[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Potentiometric Titration Method for Fluorine

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Introduction

A potentiometric titration of fluorine requires an indicator electrode for fluoride ions or for the substance that is reacting with the fluoride. Since no electrodes are available for the fluoride ion an electrode must be selected which changes its potential with the concentration, or activity, of the ions of the reagent. The fluoride may be precipitated or caused to form a complex ion such as $FeF_6^{\equiv}$ or $AlF_6^{\equiv}$. Treadwell and Köhl[2] were the first to propose a potentiometric method for fluorine, their procedure being based on the formation of $FeF_6^{\equiv}$, a volumetric method which had been previously investigated by Greeff[3] using potassium thiocyanate as a color indicator. Later these two authors made use of aluminum chloride for the titration,[4] the aluminum ions decomposing the iron cryolite complex, and Treadwell and Bernasconi applied the method to the determination of aluminum and magnesium in the presence of each other.[5] In the papers of Treadwell and Köhl the conductimetric titration of pure fluoride solutions with aluminum ions was reported.

The insoluble fluorides are few in number and the precipitation titrations are limited to the formation of the fluorides of the alkaline earths, thorium and the rare earths. Most of the volumetric methods are based on the precipitation of calcium fluoride, although one useful and interesting method involves the titration of chloride secured from lead chlorofluoride.[6] Potentiometric methods depending purely on the precipitation of an insoluble fluoride are still further limited because of the lack of suitable indicator electrodes, and thus far no such methods have been advanced.

Kurtenacker and Jurenka[7] titrated fluoride with cerous nitrate using methyl red as an indicator and their work indicates that cerous fluoride is quite insoluble and very stable. Batchelder and V. Meloche[8] did further work on the titration using methyl red and their work corroborates the statement anent the insolubility of cerous fluoride. The stability of the precipitate is shown by the results secured by Batchelder and V. Meloche using their indirect method for fluorine in which an excess of cerous nitrate is added and the excess determined by potassium permanganate using the method of Lenher and C. Meloche.[9] Thus precipitation of fluoride as

(1) J. T. Baker Chemical Company Fellow in Analytical Chemistry.

(2) Treadwell and Köhl, *Helv. Chim. Acta*, **8**, 500 (1925).

(3) Greeff, *Ber.*, **46**, 2511 (1913).

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

(5) Treadwell and Bernasconi, *ibid.*, **13**, 500 (1930).

(6) Hawley, *Ind. Eng. Chem.*, **18**, 573 (1926).

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

(8) Batchelder and V. Meloche, THIS JOURNAL, **53**, 2131 (1931); **54**, 1319 (1932).

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

cerous fluoride seems particularly suited for a potentiometric method provided some electrode can be obtained to serve as an indicator for cerous ions.

Development and Theory of Method.—Unfortunately a cerous–ceric combination cannot be used as an indicator since ceric fluoride is only slightly soluble also, but still more soluble than the cerous salt. A suitable electrode for cerous cerium has been found in an application of the ferri–ferrocyanide electrode.[10]

Cerous cerium has been determined by oxidation with potassium ferricyanide by Tomiček,[11] by precipitation as $Ce_4[Fe(CN)_6]_3$ by Treadwell and Chervet[12] and by precipitation as $CeKFe(CN)_6$ by Atanasiu.[13] Atanasiu performed the titration at 65° in a solution containing 30% ethyl alcohol. A repetition of this work checked his results and it was found possible to determine fluoride indirectly by adding an excess of cerous nitrate and determining the excess potentiometrically with potassium ferrocyanide. However, a direct method was desired and the insoluble $CeKFe(CN)_6$ was used to furnish an indicator electrode for cerous ions in the following manner. Kolthoff[14] employed a mixture of potassium ferricyanide and lead ferrocyanide in contact with a platinum electrode as an indicator for lead ions in the potentiometric titration of sulfate with lead nitrate. We have found that a ferricyanide–cerous potassium ferrocyanide mixture acts as a good indicator for cerous ions. The potential of a ferri–ferrocyanide mixture in contact with platinum at 25° is represented by

$$E = e_0 + 0.0591 \log \frac{[Fe(CN)_6^{\equiv}]}{[Fe(CN)_6^{==}]}$$

If the ferrocyanide ions are furnished only by a saturated solution of cerous potassium ferrocyanide, then for the saturated solution

$$[Ce^{+++}]\cdot[K^+]\cdot[Fe(CN)_6^{==}] = \text{Solubility product of } CeKFe(CN)_6$$

and

$$[Fe(CN)_6^{==}] = \frac{k}{[Ce^{+++}]\cdot[K^+]}$$

The potential of the electrode becomes

$$E = e_0 + 0.0591 \log \frac{[Fe(CN)_6^{\equiv}]\cdot[Ce^{+++}]\cdot[K^+]}{k}$$

and if $[Fe(CN)_6^{\equiv}]$ and $[K^+]$ are constant, dilution of the solution during titration being disregarded

$$E = e_0' + 0.0591 \log [Ce^{+++}]$$

The electrode potential is thus shown to be directly proportional to the logarithm of the molar concentration of the cerous ion. Actually such a

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[10] An extended treatment of the ferri–ferrocyanide electrode is given by Kolthoff and Furman "Potentiometric Titrations," second ed., John Wiley and Sons, New York, 1931, pp. 64–69 and 318–34.

[11] Tomiček, *Rec. trav. chim.*, **44**, 410 (1925).

[12] Treadwell and Chervet, *Helv. Chim Acta.* **6**, 550 (1923).

[13] Atanasiu, *J. chim. phys.*, **23**, 501 (1926); *Compt. rend.*, **182**, 519 (1926).

[14] Kolthoff and Furman, Ref. 10, pp. 66 and 331.

simple relation does not apply due to the dependence of the potential of the ferri–ferrocyanide electrode upon the salt concentration of the solution. For large quantities of fluoride or in the presence of large amounts of foreign salts no breaks in potential were obtained at the equivalence point.

Experimental

Apparatus and Materials.—The indicator electrode was a spiral of bright platinum wire and the reference electrode was a saturated calomel cell of the type recommended by Müller and by Kolthoff and Furman.[15] This cell was connected by a long salt bridge of saturated potassium nitrate with the solution to be titrated, a long bridge being necessary because all titrations were performed at 70°. The potentiometer was a Leeds and Northrup Potentiometric Unit, No. 4908. Titrations were made in open beakers using motor stirring and holding the temperature to within 1° of 70° with a small Bunsen flame.

Standard solutions of sodium fluoride of normalities 0.1000, 0.0100 and 0.0050 were prepared by the method used by Hawley[16] and by Allen and Furman.[17] Various amounts were measured out from calibrated pipets.

The cerous nitrate used was a C. P. product which was recrystallized once from water. The cerium content of the solution prepared was determined by oxidizing measured portions to the ceric state with ammonium persulfate using silver nitrate as a catalyst[18] and titrating back with ferrous sulfate which had been checked against standard potassium permanganate. Other analyses were made by evaporating down definite volumes of the solution and igniting the residue to constant weight; the cerium content of the ignited residue was then determined as above. Such analyses gave an average of 97.82% ceric oxide in the residue. The original cerous nitrate contained as impurities nitrates of the other rare earths but as Batchelder and Meloche[19] have pointed out such impurities may be disregarded and the normality of the solution calculated from the weight of the ignited residue, assuming it to be pure ceric oxide. In the present case this method was used since the other rare earth nitrates would change the normality of the solution to fluorine only by about 0.1%.

The potassium ferricyanide was used as an approximately 0.1 molar solution of a C. P. salt free from ferrocyanide. The cerous potassium ferrocyanide was precipitated by mixing equivalent volumes of cerous nitrate and potassium ferrocyanide and the precipitate was washed repeatedly with distilled water by decantation. This substance was used as a suspension in water. It is possible that the precipitate contained some $Ce_4[Fe(CN)_6]_3$, but this would not affect the results in any way.

Outline of the Method.—Some preliminary work had shown that cerous fluoride was precipitated in a gelatinous state and that it adsorbed excess cerous ions to a high degree; no gravimetric determination of fluorine as cerous fluoride could be made. This finding checks the results of Batchelder and Meloche.[8] On the other hand, at 70° and in a solution containing 50% ethyl alcohol by volume good results were secured by the potentiometric titration method. Other temperatures were tried but 70° gave the best results. This is about the same temperature that Atanasiu[13] used in his work. In accordance with the experience of Kolthoff with the sulfate titration, steady potentials were obtained only with 50% alcohol, other concentrations gave erratic readings. The procedure for the titrations recorded in Table I follows. The volumes of sodium fluoride

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(15) Ref. 10, pp. 79–81.

(16) Hawley, *Ind. Eng. Chem.*, **18**, 573 (1926).

(17) Allen and Furman, THIS JOURNAL, **54**, 4625 (1932).

(18) Willard and Young, *ibid.*, **50**, 1379 (1928).

(19) Ref. 8, p. 2132.

used were measured out by pipets and diluted with water and 95% ethyl alcohol so that the final volume contained 50% alcohol. The total volume of the solution titrated was 70–80 ml. for Titrations 1–22, 50 ml. for 23–34 and 25–30 ml. for 35–44. Three to five drops of 0.1 *M* potassium ferricyanide (about 0.25 ml.) and about 10 mg. of the cerous potassium ferrocyanide suspension were then added. The exact amount of the ferrocyanide used may vary somewhat but it should be cut down for the smaller quantities of fluorine. The amount of ferricyanide must be kept fairly constant at the value given. The solution was then heated to 70° and the titration performed at that temperature, not deviating more than one degree. With a 50-ml. buret, volume increments of 0.05 ml. were used near the equivalence point and with the micro-buret the increment was 0.02 ml. The equivalence point was located by computing the difference quotients in the usual manner. With volume increments of 0.05 ml. the break in potential at the equivalence point ranged from about 20 millivolts for the larger amounts of fluorine to about 90 mv. for the smaller quantities. Volume increments of 0.02 ml. used in the case of the micro-buret gave breaks of 30-40 millivolts. The potential curve for Titration No. 40 is given in Fig. 1, and is typical of the course of the potential during every titration.

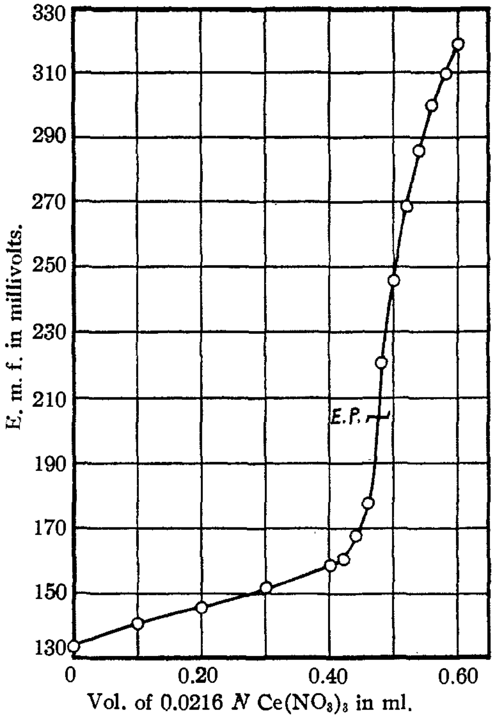

Fig. 1.—Titration of 0.19 mg. of fluorine with 0.0216 *N* cerous nitrate.

TABLE I

TITRATION OF FLUORIDE WITH CEROUS NITRATE SOLUTION

A. Using 50-ml. buret

Nos.	NaF, ml.	F pres., mg.	Mean vol. $Ce(NO_3)_3$, ml.	N of soln.	Mean wt. of F found, mg.	Deviation from correct wt. F Av., mg.	Max., mg.
1- 6	24.98	47.46	25.19	0.0992	47.48	±0.07	−0.17
7–11	9.96	18.92	10.02	.0992	18.89	− .03	− .05
12–17	4.99	9.48	5.08	.0992	9.57	± .09	+ .15
18–22	2.02	3.84	2.01	.0992	3.79	− .04	− .09
23–28	9.96	1.89	2.00	.0500	1.90	± .01	+ .04
			B. Using micro-buret				
29	10.06	0.96	0.464	0.1080	0.95	−0.01	−0.01
30–34	9.96	.95	0.994	.0500	.95	± .00	− .02
35–39	4.99	.47	1.200	.0216	.49	+ .02	+ .03
40–44	2.02	.19	0.476	.0216	.20	+ .01	+ .01

Discussion of Results.—The amount of fluorine that may be titrated by the method ranges from about 0.1 mg. to 50 mg. With a quantity greater than this upper value no break in potential is observed. This is undoubtedly due to the effect of a high salt concentration on the ferri–ferrocyanide potential, but the volume of the solution must not be too large as the method is a precipitation titration and depends on the separation of the cerous fluoride. 0.1 mg. is the lower limit set by the volumes that must be taken. In order to titrate an amount of fluorine smaller than this a more dilute solution of cerous nitrate would have to be used and then the dilution would be so great that the break in potential would not be observed at the equivalence point.

Cerous fluoride is less soluble than cerous potassium ferrocyanide so with large amounts of fluorine all of the ferrocyanide goes into solution as shown by the equation

$$3F^- + CeKFe(CN)_6 \longrightarrow CeF_3 + K^+ + Fe(CN)_6^{---}$$

As cerous nitrate is run in the excess fluoride is first precipitated and when this reaction is completed the ferrocyanide begins to reprecipitate. There is of course no indication of the completion of the cerous fluoride precipitation but since an amount of cerium equivalent to the fluoride precipitated in the beginning will be required for the ferrocyanide the correct equivalence point is shown by the break in the ferri–ferrocyanide potential. With small amounts of fluorine perhaps all of it is precipitated and the method then becomes simply a titration of ferrocyanide with cerous cerium.

The gelatinous nature of cerous fluoride and the presence of cerous potassium ferrocyanide cause poisoning of the platinum electrode. After several titrations the electrode responds very sluggishly and the magnitude of the potential breaks decreases rapidly, hence the electrode must be cleaned often by standing in cleaning solution, then washing with distilled water and igniting.

Interfering Substances.—Ions which give precipitates with cerous cerium must be absent, thus excluding hydroxide, carbonate, phosphate, etc. The solution cannot be acid, as the cerous potassium ferrocyanide is readily soluble in dilute acids. Large amounts of salts completely obscure the potential break but with only small amounts present the titration may be performed. In some experiments with 19 mg. of fluorine good results were secured in the presence of 0.5 g. of sodium chloride. Successful titrations were also made in the presence of 0.5 g. of potassium chloride, of sodium nitrate and potassium nitrate; 0.5 g. of sodium sulfate, however, completely obscured the potential break; in the presence of about 0.2 g. the determination could be made. The breaks in potential with solutions containing foreign salts are not as large as with solutions of pure fluorides. A solution of sodium fluoride containing 19 mg. of fluorine and 50 mg. of sodium silicate and another one with 32 mg. of sodium borate were neutralized to phenolphthalein and titrated. Potential breaks were secured but they came at too large a volume of cerous nitrate.

The method was applied to the determination of the percentage of fluorine in the Bureau of Standards sample of fluorspar, No. 79. The fluorine was extracted by the Berzelius method using a double fusion as outlined in a previous paper.[17] Since the titration works well only with small amounts of fluorine and foreign salts must be present in small concentrations, it was necessary to resort to the use of aliquot parts of the prepared solutions of fluoride. The analyses are recorded in Table II.

TABLE II

DETERMINATION OF FLUORINE IN FLUORSPAR

Using micro-buret, $Ce(NO_3)_3$ 0.1080 *N*

Sample, g.	Tot. vol., ml.	Vol. for titr., ml.	Vol. $Ce(NO_3)_3$			% F			Av. % F
			A	B	C	A	B	C	
0.2427	249.92	10.06	2.244	2.234	2.224	47.13	46.92	46.71	46.92
.3075	249.92	10.06	2.796	2.816		46.35	46.68		46.52
.3648	249.85	10.06	3.309	3.319	3.299	46.23	46.37	46.09	46.23

Average of all titrations, 46.56%. Bureau of Standards value, 46.20%.

The potential breaks at the end-points ranged from 15 to 25 millivolts for 0.02 ml. of reagent. The results run slightly high; this may be due to the foreign salts present or to a slight amount of carbonate which might not have been removed. Considering the small samples involved in the taking of aliquots and the relatively high concentrations of sodium and potassium nitrates in the solutions, the results exhibit a fair degree of accuracy.

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Summary

A potentiometric titration method for fluorine involving the precipitation of cerous fluoride has been developed through a new application of the ferri-ferrocyanide electrode.

The method gives good results for amounts of fluorine ranging from 0.1 mg. to 50 mg. Small amounts of foreign salts may be present but large amounts mask the equivalence point. Ions which precipitate cerous cerium must be absent. Fluorspar has been analyzed by the method.

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