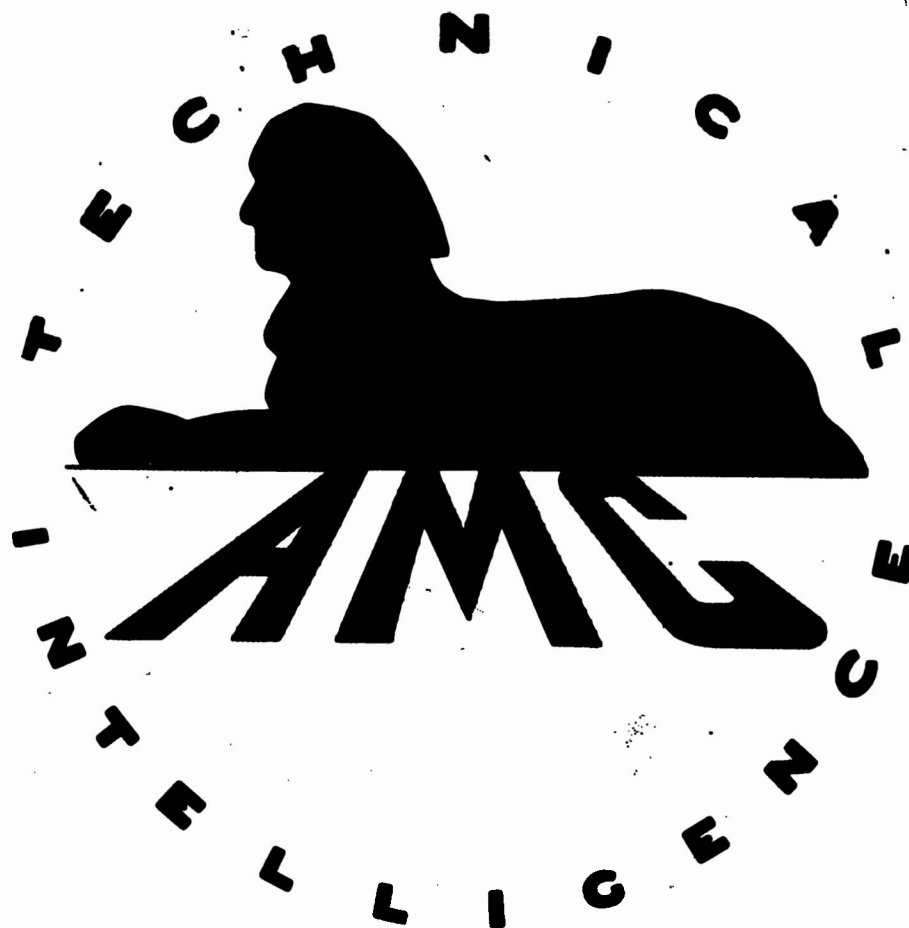


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Division 9
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

DETERMINATION OF ~~UNKNOWN~~ IN FLUORO-ORGANIC COMPOUNDS
IN LOW CONCENTRATIONS IN AIR

to
June 6, 1944
by
John H. Yoe (Official Investigator),
Jason M. Salisbury and James W. Cole

Report OSRD No. 3830

Copy No. 45

Date: June 27, 1944

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NATIONAL DEFENSE RESEARCH COMMITTEE
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SECTION 9:3

DETERMINATION OF FLUORINE IN FLUORO-ORGANIC COMPOUNDS
IN LOW CONCENTRATIONS IN AIR

Service Directive CWS- 6

Endorsement (1) Henry E. Bent, in charge - Section 9:3:1 to
Walter R. Kirner, Chief Division 9.

Forwarding report and notings:

In this method, the fluoro-organic compound is removed from air by scrubbing with 1-hexanol, in which solvent the fluoro compound is decomposed by refluxing with sodium. The sodium fluoride formed is extracted with water and is estimated titrimetrically with thorium nitrate solution, using Solochrome Brilliant Blue BS as indicator. The method has been tested with methyl fluoroacetate, 2-fluoroethanol and di-isopropylfluorophosphate in the range of 0.002 to 2 mg. of fluoride which is equivalent to 0.01 to 8 mg. of fluoro-organic compound per liter.

(2) from Walter R. Kirner, Chief Division 9 to
Irvin Stewart, Executive Secretary of the National Defense
Research Committee
Forwarding report and concurring: . . .

This is a formal report under Contract 9-344 OMSr-139 with University of Virginia.

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Division B
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
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Formal Report No.

Section 9-3

Determination of Fluorine in Fluoro-Organic Compounds in
Low Concentrations in Air

By

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

University of Virginia

Proposal B-544

Contract No. ONMSr-159

June 3, 1944

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Determination of Fluorine in Fluoro-Organic Compounds in
Low Concentrations in Air

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

A B S T R A C T

An apparatus for the preparation of mixtures of fluoro-organic compounds and air, and a method for the determination of fluorine in such compounds are described. The analysis involves (1) removing the fluoro-organic compounds by scrubbing the air mixture with 1-hexanol, (2) decomposing the fluoro-organic compound by refluxing with sodium, (3) extracting with water the sodium fluoride thus formed and (4) titrating the fluoride ion with thorium nitrate solution, using Solochrome Brilliant Blue BS as indicator. This method has been tested in the concentration range of 0.002 to 2 mg. of fluoride which is equivalent to 0.01 to 8 mg. of fluoro-organic compound per liter of air.

Three fluoro-organic compounds were analysed. With methyl fluoroacetate in the range 0.01 to 8 mg. per liter, a recovery of about 90% was obtained. About 90% of 2-fluoroethanol was recovered from air mixtures when the concentration was 0.02 to 3 mg. per liter; when the concentration was 0.01 to 0.03 mg. per liter, the recovery was only about 75%. The recovery of di-isopropylfluorophosphate is 72% at a concentration of 0.02 - 0.04 mg. per liter, 84% at 0.07 - 0.15 mg. per liter, and 68% at 1 - 2 mg. per liter. By using two scrubbers in series, 90% of di-isopropyl fluorophosphate was recovered at a concentration of 1 to 2 mg. per liter.

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Determination of Fluorine in Fluoro-Organic Compounds in
Low Concentrations in Air

INTRODUCTION

A survey of the literature reveals that three procedures have been developed for the analysis of mixtures of fluoro-organic compounds in air: (1) pyrolysis of the gas in a methyl alcohol flame¹ or by passage over a heated platinum wire²; (2) oxidation by a solution of ammonium sulfate in sulfuric acid or chromic acid and detection of HF by etching of the glass container³; (3) scrubbing the gas with ammonia and decomposing the fluoro-organic compound^{4,5}. Usually the inorganic fluoride was detected or estimated by standard methods.

In this report a procedure is described for the determination of fluorine in methyl fluoroacetate, 2-fluoroethanol and di-isopropylfluorophosphate at low concentration in air. The compounds are scrubbed out of the air mixture by passing the latter through a CWS scrubber containing 1-hexanol. The 1-hexanol solution is then refluxed with sodium to decompose the fluoro-organic compound⁶, and the sodium fluoride is extracted with water. Aliquots are titrated with thorium nitrate solution, using Solochrome Brilliant Blue BS⁷ as indicator.

PROCEDURE

Preparation of the Gas Mixture. To obtain gas mixtures of low concentration, a known amount of the fluoro-organic compound must be volatilized in a definite volume of air. This may be accomplished by passing air over the compound and diluting the vapor to a known volume with air. The amount of substance vaporized is determined by the loss in weight of the vaporizer. The total volume of gas is calculated by multiplying the rate of flow of air by the total time. The concentration of the fluoro-organic compound in the air is then calculated by

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dividing the weight of compound volatilized by the total volume of air.

1. Apparatus. The apparatus is shown schematically in Figure 1.

Compressed air is dried in tower A by anhydrous calcium chloride. The rate of flow through the system is adjusted at pressure releases B or C. When pressure release C is used, the rate of air flow is regulated by the height of the water column. If more pressure is required than can be obtained with C (3 ft. of water), part of the water may be replaced by mercury; or pressure release B (ordinary two way stopcock) may be used. Pressure release C insures a constant rate of flow, but when B is used, the flow is maintained constant by manual adjustment of the size of the orifice. The dried air passes through flowmeter D and is divided into two streams; one goes through flowmeter E, vaporizer J and into the mixing chamber M, while the other stream goes directly to mixing chamber M, which is packed with glass wool. The volume of air going through the vaporizer is determined by the position of stopcock G. The compound to be volatilized is contained in vaporizer J which consists of a glass tube 7 mm. in diameter and 40 mm. tall with glass side arms 2 mm. in diameter.

The concentration of the fluoro-organic compound in the air is determined by (1) the rate of flow and volume of air passing through the vaporizer J, (2) the temperature of the vaporizer, (3) the volume of liquid in the vaporizer, and (4) the volume of the mixture after dilution. The diluted mixture is divided into two portions as it issues from the mixing chamber. Most of the mixture is vented at N, the rest going through stopcock I into scrubber O and flowmeter F. The scrubber is immersed in the cooling bath contained in a two quart Dewar flask, P.

The type of scrubber used is very important because each has its own characteristics. A scrubber (Plate 1) obtained from the Chemical Warfare Service, Technical Division, Edgewood Arsenal, was used for most of these experiments.

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In most of the tests described in this report the rate of flow of air, as shown by flowmeter D, was 10.0 liters per minute, and the gas was scrubbed at a rate of 1.0 liter per minute. The other nine liters of gas was vented at N. Stopcock I is a three way stopcock to allow the gas to by-pass the scrubber when desirable. The rate of flow of gas through the scrubber is measured by flowmeter F.

Scrubbing Operation. The scrubbing operation is performed in the following manner. Place the compound to be volatilized in vaporizer J and weigh. Attach the vaporizer to the rest of the apparatus with rubber connections. The connection at K must be glass to glass because the vapors pass through it. Close stopcock H and adjust stopcock I so the gas will by-pass the scrubber. Charge the CWS scrubber with 40 ml. of 1-hexanol; immerse in a bath at $-40^{\circ}\text{C}.$; then attach it to the apparatus through connection L. This connection must be glass to glass. Close the stopcock at B and open the stopcock to C. Pass the air into A at a rate in excess of ten liters per minute, and adjust the water level in pressure release C so that 10.0 liters of air per minute passes through flowmeter D. Adjust the stopcock at N till a flow of about one liter per minute is registered by flowmeter F. Turn I so the air will go through scrubber O and make final adjustment at N till a flow of 1.0 liter per minute passes through flowmeter F. Open stopcock H and time (stopclock) the period that air goes through H. Flowmeters D and F should be checked occasionally during the period of scrubbing. When the scrubbing is completed, close stopcock H; turn stopcock I so gas by-passes the scrubber, and turn off the air.

Disconnect vaporizer J and weigh. The loss in weight of the vaporizer divided by the total volume (in liters) of air used gives the concentration of fluoro-organic compound per liter.

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Disconnect the scrubber at L and take it out of the cooling bath. Drain the solution through the lower stopcock into a 100 ml. gr. j. round bottom flask.

Wash down the center tube with 10 ml. of 1-hexanol and combine the two solutions.

Decomposition of Fluoro-Organic Compound⁶. (See Appendix for a list of the reagents) Add 0.2 g. of sodium to the 1-hexanol solution and attach a water condenser. Reflux the mixture gently for ten minutes. After cooling for about a minute, extract the hot solution with two 10 ml. portions of water. Analyse the aqueous (lower) layer for inorganic fluoride.

Titration of Inorganic Fluoride⁷. Add an aliquot of the aqueous solution containing up to 100 μ g. of fluoride to water in a 50 ml. Nessler tube (125 mm. tall). Make the solution acid to phenolphthalein with 3% perchloric acid and add 1 ml. of Solochrome Brilliant Blue indicator solution. Add 3% perchloric acid carefully until the solution just turns red; then add 0.5 ml. of the chloroacetic acid buffer solution. Dilute the solution to 50 ml. To a similar Nessler tube add water, 1 ml. of Solochrome Brilliant Blue indicator solution; dilute to 50 ml. and add exactly 0.10 ml. of thorium nitrate solution. Titrate the sample solution with thorium nitrate solution until its color matches that of the blank. Subtract 0.10 ml. from the volume of thorium nitrate solution used; the result is converted to μ g. of fluoride ion by comparison with a previously prepared calibration chart.

Notes. 1. The vaporizer is weighed with the rubber connections the ends of which are stoppered with short pieces of glass rods. The vaporizer should be carefully wiped with a piece of linen before each weighing.

2. A drop of glycerine put in rubber connection L will keep it lubricated for a long time.

3. The liquid in the flowmeters is water; hence the gas passing into the scrubber contains a small amount of moisture. The latter condenses in the

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upper part of the inner tube of the scrubber. When this tube is washed down with 10 ml. of 1-hexanol, the ice melts and goes into solution. This small amount of water does not interfere when the solution is refluxed with sodium.

4. A temperature of -40°C . is obtained by adding solid carbon dioxide to chlorobenzene.

5. The reaction mixture must be cooled about a minute before it is extracted with water in order to avoid a vigorous reaction.

6. Care must be exercised in acidifying the aqueous solution of sodium fluoride. Unless the correct amount of acid is used, the indicator will not turn purple when an excess of thorium nitrate solution is added. Should too much acid be added, it should be neutralized with 5% sodium hydroxide before the buffer solution is added.

7. Perchloric acid is employed to neutralize the aqueous solution of sodium fluoride because sodium perchlorate has less effect on the endpoint of the titration than sodium chloride, acetate, carbonate, sulfate, or phosphate⁷.

8. The titration must be carried out in a Nessler tube; a low result is obtained when an Erlenmeyer flask is used⁶.

DISCUSSION

To ascertain the optimum conditions for determining the concentration of fluoro-organic compounds in air nine variables were studied: (1) the solvent used to scrub the fluoro-organic compound out of air; (2) the size of the sample to be analysed; (3) the completeness of the extraction of sodium fluoride from the reaction mixture; (4) the time of refluxing necessary to obtain quantitative decomposition of the sample; (5) the dye used to indicate the endpoint of the thorium nitrate titration of fluoride; (6) the concentration of the fluoro-organic compound

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(7) the temperature of the scrubber; (8) the volume of the scrubbing liquid, and (9) the rate of flow of the gas through the scrubber. The effect of the first five variables will be discussed in this section and the last four in the section on methyl fluoroacetate.

Solvent The success of the scrubber depends upon the nature of the solvent. High boiling aliphatic alcohols were tested as solvents because they would also serve as the reflux medium for the decomposition of the fluoro-organic compound by sodium. Both 1-hexanol and 1-octanol proved to be suitable as the scrubbing solvent, but further experiments showed 1-hexanol to be the better. 1-Hexanol can be cooled without solidification to -40°C ., the temperature required for satisfactory scrubbing of low concentrations of the fluoro-organic compounds; 1-octanol freezes at -58.5°C . After the decomposition mixture is extracted with water, the 1-hexanol may be recovered by distillation followed by fractionation.

Size of Sample. The aliquot to be titrated with thorium nitrate solution using Solochrome Brilliant Blue indicator must contain between 1 μg . and 100 μg . of fluoride ion. The endpoint in the titration is dependent to some extent on the concentration of sodium perchlorate; hence a blank should be made by refluxing 50 ml. of 1-hexanol with 0.2 g. of sodium, extracting with water, and titrating the same size aliquot as used for the fluorine titration.

When the sample to be analysed contains less than 100 μg . of fluoride ion, the entire sample must be used for the thorium nitrate titration. Better results were obtained in this case if the procedure was modified in the following manner: Collect the sample by scrubbing; then reflux with sodium according to the standard procedure. Extract the reaction medium with 10 ml. of water and separate the aqueous (lower) layer. Add two drops of phenolphthalein to the aqueous solution and neutralize with 60% perchloric acid. Extract the 1-hexanol solution (upper

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layer) with another 10 ml. of water, and add the aqueous (lower) layer to the neutralized aqueous solution. Neutralize the combined aqueous solution with 3% perchloric acid and analyse for fluoride in the usual way.

Extraction of Fluoride. Practically all the sodium fluoride is extracted from the reaction mixture by two 10 ml. extractions with water. A third extraction yields less than 0.5% additional fluoride ion.

Reflux Time. Ten minutes of reflux with 0.2 g. of sodium in 1-hexanol has been shown to be sufficient decompose completely methyl fluoroacetate, di-isopropylfluorophosphate, and 2-fluoroethanol⁶.

Indicator. The aqueous solution of sodium fluoride may be titrated with thorium nitrate, using sodium alizarin sulfonate as indicator⁶. This indicator will not detect less than 10 µg. of fluoride ion, but Solochrome Brilliant Blue will detect 1 µg. of fluoride; hence the latter was used for most of the thorium nitrate titrations.

RESULTS

Analysis of Methyl Fluoroacetate in Air. The recovery of low concentrations of methyl fluoroacetate from air was found to depend on four factors: (1) the concentration of methyl fluoroacetate; (2) the temperature of the bath in which the scrubber was immersed; (3) the volume of 1-hexanol used in the scrubber; and (4) the rate of flow of the gas through the scrubber. About 90% of the methyl fluoroacetate in air containing from 0.01 mg. to 8 mg. per liter is recovered if the gas is passed at a rate of 1.0 liter per minute into 40 ml. of 1-hexanol in a CWS scrubber cooled in an ice bath at -40°C.

1. The effect of temperature and concentration. Satisfactory recovery was obtained at 20°C. and 0°C. when the concentration was above 0.07 mg. per liter,

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but a temperature of -40°C . is necessary to get 90% recovery when the concentration drops to 0.01 mg. per liter. The data in Table 1 were obtained using a rate of flow of one liter per minute and 40 ml. of 1-hexanol.

Table 1. Effect of Temperature on the Analysis of Mixtures of Methyl Fluoroacetate and Air.

Conc. Comp. Mg./l.	Volume analysed liters	Mg. Fluorine Found	Calc. (a)	Recovery, % Average
--------------------------	------------------------------	-----------------------	-----------	------------------------

Bath Temperature: 20°C .

6.79	5.0	5.64	6.77	83
3.20	5.0	2.59	3.18	81
1.66	5.0	1.47	1.64	90
1.60	5.0	1.35	1.58	85 ± 3
0.210	10.0	0.352	0.415	85
0.274	10.0	0.530	0.595	89
0.160	10.0	0.287	0.317	91 ± 2
0.0270	20.0	0.0736	0.106	74
0.0145	20.0	0.0370	0.0573	65
0.0140	20.0	0.0351	0.0554	63
0.0135	20.0	0.0351	0.0534	66 ± 4

Bath Temperature: 0°C .

1.88	5.0	2.15	1.86	115
1.72	5.0	1.72	1.70	101
1.66	5.0	1.65	1.64	100 ± 6
0.140	10.0	0.247	0.276	90
0.168	10.0	0.297	0.332	90
0.110	10.0	0.207	0.217	95
0.142	10.0	0.223	0.280	80
0.203	10.0	0.374	0.400	94
0.238	10.0	0.404	0.470	86
0.210	10.0	0.379	0.415	91
0.226	10.0	0.424	0.447	95
0.201	10.0	0.343	0.397	86
0.198	10.0	0.352	0.392	89 ± 3
0.068	20.0	0.245	0.269	85

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Table 1 (Cont.)

Conc. Comp. Mg./l	Volume analysed liters	Mg. Fluorine		Recovery, %	
		Found	Calc.(a)	Average	
0.016	10.0	0.0167	0.0317	53	
0.011	10.0	0.0125	0.0218	57	
0.021	11.0	0.0286	0.0415	69	
0.013	10.0	0.0182	0.0258	70	
0.015	20.0	0.0410	0.0594	69	63 ± 7

Bath Temperature: -40°C.

3.40	5.0	3.53	3.36	99	
3.56	5.0	3.80	3.51	108	
4.46	5.0	4.59	4.81	99	102 ± 4
0.376	10.0	0.613	0.745	82	
0.311	10.0	0.530	0.614	86	
0.297	10.0	0.561	0.588	95	
0.279	10.0	0.555	0.628	87	83 ± 3
0.0270	20.0	0.0878	0.106	83	
0.0105	20.0	0.0370	0.0415	89	
0.0120	20.0	0.0330	0.0475	82	
0.0113	15.0	0.0308	0.0336	92	87 ± 4

(a) Based on assay of 98% methyl fluoracetate.

2. The effect of volume of 1-hexanol. As expected, increasing the volume of liquid in the scrubber increases the recovery of methyl fluoracetate. When the volume of 1-hexanol was increased from 20 ml. to 50 ml., the recovery increased from 82% to 93% with the scrubber at 0 C. and a rate of flow of one liter per minute. (See Table 2.)

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Table 2. Effect of Volume of 1-hexanol on the Analysis of Mixtures of Methyl Fluoroacetate and Air

Conc. Comp. Mg./l.	Volume 1-hexanol ml.	Volume analysed liters	Mg. Fluorine Found Calc.(a)		Recovery, % Average
0.395	20	10.0	0.623	0.782	80
0.385	20	11.0	0.670	0.779	86
0.375	20	12.0	0.784	0.746	90 82 ± 5
0.298	40	12.0	0.474	0.400	94
0.238	40	12.0	0.404	0.449	86
0.210	40	12.0	0.379	0.415	91 90 ± 5
0.275	50	10.0	0.740	0.741	100
0.375	50	10.0	0.626	0.756	83
0.312	50	10.0	0.864	0.817	92
0.331	50	12.0	0.617	0.384	94 93 ± 4

(a) Based on assay of 96% methyl fluoroacetate.

3. The effect of the rate of flow. The recovery of methyl fluoroacetate is decreased when the rate of flow of the gas is increased from one liter per minute to two liters per minute. At 0°C. a recovery of 38% is obtained with a flow of one liter per minute, and only 12% recovery is obtained at a flow of two liters per minute when a mixture containing about 0.3 mg. per liter is scrubbed with 40 ml. of 1-hexanol. At 30°C. a recovery of 90% at one liter per minute and 83% at two liters per minute is obtained. (See Table 3).

Table 3. Effect of Rate of Flow on the Analysis of Mixtures of Methyl Fluoroacetate and Air.

Conc. Comp. Mg./l.	Flow rate l./min.	Mg. Fluorine Found Calc.(a,b)		Recovery, % Average
Bath Temperature: 30°C.				
	1.0	See Table 1		90 ± 3
0.450	2.0	1.830	1.15	78
0.371	2.0	0.855	1.37	63
0.349	2.0	1.23	1.45	63
0.386	2.0	1.09	1.41	76
0.287	2.0	0.868	1.06	81 87 ± 4

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Table 3 (Cont.)

Conc. Comp. Mg./l.	Flow rate l./min.	Mg. Fluorine		Recovery, % Average
		Found	Calc. (a,b)	
Bath Temperature: 20°C.				
ca. 0.3	1.0	See Table 1		88 ± 2
0.438	2.0	0.999	1.73	58
0.490	2.0	1.175	1.93	61
0.348	2.0	0.825	1.38	60
0.403	2.0	0.906	1.59	57 59 ± 2

(a) Based on assay of 96% methyl fluoroacetate.

(b) Ten liters of gas analysed.

Analysis of Di-isopropylfluorophosphate in Air. The percentage recovery varies with the concentration when air containing low concentrations of di-isopropylfluorophosphate is passed at a rate of one liter per minute through a CWS scrubber containing 40 ml. of 1-hexanol and cooled in a bath at about -40°C. Recoveries were as follows: 72% at a concentration of 0.02 - 0.04 mg. per liter, 84% at 0.07 - 0.15 mg. per liter, and 68% at 1 - 2 mg. per liter. The precision is good for concentrations up to 0.15 mg. per liter, but inconsistent results were obtained in the range 1 - 2 mg. per liter. With two scrubbers in series, consistent recovery of 90% of the di-isopropylfluorophosphate is obtained at a concentration of 1 to 2 mg. per liter. However, two scrubbers in series did not appreciably increase the recovery when the gas concentration was only 0.05 mg. per liter. These data are summarized in Table 4.

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Table 4. Analysis of Mixtures of Di-isopropylfluorophosphate and Air.

Conc. Comp. Mg./l.	Volume analysed liters	Mg. Fluorine Found	Calc.	Recovery, % Average	
1.60	10.0	1.04	1.65	63	
1.52	10.0	0.90	1.56	58	
1.35	10.0	1.06	1.39	76	
1.48	10.0	1.28	1.53	84	
1.90	13.0	1.52	2.59	59	
1.25	12.0	1.05	1.51	70	68 ± 8
1.53	10.0	1.36(a) } 0.0736(b) }	1.575	86(a) } 5(b) }	91
1.63	10.0	1.11(a) } 0.123(b) }	1.37	84(a) } 7(b) }	91
1.76	10.0	1.226(a) } 0.549(b) }	1.81	67(a) } 19 }	86 90 ± 2
0.141	10.0	0.115	0.145	79	
0.130	10.0	0.111	0.134	83	
0.105	15.0	0.130	0.162	80	
0.087	15.0	0.121	0.134	90	
0.0693	25.0	0.160	0.177	90	
0.079	15.0	0.0883	0.108	81	64 ± 4
0.0281	25.0	0.0480	0.0732	66	
0.0260	25.0	0.0820	0.0721	72	
0.0233	25.0	0.0690	0.0686	79	
0.0210	25.0	0.0432	0.0618	80	
0.0260	25.0	0.0427	0.0660	64	
0.0264	25.0	0.0419	0.0628	67	
0.0356	25.0	0.0636	0.0863	74	
0.0410	20.0	0.0620	0.0845	73	72 ± 5
0.0437	30.0(c)	0.141(a) } 0.002(b) }	0.190	74(a) } 1(b) }	75
0.0516	30.0	0.115(a) } 0.003(b) }	0.160	75(a) } 2 }	77 76 ± 1

(a) Two scrubbers used in series. This value was obtained in the first scrubber.

(b) Two scrubbers used in series. This value was obtained in the second scrubber.

(c) Rate of flow was 1.35 liters per minute.

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Analysis of 2-Fluoroethanol in Air. When mixtures containing between 0.2 and 5 mg. of 2-fluoroethanol per liter of air are passed into a CWS scrubber containing 40 ml. of 1-hexanol and cooled in a bath at about $-40^{\circ}\text{C}.$, a recovery of approximately 90% is obtained. Under the same conditions a recovery of only 50% is obtained when the concentration is 0.01 to 0.03 mg. per liter of air. When 1-hexanol recovered from previous analyses by distillation and fractionation b.p., $156.7 - 157.7^{\circ}\text{C}.$, was used to scrub gas containing 0.01 to 0.03 mg. of 2-fluoroethanol per liter, a recovery of about 75% was obtained. Two scrubbers in series, using fractionated 1-hexanol did not improve the recovery in this concentration range; in no case did the second scrubber pick up any fluoro-organic compound. These data are summarized in Table 5.

Table 5. Analysis of Mixtures of 2-Fluoroethanol and Air.

Conc. Comp. Mg./l.	Volume analysed liters	Mg. Fluorine Found	Calc. (a)	Recovery, % Average
1-Hexanol (practical grade)				
1.40	6.0	1.86	2.22	84
2.68	5.0	3.04	3.52	86
1.56	5.0	1.94	2.06	94
1.70	6.0	2.38	2.70	88 $\pm$ 3
0.203	9.0	0.505	0.536	94
0.246	10.0	0.635	0.650	98
0.254	10.0	0.648	0.671	97
0.265	10.0	0.681	0.700	97
0.241	10.3(b)	0.627	0.637	98
0.227	10.5(b)	0.591	0.300	98 $\pm$ 1

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Table 5 (Cont.)

Conc. Comp. Mg./l.	Volume analysed liters	Mg. Fluorine Found	Calc. (a)	Recovery, % Average
0.0225	20.0	0.0696	0.119	59
0.0109	22.0	0.0312	0.0634	49
0.0155	20.0	0.0456	0.0819	56
0.0150	20.0	0.0410	0.0793	51
0.0124	21.0	0.0336	0.0687	49
0.0140	20.0	0.0315	0.0740	43
0.0115	20.0	0.0275	0.0617	45
0.0130	23.0	0.0456	0.0792	58
0.0155	20.0	0.0352	0.0820	43
0.0318	21.0	0.0303	0.0765	40
0.0155	20.0	0.0361	0.0820	44 49 $\pm$ 4

Recovered 1-hexanol (fractionated)

0.0150	20.0	0.0604	0.0794	76
0.0160	20.0	0.0688	0.0846	81
0.0130	20.0	0.0439	0.0635	69
0.0130	20.0	0.0500	0.0687	73
0.0150	20.0	0.0612	0.0794	77
0.0168	22.0	0.0667	0.0978	68 74 $\pm$ 4
0.0180	30.0	0.119(c)	0.143	83
0.0162	32.0	0.0903(c)	0.137	66
0.0317	30.0	0.199(c)	0.250	80 76 $\pm$ 7

(a) Based on assay of 89% 2-fluoroethanol.

(b) Rate of flow was 1.03 liters per minute.

(c) Two scrubbers used in series. This value was obtained in the first scrubber.

SUMMARY

A method has been described for the determination of Fluorine in low concentrations of three fluoro-organic compounds in air. It is based on (1) scrubbing the fluoro-organic compound out of air with 1-hexanol; (2) decomposing the sample by refluxing the solution with sodium; (3) extraction of the sodium fluoride with water; and (4) titration of the aqueous layer with thorium nitrate solution, using Solochrome Brilliant Blue BS as indicator. The results may be summarized as follows: About 90% of the methyl fluoroacetate is recovered when

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the concentration is between 0.01 mg. and 8 mg. per liter of air. About 90% of the 2-fluoroethanol is recovered when the concentration is 0.2 - 3 mg. per liter, but only 75% in the range of 0.01 to 0.03 mg. per liter. The recovery of di-isopropylfluorophosphate is 75% at a concentration of 0.02 - 0.04 mg. per liter, 84% at 0.07 - 0.15 mg. per liter, and 68% at 1 - 2 mg. per liter. The use of two scrubbers in series yields 90% recovery at a concentration of 1 to 2 mg. of di-isopropylfluorophosphate per liter.

An apparatus for preparing mixtures of fluoro-organic compounds and air of accurately known concentration is described.

BIBLIOGRAPHY

1. "Progress of Work on Fluoroacetates and Fluorophosphates, First Interim Report", Porton Report No. 4280, November 2, 1943.
2. N. L. Drake's monthly reports to NDRC from February to May, 1944.
3. "Detection of C. W. Agents Containing Fluorine", Second Interim Report", Porton Report No. 4260.
4. R. Milton and J. E. Chivers, "The Estimation of Organic Fluorine Compounds, Part I. Methyl Fluoroacetate", Porton Report No. 2556.
5. R. Milton and J. E. Chivers, "The Estimation of Organic Fluorine Compounds, Part II. Dialkyl Fluorophosphates", Porton Report No. 2557, February 4, 1944.
6. J. H. Yoe, J. M. Salsbury, and J. W. Cole, "Determination of Fluorine in Fluoro-Organic Compounds", NDRC Formal Report, February 29, 1944.
7. R. Milton, H. F. Liddell, and J. E. Chivers, "A New Titrimetric Method for the Estimation of Fluorine", Porton Report No. 2549, October 8, 1943.

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APPENDIX

Reagents. 1. Thorium Nitrate Solution. Dissolve 0.69 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 0.005 N.

2. Solochrome Brilliant Blue BS Indicator Solution. Dissolve 0.02 g. of Solochrome Brilliant Blue BS in 100 ml. of water. Solochrome Brilliant Blue obtained from different sources may vary some 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.

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

4. 1-Hexanol. Eastman (practical grade), b.p., 155 - 158°C.

5. Perchloric Acid, 60%. Dilute 86 ml. of 70% perchloric acid (reagent grade) to 100 ml. with water.

6. Perchloric Acid, 3%. Dilute 5 ml. of 60% perchloric acid to 100 ml. with water.

7. Sodium hydroxide, 5%. Dissolve 3.0 g. of sodium hydroxide (reagent grade) in 97 ml. of water.

8. Sodium. Cut sodium (reagent grade) into small pieces weighing 0.2 ± 0.02 g. and store under kerosene.

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An apparatus for the preparation of mixtures of fluoro-organic compounds and air, and a method for the determination of fluorine in such compounds are described. The analysis involves: removing the fluoro-organic compounds by scrubbing the air mixture with 1-hexanol; decomposing the fluoro-organic compound by refluxing with sodium; extracting with water the sodium fluoride thus formed; and titrating the fluoride ion with thorium nitrate solution, using Solochrome Brilliant Blue BS as indicator. This method has been tested in the concentration range of 0.002 to 2 megacycles of fluoride which is equivalent to 0.01 to 8 megacycles of fluoro-organic compound per liter of air.

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