PHOTO-ELECTRIC COLORIMETRIC METHOD FOR THE ESTIMATION OF FLUORINE

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Summary

Photoelectric colorimetric method for the determination of fluorine is described. The method is based on the bleaching effect of fluorine on the colour produced as a result of reaction between ferron and ferric chloride.

The accuracy in the estimation of fluorine obtainable by this method is compared with that obtained in thorium nitrate titration method.

Micro Determination of Fluorine

In the Second Part, for the determination of micro-quantities of fluorine, the method has been described, wherein, fluorine is first converted into hydrofluosilicic acid by distilling it with silicon carbide and sulphuric acid, and the evolved hydrofluosilicic acid is then titrated with thorium nitrate solution, using alizarin red as the indicator. The method, when carried out in the manner prescribed, though is accurate and reliable, still suffers from the following drawbacks: (i) It is time consuming. (ii) The precise determination of the end point of the titration, which depends upon the appearance of purple lake, according to some workers, requires practice on the part of the worker. This may be expected to be overcome with experience. (iii) The accuracy of the method is impaired even by very small quantities of halides, NO_3^-, ClO_4^-, SO_3^{--}, SO_4^{--}, PO_4^{---}, AsO_3^{---} and AsO_4^{---}. Though the methods for the elimination of interference due to halides, sulphate, perchlorate and phosphate have been presented, the interference due to the remaining ions has not been successfully obviated; and as stated, it is of course not feasible to make appropriate corrections in the calculation of fluorine for the interference due to these ions, for that would involve a separate determination of each impurity and its corresponding interfering effect. (iv) For correct detection of the end point, it is desirable to employ, for the titration, as small an aliquot of the distillate as possible. This is likely to lead to higher results due to considerable multiplication of the original error. (v) The distillate cannot be concentrated by evaporation, as it is attended by a considerable loss of fluorine. With a view to developing, for the determination of fluorine, a method free from some of or, if possible, all these drawbacks, a new method has been investigated. In the following paragraphs is presented the photo-electric colorimetric method for the determination of fluorine.

Principle of the Method

It is based on the observation that the intensity of the colour produced with ferron (7-iodo-8-hydroxy quinoline 5-sulphonic acid) by ferric chloride is more than that produced in the presence of fluoride, and under certain conditions, as is shown later, the fall in the intensity of the colour is a measure of and proportional to the quantity of fluoride present.

Ferron was first described by Yoe (1932) as a colorimetric agent for ferric ion, and was later employed by Fahey (1939) for the colorimetric determination of fluorine in rock phosphate.

Reagents Required

(1) *Saturated Solution of Ferron.*—Ferron is shaken for one hour in fluorine-free distilled water and filtered; fluorine-free water is prepared by distilling alkaline water.

(2) *N/100 hydrochloric acid.*

(3) *N/10 Ferric Chloride Solution.*—This is prepared from a more concentrated solution of ferric chloride which is standardised iodometrically. The solution should be stored in a dark bottle.

(4) *Ferron-Iron Reagent.*—It is prepared by mixing the above solutions in the following proportions:

Saturated ferron solution = 45 c.c.
N/10 Ferric chloride = 5 c.cs.
N/100 HCl .. to give the required H^+ ion concentration.
Volume is made up to 100 c.c.

Details of the Method

The method for the determination of fluorine in organic and interfering matter consists of the following steps: (i) isolation of fluorine as hydrofluosilicic acid by distilling the ashed material with sulphuric acid and silicon carbide; (ii) making up the distillate to a known volume, and the determination and adjustment of its acidity; (iii) addition of the ferron-iron reagent to a fluorine solution, and (iv) photo-electric colorimetric measurement of the fall in the intensity of the colour of ferron-iron reagent by using a suitable filter.

(i) *Isolation of Fluorine.*—Fahey (1939) isolated fluorine from rock phosphate as sodium fluoride by fusing the material with sodium carbonate, and by extracting the fused material with water, and by treating the extract with zinc-oxide to remove many interfering salts including vanadates and phosphates. Besides fluorides, the extract contains other salts of sodium. Firstly, the complete extraction of fluorine by this procedure is questionable, and secondly, the salts of sodium contained in the extract will interfere with the accurate determination of fluorine by exerting a general salt effect. To obviate the salt effect, it is not feasible to introduce any compensatory method, for that would involve the determination of the total solids content of each extract, and in some cases, the percentage of its components and their corresponding interference effect. This would render the method very tedious and time consuming. Fluorine is isolated from its associated organic matter, first, by ashing the material in the presence of a fixative, and then by separating fluorine as hydrofluosilicic acid by distilling the ashed material with silicon carbide and sulphuric or perchloric acid in the manner indicated in the Second Part. When using pure fluorides, it is not necessary to isolate fluorine as hydro-fluosilicic acid but it may be estimated as such. For the same quantity, the bleaching effect of fluorine, as sodium fluoride, on the colour of the ferron-iron reagent is more than that of fluorine, as hydrofluosilicic acid. The data for the bleaching effect of fluorine as sodium fluoride and hydrofluosilicic acid, when plotted, fall on two different lines (Fig. 3). In the computation of the results, this difference should be taken note of.

Selection of Filter.—For best results with photo-electric colorimeter, it is necessary to ensure a high degree of sensitivity. This is obtained by using the filter whose spectral transmission is opposite to that of the solution being studied or the filter which transmits most light over the range where the solution absorbs most light. Selection has been made between blue filter No. 42 and red filter No. 66. The intensity of the colour of the reagent has been determined at different pH for both these filters. The data are graphically shown in Fig. 1. It is clear that higher sensitivity and linear relationship between fluoride and its bleaching effect are obtained by using the red filter No. 66.

Effect of pH on the Bleaching Action of Fluorine

To determine conditions, wherein a fixed proportionality can be obtained between fluoride concentration and its effect on the intensity of the colour produced with ferron by ferric chloride, a series of determinations was carried out at different H^+ ion concentrations. The results are graphically shown in

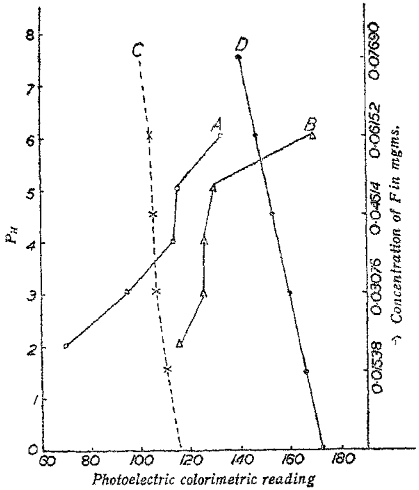

FIG. 1. Intensity of the colour of the reagent at different pH with filters 42-A and 66 B Relationship between the concentration of fluorine and its bleaching effect as revealed by filters 42-C and 66-D

Fig. 2. It will be seen that a linear relationship between fluoride concentration and its effect on the intensity of the colour is obtained when the reaction is carried out at pH 4·2.

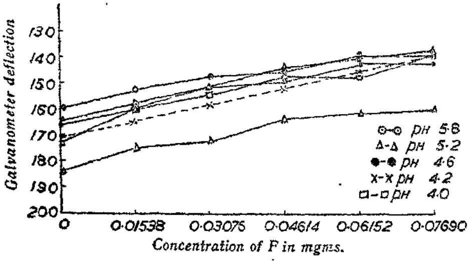

FIG. 2. Relationship between the concentration of fluorine and its bleaching effect at different pH

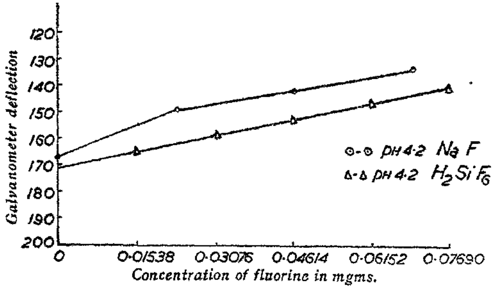

FIG. 3. **Bleaching effect of the same quantity of fluorine as sodium fluoride and hydrofluo silicic acid**

After fluorine is distilled over as hydrofluosilicic acid, the distillate is made up to known volume. A small aliquot is taken, the distillate is invariably acidic, and is adjusted to pH 7·0, and the volume of N/50 alkali required is noted. 20 c.c. or less of the distillate are taken in 25 c.c. volumetric flask together with the calculated volume of N/50 alkali required to neutralise it. To this are added 2·5 c.c. of the ferron-iron reagent, and the volume is made up to mark with distilled water. The ferron-iron reagent is prepared in the following manner so that when 2·5 c.c. of this are mixed with 20 c.c. of the neutralised distillate and made up to 25 c.c., the solution has the pH 4·2.

The composition of the ferron-iron reagent:

Saturated ferron solution	45 c.c.
N/10 Ferric chloride	5 c.c.
N/100 Hydrochloric acid	8 c.c.

Volume is made up to 100 c.c.

The colour of the reagent is stable, and its intensity is measured in a photo-electric colorimeter, using red filter No. 66.

Interference by Other Ions

It is obvious that the accuracy of the method will be severely impaired by the presence of coloured salts. The intensity of the colour of ferron with ferric chloride is seriously interfered with by oxidising and reducing substances. Colour is destroyed by nitric acid and sulphites. Ordinary sodium sulphate which contains some impurity, and the reducing agents like stannous chloride behave similarly. Thorium nitrate, zirconium nitrate and sodium silicate, when present even in small amounts, considerably reduce the intensity of the colour. Other forms of interference in the accurate determination of fluorine by this method are listed below.

(1) *Interference Due to Metals like Silver, Lead and Mercury.*—These form insoluble chlorides, are precipitated in the presence of hydrochloric acid, and result in turbid solutions and consequent abnormal values.

(2) *Interference Due to Salt Concentration.*—The intensity of the colour of ferron with ferric chloride is significantly lowered in the presence of salts. In the case of certain salts, the reduction in the intensity of the colour is independent of the nature of the salt and, within certain limits, of the concentration of the salt in the reaction mixture (Table I). The salt effect, in such cases, is noticeable only in the absence of fluorine.

TABLE I. *Effect of salt concentration on the intensity of colour of ferron with ferric chloride*

Description of the reaction mixture	Colorimetric reading
Reagent (Ferron + $FeCl_3$)	179
Reagent + H_2SiF_6 ($F = 15 \cdot 40\mu$)	170
Reagent + F ($15 \cdot 40\mu$) + NaCl 10 mgm.	170
Reagent + F ($15 \cdot 40\mu$) + NaC 120 mgm.	170
Reagent + No Fluorine + NaCl 10 mgm.	170
Reagent	157
Reagent + H_2SiF_6 ($F = 15 \cdot 40\mu g$)	148
Reagent + F ($15 \cdot 40\mu g$) + $NaNO_3$ 10 mgm.	148
Reagent + F ($15 \cdot 40\mu g$) + $NaNO_3$ 20 mgm.	148
Reagent + No Fluorine + $NaNO_3$ 10 mgm.	148
Pure sodium sulphate behaves similarly	

For certain salts, within certain limits, the reduction in the intensity of the colour is independent of the concentration of the salt, and is greater when both fluorine and salts are present than when each of them alone is present (Table II).

TABLE II. *Effect of salt concentration on the intensity of colour of ferron with ferric chloride*

Description of the reaction mixture	Colorimetric reading
Reagent	178
Reagent + H_2SiF_6 ($F = 15 \cdot 40\mu g$)	169
Reagent + F ($15 \cdot 40\mu g$) + $CaCl_2$ 10 mgm.	165
Reagent + F ($15 \cdot 40\mu g$) + $CaCl_2$ 20 mgm.	165
Reagent + No Fluorine + $CaCl_2$ 10 mgm.	171
Reagent	202
Reagent + H_2SiF_6 ($F = 15 \cdot 40\mu g$)	193
Reagent + F ($15 \cdot 40\mu g$) + $ZnSO_4$ 10 mgm.	184
Reagent + F ($15 \cdot 40\mu g$) + $ZnSO_4$ 20 mgm.	184
Reagent + No Fluorine + $ZnSO_4$ 10 mgm.	188

Magnesium sulphate, cadmium chloride, barium, strontium and beryllium salts behave in the same manner.

In some cases, the lowering in the intensity of the colour is determined by the chemical nature of the salt and its concentration (Table III).

TABLE III. *Effect of salt concentration on the intensity of colour of ferron with ferric chloride*

Description of the reaction mixture	Colorimetric reading
Reagent	202
Reagent + H_2SiF_6 (F = 15·40μg)	193
Reagent + F (15·40μg) + KBr 10 mgm.	190
Reagent + F (15·40μg) + KBr 20 mgm.	184
Reagent + No Fluorine + KBr 10 mgm.	188
Reagent	179
Reagent + H_2SiF_6 (F = 15·40 μg)	170
Reagent + F (15·40μg) + $Al_2(SO_4)_3$ 10 mgm.	153
Reagent + F (15·40μg) + $Al_2(SO_4)_3$ 20 mgm.	126
Reagent + No Fluorine + $Al_2(SO_4)_3$ 10 mgm.	149

Potassium iodide, arsenate, antimony tartrate, molybdate and phosphate behave in this manner.

The interference of the types just mentioned above is likely to be seriously encountered with, when fluorine is isolated by fusing the material with sodium carbonate, and by extracting it with water. In the isolation of fluorine from ashed material as hydrofluosilicic acid by distilling it with silicon carbide and sulphuric or perchloric acid, the cations are completely held back in the distillation flask. However, in the estimation of fluorine in biological materials, one comes across with the presence, in the distillate, of halides, nitrate, sulphate, phosphate, perchlorate, arsenate and other ions in concentration likely to affect the accuracy of the method. Methods for the elimination of interference due to sulphate, phosphate, perchlorate and halides have been given in the Second Part.

By estimating 15·40μg of fluorine as hydrofluosilicic acid in 25 c.c. volume in the presence of interfering ions, the permissible concentration of the interfering ions has been determined and is given in Table IV.

It will be seen that the salt concentration effect is much more pronounced in the reaction between fluorine and ferron-ferric chloride than it is in the reaction between fluorine and thorium nitrate (*vide* Table V, Part II). This renders the method less accurate in the presence of salts. It is not feasible to evolve a compensatory technique when the interference is due to more than one ion, and when the different ions have different interference effect at the same concentration. To obviate the interference, when it is due

TABLE IV. *The permissible concentration of the interfering ions*

Anions	Permissible concentration	Anions	Permissible concentration
Cl^-	$10^{-4} \times 8 \cdot 62$ M	SO_4^{--}	$10^{-1} \times 7 \cdot 25$ M
Br^-	$10^{-1} \times 4 \cdot 66$ M	SO_3^{--}	$10^{-6} \times 5 \cdot 20$ M
I^-	$10^{-4} \times 2 \cdot 93$ M	PO_4^{---}	$10^{-1} \times 2 \cdot 35$ M
NO_3^-	$10^{-4} \times 3 \cdot 15$ M	AsO_3^{---}	$10^{-6} \times 1 \cdot 02$ M
ClO_4^-	$10^{-1} \times 2 \cdot 12$ M	AsO_4^{---}	$10^{-6} \times 1 \cdot 96$ M

to one single ion, the following procedure is adopted: (i) An aliquot of the acidic distillate is neutralised with N/50 sodium hydroxide, and the volume required is noted. (ii) The noted volume of N/50 alkali is taken and neutralised with the requisite acid, and the volume of the acid is noted. (iii) To the reagent are then added the noted volumes of acid and alkali to introduce the same salt concentration in the reagent blank.

Limits of Estimation

The minimum quantity of fluorine, as hydrofluosilicic acid, that can be estimated by this method, is $1 \cdot 7 \mu g$ of fluorine in 25 c.c. reaction mixture, *i.e.*, 0·068 p.p.m., which corresponds to 1 division on the colorimetric scale, and the maximum quantity of fluorine that can be estimated accurately is about $170 \mu g$, *i.e.*, 6·8 p.p.m., and by doubling the concentration of iron in the ferron-iron reagent, it is possible to estimate accurately larger quantities of fluorine.

Evaluation of the Method

In Table V are presented the data obtained by the analysis of fluorine as hydrofluosilicic acid by the thorium nitrate titration method and by the photo-electric colorimetric method.

It will be seen that the photo-electric colorimetric method, even in the absence of any interference due to other ions, is not as accurate as the thorium nitrate titration method. The accuracy obtainable by the latter method is very high, provided that the end point of the titration is located correctly, which, according to some, requires considerable experience on the part of the worker, whereas, no particular skill is required in the first method. The personal errors are eliminated, but a variation in the colorimetric reading by 1 division would introduce an appreciable error in the estimation of very small quantity of fluorine. The error, of course, will

TABLE V. *Estimation of fluorine as hydrofluosilicic acid by the titration and colorimetric method*

Sl. No.	Fluorine present	Fluorine found			
		Colorimetric method	% Error	Titration method	% Error
	μg	μg		μg	
1	15·40	15·40	0·00	14·30	0·65
2	20·50	20·40	0·48	20·51	0·04
3	25·00	25·50	2·00	25·11	0·44
4	30·00	30·60	2·00	29·87	0·43
5	41·50	40·80	1·68	41·75	0·60
6	50·75	51·00	0·49	51·20	0·88
7	60·25	59·50	1·25	60·75	0·83
8	70·00	68·00	2·85	71·01	1·40
9	75·00	73·10	2·53	74·45	0·73
10	85·75	83·30	2·85	86·37	0·72

tend to diminish as larger quantities of fluorine are employed for estimation. The colorimetric method has the following advantages over the thorium nitrate titration method: (i) It is less time consuming, particularly when large number of estimations is to be carried out. (ii) When extremely small quantity of fluorine is to be estimated, a much larger aliquot can be employed than that would be possible with thorium nitrate titration method. (iii) Personal errors are eliminated.

At the same time the colorimetric method is not as accurate as the titrimetric method, and at the same salt concentration, the general salt effect is more in colorimetric than in titrimetric method.

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