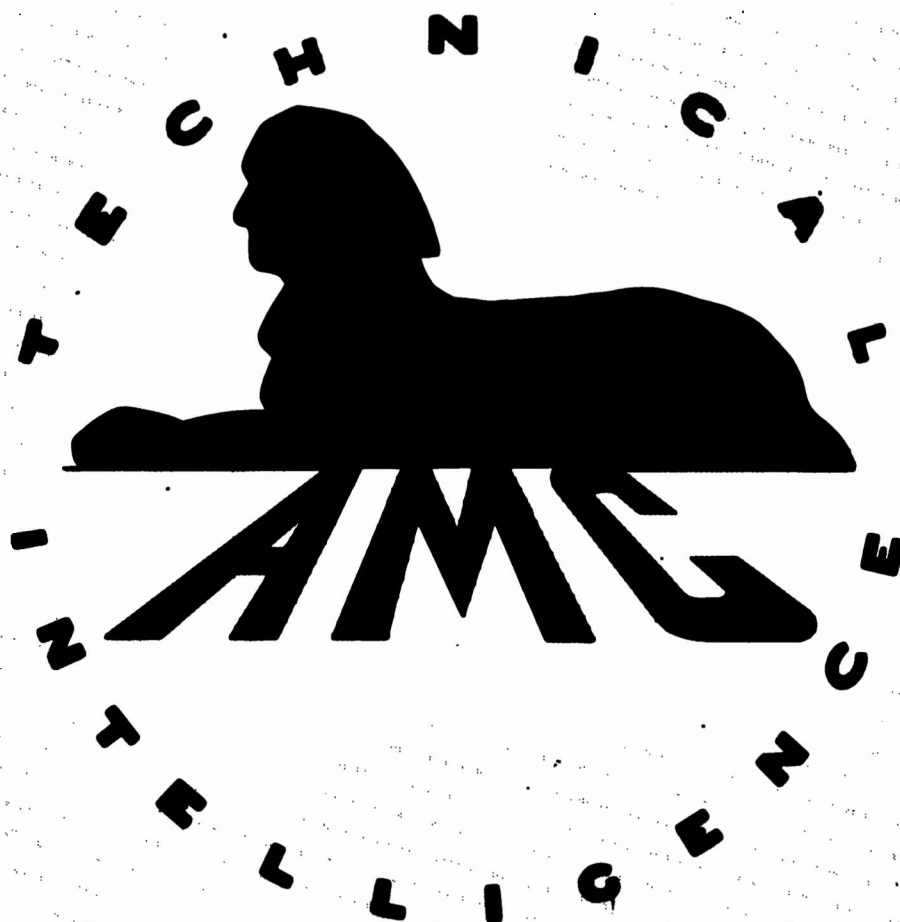


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Division 9
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

DETERMINATION OF FLUORINE IN CERTAIN FLUORO-ORGANIC
COMPOUNDS IN WATER

to
November 20, 1944
by
John H. Yoc (Technical Representative)
Jason M. Salsbury and James W. Cole

Report OSD No. 4414
Copy No. 45
Date: November 30, 1944

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Division 9
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

DETERMINATION OF FLUORINE IN CERTAIN FLUORO-ORGANIC
COMPOUNDS IN WATER

Service Directive: CWS-6

Endersement (1) Carl Niemann, Member, Division 9 to
Dr. Walter R. Kirner, Chief, Division 9.

Forwarding report and noting:

"A method for the determination of F in sodium fluoroacetate, AF-1, FE, and PF-3 in water, in which from 97-100% of the F is recovered, is described. Potassium meta periodate, silver perchlorate, perchloric acid and glass wool are added to an aqueous solution of the fluoro-organic compound; the mixture is refluxed, and then distilled at 135-145°C., maintaining the temperature by the addition of 100 ml. of water until 100 ml. of distillate is collected. Aliquots of the distillate are analyzed for fluoride ion by titrating with thorium nitrate solution using Solochrome Brilliant Blue as indicator. Ions commonly present in potable waters do not interfere."

(2) from 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 University of Virginia.

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Determination of Fluorine in Certain Fluoro-Organic
Compounds in Water

By

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

University of Virginia

A B S T R A C T

A method for the determination of fluorine in sodium fluoroacetate, methyl fluoroacetate, 2-fluoroethanol, and diisopropyl fluorophosphate in water is described. It involves addition of the aqueous solution of the fluoro-organic compound to potassium meta periodate, silver perchlorate, perchloric acid and glass wool; the mixture is refluxed, then distilled: the temperature is held at 135° - 145°C. by the addition of water until 100 ml of distillate is collected. Aliquots of the distillate are then analysed for fluoride ion by titrating with thorium nitrate solution using Solochrome Brilliant Blue as indicator.

From 97% to 100% of the fluorine was recovered. Ions commonly present in potable waters do not interfere seriously. The time required for a determination is about one hour.

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SUPPLEMENT

to

Report on the "Determination of Fluorine in Certain Fluoro-Organic Compounds in Water", Yoe, Salisbury and Cole, Nov. 20, 1944.

At the time our work was done a fluorine-free glass wool was not available. We used a Corning product (Cat. L P 21, No. 790, made from Pyrex Brand Glass No. 719) which contains about 1% of fluorine. This accounts for the high values (40-60 μg) for reagent blanks and the necessity of weighing the glass wool to a centigram and controlling the reflux and distillation times.

After our Nov. 20th report was completed, Corning supplied us with a small lot of fluorine-free glass wool. When using this material the value for the reagent blank was much lower (3-4 μg F) and was independent of the quantity of glass wool used (0.05-0.4 g) and of the time for reflux and distillation (30-90 minutes). A tenth of a gram of the fibre, well distributed in the reaction mixture, is adequate.

The Corning Glass Works is developing a fluorine-free glass wool and expect to have it available in the near future. In the meantime, Dr. W. W. Shaver, Director of Product Development, Corning Glass Works, has very kindly offered to send samples of fluorine-free glass wool to two or three laboratories upon request. He should be addressed at Corning, N. Y.

University of Virginia

Dec. 8, 1944.

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Determination of Fluorine in Certain Fluoro-Organic
Compounds in Water

INTRODUCTION

There are several methods for determining the fluorine content of fluoro-organic compounds in organic solvents¹, or in gas mixtures². Very few methods, however, are available for determining the fluorine in aqueous solutions of fluoro-organic compounds. Milton and Chivers³ report that ammonia will decompose aqueous solutions of methyl fluoroacetate quantitatively if the mixture is heated in a sealed tube at 150°C. for two hours. On the other hand, Kimber⁴ found that fluoroalcohols and fluoroacetates must be heated at 170° - 175°C. for two hours with 1:1 aqueous ammonia in a sealed tube for good results. Later, Milton and Chivers⁵ reported that dialkyl fluorophosphates may be decomposed by evaporating an aqueous ammonia solution to dryness.

Buswell⁶ reported that the presence of alkyl fluoroacetates in distilled water can be detected by evaporating 2 ml of a dilute alkaline solution to dryness in a small beaker, heating for 2 minutes, cooling slightly and then adding an indicator solution containing Solochrome Brilliant Blue, chloroacetic acid buffer (pH 5) and thorium nitrate. The color is compared with that of a blank in which ethyl acetate is used instead of the fluoroacetate. Buswell also reported that the equivalent of as little as 5 µg of organic fluorine in 1 ml of water may be detected if the aqueous solution is mixed with four volumes of ethanol and the mixture burned in an alcohol lamp. The vapors are absorbed in water and the solution tested for fluoride ions by adding Solochrome, buffer and thorium nitrate solution. The color is compared with a blank.

The method described in this report has been applied to the determination of fluorine in sodium fluoroacetate, methyl fluoroacetate, 2-fluoroethanol, and diisopropyl fluorophosphate in water; 97-100% of the fluorine is recovered as

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2.

inorganic fluoride. The procedure involves addition of the aqueous solution of the fluoro-organic compound to potassium meta periodate, silver perchlorate, perchloric acid, and glass wool. The mixture is refluxed and then distilled in a manner similar to the Elsworth and Barritt⁸ modification of the Willard and Winter⁷ procedure. The temperature is held at 135° ~ 145°C. by the addition of water; 100 ml of distillate is collected. Aliquots of the distillate are then analysed for inorganic fluoride by titration with thorium nitrate solution using Solochrome Brilliant Blue as indicator. About an hour is required to make a determination.

EXPERIMENTAL

A. Materials and Procedure.

Reagents. 1. Thorium Nitrate Solution. Dissolve 0.55 g of thorium nitrate, $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (reagent grade), in water and dilute to one liter. The solution is approximately 0.004 N.

2. Solochrome Brilliant Blue BS Indicator Solution. Dissolve 0.05 g of Solochrome Brilliant Blue BS^{*} in 250 ml of water. A fresh indicator solution should be made up every three weeks because a dark precipitate settles out of solutions that have stood for longer periods. Solochrome Brilliant Blue obtained from different sources may vary in its indicator action; hence standardization and analyses must be made with the same lot of indicator unless the different lots have been checked as to identity.

^{*}The Geigy Company, Inc., 89-91 Barclay Street, New York, N. Y., sells a dye under the name "Chrome Azurol 2 Conc." which, according to the Dye Index, is the same product as Solochrome Brilliant Blue BS. Dr. N. L. Drake¹⁰ of the University of Maryland, has recently examined spectrophotometrically some of the Geigy Dye and found its absorption spectrum the same as that of Solochrome Brilliant Blue BS. A 0.0153% solution of the former is equivalent to a 0.020% solution of Solochrome Brilliant Blue BS.

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3. Chloroacetic Acid Buffer Solution. Dissolve 22.7 g of chloroacetic acid and 4.8 g of sodium hydroxide in water and dilute to 1 liter.

4. Potassium meta Periodate. The salt was obtained from Eastman Kodak Co.

5. Silver Perchlorate. Reagent grade silver perchlorate, $\text{AgClO}_4 \cdot \text{H}_2\text{O}$, was obtained from G. Frederick Smith Chemical Co.

6. Perchloric Acid, 70%. Reagent grade perchloric acid, 70%, was obtained from Merck and Co. and J. T. Baker Chemical Co.

7. Perchloric Acid, 0.2 N.

8. Sodium Hydroxide, 0.2 N.

9. Glass Wool, low in fluorine.

Apparatus. The apparatus used in decomposing the fluoro-organic compounds is shown in Figure 1. It consists of: (A) a 100 ml round bottom, ground joint, pyrex flask (Corning Glass Works Catalogue No. 4320) into which a thermometer well is sealed; (B) a ground joint connecting tube with parallel side arm (Corning Glass Works Catalogue No. 9040) which is wrapped with asbestos cord; (C) a ground joint connecting tube, 75 angle (Corning Glass Works Catalogue No. 8920) which is wrapped with asbestos cord; (D) a 250 ml ground joint, pyrex separatory funnel (Scientific Glass Apparatus Co. Catalogue No. J-1866) to which is sealed a capillary tube extending almost to the bottom of the flask (A); and (E) two West condensers (Corning Glass Works Catalogue No. 2600) connected in series (not shown in Figure 1.). The ground joint between flask (A) and connecting tube (B) is lubricated at the top with a narrow ribbon of Lubrisal grease. The other joints are not lubricated. Enough mercury is put in the thermometer well to cover the bulb of the thermometer.

Decomposition of the Sample. To flask (A) add 0.2 g potassium meta periodate (KIO_4), 2 g silver perchlorate ($\text{AgClO}_4 \cdot \text{H}_2\text{O}$) and 15 ml of 70% perchloric acid [Note 1] Pour 20 ml of aqueous solution of the fluoro-organic compound into the mixture and

shake well. Powder any undissolved solid [Note 2] and add 0.2 g of glass wool weighed to the nearest 0.01 g. Reflux for 15 minutes; cool. Connect the flask to the apparatus as shown in Figure 1 and heat the mixture [Caution! See Note 3]; distillation begins at 110° - 120°C . Continue heating, hold the temperature at 135° - 145°C . by the addition of water from the separatory funnel, and collect 100 ml of distillate in a 100 ml volumetric flask. Twenty-five to thirty minutes should be required to collect the distillate.

Titration of Inorganic Fluoride. Transfer an aliquot (containing not more than 100 μg . of fluoride to a 50 ml low form Nessler tube [Note 4]. Add 0.2 N sodium hydroxide until the solution is alkaline to phenolphthalein; then add 0.2 N perchloric acid until the pink color just disappears [Note 5]. Now add 1 ml of Solochrome Brilliant Blue indicator (the resulting solution should have a yellow color; pink here indicates an excess of perchloric acid.) Add one drop (0.05 - 0.06 ml) of 0.2 N perchloric acid which turns the solution pink, then 0.5 ml of chloroacetic acid buffer and dilute to the 50 ml mark with distilled water [Note 6].

To a similar Nessler tube add 48 ml of water, 1 ml of indicator, one drop (0.05 - 0.06 ml) of 0.2 N perchloric acid, 0.5 ml of chloroacetic acid buffer, 0.10 ml of 0.004 N thorium nitrate solution and mix [See page 17].

The unknown is titrated with 0.004 N thorium nitrate solution until its color matches the bluish purple of the blank. Subtract 0.10 ml from the volume of thorium nitrate used, and convert the corrected volume to μg . of fluoride ion by means of a previously prepared calibration chart^{1,9}.

Notes. 1. A determination of fluoride in the reagents must be run and the analyses corrected for the positive value invariably found⁹. This is done by substituting 20 ml of distilled water for the sample and carrying out the analysis in the usual way. Most of the fluorine appears to come from the glass wool; hence it must be weighed to the nearest 0.01 g.

2. The addition of water to a mixture of potassium meta periodate, silver perchlorate, and perchloric acid forms a difficultly soluble yellow solid. Failure to powder finely this solid results in low recovery of fluorine. Black flakes in the yellow solid indicate that the potassium meta periodate and silver perchlorate became damp before the addition of the perchloric acid. When the solid is powdered the black flakes turn yellow or dissolve. Failure to eliminate this dark material results in a yellow distillate which is unsatisfactory for the titration of fluoride.

3. There is danger of explosion when heating a mixture of organic materials and perchloric acid. The operator should be protected by a safety glass barrier and a face shield. No explosion occurred in any of the many distillations made in the course of this investigation.

4. The titration must be carried out in a low form Nessler type tube (150 x 25 mm.); low fluoride values are obtained when an Erlenmeyer flask is used¹. Satisfactory titration cylinders may be prepared from 150 x 25 mm. or 200 x 25 mm. pyrex glass test tubes by flattening the closed ends.

5. The phenolphthalein endpoint must not be overrun by more than 0.01 ml of 0.2 N acid or the solution will not have the proper pH value.

6. The following alternate procedure has been found to give solutions of uniform pH: Dilute a mixture of 50 ml of indicator, 25 ml of buffer, and 3.0 ml of 0.2 N perchloric acid to 500 ml. Add 10.0 ml of this solution to the neutral fluoride solution, dilute to 50 ml, and titrate with thorium nitrate. This assures identical concentration of indicator, buffer, and acid in the blank and in successive titrations.

B. Analysis of Certain Fluoro-Organic Compounds.

The purity of the fluoro-organic compounds used to prepare the aqueous solutions was determined by the sodium in 1-hexanol method¹. The values listed in the first column of each table were obtained by multiplying the weights of the samples

by the purity factor.

Unless otherwise noted, all analyses were made by the procedure given in the section "Materials and Procedure" but without the refluxing. The increase in precision and recovery gained by refluxing was not noted until late in the investigation. Most of the analyses were made without refluxing.

Analysis of Sodium Fluoroacetate. The purity of the sodium fluoroacetate samples ranged from 81% to 88%. The samples also contained 8% to 11% sodium fluoride. Since the inorganic fluoride is completely recovered in the distillate, the values for organic fluorine rather than for total fluorine are reported in Table I (also in Tables V and VIII).

On an average, 90% of the fluorine in aqueous solution of sodium fluoroacetate was recovered in the distillate. The data are given in Table I. By comparison with Tables II and III, the recovery of 97% to 99% of the organic fluorine would be expected if the mixture were refluxed before the distillation.

Analysis of Methyl Fluoroacetate. The sample of methyl fluoroacetate, boiling range $103.5^{\circ} - 104.2^{\circ}\text{C.}$, used in these experiments assayed 99% pure.

On an average, 90% of the fluorine was recovered from aqueous solutions of the methyl fluoroacetate when distilled without refluxing; 97% was recovered when refluxing preceded the distillation. The data are given in Table II.

Table I. Determination of Fluorine in Aqueous Solutions of Sodium Fluoroacetate

Conc. of Compound µg/ml	Organic Fluoride Present µg/20 ml sample	Found µg	Recovery %
(Salsbury, Analyst)			
89.6	341	299	88
90.3	343	316	92
90.3	343	322	94
79.5	302	299	99
79.5	302	283	94
79.5	302	269	89
79.5 (a)	302	263	87
79.5 (a)	302	266	88
106.0	405	374	93
106.0	403	345	85
106.0	403	360	89
78.5	298	276	92
78.5	298	276	92
78.5	298	262	88
79.5	302	265	88
79.5	302	275	91
79.5	302	264	88
79.5	302	246	82
79.5	302	303	100
157.0	596	553	93
(Armstrong, Analyst)			
150	570	502	88
150	570	504	88
140	533	450	85
140	533	470	88
11.4	43.2	39	90
11.4	43.2	39	90
11.4	43.2	30	90
11.4	43.2	38	88
2.26	8.6	12	140
2.26	8.6	6	70
2.26	8.6	9	105

(a) Potassium periodate was dissolved in the aqueous solution of sodium fluoroacetate, silver perchlorate added, then the perchloric acid was added.

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Table II. Determination of Fluorine in Aqueous Solutions of Methyl Fluoroacetate.

Conc. of Compound µg/ml	Organic Fluorine Present µg/20 ml sample	Found µg	Recovery %
(Salsbury, Analyst)			
88.3	364	297	82
88.3	364	332	91
88.3	364	296	81
88.3	364	353	97
88.3	364	360	99
88.3	364	308	84
88.3	364	334	91
(Armstrong, Analyst)			
250	1010	900	89
250	1010	920	91
133	538	475	89
133	538	473	89
203	320	740	90
162	653	590	90
162	653	643	98 (a)
162	653	637	97 (a)
162	653	634	97 (a)
162	653	595	91

(a) Refluxed 15 minutes before distillation.

Analysis of 2-Fluoroethanol. The sample of fluoroethanol, boiling range 103° - 105.3°C., used in these experiments assayed 89% pure.

On an average, 64% of the fluorine was recovered from aqueous solutions of 2-fluoroethanol when distilled without refluxing; 99% was recovered when refluxing preceded the distillation. The data are recorded in Table III.

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Table III. Determination of Fluorine in Aqueous Solutions of 2-Fluoroethanol.
(Armstrong, Analyst)

Conc. of Compound µg/ml	Organic Fluoride Present µg/20 ml sample	Found µg	Recovery %
145	864	510	59
145	864	570	66
145	864	553	64
153	910	640	70
102	606	393	65
51	303	194	64
5.1	30.3	26	86
2.6	15.2	11	72
145	864	843	98 (a)
145	864	857	99 (a)
145	864	857	99 (a)
145	864	517	60

(a) Refluxed 15 minutes before distillation.

Analysis of Diisopropyl Fluorophosphate. A sample of 94% pure diisopropyl fluorophosphate was used.

Table IV shows that fluorine was completely recovered from aqueous solutions of diisopropyl fluoracetate. Refluxing is not necessary.

Table IV. Determination of Fluorine in Aqueous Solutions of Diisopropyl Fluorophosphate. (Armstrong, Analyst)

Conc. of Compound µg/ml	Organic Fluorine Present µg/20 ml sample	Found µg	Recovery %
202	417	417	100
81	167	168	101
40.4	83.4	81	97
16.2	33.4	34	102

C. Optimum Experimental Conditions.

Ten variables were studied to find the optimum conditions for determining the fluorine in aqueous solutions of fluoro-organic compounds: (1) The acid used in the reaction medium, (2) the type and quantity of oxidizing agent necessary to decompose all the fluoro-organic compound present, (3) the relation between the amount of silver perchlorate used and the recovery of fluorine, (4) source of silica, (5) the order of the addition of the reagents, (6) the effect of refluxing the reaction mixture, (7) the temperature necessary to decompose the fluoro-organic compound and distill over all of the inorganic fluoride, (8) the rate of distillation, (9) the volume of the distillate that must be collected to insure complete removal of the fluoride ions from the reaction mixture, and (10) the effect of diverse ions in the sample.

1. Perchloric Acid. A strong acid medium is needed when distilling fluoride out of the reaction mixture. Both sulfuric⁷ and perchloric acid^{7,8,9} have been used successfully for this purpose; perchloric acid, however, was chosen because it has a smaller effect in the thorium nitrate titration for fluoride ions using Solochrome Brilliant Blue as indicator [See page 20].

2. Effect of Potassium meta Periodate. When an aqueous solution of sodium fluoroacetate was heated in a mixture of perchloric acid, silver perchlorate and glass wool according to the procedure (p. 8), but in the absence of potassium periodate, only 4% of the sodium fluoroacetate was decomposed into fluoride ion [See Table V]. This was taken to indicate that some oxidizing agent, in addition to the mixture of perchloric acid and silver perchlorate, is required to decompose sodium fluoroacetate in aqueous solution.

In some preliminary experiments when 0.1 g of potassium permanganate was used in place of potassium periodate, about 70% of the fluorine was found in the distillate as inorganic fluoride. The distillate contained solid silver chloride and

hence had to be filtered. It was necessary to heat the reaction mixture very slowly in order to avoid bumping (about two hours being required to collect 100 ml of distillate). The precision of the results was poor because of the presence of an oxidizing agent (probably hypochlorous acid) in the distillate which slowly decolorized the Solochrome Brilliant Blue indicator. When potassium periodate was used instead of potassium permanganate, no silver chloride was carried over and no oxidizing agent appeared in the distillate.

The results summarized in Table V indicate that in some solutions the recovery of fluorine obtained with 0.1 g potassium meta periodate was equal to that with 0.2 g. Other solutions, however, required 0.2 g of potassium periodate for maximum recovery. The use of 0.5 g of potassium periodate did not affect appreciably the recovery of fluorine. In view of a lack of consistency with less than 0.2 g of potassium periodate, this quantity is recommended in the procedure.

3. Effect of Silver Perchlorate. The role of silver perchlorate in the decomposition of sodium fluoroacetate is unknown, but its presence is essential as is shown by the data in Table V. At least 1 g of silver perchlorate must be in the reaction mixture and 2 g appears desirable. With less than 1 g of silver perchlorate, the recovery of fluorine is decreased markedly, only about one-half as much being obtained with 0.03 g of silver perchlorate as with 1 g.

4. Source of Silica. Silica must be available in the reaction mixture to form H_2SiF_6 . Glass wool is the best material for this purpose⁹. From 0.05 g to 0.2 g was employed; the larger value was selected for the standard procedure because it reduced bumping. The distillate gave a titer equivalent to 2 μg of fluoride for each 0.01 g of pyrex glass wool used; a glass wool giving a much lower titer would be desirable.

Table V. Effect of Potassium Periodate and Silver Perchlorate on the Determination of Fluorine in Aqueous Solutions of Sodium Fluoroacetate. (Salsbury, Analyst)

Conc. of Compound µg/ml	Potassium Periodate g.	Silver Perchlorate g	Organic Fluorine Found µg/20 ml sample	%
67.6	0.0	1.0	10	4
67.6	.1	0.03	167	65
67.6	.1	0.03	121	47
67.6	.1	0.5	202	79
67.6	.1	1.0	235	92
67.6	.1	1.0	236	92
67.6	.1	1.0	223	87
67.6	.1	1.0	234	91
89.6	.1	1.0	239	70
89.6	.1	1.0	244	72
89.6	.1	1.0	272	80
89.6	.1	1.0	220	65
89.6 (a)	.2	2.0	Average	88
90.3	.1	1.0	524	94
90.3	.1	1.0	517	93
90.3 (a)	.2	2.0	Average	93
79.5	.1	1.0	222	74
79.5 (b)	.1	1.0	234	73
79.5 (b)	.1	1.0	241	80
79.5 (a)	.2	2.0	Average	91
79.5	.3	3.0	263	87
78.5	.1	1.0	233	78
78.5	.1	1.0	253	85
78.5	.1	1.0	227	77
78.5 (a)	.2	2.0	Average	91
79.5	.1	1.0	252	84
79.5 (a)	.2	2.0	Average	90
179.2	.1	1.0	485	71

(a) See Table I.

(b) Potassium periodate was dissolved in the aqueous solution of sodium fluoroacetate, silver perchlorate added; then the perchloric acid added.

5. Order of Addition of Reagents. When silver perchlorate was added to aqueous solutions of potassium meta periodate a dark precipitate formed. Treatment of this mixture with perchloric acid caused the solid first to turn yellow and then dissolve. The dark precipitate may be silver meso periodate (Ag_3IO_5) which has been reported¹¹ to be formed when silver meta periodate (AgIO_4) hydrolyses. It was thought there may be a difference in the percentage of fluorine recovered from sodium fluoroacetate depending on: (1) whether potassium meta periodate is dissolved in the aqueous solution of sodium fluoroacetate and silver perchlorate added, followed by perchloric acid, or (2) perchloric acid is added to a mixture of potassium meta periodate and silver perchlorate and then the aqueous solution of sodium fluoroacetate added. The data in Tables I and V indicate that the order of addition of the reagents has very little effect, if any, on the recovery of fluorine.

6. Effect of Refluxing the Reaction Mixture. Early in the investigation, in an effort to improve the recovery of fluorine from aqueous solutions of sodium fluoroacetate, the reaction mixture was refluxed for periods of 0.5, 1, and 2 hours at 120°C . An average of 95% of the fluorine was recovered after refluxing. Since 90% recovery was obtained without refluxing, the small increase in recovery did not seem to warrant the additional time-consuming step.

Late in the investigation, the perchlorate-periodate method was applied to the determination of fluorine in aqueous solutions of 2-fluoroethanol. In the analysis of this compound a 15 minute refluxing period before the distillation increased the recovery of fluorine from 64% to 98%; the precision was also increased [See Table III].

Meanwhile, improvements had been made in the procedure, and a second investigation showed the recovery of fluorine from fluoroacetate solutions is increased from 90% to 98% by refluxing the reaction mixture for 15 minutes before

distillation [See Table II].

The recovery of fluorine from aqueous solutions of diisopropyl fluorophosphate is complete without use of a refluxing period [See Table IV].

7. Temperature of the Reaction Mixture. It is reported that a temperature of at least 135°C. is required for complete removal of fluoride ion from the reaction mixture by distillation with perchloric acid^{8,9}. At temperatures above 145°C. an excessive amount of perchloric acid is carried into the distillate and interferes with the titration for fluoride. Hence, it is important that the temperature of the reaction mixture during distillation be held at 135° - 145°C.

8. Rate of Distillation. The time required for the collection of 100 ml of distillate was varied from 20 to 75 minutes. Rapid distillation increased the perchloric acid content of the distillate [See section D: Titration of Fluoride]. As the amount of fluoride in the "blank" on the reagents [Note 1, p. 4] increases with increase in distillation time, it is believed that the reagents react with the glass wool to liberate fluoride ions from the latter. Unless fluoride-free glass wool can be obtained, the time for distillation should be held within a narrow time range; 28 ± 3 minutes has been found satisfactory.

9. Volume of Distillate. Distillation of standard solutions of potassium fluoride with a mixture of 0.1 g potassium periodate, 1 g silver perchlorate, 15 ml 70% perchloric acid and a wad (0.1 g) of glass wool by the procedure given above indicates that it is necessary to collect at least 100 ml of distillate in order to recover the fluoride satisfactorily. Table V $\frac{1}{2}$ shows a typical result obtained by analysing 25 ml fractions of the distillate; the original solution contained 843 μ g of fluoride.

When aqueous solutions of sodium fluoroacetate were decomposed and the fluoride ions removed by distillation, a maximum of 2% of the fluoride ions was

Table VI. Recovery of Inorganic Fluoride as a Function of the Volume of Distillate (Salsbury, Analyst)

Fraction ml	Fluoride µg	Found %
0 - 25	368	44
25 - 50	238	34
50 - 75	124	15
75 - 100	<u>34</u>	<u>4</u>
Total	814	97

found in the second 100 ml of distillate; in the majority of determinations no fluoride was found. Hence collection of the first 100 ml distillate appears adequate.

10. Effect of Diverse Ions. Calcium, chloride, sulphate, and phosphate are ions commonly present in natural waters that might be expected to interfere either with the decomposition of the fluoro-organic compounds or with the distillation and titration of the inorganic fluoride formed. These ions are seldom present in excess of 150 p.p.m. Ca, 8000 p.p.m. SO_4 , or 53 p.p.m. PO_4 . Aluminum might be introduced in water treatment; hence it is included in this study.

The data in Table VII show that in the absence of diverse ions, the fluoride is completely recovered in the first 100 ml of distillate. The recovery of 97 - 98% of the fluoride in the presence of Ca, SO_4 , BO_3 or PO_4 ions may be due either to a slight reduction in the rate of distillation of the fluoride in the presence of these ions, or to experimental error.

The values in Table VIII show a slightly lower recovery of fluorine from sodium fluoroacetate when the decompositions and distillations are carried out in the presence of Al, Ca, BO_3 or SO_4 and PO_4 . Here too, the differences are within the experimental error.

Table VII. The Recovery of Fluoride from Aqueous Solutions of Potassium Fluoride Containing Diverse Ions. (Armstrong, Analyst)

F Introduced µg	Diverse Ions in the 20 ml sample	Recovery of Fluoride	
		µg	%
443	None	443	100
443	None	440	99
443	8000 ppm SO ₄	437	98
443	8000 ppm SO ₄	431	97
443	33 ppm PO ₄	431	97
443	8000 ppm SO ₄ ; 33 ppm PO ₄	443	100
443	8000 ppm SO ₄ ; 33 ppm PO ₄	445	100
443	150 ppm B	443	100
443	100 ppm Ca; 175 ppm Cl	433	98

Table VIII. Determination of Fluorine in Aqueous Solutions of Sodium Fluoroacetate Containing Diverse Ions. (Armstrong, Analyst)

Conc. of Compound µg/ml	Diverse Ions in the 20 ml sample	Organic Fluorine		
		Present µg	Found µg	%
150	None	570	502	88
150	None	570	504	88
150	150 ppm Ca; 265 ppm Cl	570	492	86
150	150 ppm Ca; 265 ppm Cl	570	489	86
150	77 ppm Al; 1400 ppm NO ₃	570	480	84
140	None	533	450	85
140	None	533	470	88
140	8000 ppm SO ₄ ; 33 ppm PO ₄	533	473	88
140	150 ppm B	533	420	79

The effect of Ca, SO₄ and PO₄ on the recovery of fluorine from methyl fluoroacetate is shown in Table IX. Analyses of aqueous solutions of methyl fluoroacetate are less precise than those of sodium fluoroacetate [cf. Tables I and II]. Hence the differences in recovery noted in Table IX cannot be definitely attributed to the diverse ions.

A survey of Tables VII, VIII and IX shows that the recovery of fluorine is 2 to 3% lower in the presence of 150 p.p.m. Ca. The presence of SO₄, or PO₄, or both, either does not affect the recovery of fluorine or lowers it only slightly. Hence it may be concluded that the inorganic ions commonly present in potable waters interfere only slightly, if at all, with the determination of fluorine in fluoro-organic compounds by the perchlorate-periodate procedure.

Table IX. Determination of Fluorine in Aqueous Solutions of Methyl Fluoroacetate Containing Diverse Ions. (Armstrong, Analyst)

Conc. of Compound µg/ml	Diverse Ions in the 20 ml sample	Organic Fluorine		%
		Present µg	Found µg	
245	None	1010	900	89
245	None	1010	920	91
245	150 ppm Ca; 265 ppm Cl	1010	880	87
245	None	1010 (a)	860	85
245	None	1010 (a)	860	85
245	150 ppm Ca; 265 ppm Cl	1010 (a)	840	83
245	150 ppm Ca; 265 ppm Cl	1010 (a)	840	83
131	None	538	475	89
131	None	538	478	89
131	8000 ppm SO ₄	538	440	82
131	8000 ppm SO ₄	538	425	79
131	None	538	475	89
131	33 ppm PO ₄	538	460	86
200	None	820	740	90
200	8000 ppm SO ₄	820	750	91
200	8000 ppm SO ₄	820	720	89

(a) The use of this value assumes the stability of the solution of methyl fluoroacetate over a 24 hour interval. The recovery of only 860 µg F compared to 900 and 920 µg F by the same procedure on the previous day indicates about 5% loss of methyl fluoroacetate from the solution between the two measurements.

D. Titration of Fluoride.

Manipulation. The titration is performed in 25 x 150 mm flat bottom cylinders (low form Nessler tubes or equivalent). Two of these, blank and unknown, are held in the left hand: the fingers serve as a shield reducing the light entering the sides of the tube. Light from a tungsten lamp placed behind (12-18 in.) and above (6-12 in.) the titration stand is reflected from the white porcelain base through the bottoms of the tubes. Stirring is accomplished by the vertical motion of a 4-5 mm glass rod with the lower end flattened to a 15 mm button.

Blank. The blank should be tested each day by titration against a standard fluoride solution. An error of 0.01 ml in the volume of thorium nitrate solution in the blank introduces a titration error of 0.04 ml with 50 µg F; with 100 µg F the error is 0.07 ml. In precise work a fresh blank should be prepared each day because of a slow change in its color.

Effect of pH^{*}. In Porton Report No. 2549 the necessity of careful control of the acidity is discussed without stating the pH of the solutions titrated^o. Drake¹⁰ finds solutions prepared according to the directions in the Porton Report have pH 3.17 - 3.20.

If, to the neutral solution of fluoride and 1 ml of 0.02% Solochrome indicator, 0.05 N perchloric acid is added "until the yellow of the dye just changes to pink"^o, then 0.5 ml of buffer added and diluted to 50 ml, the solution has pH 3.19 - 3.23, depending upon which shade of pink the addition of acid is stopped. On the other hand, if to the neutral fluoride solution are added one drop (0.05 - 0.06 ml) of 0.2 N perchloric acid, 1 ml indicator, 0.5 ml buffer, and water to 50 ml, the solution has pH 3.17 - 3.20. In case a number of titrations are to be made, uniform concentrations of the reagents are conveniently obtained by mixing 50 ml of indicator, 25 ml buffer, and 3.0 ml 0.2 N perchloric acid, diluting to 500 ml, and then adding a 10.0 ml portion of the solution to each sample of neutral fluoride solution.

Blanks prepared according to directions in the Porton report have pH 3.25 - 3.27; these are distinctly blue in color compared to blanks of lower pH (3.17 - 3.20). A blank prepared from 10 ml of the indicator-buffer-acid solution mentioned above, 40 ml water, and 0.10 thorium nitrate has the same pH as fluoride solutions similarly prepared.

To determine the effect of pH, solutions containing 44.3 µg F, 1.00 ml indicator, 0.5 ml buffer, and from 1 to 11 ml of 0.002 N perchloric acid were titrated with thorium nitrate solution until they matched a blank having pH 3.17. The data in Table X show that if the variation from this pH exceeds 0.02, appreciable error is introduced.

* All pH values were determined with a Coleman Model 3D meter calibrated against 0.2 N potassium acid phthalate. A Beckman pH meter, calibrated against the same standard, registered all values in the 3.0 - 3.2 range from 0.04 to 0.05 lower.

Table X. Effect of pH on the Titration of Fluoride^(a). (Armstrong, Analyst)

0.002 N HClO ₄ , ml	Equivalent volume of 0.2 N acid, ml	pH	0.004 N Thorium Nitrate, ml
1	0.01	3.23	1.41
4	.04	3.19	1.45
6	.06	3.17	1.47
6	.06	3.17	1.47
8	.08	3.13	1.49
11	.11	3.08	1.54 (b)
11	.11	3.08	1.53 (b)

(a) Each solution contained 44.3 µg F, 1 ml indicator, 0.5 ml buffer and water to make 50 ml; each was titrated to match a blank with pH 3.17.

(b) Off tint, endpoint difficult to determine.

Drake¹⁰ suggested the addition of "two drops" of 0.2 N perchloric acid and 0.75 ml of buffer to each neutral solution of fluoride thus establishing a pH 3.00 for the titration. The data for titrations near pH 3.0, Table XI, show no increase in tolerance to differences in pH over titrations performed around pH 3.17. The endpoint is more difficult to determine in solutions of pH 3.00 than of 3.17. Table XI. Titration of Fluoride at pH's near 3.00 (Armstrong, Analyst)

0.002 N HClO ₄ , ml	Equivalent volume of 0.2 N acid, ml	pH	0.004 N Thorium Nitrate, ml
7	0.07	3.06	1.57
12	.12	3.02	1.60
12	.12	3.02	1.62
17	.17	2.96	1.66

Each solution contained 44.3 µg F, 1 ml indicator, 0.75 ml buffer, and water to make 50 ml; each was titrated to match a blank with pH 3.02.

These experiments indicate that the titration of fluoride with thorium nitrate is satisfactory at any pH between 3.00 and 3.23. The analyst should select the lower pH if he finds the reddish tints easier to match; the higher pH if he prefers to match solutions of a bluish tint. However, once a pH value for the titrations is selected, this value should be maintained as rigidly as possible. It is believed that most analysts will find pH 3.17 or pH 3.20 gives solutions

that are most easily matched. If a pH of 3.40 is selected, it is readily attained by using 2.0 ml 0.2 N HClO_4 per 500 ml of indicator-buffer-acid solution described on page 18; 3.0 ml of the acid gives a pH of 3.17.

It should be obvious that to maintain the pH within narrow limits, extreme care is required in neutralizing the fluoride solution. In establishing the phenolphthalein endpoint an excess of more than 0.01 ml of 0.2 N acid is to be avoided. The use of a 0.05 N HClO_4 solution for this neutralization has the advantage that drops need not be split.

Effect of Sodium Perchlorate and Sodium Sulfate. The decomposition of fluoro-organic compounds by sodium in 1-hexanol¹ yields a fluoride solution containing 5 millimols of sodium hydroxide. In the perchlorate-periodate method the distillate contains 0.4, 2, or 8 millimols of perchloric acid for distilling times of 40, 27, or 22 minutes respectively. Thus, after neutralization, a one-tenth aliquot of the fluoride solution from the sodium-1-hexanol procedure contains 0.5 millimol of sodium perchlorate; that from the perchlorate-periodate procedure contains from 0.04 to 0.8 millimol of the salt.

The data in Table XII show that the presence of sodium perchlorate in the above quantities leads to high volumes in the titration of fluoride samples and to slightly high volumes in the so-called "blank" determination of fluoride in the reagents. Fluoride values calculated from these larger titration volumes are 2% (0.2 millimol NaClO_4) to 3% (0.5 - 1.0 millimol NaClO_4) high.

The presence of sodium sulfate is to be avoided as it causes high titration volumes.

Table XII. Effect of Sodium Perchlorate and Sodium Sulfate on the Th-F Titration. (Armstrong, Analyst)

F Present µg	Salt Present millimols milligrams		0.004 N Thorium Nitrate, ml
Sodium Perchlorate			
0	0	0	0.10
0	0.5	61	0.11
0	1.0	122	0.13
44.3	0	0	1.49
44.3	0.5	61	1.49
44.3	1.0	122	1.54
88.6	0	0	2.74
88.6	0.2	24	2.82
88.6	0.5	61	2.86
88.6	1.0	122	2.88
Sodium Sulfate			
50.0	0	0	1.64
50.0	0.001	0.14	1.67
50.0	0.002	0.28	1.72
50.0	0.004	0.57	1.83

Each solution contained 1.0 ml indicator, 0.5 ml buffer, 0.06 ml of 0.2 N HClO_4 , and water to make 50 ml; pH 3.17.

SUMMARY

A method for determining the fluorine in sodium fluoroacetate, methyl fluoroacetate, 2-fluoroethanol, and diisopropyl fluorophosphate in water has been described. It is based on (1) adding the aqueous sample to potassium meta periodate, silver periodate, perchloric acid, and glass wool, (2) refluxing for a 15 minute period, (3) heating the mixture and holding its temperature at $135^\circ - 145^\circ\text{C}$. by the addition of water while 100 ml of distillate is collected, and (4) analysing aliquots of the distillate for fluoride ions by titrating with thorium nitrate solution using Solochrome Brilliant Blue as indicator. An analysis requires about an hour.

The recovery of fluorine from solutions of the fluoro-organic compounds was 97-100%. When the reaction mixture was distilled without refluxing the recovery of fluorine was 90% for fluoroacetates, 64% for 2-fluoroethanol, and 100% for diisopropyl fluorophosphate.

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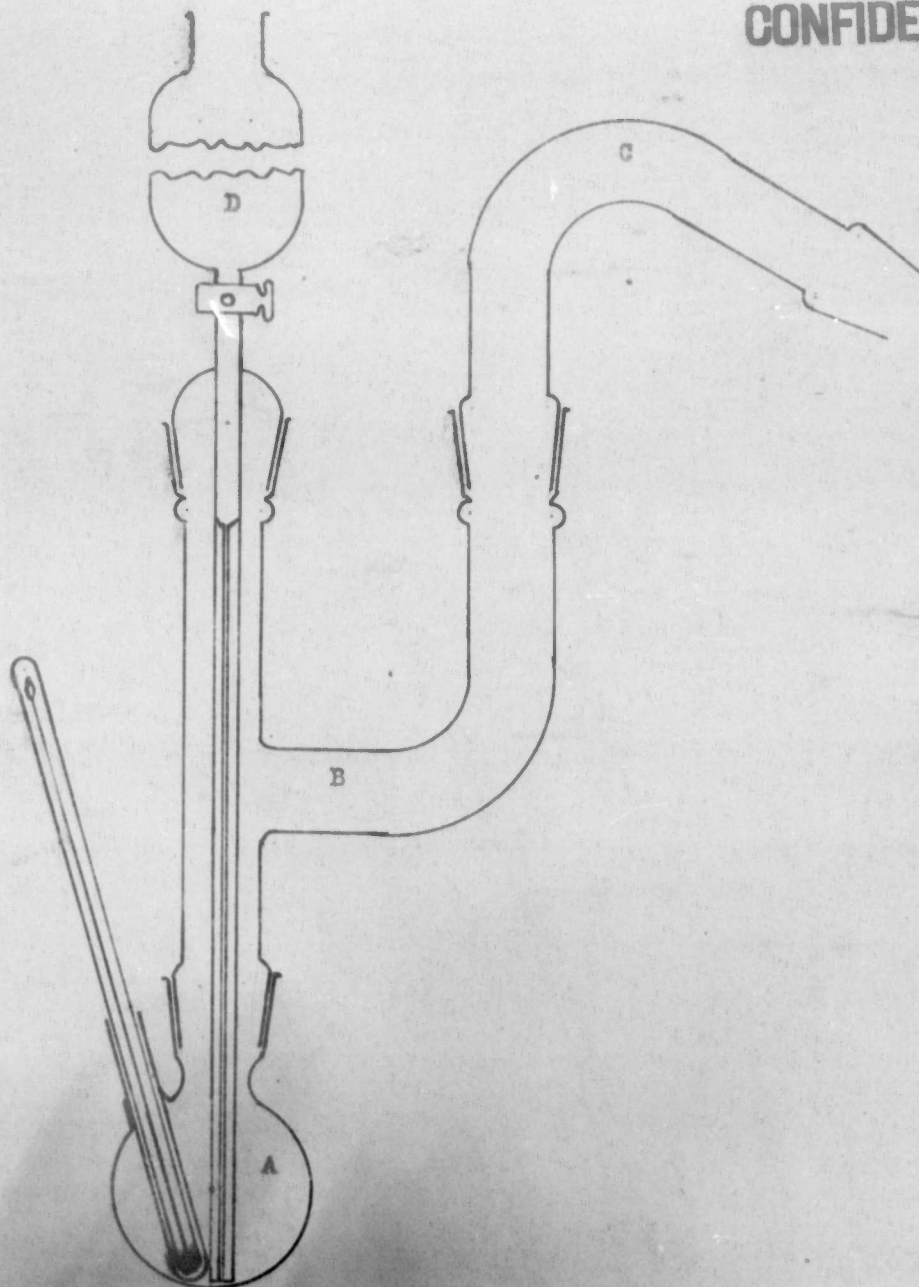
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FIGURE 1.

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ABSTRACT:

A method for the determination of fluorine in sodium fluoroacetate, methyl fluoroacetate, 2-fluoroethanol, and diisopropyl fluorophosphate in water is described. It involves addition of the aqueous solution of the fluoro-organic compound to potassium meta periodate, silver perchlorate, perchloric acid, and glass wool. The mixture is refluxed, then distilled. Temperature is held at 135° - 145°C by the addition of water until 100 ml of the distillate is collected. Aliquots of the distillate are then analysed for fluoride ion by titrating with thorium nitrate solution using Solochrome Brilliant Blue as indicator. From 97% to 100% of the fluorine was recovered. Ions commonly present in potable waters do not interfere seriously. The time required for a determination is about one hour.

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