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CHEMICAL INSPECTORATE

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THE DETERMINATION OF SMALL AMOUNTS OF FLUORINE.

PART II

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CHEMICAL INSPECTORATE

MINISTRY OF SUPPLY

THE DETERMINATION OF SMALL AMOUNTS OF FLUORINE.

PART II: THE ESTIMATION OF FLUORIDE USING ALUMINIUM AND HAEMATOXYLIN

by

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THE DETERMINATION OF SMALL AMOUNTS OF FLUORIDE

Part II. The Estimation of Fluoride using Aluminium and Haematoxylin.

Summary: The colour developed by aluminium with haematoxylin is destroyed by fluoride ions and this is used as a sensitive method for determining small quantities of fluoride.

INTRODUCTION.

A number of papers have been published giving evidence that fluoride ions interfere in many reactions (1-4), preventing the complete formation of a coloured product and in some cases destroying such a product if it has already formed. In seeking a sensitive method for estimating fluoride ions, a selection of such reactions was tested and the magnitude of the effect of fluoride noted. Some eight likely reactions with positive ions were tested; of these, the one with aluminium was most sensitive to the presence of fluoride and the reactions of aluminium were therefore subjected to further study.

The reaction between aluminium and aurine tricarboxylate (aluminon) was found to be quantitatively effected by fluoride ions and could form the basis of a method for estimating this ion; the effect, however, was small and the experimental error of such a method is likely to be relatively high. In addition, the fading of the aluminon complex itself was sufficiently rapid to cause trouble.

Experiments indicated that the effect was due to the formation of an unionised aluminium complex with fluoride which prevented the aluminium reacting with the reagent. Thus it seemed probable that, if a reaction could be found sensitive to very small changes in concentration of ionic aluminium, a sensitive method for fluorine could be developed. Such a reaction was found in the interaction of aluminium and haematoxylin which gives a purple coloured compound formed only in the presence of ionic aluminium, and which has been used as a method for estimating that element (5); this complex proved very sensitive to small quantities of fluoride and it afforded a basis for the development of a satisfactory method for estimating the latter. During the course of these investigations, it was found that a similar method had been used by Okuno (7) for fluorides in water; approximate concentrations of fluoride were obtained by matching colour developed in Nessler vessels.

EXPERIMENTAL

The basis of the method was as follows:

A stock solution of aluminium-haematoxylin complex was prepared and an aliquot added under standard conditions to known quantities of sample or standard fluoride solution. After standing for a predetermined time, the absorbancy of the sample or solution containing fluoride was determined against the same aliquot of pure stock solution diluted with a volume of water equal to that of the fluoride solution used.

The aluminium-haematoxylin stock solution was prepared by adding 9 mls. of 0.1 per cent haematoxylin solution to 500 micro-gm. of aluminium (as aluminium ammonium sulphate) in 250 mls. of water, to which 5 mls. of 20 per cent ammonium carbonate solution and 3 mls. of 5 per cent gum arabic solution had been added; after standing for 15-20 mins. the solution was adjusted to pH 4.9 with acetic acid. The gum arabic acts as a stabiliser, and its significance will be discussed in another part of this report. The standing time specified is sufficient for complete formation of the aluminium-haematoxylin complex, as indicated below.

Development of Method.

Early experiments showed that with suitable adjustment of quantities of aluminium and haematoxylin in the stock solution, an approximately straight line relationship could be obtained between the absorbancy of the solution and the quantity of fluoride present. (Table I).

TABLE I

Effect of Fluoride on the Aluminium-Haematoxylin Complex

Absorbancy x 10^3

micro-gm of F' added per total of 25 mls. of solution

5	10	15	20	25
141	247	371	456	540
135	242	370	480	586
139	258	372	506	608
135	243	356	473	587
145	268	369	480	623
133	247	378	513	638

Although variations shown in these calibration tables were greater than had been expected, it was considered that provided a calibration curve was constructed for each determination or series of determinations, satisfactory results might be achieved.

Accordingly the method was applied to distillates obtained from known amounts of sodium fluoride by the standard procedure for separating fluoride from other ions by perchloric acid distillation as hydrofluosilicic acid (8, 9). The distillate was carefully neutralised to phenolphthalein with caustic soda and the fluoride estimated in the manner already described. Recoveries were, however, far from satisfactory, ranging from 20 per cent high to 50 per cent low. Careful checking of the fluoride in the distillates by titration with thorium nitrate proved that the trouble lay, not in the distillation technique, but in the absorptiometric determination.

A long series of experiments had been carried out meanwhile, to determine precisely the magnitude and spread of errors encountered in obtaining calibration curves and the results showed that, despite every care, an error amounting to ± 30 per cent was possible in the method as it stood. An analysis of the figures showed that, whilst there were insufficient results for complete statistical treatment, a consideration of mean values and ranges did indicate that the day to day variation was by far the most important and probably large enough to swamp all others, whereas the reproducibility on any particular day was reasonably good. Variation between operators appeared to be negligible and well within day to day variations. Table II shows analyses of the results on 25 micro-gm. of fluoride. A similar number of experiments were carried out with 5, 10, 15 and 20 micro-gm. of fluoride but those quoted are typical of the general effect.

TABLE II

Daily and Operator Variation (Mean and Range) in the Effect of Fluoride on the Colour Intensity of the Aluminium-Haematoxylin Complex.

Absorbancy caused by 25 micro-gm. of Fluoride. Mean and Range.	Results Considered
$697 \pm \genfrac{}{}{0pt}{}{155}{221}$	Results obtained between 15.8.50 and 21.8.50.
$524 \pm \genfrac{}{}{0pt}{}{47}{48}$	Results obtained on 15.8.50.
$771 \pm \genfrac{}{}{0pt}{}{71}{79}$	" " " 16.8.50.
$703 \pm \genfrac{}{}{0pt}{}{22}{21}$	" " " 17.8.50.
$714 \pm \genfrac{}{}{0pt}{}{21}{14}$	" " " 18.8.50.
$772 \pm \genfrac{}{}{0pt}{}{40}{90}$	" " " 21.8.50.
$750 \pm \genfrac{}{}{0pt}{}{62}{47}$	Results by operator H.
$739 \pm \genfrac{}{}{0pt}{}{103}{57}$	" " " E.
$741 \pm \genfrac{}{}{0pt}{}{64}{41}$	" " " T.

It was clear therefore that satisfactory recoveries ought to be possible if calibration curves were made daily.

Consideration of the technique employed in treating distillates suggested two possible sources of interference, one due to variation of pH during the addition of the stock solution, and another arising from reaction due to the presence of perchlorate.

It was therefore decided that the distillate should be buffered to a standard pH prior to addition of the aluminium haematoxylin complex. In early experiments a pH of 4.6 was used, but later, as a result of investigation on the effect of pH, a value of 4.9 was decided upon as the best value for use. Tests carried out under conditions of controlled pH showed that the day to day variation had largely been eliminated (Table III).

TABLE III

Effect of Fluoride on the Colour Intensity of the Aluminium-Haematoxylin Complex.
Fluoride buffered to pH 4.9 before addition of complex.

Change in absorbancy due to 25 micro-gm. of Fluoride	585	581	592	587	588	531	525	528	591	Mean value & range $568 \pm \genfrac{}{}{0pt}{}{24}{43}$
Date	4/9	19/9	19/9	19/9	25/9	27/9	28/9	2/10	3/10	

The relatively volatile nature of perchlorate acid renders extremely difficult the production of distillates free from this acid which, at the same time, contain all the fluoride present. It was discovered that whereas small quantities of perchlorate do not interfere with the aluminium-haematoxylin estimations of fluoride, the relatively large amounts commonly present in distillates did cause serious trouble. Sulphuric acid was therefore substituted for perchloric acid in the distillation.

Using the above modifications in further tests on the amount of fluoride that could be recovered from distillates, anomalous results were again obtained, but whereas previous experiments had given low results, those now obtained were commonly too high, ranging from 96 - 132 per cent. One obvious explanation of these anomalies suggested itself, namely that distillates of necessity contained some sodium sulphate, whereas solutions used for the preparation of calibration curves and for the reference cell did not. The effect of sodium sulphate was therefore tested, and it was found that whereas this salt caused intensification of the colour of the aluminium-haematoxylin complex, provided all solutions contained equivalent amounts of sodium sulphate no effect on the determination of the complex by fluoride was detectable.

A series of tests, in which sodium sulphate equivalent to the amount present in distillates was added to the reference (blank) solution, showed that with this modification satisfactory recovery of fluoride could be obtained. Results are shown in Table IV.

TABLE IV

Recovery of Fluoride by Distillation and Estimation by Aluminium-Haematoxylin Reagent.
Sulphuric Acid Distillation; Sulphate Adjustment of Blank

Micro-gm. F added	Micro-gm. F recovered
25	23, 25, 24, 27, 25, 27, 24, 24.
50	51, 50, 51, 51, 50, 48.5, 48, 51, 51
75	74, 74, 78, 77, 72
100	96, 95, 94.5, 97.

The modified method consisted of the following steps:-

(i) The fluoride was separated from other ions by the standard distillation technique (8) using sulphuric acid.

(ii) The distillate was neutralised to phenolphthalein with caustic soda.

(iii) To an aliquot of the neutralised distillate a standard amount of ammonium acetate buffer was added. This brings the pH to 4.9.

(iv) A known quantity of aluminium-haematoxylin stock solution was then added.

(v) A blank was made up using distilled water to which sodium sulphate equivalent to that in the sample solution was added.

(vi) After the solution had stood for one hour, the absorbancy of the sample solution was measured against that of the blank.

(vii) Calibration curves were constructed by using known amounts of fluoride in place of the sample.

The times of standing used in step (vi) above, and also in preparing the aluminium-haematoxylin complex, were determined by plotting absorbancy of these solutions against time; these experiments showed that, the complex had completely formed in 15-20 minutes, and the fluoride reaction was substantially complete in one hour.

As a final check of the method a comparison was made with the thorium nitrate titration method on a distillate containing fluoride. An operator skilled in the thorium nitrate titration method was able, by adopting extraordinary precautions, to obtain reasonably concordant results by the two methods. The presence of sulphate interferes seriously with the thorium nitrate titration, whilst that of perchlorate interferes to some extent with the aluminium-haematoxylin method, and accordingly the distillate for these comparative tests was obtained from perchloric acid with careful control of temperature and rate of distillation so that insufficient perchloric acid passed over to interfere with the aluminium-haematoxylin method. The advantage of the method of the present report over the thorium nitrate method is that lengthy experience in its use, which is essential with the latter method before accurate and consistent results are attained, is not required. Results are shown in Table V.

TABLE V

Comparison of Recoveries of Fluoride from Distillates, by Aluminium-Haematoxylin Method, and by Thorium Nitrate Titration.

Micro-gm. of F added	F Recovered by Aluminium Haematoxylin Method.	F Recovered by Thorium Nitrate Titration.
25	16 x	17 x
25	17 x	15 x
25	25	25
50	48	51
75	72	75
100	84 x	85 x
100	96	94

x These low results are due to the attempt to keep perchloric acid in the distillate to a minimum, resulting in too low a distillation temperature being used. The lost fluoride was subsequently found in the distillation flask.

Effect of variation in reagents.

Although a workable method had at this stage been attained, especially when a calibration curve was plotted at the same time as the determinations were carried out, it was still necessary to check the effect of different batches and sources of reagents, and the effect of the controllable variables (temperature, pH, etc.) on the method.

Haematoxylin.

This is described in American literature as a white crystalline solid, but most products available in this country do not attain a similar standard of purity. The best product available was Hopkins and Williams preparation for use as indicator or microscopical stain, but even this is somewhat discoloured.

Early experiments in preparing a solution showed that the normal procedure of dissolving the haematoxylin in warm water did not give solutions of a strength which could be reasonably repeated, and it was found more satisfactory to dissolve the material in a minimum of alcohol and dilute to the required volume with water.

The literature suggests that a solution of haematoxylin keeps satisfactorily for about a week only; our observations indicated that this is probably due to slow oxidation. The mechanism of oxidation of the haematoxylin molecule to haematein involves the loss of two atoms of hydrogen, and it was thought that if the mechanism involved (as is possible) a primary ionisation step then haematoxylin would prove to be more stable in an acid solution. This in fact proved to be the case, and acid or buffered haematoxylin solution keeps quite satisfactorily for up to six weeks. These findings are confirmed by Houghton (10), who also found that acid haemtoxylin keeps well.

It was found that the haematoxylin solution was susceptable to mild attacks of mould growth, but this was easily prevented by the addition of small quantities of chloroform (0.05%) about once a week.

Ammonium Carbonate. Certain anomalous results were obtained when changing from one supply of this reagent to another, but investigation has shown that these results are due to pH variations arising from changes in the ammonia content of the solutions prepared.

It appeared that, with the material available, it was not possible to prepare solutions as strong as those employed by Hatfield (5) in his use of the aluminium-haematoxylin complex as a means of estimating aluminium. Different methods of preparing a saturated solution resulted in considerable variation in ammonia content, and better results were obtained by preparing a solution which, while not quite a saturated one, was satisfactorily reproducible.

Whilst the pH (9.0) at which the complex is formed was accurately obtained with any ammonium carbonate solution between 10 per cent and saturation, the pH obtained on subsequently adding a standard amount of acetic acid varied considerably (4.6 - 5.2) for changes in ammonia content of the solution, a point of the utmost importance. These changes of pH had a considerable influence on the amount of complex present in acid solution, and also on its rate of destruction by fluoride. These points are further discussed below in connection with the effect of pH variation.

Gum Arabic. Samples of gum arabic vary considerably and it is difficult to make a solution with accurately reproducible properties. It is important that sufficient be present during a determination as otherwise the stabilising action on the complex is not complete; 3 mls. of 5 per cent aqueous solution in approx. 250 ml. of aluminium-haematoxylin stock solution, as directed above, were usually found to be quite satisfactory. The efficiency of the solution deteriorates with time and a solution should not be used if it is more than a week old.

It has been found advisable with new batches of gum arabic to check the amount required to stabilise the acid aluminium-haematoxylin stock solution. Aluminium-haematoxylin stock solution is made up as described using 3 mls. of a 5 per cent aqueous solution of the gum arabic; if the gum arabic has the correct strength, the change in absorbancy of this solution over a period of two hours should be negligible. Should the absorbancy decrease, the addition of a greater quantity of gum arabic may achieve the desired stability, but it is considered that such a material is unsatisfactory, and a fresh batch should be used.

Effect of Variations in Experimental Conditions.

The Effect of pH. Experiments on ammonium carbonate had already indicated that considerable differences in pH could be obtained if a standard quantity of acetic acid was added to make the alkaline aluminium-haematoxylin stock solution acid, and experiments were therefore undertaken to determine the effect of pH variations. In these experiments, the stock solution was prepared in the manner already described, the adjustment of pH being carried out with the aid of a pH-meter. Calibration tables for the effect of fluoride on the complex were thus made at known pH. The absorbancy of the stock solution alone was also determined against water. Results are shown in Table VI.

TABLE VI

Effect of pH on the Variation of Colour Intensity of the Aluminium-Haematoxylin Complex produced by Fluoride.

pH of acid stock	Absorbancy of solution x 10^3					x Absorbancy x 10^3 of blank solution against water
	micro-gm. of F added per total of 25 mls. of solution:					
	5	10	15	20	25	
4.6	147	293	425	519	597	805
4.8	117	252	379	490	593	1036
4.92	113	257	374	496	588	1158
5.2	119	186	282	360	445	>1300

x Figures in this column give a measure of the amount of complex present.

From the above table it is clear that the lower the pH, the greater the effect produced by fluoride, and the greater the sensitivity; against this, however, the lower the pH, the less is the amount of complex available in a given solution, and hence the narrower the concentration range of fluoride which can conveniently be estimated. The increase in sensitivity to fluoride with decrease in pH is linked with a decrease in stability of the complex with increase of hydrogen ion concentration; which in some cases leads to fading of the blank. After careful consideration it was decided that a pH of 4.9 was probably the most suitable, and all further work was carried out at that value.

The Effect of Temperature. The reactions involved in the method, viz. (a) the formation of the complex and (b) the destruction of the complex by fluoride, are by no means instantaneous, but as the times of standing have been chosen so as to ensure that both reactions are virtually complete, the effect of variation of temperature by plus or minus two or three degrees has little effect on the method. In investigating the mechanism of the reactions involved (to be discussed in a further part of this report) special attention is being paid to effect of temperature. Provided calibration curves are made at the same time as determinations are carried out, little trouble with slight temperature variation is to be expected.

Interfering Substances.

Although fluoride is normally freed from other ions by distillation, it was thought possible, that in certain cases, the aluminium haematoxylin method might be used directly, and an investigation into interfering ions was carried out. The results obtained are collected in Tables VII and VIII.

Four types of interference were expected:-

(a) That arising from ions which oxidise haematoxylin, thus destroying the complex, and forming haematein. (Haematoxylin is very easily oxidised to haematein, a stream of air sufficing under strongly alkaline conditions).

(b) Interference from substances which themselves form complexes with haematoxylin.

(c) Interference from substances which form complexes with fluoride ions.

(d) Interferences from substances which form strong complexes with aluminium.

In class (a) cerium, dichromate, permanganate, peroxides and other oxidising agents would all be expected to interfere, and are indeed found to do so. Unexpectedly nitrite interferes; it is considered in this case, that the ion acts as an oxidising agent.

In class (b) iron (11), chromium, (11), tin (11), antimony (11), copper (11), zinc (11), bismuth (11) and some others might be expected to cause interference. In point of fact zinc does not interfere; antimony was not tried, but the remainder vitiate the method.

The ions causing interference due to complexing with fluoride, class (c), are aluminium, iron and zirconium, but the effect is masked by their reactions with haematoxylin.

The only ion found in class (d) was oxalate.

From the full list of ions tested and their reactions given in Tables VII and VIII, it is apparent that the number of interferences encountered renders the direct application of this method to most samples impracticable, though in certain cases, viz., sea water, water, plant ash, etc., direct application might be possible.

The effects of the ions listed in the tables were determined as follows: Two calibrations of a given stock solution were performed simultaneously using 5, 15, and 25 micro-gm. of fluorine (per 25 ml. flask) in each. The ion was added, in the amount indicated in column 2 of the tables, to all the solutions (including the blank) in one of the calibrations. The solutions were

TABLE VII

The Effect of Various Positive Ions on the Determination of Fluoride with Aluminium-Haematoxylin Reagent.

Ion	Concentration (p.p.m.)	Effect on Fluoride Determination	Nature of Interference	Remarks
Na^+	2.3×10^3	Nil	None	
K^+	1×10^5	Nil	None	
Cu^{++}	40	Marked loss of sensitivity	Itself complexes with haematoxylin	Removal is essential
Ag^+	40			Removal essential as precipitates are formed with traces of Cl^- in reagents
Be^{++}	40	Method fails	Complexes F^-	Removal essential
Mg^{++}	40	Nil	None	
Ca^{++}	4	Nil	None	
Ba^{++}	60	Nil	None	
Zn^{++}	4	Nil	None	
Cd^{++}	4	Nil	None	
Hg^{++}	40	Slight loss of sensitivity		Calibrate in presence of an equal amount of the ion
Al^{+++}				Removal essential since it upsets the proportion of Al in reagent and complexes F^- without destroying reagent
Bi^{+++}	40	Method fails	Itself complexes with haematoxylin	Removal essential
La^{+++}	4	Nil	None	
Ce^{++++}	40	Method fails	Reagent destroyed by oxidation	Removal essential
Zr^{++}	40	Method fails	Itself complex with haematoxylin also with F^-	Removal essential
Sn^{++}	4	Method fails	Itself complexes with haematoxylin	Removal essential
Pb^{++}	4	Nil	None	
Cr^{+++}	4	Marked loss of sensitivity	Complex destroyed	Removal essential
UO_2^{++}	30	Nil	None	
Mn^{++}	4	Nil	None	
Fe^{++} Fe^{+++}	4	Method fails	Itself complexes with haematoxylin	Removal essential
Co^{++}	40	Nil	None	
Ni^{++}	4	Nil	None	
Ru^{+++}	4	Marked loss of sensitivity	Itself complexes with haematoxylin	Removal essential

TABLE VIII

The Effect of Negative Ions on the Determination of Fluoride with Aluminium-Haematoxylin Reagent.

Ion	Concentration (p.p.m.)	Effect on Fluoride Determination	Nature of Interference	Remarks
Arsenate Arsenite	40	Slight loss of sensitivity		Calibrate in presence of an equal amount of the ion or remove it
Chloride	3×10^3	Nil	None	
Bromide	6×10^4	Nil	None	
Iodide	4	Nil	None	
Nitrate	1.5×10^5	Nil	None	
Nitrite	Trace	Method fails	Destruction of reagent	Removal essential
Phosphate	4	Nil	None	
Sulphate	4.8×10^3	Nil	None	
Silicate	40	Marked loss of sensitivity		Removal essential
Dichromate	40		Destruction of reagent by oxidation	
Permanganate	40	Method fails	As for dichromate Also colour of ion interferes	Removal essential
Perchlorate	Less than 30	Nil	None	
Molybdate	40	Marked loss of sensitivity	Intensification of reagent colour	Removal essential
Vanadate	40	Marked loss of sensitivity	Reagent destroyed	Removal essential
Borate	40	Nil	None	
Formate	40	Nil	None	
Oxalate	4	Method fails	Destroys reagent by competing for Al	Removal essential
Tartrate	40	Method fails	Destroys reagent by competing for Al	Removal essential

compared in the normal way, and in addition the two blank solutions containing no fluoride were compared.

In cases where interference is only moderate, a modified procedure can be used to estimate fluoride, although some sensitivity may be lost thereby; calibration curves and blanks are prepared containing the same amount of interfering ion as is present in the sample, and in this way the effect of the ion can be overcome.

CONCLUSION

The destruction of aluminium-haematoxylin complex by fluoride provides a method for estimating this ion. Experiments numbering several hundred have indicated that an accuracy of ± 10 per cent over a range of 1-25 micro-gm. of fluorine in 15 mls of solution is obtainable, although, provided a calibration curve is constructed at the same time as the samples are analysed, better results than this can normally be expected. Particular care must be taken that pH is rigidly controlled. Full details of procedures to be adopted are given elsewhere (12).

Owing to interference of certain ions, it is usually necessary to separate the fluoride; to do this the standard distillation procedure is used, but it is hoped in the future to replace this by other methods.

In developing this method, recovery of fluoride from water has been used, but work on the application to several other materials is in hand.

In the application of this method to fluoride in new substances, great care must be taken that no interfering ions are introduced into the distillate; it is in the separation of fluoride from the sample that difficulties arise, but, with careful planning, they can be overcome.

The method here described has the great advantage that no special training or skill is needed in using it, and for this reason, is to be preferred to the thorium nitrate titration, in the use of which considerable training and experience are required.

Further work is now in hand to extend the range of the method to smaller amounts of fluoride, and a theory has been developed to explain the various reactions and effects observed.

February, 1951.

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