(MACRO) DETERMINATION OF FLUORINE

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From its accompanying organic or other interfering material, fluorine is separated either as sodium-potassium fluoride by first fusing the material with sodium-potassium carbonate and then leaching it with water, or as silicon tetrafluoride by first suitably ashing the material and then distilling it with sulphuric acid.

In the first case, the dissolved fluoride is precipitated as calcium fluoride from an acidic medium which prevents the co-precipitation of insoluble carbonate and phosphate of calcium. The precipitated calcium fluoride, after drying, is either weighed as such or is further converted into calcium sulfate by treatment with sulphuric acid, and then is dried and weighed. Sometimes the dissolved fluoride is precipitated as lead chlorofluoride ($PbClF$) which is weighed, or its chlorine, after dissolving the precipitate in dilute HNO_3, is estimated either by direct titration with silver nitrate, using potassium chromate as the indicator, or by first adding an excess of silver nitrate and then determining the excess of silver by titration with potassium thiocyanate, using ferric alum as the indicator.

In the second case, the evolved silicon tetrafluoride is estimated in one of the following ways:

(i) It is determined gasometrically or gravimetrically.

(ii) It is titrated directly with an alkali of suitable strength in a medium of 50% alcohol ($H_2SiF_6 + 2KOH = K_2SiF_6 + 2H_2O$).

(iii) It is first treated with an excess of neutral calcium chloride solution and then titrated with standard sodium hydroxide, using methyl red as the indicator ($H_2SiF_6 + 3CaCl_2 + 6NaOH = 3CaF_2 + 6NaCl + H_4SiO_4 + 2H_2O$).

(iv) It is absorbed in 50% alcoholic potassium chloride solution, and the evolved hydrochloric acid is titrated with standard sodium hydroxide, using cochineal or methyl red as the indicator ($3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$; $2H_2SiF_6 + 4KCl = 2K_2SiF_6 + 4HCl$). Sometimes, the precipitated potassium silico fluoride is weighed.

(v) The evolved hydrofluosilicic acid is decomposed with sodium and ammonium carbonate into sodium fluoride and silicic acid ($H_2SiF_6 + 3Na_2CO_3 = 6NaF + H_2SiO_3 + 3CO_2$), and the dissolved sodium fluoride either is precipitated as calcium fluoride and weighed as such, or is precipitated with a known quantity of calcium chloride, and the excess calcium is estimated by precipitating it as oxalate and titrating it with permanganate.

Based on the reaction between hydrofluosilicic acid and thorium nitrate, resulting in the formation of H_2ThF_6, the following methods have been investigated for the macro-determination of fluorine. By the process of ashing and distillation, outlined in the Second Part, fluorine is isolated as hydrofluosilicic acid which is treated with a slight excess of thorium nitrate solution. The precipitated thorium compound is then quantitatively collected on a sintered glass crucible, dried at 100° C., cooled in a desiccator and weighed. Employing the above reaction between hydrofluosilicic acid and thorium nitrate, the quantity of fluorine present is calculated from the weight of the precipitate. Some of the results obtained are presented in Table I.

TABLE I. *Gravimetric estimation of fluorine*

Fluorine present	Weight of the ppt. H_2ThF_6	Fluorine found	% Error
mg.	mg.	mg.	
30·00	93·12	30·50	1·66
40·00	124·7	40·84	2·10
50·00	155·8	51·02	2·04
75·00	235·6	77·18	2·90
90·00	281·0	92·04	2·26

The method yields values which are higher than the theoretical, mainly due to the deposition of silicic acid in the pores of the sintered crucible. As the error involved in the method is mainly due to the deposition of silicic acid, firstly, the method will not be found suitable for the estimation of large quantities of fluorine, for larger the quantity of fluorine as hydrofluosilicic acid, larger will be the quantity of silicic acid produced, precipitated and deposited together with the thorium compound, and secondly, the method will be found quite suitable and accurate, if the step, requiring the weighing of the precipitate, is eliminated from this procedure. Such an elimination has been achieved in the following manner. The hydrofluosilicic acid, distilled off in the manner indicated in the Second Part, is treated with a slight excess of the thorium nitrate solution. The precipitated thorium compound is then quantitatively collected in a 75 c.c. centrifuge cup. The collected precipitate is then heated with a minimum quantity of sulphuric acid till no more fumes are given off. The centrifuge cup is then allowed to cool. The thorium content of the treated precipitate is then determined by precipitating thorium as oxalate and titrating it with permanganate solution. All the steps, *i.e.*, collection of the precipitate, heating it with sulphuric acid, precipitating thorium as oxalate, and washing the precipitate free from oxalate, and then titrating it with permanganate, are carried out in the same centrifuge cup with a view to eliminating the errors incidental to the transfer of the material from one receptacle to another. Employing the above reaction between hydrofluosilicic acid and thorium nitrate, the quantity of fluorine present is calculated from the thorium content of the precipitate. Some of the results obtained by this method are presented in Table II.

TABLE II. *Macro determination of fluorine*

Fluorine present mg.	Th present in the precipitate mg.	Fluorine corresponding to the Th present in the precipitate mg.	% Error
30·00	61·28	30·10	0·333
40·00	81·78	40·16	0·399
50·00	102·8	50·48	0·959
75·00	153·2	75·25	0·333
90·00	184·0	90·36	0·400

It will be seen that this method yields results which are in very close agreement with the theoretical values.

The method, so far, has been applied to known solutions of pure fluorides.

The thorium compound precipitated dissolves in too large an excess of the thorium salt.

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REFERENCES

The details of the methods cited above are given in the following two books :

Treadwell, F. P. and Hall, W. T. .. *Analytical Chemistry*, 1921, Vol. II, John Wiley & Sons, Inc., New York.

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