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DETERMINATION OF FLUORINE IN FLUORO-ORGANIC COMPOUNDS

to
February 29, 1944
by
John H. Yoe, Official Investigator
Jason M. Salsbury and James W. Cole

Report OSRD No. 3481
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NATIONAL DEFENSE RESEARCH COMMITTEE
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Section 9-3-1

DETERMINATION OF FLUORINE IN FLUORO-ORGANIC COMPOUNDS

Service Directive: CWS-6

Endorsement (1) From Dr. Carl Niemann, Division Member in Charge to Dr. Walter R. Kirner, Chief, Division 9.

Forwarding report and noting:

> "The fluorine content of organic fluorine compounds can be determined by refluxing the sample, in solution in hexanol-1, with sodium, extracting the liberated fluoride ion with water, and titrating the fluoride ion in the aqueous extract with thorium nitrate using sodium alizarin sulfonate as an indicator. The method is applicable to those cases where hexanol solution of the sample can be prepared."

(2) From Dr. Walter R. Kirner, Chief, Division 9 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and concurring.

This is a progress report under Contract 9-344, OEMsr-139 with The Rector and Visitors of the University of Virginia.

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Determination of Fluorine in Fluoro-Organic Compounds

By

John H. Yoe (Official Investigator)
Jason M. Salsbury and James W. Cole

ABSTRACT

An analytical procedure is described for the determination of fluorine in fluoro-organic compounds based on (1) decomposition of the sample by refluxing with sodium in 1-hexanol, and (2) titration of fluoride ion with thorium nitrate using sodium alizarin sulfonate as indicator. The analysis requires about thirty minutes.

Four fluoro-organic compounds were analysed. Fluorine in sodium fluoroacetate was about 3% above the calculated quantity; values for methyl fluoroacetate were about 4% low. The average value for di-isopropylfluorophosphate was approximately 1% below the theoretical, while in β-fluoroethanol the fluorine values averaged about 11% low. In all analyses the average deviation from the mean was about ±2%.

Purified di-isopropylfluorophosphate in a 45% ethanol solution contained 0.15% fluoride ion, but no fluoride ion was found in either methyl fluoroacetate or β-fluoroethanol. Samples from two lots of sodium fluoroacetate contained 8.5% sodium fluoride.

In the hope of enhancing the color change at the end-point in the thorium nitrate titration, fifty-four dyestuffs in mixtures with sodium alizarin sulfonate were tested. Only one appears to be of value.

A comparison of Solochrome Brilliant Blue BS with sodium alizarin sulfonate showed each indicator to have some advantage, depending on the concentration range of fluorine; the former is more sensitive at lower concentrations.

Determination of Fluorine in Fluoro-Organic Compounds

INTRODUCTION

Much difficulty has been encountered in quantitatively converting fluorine in fluoro-organic compounds to fluoride ion. A number of methods have been tried with varying degrees of success. Fluoro-organic compounds have been (a) split by refluxing several hours with sodium in an alcohol[1], (b) burned to HF in a gas stream[2], (c) ignited in a Parr bomb[3], (d) ruptured by heating with ammonia under pressure[4], (e) cleaved with potassium metal at 400°C.[5], and (f) reduced with nickel-aluminum alloy and aqueous alkali[6]. In most cases the fluoride ion formed was titrated with thorium nitrate.

Fluorine in sodium fluoroacetate, methyl fluoroacetate and di-isopropylfluorophosphate has been determined satisfactorily by the method described in this report. Results with β-fluoroethanol were low but may not be due to the method. The compounds are decomposed by refluxing with sodium in 1-hexanol. The sodium fluoride thus formed is extracted with water and the aqueous layer made to a known volume. Aliquots are diluted with water and ethanol to 45% ethanol by volume. After neutralization with hydrochloric acid, a buffer is added to adjust the pH to about 3 and the solution is titrated with thorium nitrate to the first permanent pink tint of sodium alizarin sulfonate indicator. A complete analysis requires about one-half hour. The titration of fluoride ion is accurate to about ±2%. Average values for fluorine, in terms of the theoretical, were as follows: sodium fluoroacetate, +3%; methyl fluoroacetate, -4% di-isopropylfluorophosphate, -1%; and β-fluoroethanol, -11%.

EXPERIMENTAL

Materials. 1. Standard Fluoride Solution. Dissolve 0.2100 g. of pure sodium fluoride or 0.4707 g. of pure potassium fluoride, $KF.2H_2O$, in water and dilute to one liter. The solution contains 0.095 mg. fluorine per ml. If the purity of the fluoride is doubtful, the solution should be standardized by the PbClF method.

2. Thorium Nitrate Solution. Dissolve 0.69 g. of thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$, (reagent grade) in water and dilute to one liter. The solution is approximately 0.005N.

3. Sodium Alizarin Sulfonate Indicator. Dissolve 0.5 g. of sodium alizarin monosulfonate (reagent grade) in 80 ml. of water, filter, and dilute the filtrate to 100 ml.

4. Buffer Solution. Dissolve 35.4 g. of C.P. chloroacetic acid and 10.0 g. of C.P. sodium hydroxide in enough water to make 500 ml. of solution.

5. Ethanol 60% (approx.). Mix 1000 ml. ethanol (95%) and 500 ml. water.

6. Hydrochloric Acid, 1.2N. Dilute 25 ml. of C.P. hydrochloric acid (sp.gr. 1.19) to 250 ml. with water.

7. 1-Hexanol. Eastman (practical grade), b.p., 153-156°C.

Procedure. 1. Determination of the Blank. Add 3 drops of sodium alizarin sulfonate indicator to a solution of 10 ml. water, 30 ml. 60% ethanol, and 1 drop of 1.2N hydrochloric acid. Add 2 ml. of the buffer solution and titrate with 0.005N thorium nitrate solution to the first permanent pink tint. The volume required is the blank.

2. Standardization of Thorium Nitrate Solution. The volume of thorium nitrate required in the titration of various quantities of standard

fluoride solution is not quite a linear function of the amount of fluoride ion. Therefore the fluoride ion equivalent of the thorium nitrate solution must be determined over the range to be used, that is, 0 to 1 mg. of fluorine per aliquot.

Add 1 ml. of standard fluoride solution to a mixture of 9 ml. water, 30 ml. 60% ethanol, 3 drops sodium alizarin sulfonate and 1 drop of 1.2N hydrochloric acid. Add 2 ml. buffer solution and titrate with thorium nitrate to the first permanent pink tint. The true volume of thorium nitrate required in the titration is obtained by substracting the blank from the volume of thorium nitrate actually used. Repeat this titration using n ml. of standard fluoride solution and (10-n) ml. water, where n = 2,3,4,5, 6,7,8,9, and 10. Plot the volume of thorium nitrate against milligrams of fluoride ion as in Figure 1. Obtain values from the curve and construct a table similar to Table I.

TABLE I

Volume of $Th(NO_3)_4$, ml.	Mg. of Fluoride	Correction[1], mg. F^-,
0.00	0.000	0.000
1.00	0.125	0.025
2.00	0.228	0.028
3.00	0.330	0.030
4.00	0.427	0.027
5.00	0.525	0.025
6.00	0.630	0.030
7.00	0.755	0.055
8.00	0.838	0.038
9.00	0.940	0.040

[1] Correction = mg. F^- - 0.1[ml. $Th(NO_3)_4$]

3. Decomposition of a Sample. (PERFORM IN A HOOD.) Weigh a sample (10 to 20 mg.) and transfer to a 50 ml. gs flask. Add 0.2 g. of sodium and 15 ml. 1-hexanol. Attach a water cooled condenser and reflux the mixture gently for ten minutes. Extract the hot solution with two 10 ml. portions of water and dilute the aqueous extract (lower layer) to 50 ml. with water. (Solution A)

4. Titration of the Sample. Add a 10 ml. aliquot of solution A to a solution of 30 ml. 60% ethanol, 15 drops of 1.2N hydrochloric acid, and 3 drops sodium alizarin sulfonate indicator. Add 1.2N hydrochloric acid dropwise until the indicator changes from purple to yellow-green. Add 2 ml. buffer solution and titrate with 0.005N thorium nitrate to the first permanent pink tint. Calculate milligrams of fluoride present -----

$$\text{mg. } F^- = 5[0.1(\text{ml. } Th(NO_3)_4 - \text{blank}) + \text{correction}].$$

Notes. 1. The blank should be determined at least once a day. It is usually about 0.6 ml. of 0.005N thorium nitrate solution.

2. In the thorium nitrate titration the yellow-green solution changes first to orange and then to pink. Consistent results could not be obtained when the end-point was taken as the first appearance of the orange tint.

3. The first appearance of the permanent pink tint in the titration is observed more easily if the solution is viewed against a background of white paper. A daylight lamp is a very satisfactory source of illumination.

4. A blank should be run on the sodium and the 1-hexanol if their purity is doubtful. Zero fluoride blanks have been found for the several lots of sodium and for all the organic liquids employed as reflux media.

5. The standardization curve should be checked occasionally.

6. To overcome the difficulty of weighing a small quantity of a volatile liquid, a larger amount of the compound was weighed into a volumetric flask containing a few ml. of 1-hexanol. The solution was diluted to a known volume, usually 10 ml., and aliquots taken.

7. A sharper end-point is obtained if the aliquot is added to the alcoholic solution containing about half of the hydrochloric acid required to neutralize the sodium hydroxide rather than adding the aliquot to a neutral alcoholic solution.

8. Gentle heating may be started as soon as sodium is added to the 1-hexanol, even though a reaction is occurring. When the boiling point of the alcohol is reached, careful regulation should be made of the heater to prevent loss of sample because of the vigorous reaction.

9. The reaction mixture should be extracted fairly soon after refluxing. High results may be obtained if more than an hour elapses before extraction.

DISCUSSION

During the development of the analytical method seven variables influencing the analysis were studied: (1) The alcohol used as the reflux medium. (2) The weight of sample. (3) Completeness of the extraction of fluoride ion from the reaction mixture. (4) The time of refluxing necessary to obtain quantitative decomposition of the sample. (5) The weight of sodium used. (6) Nature of the acid used to neutralize the sodium fluoride extract. (7) Buffer action in the thorium nitrate titration of fluoride ion.

Reflux Medium. The nature of the alcohol employed as the reflux medium is a critical factor in the analysis for the following reasons:

1. Sodium alcoholate is the active constituent of the mixture. When sodium fluoroacetate is refluxed in an alcoholic solution of a sodium alcoholate, the analytical results are identical with those obtained when the same compound is refluxed with sodium and the alcohol.

2. The reflux time is an inverse function of the boiling point of the alcohol. In isobutyl alcohol, b.p., 107-108°C., sixty minutes of refluxing is required for decomposition of sodium fluoroacetate, whereas only ten minutes is needed if 1-hexanol, b.p. 153-156°C., is used.

3. The solubility of the alcohol in water influences the end-point in the thorium nitrate titration, because organic substances in the titrating solution appear to affect the color change of the sodium alizarin sulfonate. All titrations are carried out in 45% ethanol to maintain a constant condition. It has been suggested that a water-soluble alcohol be substituted for 1-hexanol to eliminate the aqueous extraction. This is not desirable because of discoloration produced during refluxing which interferes in the titration of fluoride ion.

4. The lower the density of the alcohol, the more efficient is the aqueous extraction of fluoride ion.

The efficiency of the various alcohols as reflux media is shown in Table II. Here the percentage deviation from the theoretical composition is compared with the fluoride ion values found when 1-hexanol was the medium. The latter gives the most consistent results and was selected for the standard procedure.

TABLE II

Alcohol	Reflux time, min.	Compound analysed[1]	Percent Error alcohol	Percent Error 1-hexanol
Benzyl alcohol	15	TL-869	-45	+3
Cyclohexanol	30	TL-869	+18	+3
Isoamyl alcohol	5	TL-869	-21	-2
Isoamyl alcohol	10	TL-869	- 4	+3
Isoamyl alcohol	15	TL-869	- 5	+3
Isobutyl alcohol	10	TL-551	-10	-4
Isobutyl alcohol	30	TL-869	-19	+3
Isobutyl alcohol	45	TL-869	- 8	+3
Isobutyl alcohol	60	TL-869	- 5	+3
Isobutyl alcohol	240	TL-869	- 6	+3
2-Methyl cyclohexanol	30	TL-869	+25	+3
1-Octanol	15	TL-551	- 3	-4
1-Octanol	30	TL-741	-12	-11
Tetradecanol	20	TL-741	-12	-11
Tetradecanol	60	TL-741	-11	-11

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[1] TL-869, sodium fluoroacetate; TL-551, methyl fluoroacetate; and TL-741, β-fluoroethanol.

$$\% \text{ Error} = \frac{\text{mg. } F^-(\text{calc.}) - \text{mg. } F^-(\text{found})}{\text{mg. } F^-(\text{calc.})} \times 100$$

A white solid is formed when benzyl alcohol is refluxed with sodium. This solid interferes with the decomposition of the sample. No reason is apparent for the high results obtained with cyclohexanol and 2-methyl cyclohexanol since both give excellent blanks when refluxed with sodium in the absence of sodium fluoroacetate. It appears that complete decomposition is not obtained with either isoamyl or isobutyl alcohol regardless of the time of reflux. Tetradecanol, 1-octanol and 1-hexanol appear to be of equal value as reflux media, except a longer reflux time is necessary with tetradecanol.

<u>Weight of Sample</u>. The weight of sample should be chosen so that the aliquots titrated contain the equivalent of 0.1 to 0.9 mg. fluorine. In the procedure one-fifth aliquots are used; hence the sample should contain 0.5 to 4.5 mg. fluorine.

If the sample contains more than 4.5 mg. fluorine, the procedure should be modified as follows: Dilute the aqueous extract to 500 ml. Add a 10 ml. aliquot to a solution containing 30 ml. 60% ethanol, 2 drops 1.2N hydrochloric acid and 3 drops sodium alizarin sulfonate. Perform the rest of the titration procedure as stated above.

The size of the sample may be reduced if aliquots of more than 10 ml. are taken. If the sample contains less than 0.5 mg. fluorine, the procedure is the same except the aqueous extract should not be diluted. Instead, add it to a solution containing 20 ml. 95% ethanol, 6 drops hydrochloric acid (sp.gr. 1.19) and 3 drops sodium alizarin sulfonate. Add 1.2N hydrochloric acid dropwise until the indicator turns yellow-green, then 2 ml. of buffer solution and titrate with 0.005N thorium nitrate to the appearance of the first permanent pink tint. Calculate the milligrams of fluoride ion.

$$\text{mg. } F^- = 0.1(\text{ml. } Th(NO_3)_4 - \text{blank}) + \text{correction.}$$

The weight of the sample has been varied from the equivalent of 0.1 mg. to 35.0 mg. fluorine without appreciable effect on either the time necessary to split the fluorine to carbon bond or the volume of water required to extract the sodium fluoride.

Samples containing less than 0.1 mg. fluoride ion may be titrated with thorium nitrate using Solochrome Brilliant Blue BS indicator (Porton report No. 2543). A thorium nitrate standardization curve using this indicator must be made and a calibration chart prepared. (See Table III).

TABLE III

Typical Calibration Chart Using Solochrome Brilliant Blue BS Indicator (Values taken from smooth curve)

Ml. $Th(NO_3)_4$	µg. F	Correction
0.25	8.5	-0.3
0.50	17.2	-0.3
0.75	26.0	-0.2
1.00	35.0	0.0
1.25	44.2	+0.4
1.50	53.6	+1.1
1.75	63.0	+1.7
2.00	72.5	+2.5
2.25	81.5	+3.7
2.50	89.5	+1.9

The values for the correction are obtained in the standardization from this relationship:

$$\text{Correction} = \mu g.\ F^- - 35\ (\text{ml. } Th(NO_3)_4 - \text{blank}).$$

Then the µg. of fluorine in an aliquot may be calculated:

$$\mu g.\ F^- = 35[\text{ml. } Th(NO_3)_4 - \text{blank}] + \text{correction}.$$

Aliquots of several solutions previously analysed using sodium alizarin sulfonate indicator, were diluted tenfold and then titrated with thorium nitrate using Solochrome Brilliant Blue BS as indicator. Good agreement was obtained in the two methods. (see Table IV). Each value reported is the average of at least two aliquot titrations.

TABLE IV

Comparison of Indicators

Milligrams of Fluorine		
Found		Calculated
Sodium alizarin sulfonate	Solochrome Brilliant Blue BS	
3.56	3.41	3.61
3.47	3.37	3.61
3.45	3.41	3.61
3.48	3.45	3.61
3.51	3.51	3.61
3.47	3.64	3.61

The titration with Solochrome Brilliant Blue BS should be performed in low-form Nessler tubes. A series of samples titrated in 125 ml. Erlenmeyer flasks gave low results, an average value of 3.23 mg. fluoride ion being obtained. This compares with 3.47 mg. fluoride ion when titration was made in Nessler tubes.

Extraction of the Fluoride. The accuracy of the analytical procedure depends on the completeness of extraction of the fluoride ion formed in the decomposition of the fluoro-organic compound. To test the efficiency of extraction the following experiments were performed: Samples of potassium fluoride, $KF.2H_2O$, were dissolved in water and titrated with thorium nitrate using the alizarin indicator; additional samples were refluxed with sodium in 1-hexanol, extracted with water and titrated. The results (summarized in Table V) indicate that essentially all the fluoride was extracted from the alcoholic solution.

TABLE V

Analysis of Potassium Fluoride

Sample, mg.	Mg. Found	Fluorine Calc.	Error %
A. Potassium fluoride dissolved in water.			
6.5	1.3	1.31	0
92.2	19.3	18.6	+3.7
86.1	17.6	17.4	+1.1
B. Potassium fluoride refluxed with sodium and 1-hexanol.			
6.1	1.21	1.23	-1.6
6.4	1.27	1.29	-1.5
14.2	2.86	2.86	0

The potassium fluoride was analysed by the lead chlorofluoride method and found to be 100% $KF.2H_2O$. Hence the accuracy of the analytical procedure is about ±2%.

Time of Reflux. The time of reflux depends on the temperature. Ten minutes reflux time is sufficient for sodium fluoroacetate, methyl fluoroacetate, di-isopropylfluorophosphate, and β-fluoroethanol in 1-hexanol; less than ten minutes gave low values, but increasing the time above ten minutes did not alter the results.

Weight of Sodium. The amount of sodium does not appear to be significant provided a large excess is taken.

Neutralizing Acid. Both hydrochloric acid and nitric acid were used without appreciable difference. Hydrochloric acid was employed in most of the analyses.

Buffer Action. In the absence of the chloroacetic acid buffer unreliable data were obtained because sodium alizarin sulfonate is an acid-base indicator.

RESULTS

Analysis of Sodium Fluoroacetate. Analyses of samples of sodium fluoroacetate from Edgewood Arsenal and from the Department of Physiology, University of Chicago, were about 10% high in fluorine on the basis of 100% FCH_2COONa. Independent determinations of total sodium and of ionizable fluorine in each sample showed 8.5% sodium fluoride. The absence of ammonium and potassium ions was established by qualitative tests. When the analytical results on the samples were corrected for sodium fluoride, the fluorine content of sodium fluoroacetate was about 3% above the theoretical.

Essentially the same results were obtained with the samples from both sources. Table VI contains a summary of the analyses.

TABLE VI

Fluorine in Sodium Fluoroacetate

Reflux time, min.	Wt. of sample mg.[1]	Mg. Fluorine Found	Mg. Fluorine Calc.[2]	Error %
10 (Blank)	0	0	0	0
100	10.2	2.29	2.20	+4.1
30	10.6	2.22	2.28	-2.7
10	12.5	2.71	2.65	+2.2
10	11.4	2.53	2.43	+4.1
10	9.4	2.10	2.07	+1.7
10	8.0	1.81	1.73	+4.4
10	8.4	1.87	1.83	+2.2
5	7.9	1.69	1.67	+1.2
5	5.6	1.19	1.19	0
5	19.2	4.13	4.06	+1.7
5	12.3	2.49	2.61	-4.6
5	18.7	3.85	4.04	-4.7
5,	7.5	1.53	1.61	-4.9
5	9.8	2.11	2.12	-0.4

---

[1] This is the weight of sample as received.
[2] This is the calculated fluorine content corrected for sodium fluoride.

Analysis of Methyl Fluoroacetate. Analyses of samples of methyl fluoroacetate obtained from the Department of Physiology, University of Chicago, were 15% low in fluorine on the basis of 100% FCH_2COOCH_3. After purifying the sample by drying over anhydrous sodium sulfate and fractionation, the fraction boiling 103.0-104.5°C., at 750 mm. Hg showed values averaging 4% below the theoretical. A second sample was dried by adding benzene and distilling. The distillate was fractionated and the portion boiling 103.5-104.2°C. at 756 mm. Hg was analysed. Essentially the same results were obtained as with the 103.0-104.5° fraction. A summary of the analyses is given in Table VII.

TABLE VII

Fluorine in Purified Methyl Fluoroacetate

Reflux time, min.	Wt. of sample, mg.	Mg. Fluorine		Error %
		Found	Calc.	
B.p., 103-104.5°C. at 750 mm. Hg.				
10 (blank)	0	0	0	0
60	12.56	2.45	2.59	-5.4
10	12.56	2.54	2.59	-1.9
10	12.56	2.49	2.59	-3.8
10	12.56	2.44	2.59	-5.8
10	12.56	2.54	2.59	-1.9
B.p., 103.5-104.2°C. at 756 mm. Hg.				
10	17.53	3.56	3.61	-1.3
10	17.53	3.47	3.61	-3.9
10	17.53	3.45	3.61	-4.4
10	17.53	3.48	3.61	-3.6
10	17.53	3.51	3.61	-2.8
10	17.53	3.47	3.61	-3.9

Analysis of Di-isopropylfluorophosphate. Di-isopropylfluorophosphate obtained from the Department of Physiology, University of Chicago, was dried over anhydrous sodium sulfate and distilled under reduced pressure. The fraction boiling 68.4-69.4°C., at 9 mm. was analysed. The values were within a few per cent of the theoretical. See Table VIII.

TABLE VIII

Fluorine in Di-isopropylfluorophosphate

Reflux time, min.	Wt. of sample, mg.	Mg. Fluorine		Error %
		Found	Calc.	
10 (blank)	0	0	0	0
60	20.12	2.06	2.07	-0.5
15	20.12	2.03	2.07	-1.9
15	20.12	2.02	2.07	-2.4
10	20.12	2.05	2.07	-0.9
10	20.12	2.15	2.07	+3.9
10	20.12	2.03	2.07	-1.5
10	20.12	2.09	2.07	+1.9

<u>Analysis of β-Fluoroethanol</u>. A sample of β-fluoroethanol supplied by the Department of Physiology, University of Chicago, was dried over anhydrous sodium sulfate. The distillate boiling 103.0-103.2°C. at 752 mm. Hg was analysed for fluorine. Another sample obtained from Monsanto Chemical Company, Anniston, Alabama, was dried by distilling with benzene. The distillate was fractionated twice, and the portion boiling 103.0-103.3°C., at 754 mm. Hg was analysed. Both samples had essentially the same fluorine content and gave values averaging about 11% below the theoretical. Increasing the reflux time from ten minutes to three hundred and seventy-five minutes, or varying the reflux medium, did not affect the results. The possibility of an azeotropic mixture of β-fluoroethanol and some other non-halogen compound such as ethanol should not be overlooked. A microanalysis of the purified sample showed 38.95% carbon and 8.25% hydrogen. The theoretical percentages are: for FCH_2CH_2OH, Carbon - 37.48%; Hydrogen - 7.87%; for a mixture containing 10% ethanol, Carbon - 38.95%; Hydrogen - 8.40%.

TABLE IX

Fluorine in β-Fluoroethanol

Reflux time, min.	Wt. of sample, mg.	Mg. Fluorine Found	Mg. Fluorine Calc.	Error %
Medium: 1-Hexanol (b.p., 155-156°C.)				
10 (blank)	0	0	0	0
375	6.09	1.62	1.80	-10.0
375	6.09	1.49	1.80	-17.2
370	6.09	1.67	1.80	- 7.2
30	9.06	2.40	2.66	- 9.8
15	9.06	2.36	2.66	-11.2
10	119.3	32.5	35.4	- 8.2
10	13.47	3.52	4.00	-12.0
10	13.47	3.48	4.00	-13.0
10	9.06	2.39	2.66	-10.1
10	9.06	2.36	2.66	-11.2
10	9.06	2.37	2.66	-10.9
10	6.09	1.58	1.80	-12.2
10	6.09	1.58	1.80	-12.2
Medium: 1-Octanol (b.p., 191-193°C.)				
30 (blank)	0	0	0	0
30	9.06	2.34	2.66	-12.2
Medium: Tetradecanol (b.p., 265°C.)				
30 (blank)	0	0	0	0
60	85.1	22.5	25.3	-11.0
60	111.7	29.6	33.2	-10.8
20	6.09	1.70	1.80	- 5.5
20	6.09	1.49	1.80	-17.2
20	6.09	1.50	1.80	-16.7
Medium: 50% 1-Hexanol; 50% m-Xylene				
60 (blank)	0	0	0	0
60	13.47	3.49	4.00	-12.5
Medium: 50% 1-Hexanol; 50% Isoamyl ether				
30 (blank)	0	0	0	0
30	9.06	2.40	2.66	- 9.8

Ionizable Fluorine in Methyl Fluoroacetate, β-Fluoroethanol, and Di-isopropylfluorophosphate. Methyl fluoroacetate and β-fluoroethanol did not show any fluoride ion when each was dissolved in 45% ethanol and titrated with thorium nitrate using sodium alizarin sulfonate indicator. A freshly prepared solution of purified di-isopropylfluorophosphate in 45% ethanol contained 0.15% fluoride ion; on the other hand, di-isopropylfluorophosphate which had been made up in dilute solution in 1-hexanol and allowed to stand 17 days gave a fluoride ion value of 0.6% when titrated in 45% ethanol.

Attempts to Improve Sodium Alizarin Sulfonate Indicator. In an effort to make the sodium alizarin sulfonate end-point more easily visible, combinations of the indicator with fifty-four dyestuffs were studied. Two test solutions were prepared: (A) 40 ml. of 45% ethanol, 1 drop of 1 N hydrochloric acid and 2 ml. buffer solution; and (b) a solution identical to A but titrated with 0.005N thorium nitrate to a permanent pink tint. Twelve of the fifty-four dyes appeared to enhance the color change at the end-point when added to aliquots of solutions A and B in 10 mm. x 75 mm. test tubes. Further tests were made by adding each of the twelve dyes to solutions containing known amounts of potassium fluoride and titrating with thorium nitrate using sodium alizarin sulfonate as indicator. Only one dye, duPont Azo Blue (U.Va. No. 738B), appeared to be of value in the titration; improvement in color difference was slight, but it may be helpful to others who have difficulty with the sodium alizarin sulfonate color change.

SUMMARY

A method has been described for the analysis of certain fluoro-organic compounds, based on (a) decomposition of the sample by refluxing with sodium in a higher alcohol of low solubility in water, such as 1-hexanol, (b) extraction of sodium fluoride with water and (c) titration of the aqueous layer with thorium nitrate using sodium alizarin sulfonate as indicator. The results may be summarized as follows: Sodium fluoroacetate gave fluorine values averaging about 3% higher than theoretical; methyl fluoroacetate was approximately 4% low; di-isopropylfluorophosphate was about 1% low; and β -fluoroethanol was 11% low. The average deviation from the mean was ±2% (approx.).

Purified di-isopropylfluorophosphate was found to have 0.15% fluoride ion in equilibrium with it in 45% ethanol; β -fluoroethanol and methyl fluoroacetate gave no fluoride ions under the same conditions. The sodium fluoroacetate used contained 8.5% sodium fluoride.

Tests with Solochrome Brillianta Blue BS as indicator showed it to be useful at low concentrations of fluoride ion.

Fifty-four dyestuffs were tested as modifiers for sodium alizarin sulfonate indicator. Only one appeared to be of value.

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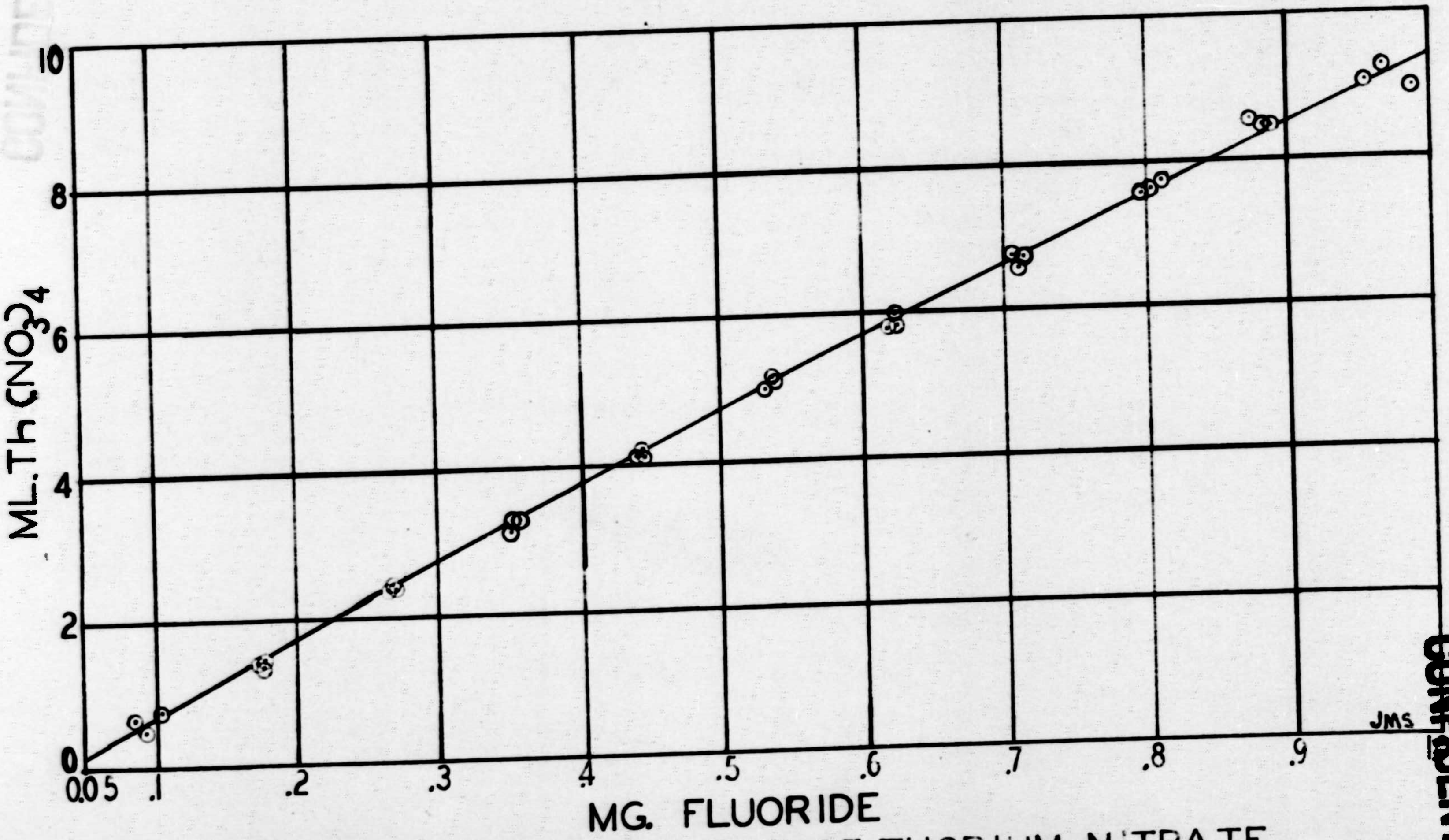

STANDANDIZATION CURVE OF THORIUM NITRATE

FIGURE I

REEL – C

1279

A.T.I.

30286

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ABSTRACT:

Sodium fluoroacetate, methyl fluoroacetate, di-isopropylfluorophosphate and β-fluoroethanol were analyzed, based on decomposition of the sample by refluzing with sodium in a higher alcohol of low solubility in water, such as 1-hexanol, extraction of sodium fluoride with water and titration of the aqueous layer with thorium nitrate, using sodium alizarin sulfonate as indicator. FCH_2COONa gave fluorine values averaging about 3% higher than theoretical, FCH_2COOCH_3 was 4% low, di-isopropylfluorophosphate was about 1% low and FCH_2CH_2OH was 11% low. Purified di-isopropylfluorophosphate was found to have 0.15% fluoride ion in equilibrim with it in 45% ethanol. Tests with Solochrome Brilliant Blue BS as indicator showed it to be useful at low concentration of fluoride ion. In an effort to make the sodium alizarin sulfonate end-point more easily visible, 54 dyestuffs were studied.

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SUBJECT HEADINGS: Fluoro-organic compounds - Fluorine determination (41603)

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fluorine
organic compounds