

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]
**THE VOLUMETRIC ESTIMATION OF FLUORINE BY MEANS OF
CEROUS NITRATE**

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Among the compounds which have been employed in the gravimetric determination of fluorine are: calcium fluoride,¹ barium fluoride,² lanthanum fluoride,³ thorium fluoride⁴ and lead chlorofluoride.⁵ While good results have been reported in most cases, none of the gravimetric methods seems to possess the accuracy and general applicability that are necessary for a standard determination.

Omitting acidimetric titrations of hydrofluoric and fluosilicic acids, a list of volumetric procedures includes the methods of Hempel and Scheffler,⁶ Wagner and Ross,⁷ Penfield,⁸ de Boer,⁹ Steiger¹⁰ and Merwin,¹¹ Guyot¹² and Greeff¹³ and Fairchild.¹⁴ The first three mentioned involve the evolution of silicon tetrafluoride which is either measured or absorbed and determined acidimetrically. Such procedures possess the advantage of being applicable in the presence of phosphates, but have the disadvantage that their accuracy depends to no small degree upon the skill and experience of the analyst. The method of de Boer depends upon the fact that the color produced by a zirconium solution when treated with sodium alizarin sulfonate is bleached by fluoride ions but not by other halogens at low acid concentrations.

The Steiger-Merwin and Guyot-Greeff methods are probably the two most widely used at the present time. The former involves the removal of the yellow color from a hydrogen peroxide titanium solution by fluorides, while the latter consists in the formation of FeF_6^{---} ion when ferric chloride is added to a fluoride solution, the indicator according to Greeff being SCN^- . Critical studies of these two procedures have been made by Fresenius¹⁵ and by Treadwell and Köhl,¹⁶ who employed

¹ Berzelius, *Pogg. Ann.*, 1, 169 (1824).

² Rose, *Ann.*, 72, 343 (1849).

³ Meyer and Schulz, *Z. angew. Chem.*, 38, 203 (1925).

⁴ Pisani, *Compt. rend.*, 162, 791 (1916).

⁵ Starck, *Z. anorg. Chem.*, 70, 173 (1911).

⁶ Hempel and Scheffler, *ibid.*, 20, 1201 (1899).

⁷ Wagner and Ross, *J. Ind. Eng. Chem.*, 9, 1116 (1917).

⁸ Penfield, *Z. anal. Chem.*, 21, 120 (1882).

⁹ De Boer, *Chem. Weekblad*, 21, 404 (1924).

¹⁰ Steiger, *THIS JOURNAL*, 30, 219 (1908).

¹¹ Merwin, *Am. J. Sci.*, 28, 119 (1909).

¹² Guyot, *Compt. rend.*, 71, 273 (1870).

¹³ Greeff, *Ber.*, 46, 2511 (1913).

¹⁴ Fairchild, *J. Wash. Acad. Sci.*, 20, 141 (1930).

¹⁵ Fresenius, Schröder and Frommes, *Z. anal. Chem.*, 73, 65 (1928).

¹⁶ Treadwell and Köhl, *Helv. Chim. Acta*, 9, 470 (1926).

the potentiometer as an end-point indicator for the ferric chloride titration. In a more recent modification of the Guyot-Greeff method, Fairchild 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. Good results were obtained when the variables, temperature, time and concentration were carefully controlled. Although very satisfactory under the proper conditions, the limited ranges of these two methods and the existence of several variables affecting their accuracy make the development of better procedures for the analysis of fluorides highly desirable.

Trivalent Cerium as a Precipitant.—The use of lanthanum acetate as a precipitant for fluoride ions by Meyer and Schulz suggested to us possibilities in the use of cerium. Attempts at a gravimetric separation of cerous fluoride were, however, unsatisfactory on account of the gelatinous character of the precipitate. What results were obtained indicated a high degree of adsorption on the surface of the cerous fluoride. This was borne out by further attempts to obtain a potentiometric end-point without filtration.

A Back Titration Method.—Since the gravimetric separation of cerous fluoride proved to be impracticable due to adsorption, a volumetric modification was investigated. It was hoped that the error introduced in the gravimetric method by adsorption might be eliminated in the volumetric procedure.

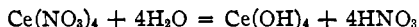
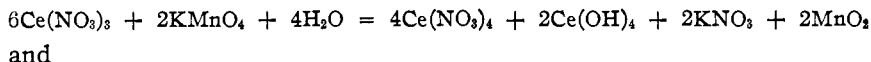
Materials.—The sodium fluoride which was used as a primary standard was prepared by adding an excess of hydrofluoric acid to sodium bicarbonate, the fluoride thus formed being dried and finally fused in platinum. The reagent quality hydrofluoric acid was specially purified for the above preparation by repeated distillation. Sodium fluoride obtained by this method gave a clear water solution. The purity of this salt was checked by conversion to the sulfate.

White reagent quality cerous nitrate was used in these experiments. Samples of this material were ignited to the oxides and the cerium content determined by Metzger's bismuthate method¹⁷ and the method of Lenher and C. Meloche.¹⁸ The results of these analyses showed the residue to consist of 98.6% CeO₂. The remainder of the sample was found to be oxides of the rare earths. Calculations indicate that in the case of the largest samples reported in the table error due to rare earth content is not greater than 0.0002 g. (about 0.00003 g. of NaF per 10 cc. of the titrating solution used). This is due to a proximity of molecular and atomic weights. Correction for impurities was therefore neglected.

Method.—The proposed method involved the addition of an excess of a known cerous nitrate solution to a neutral solution of sodium fluoride, and titration of the excess cerium by means of potassium permanganate, according to the method of Lenher and C. Meloche. This method depends upon the equations

¹⁷ Metzger, *THIS JOURNAL*, **31**, 523 (1909).

¹⁸ Lenher and C. Meloche, *ibid.*, **38**, 66 (1916).



An excess of zinc oxide is added to take care of the nitric acid produced.

Before application of the permanganate titration to the indirect determination of fluoride, it was necessary to test the accuracy of the cerium determination. Table I contains a few typical results obtained by the direct titration of cerous nitrate solutions with permanganate. The titrations were made in the usual way in the presence of zinc oxide at a temperature of 80°. The addition of 0.5–1.0 g. of zinc sulfate to the solution aided materially in the coagulation of the precipitate. In this and in all subsequent work the concentration of stock solutions was carefully checked by weighing the residues resulting from the evaporation of measured volumes.

TABLE I

Stock solution of $\text{Ce}(\text{NO}_3)_3$ —10 cc. = 0.0377 g. of CeO_2					
(a) Using macroburet			(b) Using microburet		
CeO_2 added, g.	CeO_2 calcd., g.	Vol. of sample, cc.	CeO_2 added, g.	CeO_2 calcd., g.	Vol. of sample, cc.
0.0302	0.0301	50	0.00152	0.00160	50
.0151	.0150	50	.00114	.00110	50
.0075	.0075	50	.00076	.00071	50
.0038	.0035	50	.00076	.00068	50
			.00076	.00065	50

An examination of data indicates that under optimum conditions an agreement of 0.0001 g. of CeO_2 may be expected. Since this represented a satisfactory value, the method was next applied to the estimation of excess Ce^{+++} in the fluoride titration.

The Indirect Titration of Fluorides.—A neutral solution of sodium fluoride having a volume of about fifty cubic centimeters was treated with an excess of a known solution of cerous nitrate. The solution was then heated to about 80°, 0.5 g. of zinc oxide was added and the titration was made with *N*/40 potassium permanganate. Instead of titrating the solution to the first detectable change of color in the supernatant liquid, the precipitated MnO_2 , CeF_3 and $\text{Ce}(\text{OH})_4$ were removed by means of a Gooch crucible slightly before the equivalence point was reached. The filtrate was then reheated, a slight excess of zinc oxide was added and the titration with permanganate completed. Filtration was necessary at this point since it was discovered that otherwise an over-titration was obtained due to adsorption of MnO_4^- ion.

Using this method it was possible to detect quantities of fluoride ranging from 0.1 to 0.001 g. with an accuracy of about 0.0003 g. Characteristic results are given in Table II.

Although exhibiting a fair degree of accuracy, this procedure is rather cumbersome and difficult for one not familiar with it. The color and

TABLE II

RESULTS OF EXPERIMENTS					
NaF added, g.	NaF found, g.	Volume of sample, cc.	NaF added, g.	NaF found, g.	Volume of sample, cc.
0.1502	0.1502	50	0.0108	0.0108	50
.1502	.1502	50	.0072	.0070	100
.0719	.0722	50	.0072	.0072	100
.0108	.0108	50	.0072	.0072	100

extent of coagulation of the precipitate give some indication of the point at which filtration should be made, but this cannot usually be determined without two or three trials upon fluoride solutions of equal concentration. This necessitates the use of aliquots. It is important that the filtration be performed as close to the equivalence point as possible, since the error due to adsorption is then at a minimum. Ions such as phosphate and oxalate which precipitate cerium interfere with the determination. This includes hydroxyl ion since if the *PH* be greater than the value resulting from the buffering effect of ZnO , $Ce(OH)_3$ will be precipitated.

Direct Titration.—In the search for a better scheme of analysis it was decided to try adsorption indicators, hoping that a direct titration with cerium would be possible. Samples of fluoride were titrated with cerous nitrate at room temperature, using a variety of indicators. Among these two were discovered which exhibited a color change at the stoichiometric point: amphi magenta and diiodophenolsulfonephthalein. After trying various concentrations of the phenolsulfonephthalein, the end-point (from a reddish-brown to a yellow) was not thought to be sufficiently sharp to warrant further investigation.

Amphi Magenta as an Indicator.¹⁹—The amphi magenta in a concentration of 20 mg. to a liter was found to give a very satisfactory indication of the equivalence point at which it changed from a deep blue to a less intense purple. Results using this indicator are given in Table III.

TABLE III

20 Cc. of solution containing the indicator was used in all cases. Stock solution of $Ce(NO_3)_3$ —10 cc. = 0.0401 g. of CeO_2

(a) Using macroburet		(b) Using microburet	
Stock NaF—10 cc. = 0.1502 g.		Stock NaF—10 cc. = 0.0015 g.	
NaF added, g.	NaF found, g.	NaF added, g.	NaF found, g.
0.1502	0.1503	0.00075	0.00081
.1502	.1502	.00075	.00084
.0451	.0452	.00075	.00074
.0451	.0454	.00075	.00064
.0300	.0300	.00075	.00074
.0150	.0150		

¹⁹ Amphi magenta was obtained from the National Aniline and Chemical Company and was described by them as made by diazotizing *p*-aminoethylacetanilide and coupling with 1,8-dihydroxynaphthalene-3,6-disulfonic acid.

The accuracy of this determination is seen to be about 0.0001 g. of sodium fluoride under the best conditions. Although more dilute solutions of magenta were tried, the end-point seemed most satisfactory at the concentration given. A very slight decrease in the sharpness of the color change was observed in the case of the smaller quantities of fluoride.

Methyl Red as an Indicator.—Kurtenacker and Jurenka²⁰ have recently published a procedure involving the use of methyl red as an indicator for the titration of fluorides with cerous nitrate. Samples of sodium fluoride were analyzed according to their procedure and very satisfactory results obtained. Titrations were made at a temperature of 80° as recommended. The results are given in Table IV.

TABLE IV

Stock solution $\text{Ce}(\text{NO}_3)_3$ —10 cc. = 0.0401 g.			
Using macroburet		Using microburet	
Stock solution NaF—10 cc. = 0.1502 g.		Stock solution NaF—10 cc. = 0.0015 g.	
NaF added, g.	NaF found, g.	NaF added, g.	NaF found, g.
0.1502	0.1505	0.00075	0.00071
.1502	.1500	.00075	.00071
.0300	.0297	.00030	.00044
.0300	.0298	.00030	.00023
.0300	.0296	.00030	.00022

These results exhibit an accuracy of about 0.0001, with the microburet and 0.0004 g. with the macroburet. It will be noticed that the procedure is satisfactory for the detection of quantities of fluoride amounting to less than a milligram.

It was impossible to compare these values with those of Kurtenacker and Jurenka, since similar data were not published by them. Although claiming an ability to detect a few milligrams of fluorides, Kurtenacker and Jurenka reported difficulty in obtaining results in agreement with the theoretical values based upon the cerium content of the solution added in the titration. A deviation of as much as 4% was reported in some cases. Our results were not in agreement with these findings since no such discrepancy was observed.

The anomalous results obtained by Kurtenacker and Jurenka may possibly be explained in the following manner. The change of the methyl red at the end-point was apparently attributed by them to hydrolysis of the cerous nitrate, the nitric acid liberated causing a change of P_{H} . In case the end-point is due to a change of P_{H} , it would seem logical to run a blank titration in order to determine what excess of cerous nitrate was necessary to change the color of the indicator. When an aqueous solution of the indicator was titrated with the standard cerous nitrate solution, 2.5 cc. was required to change the color of the methyl red. No color change occurred under similar circumstances with the amphi ma-

²⁰ Kurtenacker and Jurenka, *Z. anal. Chem.*, **82**, 210 (1930).

genta. If, however, fluoride is present, the titration with cerous nitrate gives a color change with the indicator when an equivalent amount of cerous nitrate has been added to the fluoride. When quantities of cerous nitrate which were insufficient to convert the indicator to the acid form were titrated with a sodium fluoride solution, the color of the methyl red gradually changed from yellow to red and at the equivalence point the solution again became yellow. The addition of excess cerium or excess fluoride now caused a change, respectively, from yellow to red or from red to yellow. From this point on the end-point was reversible. Thus it seems likely that in the presence of Ce^{+++} ions, precipitated cerous fluoride preferentially adsorbs indicator and in the presence of fluoride ions, the cerous fluoride preferentially adsorbs fluoride.

No end-point was obtained in the presence of sulfate ion either in the case of the amphi magenta or in the case of the methyl red. Attempts at varying the P_H resulted either in the precipitation of cerous hydroxide or in a change of the color of the indicator. In addition to sulfate ions, in general, any ion such as phosphate or oxalate capable of precipitating cerium will interfere with the determination.

Summary

An indirect method and two direct methods for the volumetric estimation of fluorides with cerous nitrate are given. Neutral solutions must be used in all cases.

The indirect method consists of adding a known excess of cerous nitrate to a fluoride solution and determining the excess cerium by means of a back titration with permanganate. This method is not recommended because it is cumbersome and the chance for error is relatively large.

The direct methods involve the titration of neutral fluoride solutions with cerous nitrate using methyl red and amphi magenta as indicators. These methods are very satisfactory for ordinary quantities of fluoride. The methyl red seems to be slightly better in the case of the smaller samples. Explanation of the indicator change on the basis of adsorption seems plausible.

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