9.26	9.61	9.61	9.81	88°6	10.01	9.98
Fluorine Present (mg.)	10	TO	10	TO	10	10	10	10	10	10
Th(NO3) Used (eč.)	9.18	9.15	9.50	9.50	9.65	9.65	9,85	9,87	10.04	9.96
Th(NOg) & added before filtration (cc.)	4	7	8	8	0	0	9.5	9 ° 5	9 • 8	9.8
Trial	Ч	લ્ય	ю	-	2	Q	4	ω	a	10

Table VII

It was found that long before the equivalent point was reached a pink color was developed which upon filtration left the filtrate the original yellow color. Further addition of the thorium nitrate solution resulted in an extremely sharp color change, but when the solution was again filtered and more of the precipitant added, a repetition of the same phenomenon occured. This continued until all the fluorine had been precipitated.

It was next decided to attempt some gravimetric determinations of fluorine by precipitating the fluorides of thorium, cerium, and lanthanum and converting them to the oxides. Thorium fluoride and cerous fluoride are readily ignited to the oxides, but it is questionable if a complete conversion of lanthanum fluoride to the oxide occurs.

An attempt was made to precipitate the fluorine as thorium fluoride and ignite the precipitate to thorium dioxide. Results for this are given in Table VIII.

- 29 -

TABLE	VIII.
-------	-------

Trial	Fluorine present (g.)	Fluorine found (g.)	Error (g.)
1	.0100	•0050	0050
2	.0100	•0059	0041
3	.0100	•0055	0045
4	.0100	•0068	0032

Only about fifty percent of the fluorine was recovered by this procedure. The thorium fluoride precipitate was very gelatinous and difficult to filter. It was also felt that due to its finely divided state some of the precipitate may have passed through the filter paper, thus accounting for the extremely low results obtained on all the trials.

A gravimetric separation of cerous fluoride was next tried. Batchelder and Meloche reported unsuccessful results from a similar attempt.

The sodium fluoride solution was heated

almost to boiling and a slight excess of cerous nitrate solution added drop by drop with constant stirring. Filter pulp was added to the solution and after allowing it to stand about a half hour, the solution was filtered through Whatman 42 Filter paper and washed free of the nitrate ion. The cerous fluoride precipitate was then ignited and weighed as cerium dioxide.

It was found that the addition of much more than the theoretical amount of cerous nitrate solution required to precipitate the fluoride caused the precipitate to apparently dissolve. For that reason it was impossible to add a large excess of the precipitant to drive the reaction more nearly to completion. Determinations were carried out both in ageous and fifty percent alcohol solutions. The results are shown in Table IX.

TABLE IX

Trial	Solution	F present (g.)	f found (g.)	Error (g.)
1	Water	•0100	.0094	0006
2	W	•0100	.0093	0007
3	50% alcohol	•0100	•009 7	0003
4	*	•0100	•0098	0002
5	Ħ	.0449	•038 2	0067
6	¥	•0452	•038 4	0068

As the data shows, when small amounts of fluorine were present the error was relatively small, but with larger samples the discreptancy was unproportionately greater. In no case was complete recovery of the fluorine accomplished. The cerous fluoride was very gelatinous and hard to filter. Perhaps two opposing errors were involved here: The tendency toward complex formation, and adsorption by the fluoride precipitate. This seems especially feasible since the variation in the magnitude of error was out of all proportion to the amount of fluorine present. Lanthanum was next considered as a possible precipitant for the fluorine ion. It was hoped that the fluorine could be separated as lanthanum fluoride which upon ignition at a high temperature would be completely converted to the oxide.

Both ageous and fifty percent alcohol solutions of sodium fluoride were treated with lanthanum nitrate solution and the resulting precipitate filtered, ignited, and weighed as La₂O₃. The same difficulty was encountered here as in the case of the cerium compound, i.e. the tendency toward complex formation, and the adsorption effect of the fluoride precipitate.

. The results from these determinations are given in Table X.

- 32 -

TABLE	X
-------	---

Trial	Solution	F present (g.)	F found (g.)	Error (g.)
1	Water	•010 0	•0105	+.0005
2	Ħ	.0100	.0104	+.0004
3	Alcohol	.0100	.0102	+0002
4	π	•0100	•0101	+.0001

While these results are in fairly good agreement with the theoretical, the residues after ignition were shown to contain fluorine by means of the etch test, thus confirming the suspicion that all the fluoride is not converted to the oxide even at the maximum temperature of the meeker burner.

The apparent stability of the lanthanum fluoride suggested the possibility of igniting the precipitate at a low temperature and weighing it as LaF_3 . Results from this attempt are given in Table XI.

- 34 -

TABLE XI

Trial	Solution	F present (g.)	F found (g.)	Frror (g.)
l	50% alcohol	•0100	.0101	+.0001
2	50% alcohol	•0100	•0098	0002

This procedure seemed to give theoretical results. However, when the filtrates were treated with acetic acid and ammonium acetate according to the Meyer and Schulz method for the determination of fluorine a precipitate was obtained which, by means of the etch test, was shown to contain fluorine. Thus, it has been shown that the gravimetric determination of fluorine as outlined above involves at least three errors: The tendency toward complex formation, adsorption by the precipitate, and the indefinite composition of the residue after ignition.

Meyer and Schulz precipitated lanthanum fluoride by means of lanthanum acetate in the presence of ammonium acetate and acetic acid. They then corrected for the amount of lanthanum acetate adsorbed by the lanthanum fluoride by drying and weighing the precipitate at 100°, followed by the conversion of the adsorbed lanthanum acetate to oxide by heating over a bunsen burner. The percent of fluorine was then calculated by means of the formula:

$$\% F = \frac{57 (b - 1.0647c) 100}{195.9 a}$$

in which a = the unchanged substance or sample

b = weight of LaF₃ plus La₂0₃

c = loss in weight upon heating

Using molecular weights of the substances involved the formula might also be written in the following manner:

% F = 3F
$$\left[b - \left(\frac{La_2 o_3}{2 La A o_3 - La_2 o_3} c \right) \right]$$
 100
LaF₃ x a

Since they assumed the fluoride to be stable at the moderate temperature of the bunsen burner without investigating its exact decomposition temperature, it was decided to determine the temperature at which decomposition actually began. For this purpose it was necessary to prepare some pure lanthanum fluoride. This was done by treating a solution of lanthanum nitrate in a large platinum dish with Baker's C.P. hydrofluoric acid, and washing the precipitate by decantation until the supernatent liquid no longer gave a test for the nitrate ion. The product was then dried at 100°, pulverized, and stored in platinum over calcium chloride.

In order to determine the decomposition temperature of the lanthanum fluoride thus prepared, samples were weighed out and taken to constant weight at definite temperature intervals first in the electric oven, and finally, in a calibrated muffle furnace. In order to determine the temperature at which the fluoride began to decompose the residues were twice treated with concentrated sulfuric acid and evaporated to dryness, after which they were heated to constant weight over the blast lamp. From the weights of La₂0₃ obtained the corresponding weights of LaF₃ were calculated and compared with the weights of the samples at the various temperature intervals. The results are shown in Table XII.

- 36 -

TABLE XII

		2	
Decom- position Temper- ature	540°	540°-561	540°-56(
Range of stable composition	380 ⁰ - 480°	486°-540°	688°-540°
Theretical W. of LaPs (g.)	. 2856	. 20 27	. 2014
Wt. of Legos (e.)	. 2679	. 2654	. \$68
W. of LaF ₅ at E850(g.)	. 2786?	28722	.2997
W. of Lars at 540°(g.)	3945 .	. 2935	. 266
Wt. of LaF ₅ et 488 ⁵ (g.)	373 2.	926a .	. 2067
W. of La7 ₅ at 380 ⁰ (g.)	. 2878	. 2942	. 2676
Tt. of Laf, at 2008(g.)		. 2969	8168.
W. of Lals et 1600(g.)	. 2034	. 2067	. 29.24
Wt. of LaNg at L400(g.)	9362 .	. 2035	1686
Tt. of LaP3 at 100 ³ (g.)	1902 .	3065.	\$008.
1940 L	F		10

- 37 -

It was found that the lanthanum fluoride used in these experiments could be heated to about 540° before it began to decompose, but above that temperature it lost weight quite rapidly. The weights recorded at 585° were simply the results of the last weighings made, since after heating at that temperature for 62 hours, the samples were still showing significant loss in weight.

The composition of the fluoride seemed to be stable between the temperatures of 485° and 540°.

In connection with this work it was decided to run some determinations by the Meyer Schulz method.

Before doing this, however, it was necessary to prepare some lanthanum acetate. This was accomplished in the following manner. A solution of lanthanum nitrate was treated with ammonia to precipitate lanthanum hydroxide, which was then filtered off and dissolved in acetic acid. The solution was then evaporated to dryness several times to get rid of the excess acetic acid, and the lanthanum acetate obtained dissolved in water.

- 39 -

In their article Meyer and Schulz did not specify any definite amounts of materials to be used, hence, it was necessary to use our own judgment in that respect.

Samples of sodium fluoride ranging from .05 g. to .1 g. were weighed into small casseroles and dissolved in 50 cc. of water. An excess of lanthanum acetate was added to the cold solution. followed by the addition of 3 drops of glacial acetic acid and about a gram of ammonium acetate. The solution was then boiled for about three minutes. allowed to settle and the supernatent liquid filtered through a weighed Gooch crucible. The precipitate in the casserole was then evaporated to dryness and heated at 150° for at least two hours. The residue was then taken up in hot water containing about the same amounts of acetic acid and ammonium acetate as was used before, heated, allowed to settle. filtered. and washed thoroughly with water containing a small amount of acetic acid. The precipitate was then heated to constant weight at 100°, after which it was heated at 485° until constant weight was obtained. By means of the formula

previously stated the percent of fluorine was calculated. Results are shown in Table XIII.

Trial	Wt. of NaF	Theoretical % F	% F found	Erro r (%)
1	•0994	45.23	40.88	- 4.33
2	.1010	45.23	42.36	- 2.87
3	•0998	45 .23	42.86	- 2.37
4	.1003	45.23	41.85	- 3,38
5	• 0 5 15	45.23	40.11	- 5 .12
6	• 0539	45.23	40.65	-4.58
7	• 0 50 5	45.23	39.76	- 5•46
8	•05 09	45.23	39.27	- 5 .96

TABLE XIII

As the data shows the results are far too low in every case, and no consistent variation was noted. Perhaps the final temperature used was quite different from that used by Meyer and Schulz, but on the basis of such a difference it would still be expected that more concordant results would have been obtained. It seems as if there might be an error in assuming, as Meyer and Schulz do, that pure lanthanum acetate is adsorbed by the lanthanum fluoride precipitate.

SOLUBILITY OF LANTHANUM FLUORIDE IN WATER AT 250

Historical Introduction

Practically nothing has been done in the past toward making a study of the solubilities of the fluorides of the rare earth metals.

Kohlrausch (12) has studied the solubilities of many of the other fluorides, such as the fluorides of barium, strontium, calcium, magnesium, zinc, and lead. The solubility values obtained for these compounds were found by means of electrical conductivity methods.

Spitzen (13) found that a liter of saturated solution of $\text{ThF}_4 - 4\text{H}_20$ contains .17 mg. of ThO_2 at 25°.

EXPERIMENTAL RESULTS

In attempting to determine the solubility of lanthanum fluoride in water apparatus similar to that used by Moody and Leyson (14) for measuring the solubility of lime in water was made use of. This consisted of a large, three-necked, Pyrex flask which was coated on the inside with paraffin and equipped with a mechanical stirrer and inverted thistle tube. The bulb of the thistle tube was packed with a light wad of cotton through which the solution was filtered as it was drawn from the flask.

The flask containing water and lanthanum fluoride was then immersed in a thermostat at 25° and agitated for a definite length of time, after which the fluoride was allowed to settle before the sample was withdrawn. 500 cc. of the solution was then removed through the thistle tube, evaporated to dryness in a large platinum dish, and heated to constant weight at 485°. The results are shown in Table XIV.

- 42 -

- 43 -

£				
Trial	Day s Agitated	Days Solu. in contact with LaF3	Wt. of Residue (g.)	Solubility of LaF ₃ in g. liter
1	2	2	•0028	•005 6
2	1	5	.0022	•00 44
3	1	8	.0028	•005 6
4	2	14	•0024	• 0 0 48
5	2	2	•0012	•00 24
6	2	5	•000 7	•0014
7	2	9	.0019	•0038

TABLE XIV

The first four trials were taken from one run, i.e. without changing the solution started with, while the other trials represent values that were obtained from another run starting with new lanthanum fluoride and a large volume of water. For that reason the lower solubility values obtained on trials 5 and 6 may have been due to incomplete saturation.

It was first attempted to use a flask that had not been paraffined, but the values obtained failed to reach any constant point whatever, and the fluoride finally went into a colloidal state in which form it would not settle out. Moreover, the residue left in the platinum dish after reaching constant weight was shown to contain silica by means of evolution with hydrofluoric acid, thus showing that the glass had been attacked by the fluoride.

CONCLUSIONS

The titration of fluorine by means of cerous nitrate solution using methyl red as the indicator was found to give theoretical results when no interferring substances were present, but was not applicable to the determination of fluorine in plating solutions because of the interference of sulfate and borate ions.

Both brom phenol blue and brom cresol green gave some promise as indicators in the titration of fluorine with thorium nitrate solution, but the results were not concordant.

A potentiometric titration of fluorine with cerium, thorium or lanthanum nitrate using a quinhydrone electrode is described, and from the results obtained it was concluded that Batchelder and Meloche were correct in assuming that the color change of Methyl red when used as the indicator in the titration of fluorine with cerous nitrate is due largely to preferential adsorption by the cerous fluoride precipitate.

Attempts to make gravimetric separations of fluorine by precipitating the fluorides of thorium, cerium, and lanthanum did not give theoretical results.

The decomposition temperature of lanthanum fluoride was found to be between 540° and 585° .

Determinations of fluorine by the Meyer Schulz method gave results that were far too low as compared to the theoretical percent of fluorine in sodium fluoride.

Measurements of the solubility of lanthanum fluoride in water at 25° were made but the results obtained were not in close agreement.

BIBLIOGRAPHY - 46 -(1) F. Pisani Compt. Rend. 162, 791-3 (1916)(2) W.H. Adolph J. Am. Chem. Soc. 37, 2500 (1915)(3) F.A. Gooch and M. Kobayashi Am. J. Sci. 45, 370-6 (1918) (4) R.J. Meyer and W. Schulz Z. Angew. Chemie 38, 203 (1925)(5) G. Batchelder and V.W. Meloche J. Am. Chem. Soc. 53, 2131 (1931)(6) V. Lenher and C. Meloche J. Am. Chem. Soc. 38, 66 (1916)(7) A. Kurtenacker and W. Jurenka Z. Anal. Chem. 82, 210 (1930)Ind. Eng. Chem. Anal. Ed. (8) H.H. Willard and O.B. Winter (1933) 25, 7 J. Am. Chem. Soc. 55, 1741 (9) W.D. Armstrong (1933)(10)G.A. Shuey J. Assoc. Official Agr. Chem (1933) 16, 151 (11)N. Allen and N.H. Furman J. Am. Chem. Soc. 55, 90 (1933)(12)Fr. Kohlrausch Z. Physik Chem. 44, 197 (1903)J. Russ. Phys. Chem. Soc. (13)V.I. Spitzen (1917) 49, 357 (14)G.T. Moody and L.F. Leyson J. Chem. Soc. Lond. 93, 1767 (1908)

ī . 1 . Ì • :

,





