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Investigation on Several Methods of Determination of Fluoride Ion

I. Gravimetric and Volumetric Determinations
II. Colorimetric Determinations

By

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I. GRAVIMETRIC AND VOLUMETRIC DETERMINATIONS

Introduction

Although many methods are known for determination of fluoride ion, only few investigations on the comparison of these methods have made it difficult to select the best one out of them, and it seems to be due to difficulty of setting up the standard measure of comparison. This measure may be provided, however, by application of statistical methods, and the relative accuracies and precisions of various methods are expected to be determined on the basis of statistics.

In this research it was attempted to compare the seven methods of determination of fluoride ion from the standpoints of statistics as well as of analytical chemistry.

The seven methods chosen were as follows.

(A) Gravimetric determination as PbFCl.
(B) Volumetric determination as PbFCl.
(C) Gravimetric determination as CaF_2.
(D) Offerman's method.
(E) Volumetric determination with $AlCl_3$. (Eriochromecyanine as indicator).
(F) Conductometric titration with $AlCl_3$.
(G) Volumetric determination with $Th(NO_3)_4$.

In all these cases, NaF used as sample was that manufactured by the Morita Chemical Industries, Ltd., and the effect of co-existing ion was neglected.

Experimental Results and Considerations

Table 1 shows the time of operation required by the seven methods chosen.

Table 1.

	Methods	Time required
A	Gravimetric determination as lead chlorofluoride	3.5 hrs.
B	Volumetric determination as lead chlorofluoride	2.5
C	Gravimetric determination as calcium fluoride	6.0
D	Offerman's method	1.3
E	Volumetric determination with aluminum chloride	0.3
F	Conductometric titration with aluminum chloride	1.0
G	Volumetric determination with thorium nitrate	0.6

Accuracies of these methods were studied by classifying them into two groups, one for large amount of fluoride (A, B, C and D) and the other for small amount of fluoride (E, F and G). The experiments were designed by one-way classification, and the order of the measurements was determined at random. The results are shown in Table 2.

Table 2.

Methods / No.	A	B	C	D	E	F	G
1	98.32%	98.20%	97.67%	99.81%	98.42%	98.49%	98.74%*
2	97.92	97.92	97.02	100.22	98.91	99.03	99.04
3	97.95	97.80	96.38	99.92	98.00	98.82	99.02
4	98.58	98.45	97.05	99.80	98.64	97.84	98.65
5	99.02	98.58	97.50	98.56	98.56	98.90	97.98
6	98.40	98.64	96.92	99.10	97.96	98.85	98.47
7	99.19	98.27	97.90	100.09	98.91	98.61	98.57
8	99.01	98.82	97.92	99.13	98.09	99.10	98.19
Total	788.39	786.68	778.36	796.63	787.48	789.54	788.66
Average	98.55	98.34	97.29	99.58	98.43	98.69	98.58

* percentage to theoretical value

As shown in Table 3, there is no significant difference in precision among A, B, C and D, or among E, F and G.

The results of the analysis of variance are shown in Table 4. It indicates that there is a significant difference among the mean values of A, B, C and D. Therefore a comparison of B, C and D with A was made by t-test. A significant difference at 1% level was detected between A and C and between A and D, but not between A and B.

Table 3.

Methods	Mean square
A	0.239
B	0.126
C	0.293
D	0.337
E	0.150
F	0.158
G	0.137

Table 4. Analysis of variance. (Group of A, B, C and D)

Source of estimate	Sum of squares	Degrees of freedom	Mean square	F ratio
Between methods	21.045	3	7.015	28.59**
Within method	6.970	28	0.249	
Total	28.015	31		

Analysis of variance. (Group of E, F and G)

Source of estimate	Sum of squares	Degrees of freedom	Mean square	F ratio
Between methods	0.267	2	0.134	—
Within method	3.120	21	0.149	
Total	3.387	23		

As the factors of $AlCl_3$ and $Th(NO_3)_4$ solutions for E, F and G were determined with NaF prepared from Merck's HF, it is expected that there should be no difference among the mean values of E, F and G. The results were just as expected, as shown in the lower part of Table 4.

On A, which has hitherto been considered to be a standard method, a test of accuracy was carried out. Table 5 shows the results.

Table 5.

No.	Sample taken (A) g	Determination found (B) g	B/A×100 %
1	0.1060	0.1055	99.57
2	0.2120	0.2122	100.05
3	0.3180	0.3149	99.06
4	0.4240	0.4232	99.81
5	0.5300	0.5292	99.85
6	0.6360	0.6351	99.85
7	0.7420	0.7410	99.87
8	0.8480	0.8484	100.05
9	0.9540	0.9537	99.96
10	1.0600	1.0601	99.99
Average	—	—	99.81

According to Table 5, the mean value is 99.81% (in the right column) for the weight of samples of 0.1060–1.0600 g. As the result of t-test, the mean value was found to be acceptably close to 100%. Since the standard sample for this test was NaF prepared from Merck's HF, this PbFCl-method might be said to be an accurate one. The 95% confidence limits for the mean value are 100.11% and 99.50%. On the contrary, the methods C and D are regarded to have some deviation, as there has been a significant difference between A and C and between A and D as mentioned above. The methods E, F and G, on the other hand, might be considered to have no deviation, because the method A has no difference with E, F and G, as shown in Table 2.

Experiments on E, F and G were designed by two-way classification, in which the concentrations of the sample solutions were varied from 0.01 g/*l*. to 0.1 g/*l*. The results are shown in Table 6. The analysis of variance for them is shown in Table 7.

Table 6.

Concentration of Sample g/*l*	E	F	G	Total
0.01	98.97%	98.46%	98.50%	295.93
0.02	98.56	98.35	98.77	295.68
0.03	98.60	98.65	98.91	296.16
0.04	98.72	98.76	98.62	296.10
0.05	98.16	98.92	98.43	295.51
0.06	98.03	98.44	98.47	294.94
0.07	98.61	98.72	98.52	295.85
0.08	98.54	99.01	98.73	296.28
0.09	98.45	98.81	98.79	296.05
0.10	98.92	98.58	98.56	296.06
Total	985.56	986.70	986.30	2958.56

Table 7. Analysis of variance.

Source of estimate	Sum of squares	Degrees of freedom	Mean square
Between Concentrations	0.469	9	0.052
Between Methods	0.080	2	0.040
Error	1.965	18	0.109
Total	2.514	29	

Among the mean values of E, F and G, and among the concentrations of the sample solutions, there is no significant difference.

Finally, some points may well be added, from the author's experiences, with regard to the procedures of the above seven methods.

(a) Gravimetric determination as $PbFCI$.1)

This method utilizes the precipitation of fluoride as lead chloro-fluoride, which is granular and easily filtered. Precipitation should be done at pH 3.6–5.6, and the precipitate should be allowed to stand for one hour at 15°C. The precipitate is filtered through a Gooch's crucible, and after being washed with a saturated solution of $PbFCI$, it is dried for one hour at 110–120°C and weighed. This method seems to be the easiest one for gravimetric determination of fluoride ion.

(b) Volumetric determination as $PbFCI$.2)

The precipitate of $PbFCI$ is dissolved in 5% HNO_3 and an excess of $AgNO_3$ solution is added. The precipitated $AgCI$ is filtered off, and the filtrate is titrated with standard NH_4SCN.

(c) Gravimetric determination as CaF_2.3)

This is the most common procedure but can not be said to be an accurate method. CaF_2 is fairly soluble in water and in acetic acid. It has a tendency to form a gelatinous precipitate with excess $CaCl_2$, and is difficult to filter.

(d) Offerman's method.4)

SiF_4, which is evolved by the action of H_2SO_4 upon a fluoride in the presence of silica, is received in water and the resulting compound is titrated with standard alkaline solution.

(e) Volumetric determination with $AlCl_3$.⁵⁾

This method utilizes the complex ion formation of F^- with Al^{3+}. Pure $AlCl_3$ is produced by passing dry HCl through hydrochloric acid solution of $AlCl_3 \cdot 6H_2O$ under ice cooling. The factor of $AlCl_3$ is determined by standard NaF solution, which is prepared by neutralizing Merck's HF with NaOH. This method is very convenient for the determination, because it requires only a short time of operation and the end point is recognized sharply by the use of Eriochromecyanine R as indicator.

(f) Conductometric titration with $AlCl_3$.⁶⁾

This method also utilizes the complex ion formation of F^- with Al^{3+}. The fluoride is titrated in 30% alcoholic solution.

(g) Volumetric determination with $Th(NO_3)_4$.⁷⁾

After adjustment of the pH value of a fluoride solution at 3.5 with monochloroacetic acid-sodium hydroxide buffer solution, the fluoride is titrated with $Th(NO_3)_4$ solution by the use of sodium alizarinsulfonate as indicator.

Conclusion

The comparative investigation on the seven methods for fluoride determination, (A) gravimetric determination as lead chloro-fluoride, (B) volumetric determination as lead chloro-fluoride, (C) gravimetric determination as calcium fluoride, (D) Offerman's method, (E) volumetric determination with aluminum chloride (with Eriochromecyanine R as indicator), (F) conductometric titration with aluminum chloride and (G) volumetric determination with thorium nitrate, showed the following results.

(1) There is no significant difference among precisions of A, B, C and D, but accuracies of C and D are inferior to that of A or B.

(2) Among E, F and G, there is no significant difference in both precision and accuracy.

(3) There is no significant difference among the mean values of E, F and G over a sample concentration range of 0.01–0.1 g/l.

(4) From the standpoints of precision, accuracy, easiness to operate and shortness of operating time, lead chloro-fluoride method (A) is most suitable for gravimetric analysis, and aluminum chloride method (E) for volumetric analysis.

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II. COLORIMETRIC DETERMINATIONS

Introduction

In 1936 the American Water Work Association set up a committes to find the best method for the determination of fluoride ion in many types of water. They selected the Scott's modification[1] of the Sanchis' method,[2] in which a Zirconium-Alizarin reagent, that is decolorized by fluoride ion, is used and the color is compared with standards of known concentrations. The method is simple and fairly accurate, but has some disadvantages. In recent years, the fluoridation of community water supplies to reduce dental caries has become fairly widespread. The fluoride ion is added generally in the range of 0.6–1.5 ppm. For determination of fluoride ion in water supplies or in natural water, therefore, a simple, rapid, colorimetric method is desirable.

This work was undertaken to select the most suitable method for colorimetric determination of microgram quantities of fluoride ion and to compare the accuracies and precisions of several methods of fluoride determination and to show the effect of interfering ions by the statistical methods.

Procedure and Results

Out of many colorimetric methods and their modifications that have hitherto been proposed, five were chosen (see Table 1–5) and the determinations of fluoride were

Table 1. Percentage transmittancy measured with Ferric Thiocyanate Method.

F^- added γ	Interfering ions									
	none			NaCl	$CaCl_2$	Na_2CO_3	$Mg(NO_3)_2$	Na_2SO_4	Na_3PO_4	$FeCl_3$
0	53.0	53.4	52.7	52.3	53.3	53.6	53.4	54.7	53.1	53.0
100	57.5	57.3	57.5	57.8	58.2	58.0	58.1	59.1	57.9	58.0
200	61.8	62.0	62.2	62.0	62.1	62.3	62.2	63.2	62.1	62.1
300	66.2	66.0	65.8	65.8	66.0	66.1	66.2	67.1	66.0	65.8
400	69.9	69.0	69.2	69.5	69.4	69.5	69.2	70.3	69.2	69.0

Table 2. Percentage transmittancy measured with Ferric Salicylate Method.

F^- added γ	Interfering ions									
	none			NaCl	$CaCl_2$	Na_2CO_3	$Mg(NO_3)_2$	Na_2SO_4	Na_3PO_4	$FeCl_3$
0	45.0	44.9	45.0	46.9	45.2	49.9	45.0	45.2	45.0	44.3
100	53.0	53.0	52.8	53.7	54.1	57.9	54.0	53.2	53.0	51.2
200	60.2	60.0	59.9	61.5	59.9	62.4	60.4	59.8	60.0	57.8
300	66.6	66.2	66.3	66.2	66.1	67.5	65.0	66.0	65.7	63.2
400	71.5	71.0	71.3	71.0	68.8	71.9	69.0	70.0	70.0	68.2

Table 3. Percentage transmittancy measured with Thorium-Alizarin Method.

F- added γ	Interfering ions									
	none			NaCl	$CaCl_2$	Na_2CO_3	$Mg(NO_3)_2$	Na_2SO_4	Na_3PO_4	$FeCl_3$
0	55.6	55.7	55.8	56.0	56.0	54.0	56.2	64.2	57.8	56.1
20	65.0	65.1	65.0	65.5	65.2	62.3	65.0	72.8	67.5	64.2
40	76.4	76.2	75.8	76.2	76.2	73.5	76.1	82.8	77.2	75.0
60	86.0	86.0	86.0	86.6	86.0	82.7	86.0	90.1	85.7	83.5
80	93.0	93.0	93.1	93.0	93.0	89.2	93.0	94.9	92.2	90.0

Table 4. Percentage transmittancy measured with Zirconium-Alizarin Method.

F- added γ	Interfering ions									
	none			NaCl	$CaCl_2$	Na_2CO_3	$Mg(NO_3)_2$	Na_2SO_4	Na_3PO_4	$FeCl_3$
0	45.8	45.8	45.8	47.0	46.8	41.5	47.0	47.0	47.0	45.7
40	54.0	54.1	54.8	55.2	55.0	55.0	54.9	55.8	55.2	55.1
80	65.3	65.4	65.3	66.8	66.2	66.5	66.8	67.3	66.8	66.0
120	78.2	79.0	78.8	80.2	79.7	79.9	80.2	80.7	79.9	78.4
160	91.4	90 9	91.2	93.0	92.0	92.0	92.9	92.3	92.3	89.9

Table 5. Percentage transmittancy measured with Aluminum-Hematoxylin Method.

F- added γ	Interfering ions									
	none			NaCl	$CaCl_2$	Na_2CO_3	$Mg(NO_3)_2$	Na_2SO_4	Na_3PO_4	$FeCl_3$
0	41.2	41.5	41.5	41.3	41.8	43.0	41.2	41.0	43.2	41.0
100	42.2	42.8	43.2	42.3	42.2	43.3	41.8	41.6	43.8	42.1
200	45.8	47.0	45.8	45.8	45.8	45.0	45.2	45.5	45.5	44.8
300	55.4	55.4	55.5	55.8	55.0	57.9	54.9	54.4	55.0	59.2
400	73.2	73.2	73.8	73.6	73.6	66.0	72.0	73.6	73.0	69.2

carried out according to the directions in the literature.[1,3-6]

A filter photometer with 2 cm. cells was used to measure the transmittancy. The bleaching effect of fluoride ion in the region of low concentration (0 to 10 ppm.) was studied by plotting the logarithm of precent transmittancy against the volume of fluoride solution added to the colored solution to determine whether the change in precent transmittancy obeyed the Lambert-Beer's law. To effect of various interfering ions on the color intensity of the solution, the percent transmittancy or its logarithm was plotted against the volume of fluoride solution containing an interfering ion added to the colored solution.

The chief interference in natural water would be due to Fe^{3+}, Ca^{2+}, Mg^{2+}, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, and Cl^-.

The test of interference was carried out in the presence of 60 ppm. of Ca^{2+}, 20 ppm.

of Mg^{2+}, 0.3 ppm. of Fe^{3+}, 50 ppm. of CO_3^{2-}, 0.5 ppm. of PO_4^{3-}, 50 ppm. of SO_4^{2-}, and 320 ppm. of Cl^-, respectively.

While quantitative experiments should be planned in such a manner that some accepted statistical method may readily be used to analyze the resulting data, the present data are most satisfactorily treated by a statistical procedure known as regression analysis, which was first applied by W. T. Youden(7) to the study of accuracy.

Although the relationship between the percent transmittancy and the volume of fluoride solution was not linear in the whole range, it was possible to apply the linear regression in the special range measured.

If $x_1, x_2, \cdots, x_n$ are the volumes of fluoride solution added, $y_1, y_2, \cdots, y_n$ the corresponding percent transmittancies and $y_1', y_2', \cdots, y_n'$ the corresponding percent transmittancies measured in the presense of an interfering ion, the regression line of y upon x is

$$y = bx + a$$

and that of y' upon x is

$$y' = b'x + a'.$$

If the difference between b' and b or a' and a is significant, it is concluded that the method is affected by the interfering ion.

1) Ferric thiocyanate method.(1)

Reagents

A. 12.62 g of ammonium rhodanate was dissolved in 500 ml. of water.

B. 0.26 g of ferric ammonium sulfate was dissolved in 0.01 N perchloric acid.

The red color system were developed by using 5 ml. of A, 5 ml. of B, and fluoride solutions and diluting to 50 ml. After standing for 5 minutes, the transmittancy at 530 mμ was measured.

At 530 mμ the absorbancy was almost linear from 0 to 300γ of fluoride, with a sensitivity of 0.00029 per 1γ of fluoride, and nonliner at higher concentrations.

The results of measurement and the effect of the presence of various interfering ions on the color intensity of the solution are given in Table 1 and 6.

According to the statistical test, it was found that the presence of 50 ppm. of

Table 6. Test of Significance.

Methods	Interfering ions						
	NaCl	$CaCl_2$	Na_2CO_3	$Mg(NO_3)_2$	Na_2SO_4	Na_3PO_4	$FeCl_3$
Ferric salicylate	—	—	+	—	—	—	—
Ferric thiocyanate	—	—	—	—	+	—	—
Thorium-alizarin	—	—	—	—	+	—	—
Zirconium-alizarin	—	—	—	—	—	—	—

sulfate has an appreciable effect upon the color intensity of the solution, but other ions tested have no significant effect.

The colors were stable over a long period of time.

2) Ferric salicylate method.³⁾

Reagents

A. 0.16 g of Na-salicylate was dissolved in 1000 ml. of water.

B. 5.406 g of ferric chloride was dissolved in 1000 ml. 1 N HCl.

The violet color solutions were prepared by mixing 50 ml. of A and B, and diluting to 1000 ml. and adjusting pH to 3.0, 10 ml. of this solution and fluoride solutions were diluted to 50 ml. The best condition for fluoride sensitivity was at pH 3.0.

The colors were stable over a long period of time.

The results of measurement and the effect of the presence of various interfering ions on the color intensity are given in Table 2 and 6.

It was found that 50 ppm. of CO_3^{2-} has an appreciable effect upon the color intensity, but other ions tested have no significant effect.

3) Thorium alizarin method.⁴⁾

Reagents

A. Monochloroacetic acid, 3.78 g

B. NaOH, 1.34 g

C. Na-Alizarin sulfonate, 0.30 g

D. $Th(NO_3)_4 \cdot 12H_2O$, 0.002 N solution

Above four reagents were dissolved in 1000 ml. of water. After standing for one day, 10 ml. of upper layer of this solution and fluoride solutions were diluted to 50 ml. The best condition for fluoride sensitivity was at pH 3.0.

Using a 530 mμ filter, the absorbancy was almost linear from 0 to 60 γ of fluoride with a sensitivity of 0.0029 per 1 γ of fluoride and nonlinear at higher concentrations.

The colors were unstable over a long period of time. The results of measurement and the effect of the presence of various interfering ions on the color intensity of the solution are given in Table 3 and 6.

It was found that the presence of 50 ppm. of sulfate has an appreciable effect upon the color intensity, but other ions have no significant effect.

4) Zirconium-alizarin method.⁵⁾

Reagents

A. Na-Alizarin sulfonate, 0.35 g

B. $ZrOCl_2 \cdot 8H_2O$, 0.30 g

C. H_2SO_4 (12 N), 40 ml.

D. HCl (12 N), 120 ml.

Above four reagents were dissolved in 1000 ml. of water. After standing for one day, the clear layer was diluted to the twice with water. 10 ml. of this reagent and fluoride solutions were diluted to 50 ml.

After standing for two hours, the transmittancy at 530 mμ was measured. At 530 mμ the absorbancy was almost linear from 0 to 120 γ of fluoride, with a sensitivity of 0.0019 per 1 γ of fluoride and nonlinear at higher concentrations.

The results of measurement and the effect of the presence of various interfering ions on the color intensity of the solutions are given in Table 4 and 6.

It was found that the 60 ppm. of Ca^{2+}, 20 ppm. of Mg^{2+}, 50 ppm. of CO_3^{2-}, 0.5 ppm. of PO_4^{3-}, 50 ppm. of SO_4^{2-}, 200 ppm. of Na^+, 0.3 ppm. of Fe^{3+} have no significant effect.

5) Aluminium-Hematoxylin method.⁽⁶⁾

Reagents

A. $Al_2(SO_4)_3$ solution, Al 0.05 mg/ml.

B. Hematoxylin solution, 0.5%

C. Saturated solution of Na_2CO_3

D. Acetic acid (1 : 2)

To 400 ml. of A, 250 ml. of water, 60 ml. of hematoxylin solution, 10 ml. of Na_2CO_3 solution, and 10 ml. of acetic acid were added. 10 ml. of the prepared reagent and fluoride solution were diluted to 50 ml. After standing for four hours, the transmittancy at 530 mμ was measured. The best condition for fluoride sensitivity was pH 4.6.

The colors were unstable over a long period of time. In this case, we do not test statistically the effect of the presence of various ions on the color intensity of the solution, since the percentage transmittancy or absorbancy was nonlinear over all concentrations of fluoride.

Conclusion

From the points of view of precision, sensitivity and accuracy, the Thorium-Alizarin method and the Zirconium-Alizarin method seem to be most suitable for the determination of fluoride ion in the concentration range from 0 to 5 ppm., and Ferric-salicylate method for about 10 ppm. of fluoride ion.

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