Studies on a New Volumetric Method for the Determination of Fluorine.*

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28 弗素の一新容量分析法の研究 宮原泰幸（北興化学株式会社 東京研究室，元大連満鉄中央試験所及び青島国立張店農薬廠研究室） 28. 8. 27. 受理

本報告は，アルコール溶液で硝酸第二鉄を標準液として，サルチル酸曹達を指示薬とする，弗素の一新容量分析法，並に該方法を弗化曹達及び其他の弗化物の分析への応用に就て記載した。

先づ，サルチル酸曹達の感度と用量，滴定液の pH 及びアルコール濃度，供試弗化物濃度，アルコールの添加時期等，滴定精確度に関係ある諸因子の影響を検討し，最後に迅速で精確な容量法を提案した。

本法は，緩衝液で pH 3 に調節した溶液中で微量の $Fe^{\cdots}$ イオンに対して鋭敏な紫の呈色反応を呈するサルチル酸曹達を指示薬として用ひ，硝酸第三鉄の標準液で滴定し，滴定中溶液が橙黄色を呈するに到り，適量のアルコールを加へて（終点に於けるテルコール濃度 50% by volume 以上とす）脱色し，再び滴定を継続して，微紅色の出現を滴定終点とする。

二価以上の金属イオン，燐酸，珪酸，硼酸，炭酸等の陰イオン，硫化物，其他 Fe イオンに作用する還元性物質は障害があるから，予め除去する必要がある。

本法を弗化曹達液の分析に応用した処，従来農薬分析の公定法として採用されている塩弗化鉛法の結果とよく一致する値を示した。

In view of the necessity of the rapid and accurate process for the determination of fluorine applicable in the studies and in the technical analyses of sodium fluoride industrially produced, the author has established a new volumetric process using ferric nitrate as a standard solution. The proposed method is characteristic in using the optimum amount of alcohol in the course of titration and using sodium salicylate as indicator that shows sharp violet color with minute amounts of ferric ion under the proper pH value.

Among the insoluble compounds which have been employed in the gravimetric or volumetric determination of fluorine are : calcium fluoride [1,2] barium fluoride[3], lanthanum fluoride[4], thorium fluoride[5,6], cerous fluoride[7], lead chlorofluoide[8,9,10], aluminium fluoride complex [11,12], and ferric fluoride complex[13,14,15] etc. Above all, the gravimetric or volumetric process of the lead chlorofluoride[10], though troublesome in the process, seems to have the accuracy and general applicability. Also the volumetric method of thorium fluoride, showing comparatively high accuracy, is widely used for the direct titration of soluble fluoride.

The direct titration of fluoride with aluminium ion, using methyl red[11] or eriochromecyanine [12] as indicator, has been reported to possess fair accuracy, though leaving some scopes for discussion. As to the direct titration with ferric ion, various methods have been proposed. The Guyot-Greeff method[13,14] is the titration with a standard ferric chloride solution against sodium fluoride solution containing thiocyanate as indicator until the permanent red color is obtained. As a modification of the Guyot-Greeff method, Fairchild[15] added an excess of ferric chloride to the fluoride solution, estimating the excess of ferric chloride by the addition of potassium iodide and titration of liberated iodine by means of thiosulfate. Another process proposed by Visintin[16] is the titration of neutral sodium fluoride solution with ferric chloride using bromophenol blue as indicator. All of these methods of the titration with ferric ion based on the reaction : $6NaF+FeCl_3=Na_3FeF_6+3NaCl$, but the sodium ferric fluoride thus formed is somewhat soluble in water and makes the end point unclear, accordingly the titration can not be performed accurately. For the colorimetric determination of fluoride, some processes have been published, namely, the determination of fluoride by measuring colorimetrically the bleaching power of soluble

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fluoride against the coloring complex which is obtained by the action of ferric ion with such indicators as the salicyclic acid proposed by Kortüm-Seiler[17] or the sulfosalicylic acid proposed by Monnier and others[18]. These methods seem to have disadvantages because the procedure is tedious and can not obtain the strictly accurate results in comparison with the volumetry.

In view of the necessity of the rapid and accurate process for the determination of fluorine applicable in the studies and in the technical analyses of sodium fluoride industrially produced, the author has established a new volumetric process using ferric nitrate as a standard solution. In the titration of sodium fluoride with ferric ion according to the previously published methods, there is a defect that the end point is not so clear. This seems to be due to the fact that the following two reactions advancing simultaneously, and accordingly the formation of sodium ferric fluoride is hardly complete.

$$3NaF+Fe(NO_3)_3=FeF_3+NaNO_3,$$
$$3NaF+FeF_3=Na_3FeF_3.$$

But this reaction, according to the author's experiments, is deemed to advance almost quantitatively in the medium containing more than 50% alcohol. The proposed method is characteristic in using the optimum amount of alcohol in the course of titration and using sodium salicylate as indicator that shows sharp violet color with minute amounts of ferric ion under the proper pH value.

The present work describes the effects of several variables on the accuracy of the volumetry, namely the sensitivity and the amounts of indicator, the pH values and the concentration of alcohol in the medium, the concentration of fluoride taken, the steps for adding alcohol and finally proposed a satisfactory process under proper conditions.

Experimental

1. *The color reaction of salicylic acid with ferric ion of various concentration.*

The salicylic acid shows sharp violet color with ferric ion even in very dilute solution and is used as indicator for the colorimetric determination of minute amount of ferric ion[19,20]. The author has compared the sensitivity of salicylic acid with that of the thiocyanate and various concentrations of ferric nitrate. As shown in table I, the thiocyanate, with low concentration of ferric ion, shows light to faint yellow color and the sensitivity of thiocyanate seems to be inferior to that of the salicylic acid.

To go into details, the color obtained by salicylic acid with 0.001 to 0.0001 *N* of ferric nitrate were compared similarly. It is clear from the results given in table II, that ferric ion is detected at the normality of 0.0002 to 0.0004 *N* (Fe 0.372 to 0.745 mg per 100 cc) by salicylic acid resulting light to slight violet color.

2. *The influence of* pH *values of the medium upon the color of ferric salicylate.*

Using Walpole's buffer solutions[21] containing various proportions of sodium acetate and hydrochloric acid, these being indifferent with either ferric or salicylate ions, ferric nitrate solutions of various pH values from 1 to 5 were

Table I. *Comparison of sensitivity of salicylic acid and that of potassium thiocyanate with ferric ion.* (1 drop of 1% salicylic acid alcohol solution or of *N*/10 *KSCN* is added for every 10 cc of ferric nitrate solution of various concentrations in a test tube.)

normality of $Fe(NO_3)_3$	concentration g/100 cc		color with salicylic acid	color with *KSCN*
	as $Fe(NO_3)_3 9Aq$	as $Fe^{\cdots}$		
0,1 *N*	1,3467	0,18616	deep reddish violet	deep orange red
0,01	0,13467	0,018616	violet	orange
0,001	0,01347	0,001862	〃	light yellow
0,0001	0,00135	0,000186	slight violet	faint yellow
0,00001	0,000135	0,0000186	colorless	colorless

Table II. *Color reaction of salicylic acid with ferric ion of low concentrations.* (1 drop of 1% salicylic acid alcohol solution is added to every 10 cc of ferric nitrate solution of various concentrations in test tube, and the pH of media are about 4,0-4,5.)

normality of $Fe(NO_3)_3$	concentration g/100 cc		color with salicylic acid
	as $Fe(NO_3)_3 \cdot 9Aq$	as $Fe^{...}$	
0,0010	0,01347	0,001862	violet
0,0008	0,01078	0,001490	〃
0,0006	0,00803	0,001117	light violet
0,0004	0,00539	0,000745	〃
0,0002	0,00269	0,000372	slight violet
0,0001	0,00135	0,000186	〃

Table III. *Influence of pH value of medium upon color of ferric salicylate.* (1 drop of 1% salicylic acid alcohol solution is added to every 10 cc 0.001 *N* Fe $(NO_3)_3$ solution of various pH values in test tube.)

pH of medium	color of original solution	color after addition of salicylic acid
1,09	faint yellow	colorless
2,32	〃	light violet
3,09	slight yellow	violet
4,19	〃	light reddish violet
5,29	〃	slight reddish violet

prepared and treated with salicylic acid and the color reactions were compared as shown in table III. The color intensity of ferric salicylate is much affected by the pH value of the medium, and the optimum pH value at which deep violet color resulted is at about 3. The pH found agrees with that (pH 2.7) color reported by Mehling [20] and Kortüm-Seiler [17] for ferric salicylate and that(pH 3) obtained by Monnier and others [18] for the violet complex of ferric sulfosalicylate.

3. *The influence of the amount of indicators upon the accuracy of the titration.*

In the titration of sodium fluoride with standard ferric nitrate, the effect of the sort and the amount of indicators upon the accuracy of the titration were found empirically. Every 10 cc of 0.3 *N* sodium fluoride was placed in a small Erlenmyer flask and 5 cc of Walpole's buffer solution of pH 3.09 (34.0 g of crystalline sodium acetate and 20 cc of 38% HCl are dissolved in water and make up to 250 cc) and various amounts of indicator solution were added as described in table IV; titrate with 0.15 *N* ferric nitrate solution using a micro buret until the orange yellow color was established, this step was resulted at about 8 cc of titrant, then decolorize the solution with addition of 25 cc of absolute alcohol and stir for about 30 seconds. The alcohol concentration of the medium at the end point is about 50% by volume. Further continue the titration until the slight pink color was not discharged (over the white surface) by stirring for 30 seconds. Sodium fluoride and ferric nitrate used were E. Merck's reagents and the strength of the fluoride and the ferric nitrate solutions were determined by the lead chlorofluoride method [10] and by the Mohr's iodometry respectively.

As shown in table IV it is hard to find any difference of titrated values in every cases using salicylic acid and sodium salicylate as indicator, and the necessary amount of each indicator is about 2 cc of 0.1 Mol solution for 50 cc of total volume. But for keeping a constant pH of 3.09, the use of sodium salicylate is more advisable than that of salicylic acid.

4. *The effect of alcohol concentration of the medium upon the accuracy of the titration.*

In the case of the titration of sodium fluoride

Table IV. *Influence of amount of indicators upon accuracy of the titration.* (9.96 cc of 0.3000 *N NaF*, 5 cc of Walpole's buffer solution, 25 cc of alcohol, 0,25-3,00 cc of indicator solutions are used. For every titration using micro buret. Final volume at end point is about 50 cc.)

indicator applied	amount of indicator added, cc	$Fe(NO_3)_3$, 0,1500*N* cc	*NaF* recovery %	appearance of end point
0,1 Mol	0,25	10,08	101,2	not so sharp
salicylic	0,50	10,04	100,8	〃
acid in	1,00	9,97	100,1	〃
50%	2,00	9,96	100,0	sharp
alcohol	3,00	9,95	99,9	〃
0,1 Mol	0,25	10,07	101,1	not so sharp
sodium	0,50	10,04	100,8	〃
salicylate	1,00	9,97	100,1	sharp
in 50%	2,00	9,96	100,0	〃
alcohol	3,00	9,96	100,0	〃

Table V. *Effect of alcohol concentration of medium upon accuracy of titration.* (5.00 cc of 0.2987 *N NaF* solution, 2;5 cc Walpole's buffer solution, 1 cc of 0,1 M sodium salicylate dissolved in 50% alcohol solution, various amount of alcohol are used. Titrate with micro buret.)

alcohol conc'n. in medium vol %	alcohol added cc	$Fe(NO_3)_3$ 0,1538 *N* cc	*NaF* recovery %	appearance of end point
0	0	4,25 ?	87,54 ?	orange yellow, uncertain
17,2	2,50	4,52	93,11	light pink, unsharp
29,1	5,00	4,67	96,20	〃 〃 〃
38,0	7,50	4,76	98,05	light pink, relatively sharp
44,8	10,00	4,82	99,29	light pink, sharp
50,3	12,50	4,85	99,90	〃 〃 〃
54,8	15,00	4,85	99,90	〃 〃 〃

with standard ferric nitrate as described above, the alcohol concentration of the medium is seemed to be one of the most important factors affecting the accuracy. In these experiments various amounts of alcohol were added prior to every titration. As shown in table V, at alcohol concentrations lower than 50%, owing to the incomplete precipitation of sodium ferric flouride, the end points appeared early and were unsharp. The sufficient alcohol concentration for the reaction is found to be above 50% by volume at the end point.

5. The accuracy of the titration when various concentrations of sodium fluoride and ferric nitrate are used.

Using every 5 cc of sodium fluoride of the various normalities and ferric nitrate of the corresponding normalities, the concentration-accuracy relationships were studied and the results were tabulated in table VI. The alcohol was added in the course of the titrations when the orange yellow color was established by the addition of ferric nitrate (about 4 cc).

At lower concentrations than 0.3 *N* of sodium fluoride, especially at 0.1 *N*, the end point is not so sharp owing to the appearance of intermediate yellow color and lower results are obtained. Such results are probably caused by the low concentration and solubility of sodium ferric fluoride formed in media. The higher

Table VI. *Accuracy of titration when sodium fluoride and ferric nitrate having various normalities are used.* (4.979 cc of *NaF* having various normalities, 2,5 cc Walpole's buffer solution, 1 cc of 0,1 *M* sodium salicylate dissolved in 50% alcohol, and 12,5 cc of alcohol are used in each titration using micro buret, the final alcoholic concentration of medium is about 50 vol. % at the end point.)

conc'n of *NaF* *N*	$Fe(NO_3)_3$ sol'n. *N*	$Fe(NO_3)_3$ sol'n. cc	*NaF* recovery %	appearance of end point
0,5000	0,2500	5,02	100,8	light pink, sharp
0,4000	0,2000	5,01	100,6	〃 〃 〃
0,3500	0,1750	4,99	100,2	〃 〃 〃
0,3000	0,1500	4,98	100,0	〃 〃 〃
0,2500	0,1250	4,96	99,6	〃 〃 〃
0,2000	0,1000	4,95	99,4	〃 〃 〃
0,1000	0,0500	4,78	96,0	ligh yellowish pink, not so sharp

Table VII. *The optimum step when alcohol should be added in the course of titration.* (5 cc of 0.2935 *N NaF* solution, 2,5 cc of Walpole's buffer solution, 1 cc of 0,1 *M* sodium salicylate dissolved in 50% alcohol are used for every titration and 12,5 cc of alcohol is added at various steps of titration.)

adding alc. when following amt. of titrant were added	color of medium before adding alcchol	color of medium after adding alcohol	$Fe(NO_3)_3$ used 0,1498 *N*	*NaF* recovery %
0 cc	colorless	colorless, sl. opalescent	4,84cc	98,8
1,25	yellowish turbid	colorless opalescent	4,82	98,4
2,50	yellow turbid	colorless opalescent	4,84	98,8
3,00	yellow turbid	colorless opalescent	4,88	99,6
3,75	deep yellow turbid	colorless optalescent	4,89	99,8
4,00	orange yellow turbid	colorless opalescent	4,90	100,0
4,60	deep orange yellow turbid	colorless opalescent	4,91	100,2

results are obtained with the higher concentrations of sodium fluoride, though their end points are sharp. It is aupposed that the higher results obtained in higher normalities of fluoride are probably due to the some absorption of the color complex of ferric salicylate by the colloidal precipiation of sodium ferric fluoride formed in the media. In general it is advisable to use about 0.3 *N* of sodium fluoride (1.26 g *NaF* per 100 cc) and 0.15 *N* of ferric nitrate for attaining the high accuracy.

6. *The optimum step when alcohol should be added in the course of titration.*

In this experiment the effect of adding alcohol at an early or later time in the course of titration upon accuracy was studied and the results obtained were given in table VII.

When the alcohol is added too early in the course of titration, somewhat early end points are observed and therefore lower results are obtained, while the contrary results are obtained when the alcohol is added close to the equivalent point. For obtaining accurate results, it is desirable to add alcohol when the medium exhibits orange yellow color, and in the present case, after adding 4 cc of titrant.

7. *The proposed method and its applications in analyses of sodium fluoride and other fluorine compunds.*

Reagents :

a) Standard 0.15 *N* (0.05 *M*) ferric nitrate solution; Pure crystalline $Fe(NO_3)_3$ 9Aq(20,2g) is dissolved in 1000 cc of water and filtered if necessary. The strength of the solution is

determined by the analysis of ferric ion. 1 cc. of the solution is corresponding to 0.0057 g fluorine.

b) Buffer solution; Walpole's buffer solution of pH 3.09 is prepared by dissolving 34,0 g of crystalline sodium acetate and 20 cc of 38% hydrochloric acid in water and making up to 250 cc.

c) 0.1 *M* sodium salicylate alcohol solution; 1,60 g of pure sodium salicylate is dissolved in 100 cc of 50% alcohol and stocked in a brown bottle to shield from light.

d) Absolute or 95% alcohol; redistilled in presence of pure lime to eliminate any traces of fluorine and volatile acids.

Procedure :

Take 5 cc of about 0,3 *N* sodium fluoride solution (containing about 1,26 g *NaF* or 0,57 g fluorine per 100 cc) in a small Erlenmyer flask, add 2,5 cc of the buffer solution and 1 cc of 0.1*M* sodium salicylate alcohol solution and stir well. Here the standard 0,15 *N* ferric nitrate solution is added slowly from a micro-buret until the solution becomes orange yellow, which is then becolorized completely with the addition of 12,5 cc of absolute alcohol (or 13 cc of 95% alcohol) and stir for 30 seconds and continue the titration with standard solution. In this case the slow addition of the ferric nitrate (one drop every 2 or 3 seconds) is imporant. Near the end point the addition is still slower with good mixing, and the end point is reached when slight pink color is not discharged by stirring for 30 seconds over the white surface. In the course of the titration, few drops of 50% alcohol provided in a small washing bottle will be used for washing the wall of the flask if necessary. 1 cc of 0,15 *N* ferric nitrate is corresponding to 0,0126 g sodium fluoride or 0,0057 g fluorine. The procedure must be carried out in difuse light for fear of color fading by direct sunlight.

The alcohol may be recovered occasionally from the waste liquid by distillation in presence of excess lime.

Applications in analyses of sidium fluoride and other fluorine compounds :

In this titration, divalent and polyvalent metallic ions, phosphate, silicate, borate, carbonate, sulfide, and reducing substances acting on ferric ion etc. have the interfering action, therefore, prior to the titration, it is necessary to separate fluorine from the interfering substances by distillation of the sample according to the method of Willard and Winter[6]. The distillate is neutralized with dilute sodium hydroxide and then with hydrochloric acid to the transition point of *p*-nitrophenol. When only carbonate is present, for example, in analysis of water extract of crude sodium fluoride produced by the process of fusing fluorspar with sodium carbonate and silica, it is merely sufficient to neutralize the extract with dilute hydrochloric acid using *p*-nitrophenol as indicator and expell almost all cardon dioxide before the titration.

For determining the concentration of sobium fluoride solution containing usually about 2,8 g *NaF* per 100 cc and some sodium carbonate obtained by the extraction of the crude product

Table VIII. *Analyses of sodium fluoride solution produced by industrial process.*

sample no.	by lead chloro fluoride method*	by proposed method**
1	2,72 g *NaF* per 100 cc	2,71 g *NaF* per 100 cc
2	2,74 〃	2,75 〃
3	2,80 〃	2,80 〃
4	2,83 〃	2,83 〃
5	2,79 〃	5,81 〃
6	2,83 〃	2,83 〃

* obtained by a single analysis,

** average values of tiplicate tritration.

produced industrially as described above, take 25 cc of the clear sample solution into 50 cc measuring flask, and 1 drop of *p*-nitrophenol solution (0,25 g. *p*-nitrophenol per 100 cc of water) then neutralize with dilute *HCl* (1 : 4) with stirring to expell carbon dioxide, and make up to 50 cc. A 5 cc aliquot of the solution is used for titration by the above procedure. Some of the analytical data are shown in table VIII. Comparing with the results obtained by the lead chlorofluoride method[10], it is proved that the results obtained by the proposed method show fairly good agreement with those obtained by the lead chlorofluoride process which is recognized as standard method for the determination of fluorine in agricultural chemicals.

Summary

The present work describes on a new volumetric method for the determination of fluorine, consisting in the titration in aqueous-alcoholic medium with ferric nitrate as standard solution and sodium salicylate as indicator, and also on its application in analyses of sodium fluoride and other fluorine compounds.

This paper reports the experimental results obtained in the fundamental studies of the various factors influencing the accuracy of the volumetry, *viz.* the sensitivity aud the necessary amount of sodium salicylate used as indicator, the pH value, the alcohol concentration of the titration medium, the concentration of the fluoride taken for the determination, and the time when alcohol should be added in the course of the titration. A rapid and accurate volumetric method is then proposed.

The proposed method is characterstic in using sodium salicylate as indicator which shows sharp violet color with minute amount of ferric ion in pH 3 medium (controlled with the buffer solution), then titrating with standard ferric nitrate, and adding proper amount of alcohol (the alcohol concentration at the end point should be above 50% by volume) during the titration when the medium becomes orange yellow in order to complete the reaction.

Divalent and polyvalent methallic ions, phosphate, silicate, borate, carbonate, sulfide and reducing substances acting on ferric ion interfere. It will be necessary to seperate fluorine from these interfering substances by distillation. The interference of carbonate may be overcome simply by acidifying to *p*-nitrophenol end point.

In analyses of sodium fluoride solutions, the results obtained by the proposed method showed fairly good agreement with those obtained by the lead chlorofluoride process, which is recognized as standard method for the determination of fluorine in agicultural chemicals.

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