QUANTITATIVE DETERMINATION OF FLUORINE IN ORGANIC COMPOUNDS

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ABSTRACT

It was found that certain organic fluorine compounds, including those which are easily volatilized at room temperature, can be quantitatively analyzed for fluorine by determining the loss in weight of a tared Pyrex flask caused by the etching action of the generated hydrofluoric acid. The sample is completely destroyed by heating with small amounts of potassium nitrate in sulfuric acid solution.

The method is very simple and can be performed in 4 hours, requiring only five weighings and no expensive apparatus.

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I. INTRODUCTION

In the course of a current investigation of optical rotation and atomic dimension, it was found desirable that a simple method of quantitative determination of fluorine in organic compounds be made available. Numerous methods have been published and their number has increased rapidly in recent publications. W. Bockemueller [1] has discussed the methods up to the year 1932 and has added a new procedure himself; but since 1932 many others have appeared. This increased effort to find a simple method can be explained by increased application of organic fluorine compounds. In fact, M. Mayor [2] also gives at the end of his study on the preparation of organic fluorine derivatives the variety of applications of these compounds, such as liquids for refrigerating machines, insecticides, plastics, dyes, solvents, etc.

II. SURVEY OF EXISTING METHODS

For the quantitative determination of fluorine in organic fluoro derivatives, a conversion must first be performed from the organic fluoro compound to an inorganic fluoro compound. In the case of nonvolatile compounds this conversion has been made mostly by ignition with sodium carbonate in a nickel or platinum crucible. For organic fluorine compounds which are easily volatilized at room tem-

[1] Z. anal. Chem. 91, 81 (1932).
[2] Rev. chim. ind. Paris 49, 2–10; 30–34; 64–74 (1940).

perature, as well as for those which are gaseous at room temperature, the bomb or platinum combustion tube has been applied, which requires elaborate manipulations with special apparatus. After the fluorine in the sample has been converted to inorganically bound fluorine, it is usually quantitatively determined by weighing as calcium fluoride. This method is not satisfactory, because calcium fluoride is appreciably soluble in the wash water, and elaborate precautions, time-consuming evaporations, filtrations, and ignitions are necessary before it can be weighed.[3] H. Ost[4] determines the fluorine in the unwashed calcium fluoride (which however, must be free from silica) by the loss in weight of a glass plate used as a cover for a platinum crucible. The plate is etched by the hydrofluoric acid generated from the calcium fluoride by sulfuric acid. The method of Ost has been used by B. Helferich and R. Gootz[5] for determining the fluorine directly in nonvolatile organic fluorine derivatives. Thus the intermediate separation of calcium fluoride is unnecessary.

The investigation of the possibility of applying this simple etching process directly to volatile organic fluorine compounds has resulted in the new method described in this paper.

III. DESCRIPTION OF THE NEW METHOD

A flask of about 30-ml capacity with a small cup sealed at the flat bottom and a ground stopper of special design, as illustrated in figure 1, all made of Pyrex glass, is used in the determination. The flask is thoroughly cleaned with a hot solution of potassium bichromate in sulfuric acid, in which it is allowed to stand overnight, after which it is rinsed with distilled water and dried by drawing air through the warmed flask. Experiments showed that the flask thus cleaned can be heated to 300° C for 2 hours with pure sulfuric acid, or sulfuric acid with potassium bichromate, or sulfuric acid with potassium nitrate, without causing a decrease in weight of more than 0.2 mg.

The determination is made as follows: The stoppered flask is accurately weighed to 0.1 mg. A few small crystals of potassium nitrate (about 30 to 40 mg) are introduced in the flask outside the cup and about 8 ml of sulfuric acid is added to the same compartment by means of a long-stem funnel (A) and a 10-ml graduated cylinder. The stopper is greased with vaseline and placed upside down on the flask so that the orifice of the flask remains free from vaseline. The weight of the flask thus prepared is determined. The greased stopper is now placed aside, standing on the flat part so that no grease will be lost. The sample is introduced into the cup, using a funnel tube (B) for powders and a pipette in connection with the funnel tube (A) for volatile liquids. The curved tip of the funnel (A) can be used for tipping off the last drop to the wall of the cup, thus keeping the orifice clean. The greased stopper is used for closing the flask, and the new weight of the flask will yield the weight of the sample. This weight of the sample is regulated so that the decrease in weight of the flask, in milligrams, produced by the etching is approximately equal to the percentage of fluorine in the compound. This insures that the

[3] F. C. Hahn and E. E. Reid, J. Am. Chem. Soc. 46, 1652 (1924). D. H. Brauns, J. Research NBS 18, 322 (1937) RP978, Bockemueller, footnote 1.
[4] Ber. deut. chem. Ges. 26, 151 (1893).
[5] Ber. deut. chem. Ges. 62B, 2505 (1929).

weighing error shall not be more than 0.1 percent, when the weighings are made to 0.1 mg. After the flask is closed by the greased stopper and weighed and a rubber band hooked on to keep the stopper in place, the flask is rotated to mix the sample with the sulfuric acid. The flask is now placed in a 600-ml beaker filled with water, which is gradually heated to 70° C in the course of about one-half hour. The bath is regulated within this range for another one-half hour. Clamp-
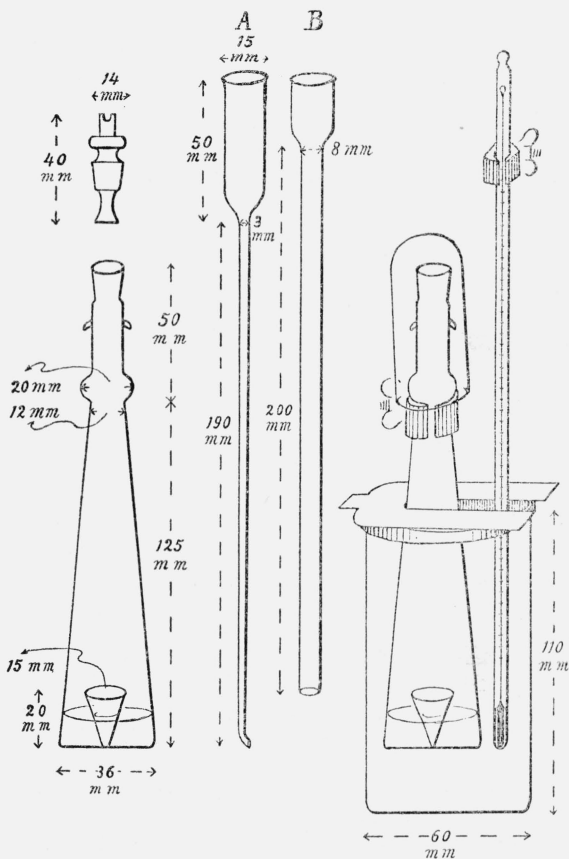

FIGURE 1.—*Quantitative fluorine determination apparatus.*

ing the flask in a stand is unnecessary if the flask is carefully handled and scratching avoided.

As the fluorine is strongly bound in 1-fluoro-2-methylbutane [6] and the compound is easily volatilized (boiling point 55.9° C), it is well-suited for a severe test of the new method. Hence, a detailed description of the fluorine determination in this compound follows. The procedure for nonvolatile fluorine derivatives could probably be shortened, but it seems advantageous to use the same method for all compounds. After the weighed sample is mixed with the sulfuric acid, as described above, one observes first that the 1-fluoro-2-

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⁶ D. H. Brauns, J. Research NBS **18**, 322 (1937) RP978.

methylbutane floats on top of the sulfuric acid. On warming, it gradually turns turbid yellow, and after one-half hour at 70° C all of the sulfuric acid has an even, transparent yellow-brown color. During this half-hour the flask is occasionally rotated so that a scrubbing action of the acid on the vapor in the neck is obtained (care being taken that the acid does not reach the stopper). The flask is now cooled in ice water or tap water. It will be noticed by removing the stopper that only little pressure exists in the flask, which indicates that there is no danger in heating to 60° to 70° C in the closed flask.[7] The open flask is now clamped in a stand and heated in an air bath consisting of a Pyrex tube supported by an iron ring and closed at the top by a thin copper plate cut out to receive the flask and a thermometer (see fig. 1). The temperature is slowly raised to about 120° C, and small crystals of potassium nitrate are dropped into the flask in the course of three-fourths hour until about 0.3 to 0.4 g has been used, the color of the liquid changing gradually from dark brown to light yellow. When brown nitrogen peroxide (NO_2) vapors are visible above the liquid after mixing by agitating the flask, sufficient potassium nitrate has been used, and the heating is now gradually increased until the temperature reaches 300° C. An inverted tube is placed over the neck of the flask as inadvertent heating above 300° C may cause the acid upon reaching the boiling point of sulfuric acid (320° to 330° C) to spurt out. As a result of this heating, undecomposed substance adhering to the neck is refluxed to the body of the liquid. The flame is now taken away, and the tube is allowed to cool, slowly at first, then more quickly by removing the air bath.

The liquid will be water-white when cold and straw-yellow when hot (dissociation of N_2O_5) if sufficient potassium nitrate has been used. To make sure that all fluorine is liberated from the organic compound and that the action of the hydrofluoric acid is complete, the heating to 300° C and cooling are repeated once or twice (compare footnote 7). For obtaining a check on the completion of the action of hydrofluoric acid on the glass, the cooled sulfuric acid solution is poured (for temporary storage) into a platinum dish or a weighed Pyrex beaker,[8] the small amount of sulfuric acid solution remaining in the flask being immaterial. The flask and stopper are rinsed with water (using a soft brush for cleaning the neck), further with pure alcohol, and then with ether to remove all acid and vaseline. The flask and stopper are then dried by a current of air. The cleaned Pyrex vessel with stopper is now allowed to stand in the balance case for 15 minutes and weighed. The sulfuric acid solution that has been put aside is poured back into the flask and the heating to 300° C and cooling are repeated, after which the flask is again cleaned and dried and the weight again determined. The weight is usually found to be constant, or there is a decrease of around 0.4 mg. The total decrease in weight in grams, multiplied by 1.0526 (conversion factor for Pyrex glass) gives the number of milligrams of fluorine, from which the percentage of fluorine in the sample is calculated.

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[7] The decomposition to carbon dioxide and water is not completed during this preliminary heating. The important point is that all hydrofluoric acid is split off by this treatment, or converted to nonvolatile carbon compounds, the greater part being combined at this stage with the sulfuric acid (see J. H. Simons, H. J. Passino, and S. Archer, J. Am. Chem. Soc. **63**, 608 (1941), the remaining part etching the glass.

[8] The beaker is weighed for detecting action of any hydrofluoric acid during storage.

IV. CONVERSION FACTOR FOR CALCULATING THE FLUORINE CONTENT

Ost (see reference 4) determined empirically the loss in weight of soft glass by etching, using weighed amounts of calcium fluoride. His results indicated a loss of 0.8 to 0.9 mg of glass for 1 mg of fluorine. Helferich and Gootz (see reference 5), using organic fluorine derivatives of sugars of known constitutions and applying the etching method of Ost, found an average of 0.85 mg loss of weight of soft glass for 1 mg of fluorine in the sample. Helferich applied slides such as are used in microscopic work for the etching. Ost applied small amounts of 78-percent sulfuric acid sufficient for wetting the sample, which was weighed in the platinum crucible. The crucible was covered with a tared cover glass and heated in a sand bath for 4 to 8 hours to 100° to 150° C, and at the end to a higher temperature until sulfuric acid vapors appeared. By repeating the procedure of Ost-Helferich with the nonvolatile fluoro-derivatives of sugars, using a platinum crucible with soft-glass covers, there was also found an average loss of weight of 0.85 mg.

It was realized, however, by the writer that not only the use of a different glass (e. g., Pyrex glass) should have an influence on the factor, but possibly also the experimental conditions under which the determination is made. Indeed, replacing the platinum crucible with a soft glass crucible of about the same size changed the factor. This is probably due to escape of hydrofluoric acid from the platinum crucible without acting on the cover glass. It may be mentioned that the changed factor now agreed accurately with the factor calculated for soft glass according to the method applied below for Pyrex glass.

For investigating the possibility of extending the Ost-Helferich method also to volatile fluoro-derivatives, a platinum-lined bomb containing a weighed glass plate was first used. Difficulties were met because of the peculiar behavior of noble metals under oxidizing conditions and the leakage which frequently occurs. Then a stoppered Pyrex flask was used in which a Pyrex weighing tube containing the sample could be opened; thus the sample was brought in contact with 10 ml of sulfuric acid in the flask and gradually decomposed by heating as potassium nitrate was added. For preventing scratching of the glass, the weighing tube was surrounded by platinum gauze or wire. Finally, the described apparatus and method were devised in which no platinum is used. Using fluoro-derivatives of known constitution, it was found that the factor for converting the loss of weight of Pyrex glass to the weight of fluorine is 1.053. We may apply a tentative theoretical calculation for obtaining a theoretical conversion factor as follows:

Using for the composition of Pyrex glass SiO_2, 81.0 percent; B_2O_3, 13.0 percent and 6 percent of basic oxides (see E. Wichers, A. N. Finn, and W. S. Clabaugh),[9] the amount of fluorine used for etching 1 mg of Pyrex glass is:

for SiO_2 (yielding SiF_4) $\dfrac{0.81 \text{ mg}}{\text{mol. wt } SiO_2} \times 4 \times$ at. wt of $F = 1.02$ mg of F

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[9] J. Research NBS **26,** 537 (1941) RP1394.

for B_2O_3 (yielding BF_3) $\dfrac{0.13 \text{ mg}}{\text{mol. wt } B_2O_3} \times 6 \times$ at. wt of $F = 0.18$ mg of F

6 percent of basic oxides will yield sulfates. Hence, a 1 mg loss of weight of Pyrex glass should correspond to $1.02 + 0.18 = 1.2$ mg of fluorine.

In conclusion, it is recommended that a blank test be made and that the conversion factor as found by the writer be checked by using a pure nonvolatile fluoro-derivative, such as fluoracetyl-glucose or -arabinose, which can be easily prepared with the aid of hydrofluoric acid now marketed in cylinders.

V. ANALYSES

The following is an example of the calculation of the fluorine in fluorotriacetylarabinose:

	Grams
Weight of empty flask + stopper (1st weighing)	42. 5252
Weight of flask + greased stopper + H_2SO_4 + KNO_3 (2d weighing)	56. 5391
Weight of flask + greased stopper + H_2SO_4 + KNO_3 + substance to be analyzed (3d weighing)	56. 6851
Weight of substance to be analyzed	0. 1460
Weight of flask + stopper after 1st etching (4th weighing)	42. 5156
Weight of flask + stopper after 2d etching (5th weighing)	42. 5156
Loss by etching _____ (42.5252 minus 42.5156) =	0. 0096

$F = 0.0096 \times 1.053 = 0.0101$ g of F.

Percentage of $F = (0.0101/0.1460) \times 100 = 6.9$.

Theory = 6.82 percent of F for $C_{11}H_{15}O_7F$.

Table 1 gives the complete analytical data.

TABLE 1.—*Analytical data obtained in the quantitative fluorine determination*

Name of substance and formula	Weight of substance	Weight loss, first etching	Weight loss, second etching	Weight of fluorine, indicated	Percentage of fluorine—	
					Indicated	Calculated
	g	*g*	*g*	*g*		
Fluorotriacetylarabinose, $C_{11}H_{15}O_7F$	0.1460	0.0096	0	0.0101	6.9	6.82
Fluorotriacetylarabinose, $C_{11}H_{15}O_7F$	.1458	.0098	.0001	.0104	7.1	6.82
1-Fluoro-2-methylbutane, $C_5H_{11}F$	.0894	.0180	0	.0189	21.2	21.09
1-Fluoro-2-methylbutane, $C_5H_{11}F$	.0945	.0189	.0003	.0202	21.3	21.09
1-Fluoro-2-methylbutane, $C_5H_{11}F$	.1583	.0308	.0006	.0331	20.9	21.09

VI. DISCUSSION

It was found by experiment that the loss in weight of glass containers in which organic fluorine derivatives are destroyed with sulfuric acid and potassium nitrate under definite conditions of procedure and apparatus is a reliable basis for the quantitative determination of fluorine in these compounds. In spite of the fact that the factor for converting the loss in weight of Pyrex glass to fluorine is only slightly more than 1 (1.053), the method yields fairly accurate results. No filtrations or ignitions are necessary and no difficult manipulations are involved. This method of decomposition is not satisfactory preliminary to determining chlorine, bromine, and iodine in organic

compounds as silver halides; also the destruction of volatile organic fluoro-chloro compounds needs a more vigorous attack.[10]

The peculiarity of the easy destruction of organic fluorine derivatives by sulfuric acid and liberation of hydrofluoric acid has been well known to investigators in this field, and Paternò and Spallino[11] have based a simple qualitative test for fluorine on this property. The present investigation has shown that this property also can be used for a simple quantitative determination of fluorine, and can give accurate results even for volatile fluorine derivatives if they are decomposed first in a stoppered flask.

[10] Preliminary experiments with stable fluoro-chloro compounds (Freon CF_2Cl_2) have shown that it may be possible to determine the fluorine in these compounds by the loss in weight of a small quartz combustion tube. Thus the advantage of a simple determination of the loss in weight would remain. These experiments may be continued at a later date.

[11] E. Paternò and R. Spallino, Gaz. chim. ital. **37**, II, 309 (1907).