

Analysis of the Residue in the Bredig Vessel.

—During the arcing process there is a moderate amount of wastage which collects in the bottom of the Bredig vessel. Part of this is light gray in color, and has the appearance of the ignited micelle. Analysis of this gray matter (Table II (iii)) shows that it is practically pure platinum. Evidently it consists of the metallic particles which for some reason have failed to collect any appreciable amount of stabilizing material during the arcing process.

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Summary

The colloidal platinum micelle, after isolation

by freezing from Bredig preparations, has been analyzed by microchemical methods. The composition of the micelle of an average preparation can be given by the formula $[3.9\text{Pt}, 1.16\text{PtO}_2, 1.0\text{H}_2\text{Pt}(\text{OH})_6]_n$.

There is evidence that the whole of the water in the micelle is present in the form of the highest hydrate, $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$, which is hexahydroxyplatinic acid.

The total amount of this acid (in the micelle and in solution) is 27.2% of the gross weight of the particles. On continued boiling the greater part of this remains in the micelle, where some appears to be in the interior.

The precipitate formed on aging is less rich in stabilizing material than is the ordinary micelle.

The light-gray wastage in the Bredig vessel is practically pure platinum.

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[CONTRIBUTION FROM MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Use of the Concentration Cell in Quantitative Analysis. II. The Determination of Fluoride¹

BY GEORGE W. LOW, JR.,² AND EVERETT H. PRYDE

The first paper in this series³ described in detail the procedure which may be used for the determination of traces of chloride by employing a simple concentration cell. It was pointed out that the technique involved should be perfectly general and should be applicable to the determination of any substance for which a suitable reversible electrode could be found. In the present paper is given a discussion of the application of this technique to the determination of fluoride. Detailed reviews of the literature on the subject of fluoride determination recently have been given⁴ and therefore need not be considered here.

Preliminary Measurements

Our first concern was to find an electrode which would behave reversibly toward fluoride ions. Allen and Furman⁵ have reviewed this subject in developing a potentiometric titration method for

fluorine. Treadwell and Köhl⁶ showed that the system $\text{Fe}^{+++}/\text{Fe}^{++}-\text{Pt}$ functions as a good fluoride electrode because of the formation of the complex iron cryolite, Na_3FeF_6 . This system seemed to offer the best possibilities for use in the concentration cell. Accordingly preliminary titrations were performed using the electrode pair, Pt-satd. calomel, in order to determine, if possible, the conditions of acidity and salt concentration which would be most suitable for the final concentration cell measurements and for what range of fluoride concentration the electrode would be expected to function. These titrations, the results of which are shown in Figs. 1, 2 and 3, give information, of a qualitative nature, which is of particular value to anyone who wishes to carry out concentration cell measurements under different conditions from those described in this paper.

Figure 1 shows typical curves for the titration of pure ferric chloride solutions of different concentrations with solutions of sodium fluoride, in the presence of a small amount of ferrous iron, potassium chloride of concentration 0.5 *M*, and hydrochloric acid 0.01 *M*. Under these condi-

(1) Presented at the 97th meeting of the American Chemical Society held at Baltimore, Md., April 3 to 7, 1939.

(2) Present address: American Viscose Corporation, Front Royal, Virginia.

(3) Furman and Low, *THIS JOURNAL*, **57**, 1585, 1588 (1935).

(4) (a) Reynolds and Hill, *Ind. Eng. Chem., Anal. Ed.*, **11**, 21 (1939); (b) McClure, *ibid.*, **11**, 171 (1939).

(5) Allen and Furman, *THIS JOURNAL*, **55**, 90 (1933).

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

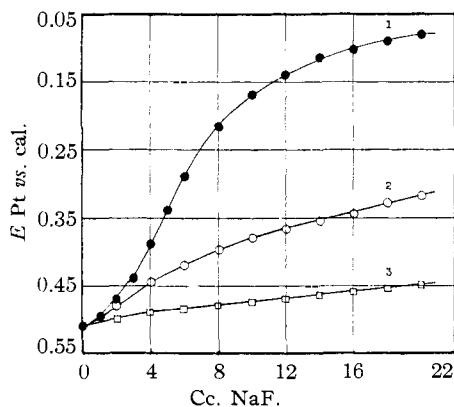


Fig. 1.—Effect of Fe^{+++} and F^- concentrations: volume at start of titration, 20 cc.

Curve	Fe^{+++}	NaF	$\text{Fe}^{+++}/\text{Fe}^{++}$	KCl	HCl
1	0.01	0.1	2/1	0.5	0.01
2	.001	.01	2/1	.5	.01
3	.0001	.001	2/1	.5	.01

tions, 1 cc. of 0.001 M sodium fluoride solution added to 20 cc. of 0.0001 M ferric chloride causes a measurable change in the e. m. f. of the electrode system. In Fig. 2 are presented a number of curves showing the effects of acidity and of potassium chloride concentration on the shape of the curves given in Fig. 1. The potassium chloride concentration is relatively unimportant, whereas if the solution is too acidic the sensitivity of the

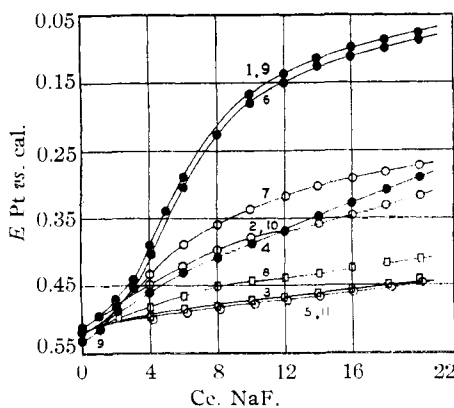


Fig. 2.—Effect of acidity and of KCl concn.

Curve	Fe^{+++}	NaF	$\text{Fe}^{+++}/\text{Fe}^{++}$	KCl	HCl
1	0.01	0.1	2/1	0.5	0.01
2	.001	.01	2/1	.5	.01
3	.0001	.001	2/1	.5	.01
4	.01	.1	2/1	.5	.10
5	.001	.01	2/1	.5	.10
6	.01	.1	2/1	.5	.0015
7	.001	.01	2/1	.5	.0015
8	.0001	.001	2/1	.5	.0015
9	.01	.1	2/1	0	.01
10	.001	.01	2/1	0	.01
11	.0001	.001	2/1	0	.01

electrode to fluoride ions is markedly decreased. On the other hand, the acidity should not be too low, because even in 0.001 M hydrochloric acid solutions hydrolysis of ferric chloride is quite rapid.⁷

Preliminary titrations of this type also give important information of a qualitative nature, with regard to the effect of impurities on the e. m. f. of the system. Anything which reacts with ferric ion, ferrous ion, or fluoride ion, would be expected to interfere with a determination of this sort.

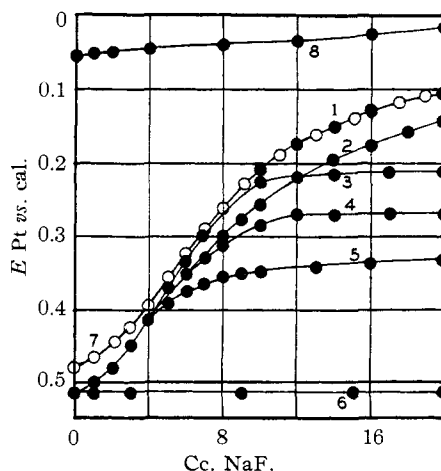


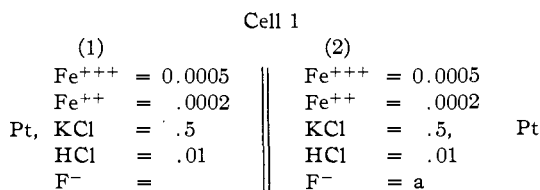
Fig. 3.—Effect of foreign salts: Fe^{+++} , 0.01; NaF, 0.1; $\text{Fe}^{+++}/\text{Fe}^{++}$, 2/1; KCl, 0.5; HCl, 0.01; foreign salt, 0.1: 1, none, KNO_3 , NaCl, NH_4Cl , KBr, ZnCl_2 ; 2, MgCl_2 ; 3, HgCl_2 ; 4, CuCl_2 ; 5, CaCl_2 ; 6, AlCl_3 ; 7, K_2SO_4 ; 8, tartrate.

Figure 3 shows the effects of a number of foreign salts on curve 1 of Fig. 1. The fact that aluminum ions interfere so completely can be interpreted as evidence that the Al-F complex is more stable than the Fe-F complex. A number of bivalent metals also affect the curve (but only after about 4 cc. of the sodium fluoride solution is added) owing, presumably, to the formation of the insoluble MF_2 . It is interesting to note that these curves give a measure of the relative insolubilities of the several fluorides involved. Interference by these ions is not encountered at the start of the titration, when the ferric ion concentration is relatively high; *i. e.*, we would expect calcium fluoride to dissolve in ferric chloride if the latter is present in great excess. Sulfate, citrate and tartrate interfere because of reaction with the ferric ion, and special means must be taken to eliminate this effect, as well as those mentioned

(7) Lamb and Jacques, *THIS JOURNAL*, **60**, 973, 1215 (1938).

above, when determining fluoride with the concentration cell.

All of the above qualitative information is valuable in considering the best conditions for determining fluoride with the concentration cell. Consideration of these curves showed that the following cell would serve as a suitable test of the concentration cell technique over the range of fluoride concentration, *a*, from 1–20 mg. per liter.



All concentrations are expressed in moles per liter.

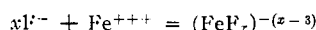
It is a simple matter to calculate what the e. m. f. of cell 1 should be if we know the reaction which takes place between ferric and fluoride ions. The following relationship would be valid at 30°

$$E = 0.0601 \log \frac{f'_1 Fe_1^{+++} / f'_2 Fe_2^{+++}}{f_1 Fe_1^{++} / f_2 Fe_2^{++}} \quad (1)$$

where the subscripts refer to sides 1 and 2 of cell 1, *f* is the activity coefficient, Fe⁺⁺⁺ and Fe⁺⁺ refer to the molar concentrations of the two ions, and *E* is the difference of potential between the two platinum wires. Since Fe⁺⁺ does not enter into the reaction with fluoride, and since *f*'₁ = *f*'₂ and *f*₁ = *f*₂ because of the high and essentially uniform ionic strength throughout, the equation may be simplified to

$$E = 0.0601 \log \frac{Fe_1^{+++}}{Fe_2^{+++}} \quad (2)$$

If the reaction between ferric and fluoride ions is:



then

$$Fe_2^{+++} = 0.0005 - \frac{1}{x} a$$

and

$$Fe_1^{+++} = 0.0005$$

where *a* is the molar concentration of fluoride and *x* - 3 represents the number of charges on the complex ion. Thus it is possible to calculate *x* from the e. m. f. of the cell if we work with known concentrations of fluoride. In Table I is given a summary of measurements made using cell 1. It is seen that *x* is not 6, as we might reasonably expect it to be, nor is it a constant. If a constant value for *x* is used in the Nernst equation, a curve (curve 1, Fig. 4) is obtained, whereas the experimental data fit a straight line

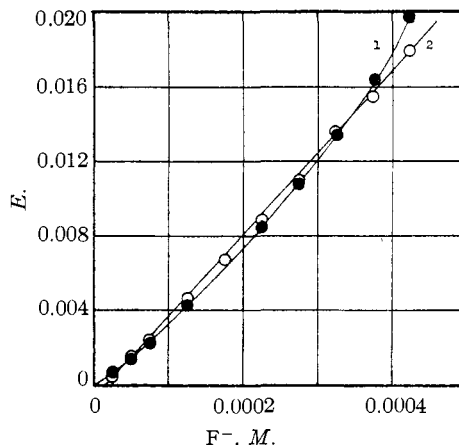


Fig. 4.—○, *E* = 2.29*a*₂ - 0.00067, at 30°; ●, *E* = 0.0601 log (0.0005/(0.0005 - 0.61*a*₁)).

(curve 2, Fig. 4) which is described by the following empirical equation

$$E = 2.29 a_2 - 0.00067 \text{ at } 30^\circ$$

where *E* is the observed e. m. f. of the cell when the fluoride concentration, *a*₂, is expressed as mg. of fluoride per liter.

TABLE I

Fluoride concn.		<i>E</i>	Fe ⁺⁺⁺ calcd. equation 2	<i>x</i>
mol., <i>a</i> ₁	mg./l., <i>a</i> ₂			
0.000025	0.48	0.00045	0.000488	2.94
.000050	.95	.0016	.000467	1.69
.000075	1.43	.0026	.000450	1.58
.000125	2.38	.0050	.000410	1.44
.000175	3.33	.0069	.000381	1.51
.000225	4.28	.0090	.000351	1.53
.000275	5.22	.0112	.000323	1.58
.000325	6.18	.0134	.000297	1.63
.000375	7.12	.0156	.000273	1.66
.000425	8.07	.0180	.000249	1.72
.000500	9.5	.0213	.000220	1.81

The preliminary measurements described above lead us to the conclusion that an empirical but reproducible relationship, suitable for analytical determinations, exists between the e. m. f. of a given cell and the fluoride concentration. Thus if it is desired to use a concentration cell for measurements of unknown fluoride concentrations it is necessary to determine experimentally the empirical curve for the particular ferric reagent being used.

Results with the Concentration Cell

Apparatus.—The glass concentration cell has been described in detail by Furman and Low.³ All e. m. f. measurements were made by means of a Leeds and Northrup type K2 potentiometer in conjunction with a Leeds and Northrup lamp and scale galvanometer No. 2420c. For most measurements the ordinary Students type potentiometer with a sensitive galvanometer should be satisfactory.

Platinum wires sealed into soft glass tubing were used as electrodes, and it is very important that they be cleaned frequently by dipping into chromic acid cleaning solution. All measurements were made after the cell had reached constant temperature in a water-bath designed to maintain the temperature constant within $\pm 0.02^\circ$.

Cell Used.—Since sulfate is likely to be encountered with fluoride in waters or in distillates resulting from the separation of fluoride from other materials, it was decided to modify cell 1 for our final series of measurements by adding sulfate to each side. In this way, the effect of small amounts of sulfate on the e. m. f. of the system is masked. This addition of sulfate merely changes the slope of the straight line of Fig. 4, and offers no inconvenience, since the empirical relationship must be determined anyway. The following cell was used for all measurements described in this paper, with the exception of a few which will be indicated specifically:

	FeCl ₃	= 0.000497 \pm 0.000002
	Fe ⁺⁺	= any value (0.0002)
Pt,	KCl	= 0.5 \pm 0.1
	Na ₂ SO ₄	= 0.15 \pm 0.01
	HCl	= 0.0094 \pm 0.0001
	F ⁻	= 0

Cell 2

	FeCl ₃	= 0.000497 \pm 0.000002	
	Fe ⁺⁺	= any value (0.0002)	
	KCl	= 0.5 \pm 0.1	
	Na ₂ SO ₄	= 0.15 \pm 0.01,	Pt
	HCl	= 0.0094 \pm 0.0001	
	F ⁻	= 0.000025 to 0.0016 (0.5 to 30 mg./l.)	

Measurements showed that the concentrations (all expressed as molarities) must be within the limits indicated in order that the e. m. f. values fit the data presented in this paper. However, it is an easy matter for any worker to determine his own empirical curve (with known amounts of fluoride) for any given ferric ion concentration. Variation of any of the concentrations outside of the above limits results in a change of the slope of the straight line. A careful study of the preliminary titrations, shown in Figs. 1, 2, and 3, was necessary in order to decide upon the various concentrations shown in cell 2, for the determination of fluoride concentrations of from 0.5 to 30 mg. per liter. For much higher concentrations of fluoride, or lower, a different concentration of ferric ion in the cell would be necessary.

Reagents and Chemicals.—It was found convenient to prepare the following reagents. All concentrations indicated need be only approximate, standardization of solutions being unnecessary since an empirical curve must be determined. Our ferric reagents were standardized, and the final ferric ion concentration is indicated in cell 2, but only because we had hoped to find that our data would fit the Nernst equation in some way.

Hydrochloric acid: one liter of 3 *M* stock solution.

Reagent 1: one liter of ferric stock solution containing 0.16 *M* FeCl₃ and 0.3 *M* HCl.

Reagent 2: ferric solution containing 0.0016 *M* FeCl₃, 0.03 *M* HCl, 1.67 *M* KCl and 0.50 *M* Na₂SO₄. One liter of this reagent can be prepared conveniently by pipetting exactly, 10 ml. of Reagent 1 and 10 ml. of hydrochloric acid stock solution (3 *M*) into a liter volumetric flask, adding the proper amounts of c. p. potassium chloride and sodium sulfate decahydrate (weighed roughly) and diluting to one liter. It is best to dissolve the potassium chloride and sodium sulfate in boiling water before adding to the volumetric flask.

(NH₄)₂SO₄·FeSO₄·6H₂O, c. p.: a stock solution of this is not prepared because of the ease of oxidation by air. Solutions are made freshly as needed.

NaF, c. p., or other material containing a known amount of fluoride: a stock solution of this is convenient, but should be kept in a paraffin lined bottle.

Procedure.—In order to make a measurement of the amount of fluoride in a given solution, the following procedure is used. Two solutions are prepared:

	Solution 1		Solution 2	
Reagent 2	3 cc.		Reagent 2	3 cc.
Fe ⁺⁺ soln.	2 cc.		Fe ⁺⁺ soln.	2 cc.
Water	5 cc.		F ⁻ soln.	5 cc.

(The ferrous ion solution is made freshly from c. p. Mohr salt and should be roughly 0.001 *M* in Fe⁺⁺ and 0.001 *M* in hydrochloric acid. The actual concentration of Fe⁺⁺ may vary a hundred-fold, as shown below,

provided the same solution is used for both solutions 1 and 2.)

Pipets are used to measure out the quantities of solutions needed above. Solution 1 is then transferred to one side of the concentration cell, solution 2 to the other, care being taken not to make the junction between the two sides, in order to avoid mixing. A platinum electrode is inserted in each side of the cell and it is then placed in the thermostat. After five minutes have elapsed, in order for the solutions to reach temperature equilibrium, the junction is made between the sides of the cell (as described by Furman and Low³) and the e. m. f. measured. The e. m. f. remains constant for at least a half hour under ordinary circumstances. Drifting of the potentials indicates that the solutions are mixing or that the electrodes are not clean and the measurement is of no value. From the e. m. f. can be calculated the amount of fluoride present by means of the empirical equation obtained below from measurements of known fluoride solutions.

Results with Pure Fluoride Solutions.—In order to determine the empirical relationship between e. m. f. of the cell and amount of fluoride present, a series of measurements was made using solutions of fluoride made from c. p. sodium fluoride. Table II shows the results obtained. In the two columns at the right the data are expressed as gamma in the 5-cc. sample taken for analysis, which is diluted to 10 cc. (see procedure) to become the "final concentration" shown in the two left columns and expressed as mg. per liter. It can be seen that the method is satisfactory for amounts of fluoride, in the 5-cc. sample taken for analysis, as small as 1

gamma. That these data fit a straight line is shown in Fig. 5. The equation for the straight line was found from a series of measurements made at different temperatures, as described below, under *effect of temperature*. If more than 30 mg. per liter of fluoride is present in the final solution, the relationship is no longer linear, and therefore the fluoride sample should be adjusted so that the amount of fluoride in the final solution falls within the range indicated. As shown below larger amounts of fluoride could also be determined using a reagent in which the ferric ion concentration is higher.

TABLE II

MEASUREMENTS OF SOLUTIONS OF PURE SODIUM FLUORIDE

Final concentrations of fluoride, mg./l. or p. p. m. Added		Fluoride in 5-cc. sample taken for analysis, γ Found ^a	
0.10	0.07	1.0	0.7
.20	.22	2.0	2.2
.30	.25	3.0	2.5
.40	.41	4.0	4.1
.48	.47	4.8	4.7
.95	.97	9.5	9.7
1.90	1.86	19.0	18.6
2.37	2.32	23.7	23.2
2.72	2.65	27.2	26.5
3.33	3.21	33.3	32.1
4.75	4.50	47.5	45.0
4.79	4.75	47.9	47.5
7.12	6.90	71.2	69.0
9.50	9.32	95.0	93.2
11.4	11.4	114	114
15.2	15.1	152	151
24.7	24.4	247	244
30.4	29.0	304	290

^a Calculated from the following equation, $g. F^-/l. = (0.490 + 0.002t) E + 0.0001$ in which E is the observed e. m. f. of the cell and t is the centigrade temperature.

Results with Known Fluoride Samples.—

A series of measurements was also made using other sources of fluoride than c. p. sodium fluoride, specifically synthetic sodium fluoride made by the method suggested by Allen and Furman⁸ from c. p. sodium carbonate and hydrofluoric acid, c. p. calcium fluoride, c. p. sodium fluosilicate, and Bureau of Standards fluorspar of known purity. The sodium fluoride was dissolved in water, but the others, being insoluble in water, were treated by a special procedure which was predicted on the basis of the preliminary titrations. To an accurately weighed sample, not over 0.1 g. was added 30 cc. of water and 30 cc. of Reagent 1 (measured by pipet). The mixture was stirred on

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

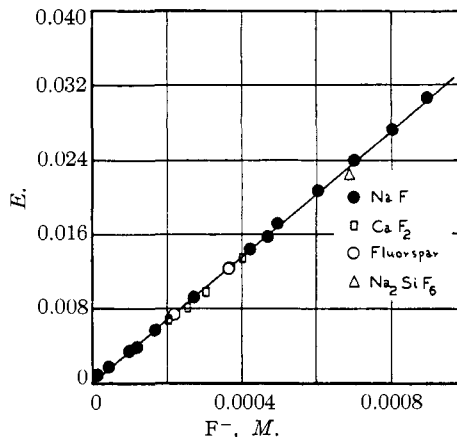


Fig. 5.

the hot-plate (80–90°) for one hour, cooled and diluted to 100 cc. in a volumetric flask. This solution was then diluted to the proper concentration for measurement in the concentration cell, with a solution of potassium chloride, hydrochloric acid and sodium sulfate. The reference side of the cell was made in exactly the same way except that no fluoride was put into it. Prolonged heating on the hot-plate was found to be necessary only for the fluorspar; the calcium fluoride and sodium fluosilicate dissolved readily in fifteen minutes of stirring at room temperature. The results obtained using a number of samples of these materials are given in Table III.

TABLE III

MEASUREMENTS OF FLUORIDE IN KNOWN SAMPLES

Substance	Final concentrations of fluoride, mg./l. or p. p. m. Added		Fluoride in 5-cc. sample taken for analysis, γ Found ^a	
	Added	Found ^a	Added	Found ^a
NaF synthetic	2.72	2.65	27.2	26.5
CaF ₂ , c. p.	2.43	2.37	24.3	23.7
CaF ₂ , c. p.	3.82	3.65	38.2	36.5
CaF ₂ , c. p.	4.73	4.50	47.3	45.0
CaF ₂ , c. p.	5.02	4.77	50.2	47.7
CaF ₂ , c. p.	5.70	5.54	57.0	55.4
CaF ₂ , c. p.	7.60	7.41	76.0	74.1
Fluorspar, B. S.	4.07	4.03	40.7	40.3
Fluorspar, B. S.	6.96	6.78	69.6	67.8
Fluorspar, B. S.	7.04	6.42	70.4	64.2
Na ₂ SiF ₆ , c. p.	13.1	12.5	131	125

^a Calculated from the equation: $g. F^-/l. = (0.490 + 0.002t) E + 0.0001$.

Effect of Ferric Ion Concentration.—It was pointed out above that the ferric ion concentration determines the slope of the straight line of Fig. 5. Quantitative data concerning the magnitude of this effect are shown in Fig. 6 and Table IV.

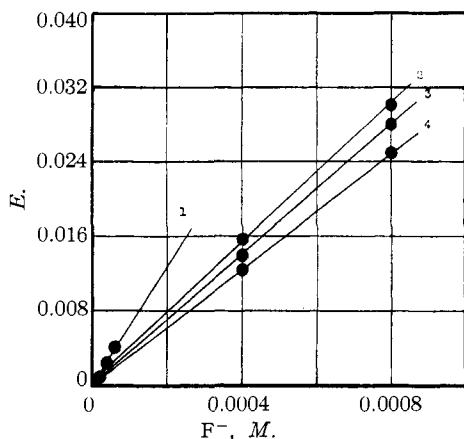


Fig. 6.—Curve 1, $\text{Fe}^{+++} = 0.0000993 M$; 2, $\text{Fe}^{+++} = 0.000398$; 3, $\text{Fe}^{+++} = 0.000497$; 4, $\text{Fe}^{+++} = 0.000597$.

TABLE IV

EFFECT OF CHANGE IN FERRIC ION CONCENTRATION
 $\text{Fe}^{+++} = 0.0000993$, Reagent 3. $\text{Fe}^{+++} = 0.000497$,
 Reagent 2.

F^- present, mg./l.	E. m. f., reagent 3	E. m. f., reagent 2
0.19	0.0003	0.00017
.38	.0009	.00052
.76	.0026	.00122
1.14	.0040	.00194

In each case the reagent differs from Reagent 2 only with respect to the ferric ion concentration; all other concentrations are the same. Thus it can be seen that if we were working with very small amounts of fluoride (under 1 mg. per liter), it would be to our advantage to use a reagent whose ferric ion concentration is lower than that of Reagent 2. This reasoning cannot be carried too far, however, because if the concentration is much lower than that indicated for Reagent 3 there is so little iron present that the e. m. f. cannot be read to as many decimal places; the system is then insensitive. On the other hand, if it is desired to measure amounts of fluoride greater than 30 mg. per liter, a reagent whose ferric ion concentration is greater than that of Reagent 2 can be used, which will again cause a different slope to the line.

Effect of Ferrous Ion Concentration.—It was assumed in the preliminary discussion that the concentration of ferrous ion in the cell should not be critical since it does not enter into the reaction with fluoride. It seemed advisable, however, to obtain quantitative data showing this assumption to be valid. Table V gives the results obtained using cell 2, with the exception that the ferrous

ion concentration was varied a hundredfold. This table shows definitely that the ferrous ion concentration may be any value within reasonable limits. It is important to note, however, that the concentration must be the same on each side of the cell in any given measurement. One other factor also must be considered: namely, that the ferrous ion concentration must be kept fairly low in order to make sure that no appreciable amount of ferric ion, which is always present as an impurity, is added to the cell.

TABLE V

Ferrous concn. in each side, M	E. m. f., v.	F^- found mg./l.
0.00002	0.0047	2.64
.0002	.00470	2.64
.002	.00475	2.67

Effect of Temperature.—It was expected that the e. m. f. value would, of course, be higher if the temperature were higher, for any particular cell. Accordingly, it was somewhat surprising to find exactly the opposite effect; *i. e.*, the e. m. f. of a given cell was lower at 30° than at 25° . Measurements were made, using cell 2, at a series of temperatures, allowing time for temperature equilibrium to be reached between readings. The temperature in the thermostat in which the cell was placed was raised from 15 to 35° and then lowered again to 15° . The same e. m. f. value, at any temperature, was obtained when approached from above or below the given temperature. In Table VI is given a summary of data showing this unexpected effect.

TABLE VI

Temp., $^\circ\text{C}.$	F^- , 0.0004 M		F^- , 0.0008 M	
	Obsd. e. m. f.	Calcd. e. m. f. ^a	Obsd. e. m. f.	Calcd. e. m. f. ^a
15	0.0143	0.0143	0.0289	0.0289
20	.0141	.0145	.0284	.0294
25	.0139	.0148	.0280	.0299
30	.0137	.0150	.0275	.0304
35	.0134	.0153	.0269	.0309

^a Calculated assuming the value at 15° to be correct; *i. e.*, the e. m. f. at 20° should be $293/288 \times$ the value at 15° .

These results are shown graphically in Fig. 7.

This unexpected phenomenon can be explained on the basis that the degree of hydrolysis of the ferric chloride is greater at the higher temperatures. A measurement carried out at 100° supports this view, inasmuch as at this temperature a precipitate was formed, presumably of ferric hy-

droxide. That the effect is due to hydrolysis rather than to a change of the extent of dissociation of the Fe-F complex was shown by a measurement made on a similar cell put together without any fluoride present in either side. The same anomalous effect was observed with this latter cell.

If consideration is taken of this observed effect of temperature on the slope of the line of Fig. 5, equation 3 is found to be the empirical equation which fits our data at any temperature between 15 and 35°. *E* is the observed e. m. f. of the cell, and *t* the centigrade temperature.

$$g. F^-/l. = (0.490 + 0.002t) E + 0.0001 \quad (3)$$

This hydrolysis in no way affects the usefulness of the method, since the fact that our reagents remained perfectly stable over a period of many months shows that this partial hydrolysis of the ferric chloride is completely reversible and not progressive. It is interesting to note that a means here suggests itself for measuring the degree of hydrolysis of salts of this type by e. m. f. measurements.

TABLE VII
EFFECT OF IMPURITIES

Impurity	Impurity molarity	Final solution impurity concn. mg./l.	Concn. in final solution, mg./l.	
			F ⁻ added	F ⁻ found
.....	7.6	7.6
KCl	0.1	K, 3900 Cl, 3500	7.6	6.7
KCl	.01	K, 390 Cl, 350	15.2	15.3
NaCl	.01	Na, 230	15.2	15.1
K ₂ SO ₄	.01	SO ₄ , 960	15.2	15.7
Na ₂ SO ₄	.0005	SO ₄ , 480	15.2	15.6
K ₂ SO ₄	.001	SO ₄ , 96	15.2	15.3
CaCl ₂	.01	Ca, 400	15.2	15.8
CaCl ₂	.001	Ca, 40	15.2	15.1
K ₂ HPO ₄	.01	PO ₄ , 950	15.2	70.1
K ₂ HPO ₄	.0001	PO ₄ , 10	7.6	8.6
H ₃ BO ₃	.01	H ₃ BO ₃ , 600	7.6	7.4
MgCl ₂	.01	Mg, 240	15.2	14.6
MgCl ₂	.001	Mg, 24	15.2	15.3
MnCl ₂	.01	Mn, 550	15.2	14.5
MnCl ₂	.001	Mn, 55	15.2	15.2
HgCl ₂	.01	Hg, 2000	15.2	14.8
HgCl ₂	.001	Hg, 200	15.2	15.1
KBr	.01	Br, 800	15.2	15.1
Tartrate	.0001		15.2	16.0
Citrate	.0001		15.2	20.7
CuCl ₂	.001	Cu, 64	15.2	15.1
NH ₄ Cl	.01	NH ₄ , 180	15.2	15.2
AlCl ₃	.0001	Al, 2.7	15.2	8.5
KNO ₃	.01	NO ₃ , 620	7.6	7.4
Na ₂ SiO ₃	.001	SiO ₃ , 75	7.6	8.1
Th(NO ₃) ₄	.001	Th, 230	7.6	0.2
NaClO ₄	.01	ClO ₄ , 1000	2.7	2.6

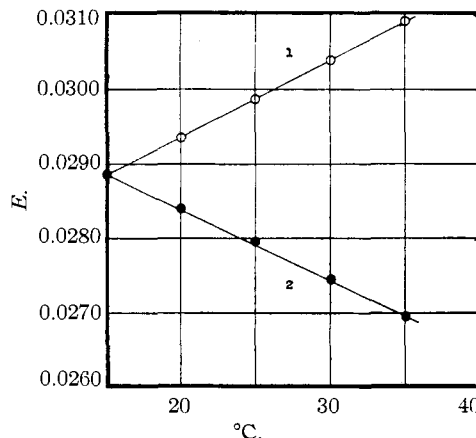


Fig. 7.—Effect of temperature: curve 1, theoretical; curve 2, experimental.

	Cell	
Fe ⁺⁺⁺ = 0.0005		Fe ⁺⁺⁺ = 0.0005
Fe ⁺⁺ = .0002		Fe ⁺⁺ = .0002
Pt, KCl = .5		KCl = .5, Pt
Na ₂ SO ₄ = .15		Na ₂ SO ₄ = .15
HCl = .01		HCl = .01
F ⁻ = 0		F ⁻ = .0008

Effect of Impurities.—In order that the method may be of value for the determination of fluoride, it must function, of course, in the presence of certain impurities. Consequently, a series of measurements was performed which was designed to study this effect. Different foreign salts were added with the fluoride to the concentration cell, and the effect of these salts, if any, on the e. m. f. was determined. Table VII summarizes the data obtained in this series. A study of this table shows that most of the common ions cause no trouble, but that high results are obtained if phosphate, citrate or tartrate is present (because of reaction with ferric ion), and low results if aluminum or thorium is present (because of reaction with fluoride). As was predicted on the basis of the preliminary titrations, calcium and other bivalent metal ions do not interfere if present in moderate amounts. It can be seen that appreciable amounts of sulfate, perchlorate or silicate, cause no trouble. This is very important, inasmuch as it means that the distillate obtained by separation of fluoride by the usual methods contains no ions which would interfere with the determination of the fluoride. It also should be noted that if the total concentration of impurity is greater than 0.01 *M*, fictitious e. m. f. values will be encountered because of a liquid junction potential.

Means of eliminating trouble due to impurities will be given below.

Distillation of Fluoride.—A very satisfactory method for the separation of fluoride from other substances has been developed by Willard and Winter.^{8a} They recommend the separation of fluoride by distillation from a perchloric acid solution. The determination of fluoride in the distillate can then be made by a number of standard methods. That our concentration cell method is satisfactory for the determination of fluoride in this distillate is shown in Table VIII. A 30-cc. sample of pure sodium fluoride solution, of the concentration shown in the table, was distilled according to the Willard and Winter procedure and the amount of fluoride in the distillate measured by the technique described here.

TABLE VIII
DISTILLATION OF FLUORIDE BY WILLARD-WINTER PROCEDURE

Concn. of 30-cc. sample, mg./l.		75 cc. of distillate		Mg. of fluoride	
Added	Found	Added	Found	Added	Found
4.7	4.7	1.4	1.4		
16.7	15.3	5.0	4.6		
30	29	9.0	8.7		
62	61	18.6	18.3		

Another procedure commonly employed is distillation from sulfuric acid solution. This offers the advantage that the temperature can be taken much higher without the danger of explosion which is attendant upon the use of perchloric acid. It is often quite difficult to separate fluoride from a sample by a single perchloric acid distillation, and it is frequently the practice to distil twice, first from sulfuric acid and then from perchloric acid.⁹ This second distillation is for the purpose of removing small amounts of sulfate which interfere with some methods of determining the fluoride. Distillation from sulfuric acid has been described in detail by Hoffman and Lundell¹⁰ and is used by them in the determination of fluoride in phosphate rock. Their determination of fluoride in the distillate is then done by a gravimetric process, precipitation as lead chlorofluoride. The concentration cell technique is applicable to the determination of fluoride in such rocks, where the percentage of fluoride is low. Table IX shows the results obtained in determining the fluoride in Bureau of Standards sample No. 56a, by means of

(8a) Willard and Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

(9) Churchill, Bridges and Rowley, *ibid.*, **9**, 222 (1937).

(10) Hoffman and Lundell, *J. Research Natl. Bur. Standards*, **20**, 607 (1938).

our technique. The distillation was carried out as described by Hoffman and Lundell, with the exception that we employed no preliminary fusion and collected the distillate in air rather than under sodium hydroxide solution. Three hundred cc. of distillate was collected, the solution made faintly alkaline to phenolphthalein, then very slightly acidic with 0.01 *M* hydrochloric acid, and diluted to 500 cc. in a volumetric flask. Five cc. of this was then taken for analysis in the concentration cell according to the procedure already described. The whole procedure, after the distillation, takes about fifteen minutes, whereas the gravimetric procedure usually employed takes much longer.

TABLE IX
ANALYSIS OF PHOSPHATE ROCK
Bureau of Standards Sample No. 56a

Sample, g.	% F ⁻ present (certificate)	% F ⁻ found	
0.3650	3.56	3.56	
.1988	3.56	3.61	3.57 ^a 3.57 ^b

^a A 50-cc. sample of the distillate from sample 2 was evaporated to dryness after making slightly alkaline with sodium hydroxide. It was then taken up with water, made slightly acidic with hydrochloric acid and diluted to 25 cc. Five cc. of this solution was then taken for analysis. The evaporation was carried out in Pyrex glass. ^b Same as ^a except that the evaporation was carried out in platinum.

These results show that distillates may be concentrated, if desired, by evaporation in either glass or platinum. Since our experiments concerning the effect of impurities showed that small amounts of silicate do not interfere, this was to be expected.

Elimination of Error Due to Phosphate.—The preceding section described the procedure which may be used for the separation of fluoride from any or all impurities, by distillation. It is possible to determine fluoride in the presence of phosphate by means of a procedure which involves no distillation. If phosphate is present with the fluoride, fictitiously high values for fluoride would be found by the usual concentration cell technique, because of the fact that phosphate reacts with ferric ions in much the same way as does fluoride. This difficulty can be eliminated in the following manner. First the "apparent fluoride" is measured in the usual way by the direct procedure. The measurement is then repeated on a different sample, with a small amount of aluminum ion in each side of the concentration cell. Thus the two solutions would be made as follows.

Solution 1		Solution 2	
3 cc. reagent 2		3 cc. reagent 2	
1 cc. Fe ⁺⁺⁺ solution		1 cc. Fe ⁺⁺⁺ solution	
1 cc. Al ⁺⁺⁺ sol. (0.015 M)		1 cc. Al ⁺⁺⁺ sol. (0.015 M)	
5 cc. H ₂ O		5 cc. F ⁻ (+PO ₄) solution	

In this second cell the aluminum ions tie up the fluoride so that it cannot react with the ferric ions, whereas the phosphate does not react with aluminum ions if ferric ions are also present. The e. m. f., therefore, is due to the phosphate alone, whereas the e. m. f. of the first cell is due to both the phosphate and the fluoride. The difference between the two values gives the e. m. f. due to the fluoride. Table X shows results obtained by this procedure. The results show that the method yields only approximate values and that distillation should be resorted to if accurate values are required.

TABLE X
DETERMINATION OF FLUORIDE IN THE PRESENCE OF PHOSPHATE

PO ₄ present mg./l.	F ⁻ present mg./l.	Aluminum procedure			
		Direct procedure E. m. f.	Apparent F ⁻ found mg./l.	E. m. f. due to phosphate	E. m. f. due to F ⁻ (by diff.)
10	1.6	0.0054	3.0	0.0024	0.0030
20	1.6	.0092	5.1	.0054	.0038
30	1.6	.0124	6.8	.0087	.0037

Analysis of Water Samples.—The technique was tested on Arizona water samples, which were kindly furnished by Professor H. V. Smith of the University of Arizona, who recently has compared¹¹ a number of standard methods used for the determination of fluoride in water. These samples had been analyzed in his laboratories, and his results are given with ours in Table XI as a means of comparison. Samples 4 and 5 had been passed through a bone filter devised by Smith and Smith¹² to remove fluoride from water; the original content of these samples was quite high in fluoride.

TABLE XI
ARIZONA WATER SAMPLES

Sample no.	Fluoride found, mg./l.		
	Direct proc.	Aluminum proc.	H. V. Smith Sanchis method
1	3.5	3.5	4.0
2	6.8	6.3	6.0
3	0.7	0.2	0.3
4	.9	.6	.3
5	.4	.1	.0
6	4.1	3.8	3.5

The table indicates that there was a small amount of phosphate in the water also, the effect of which

(11) Smith, *Ind. Eng. Chem., Anal. Ed.*, **7**, 23 (1935).

(12) Smith and Smith, *Water Works Eng.*, **Nov. 10**, 1937.

was removed by means of the "aluminum procedure" already described.

Discussion of Results

Advantages of the Technique

1. *Wide range of applicability.*—The procedure should be applicable to the determination of fluoride in any substance, since it may be applied to the filtrate obtained by distilling fluoride from impurities, from either a perchloric or sulfuric acid medium.

2. *Rapidity.*—A single measurement takes about fifteen minutes, if the fluoride is present in solution. If a solid material is being analyzed, or if many impurities are present, the time to carry out the distillation to separate the fluoride must be added to this. It is very convenient to make a number of measurements at the same time, using three or four concentration cells.

3. *Simplicity.*—Since the procedure involves only the use of a pipet and the ability to read a potentiometer, it is extremely simple. In addition, no personal error enters, as it does in certain titration methods where the end-point is difficult to distinguish.

4. *Accuracy.*—For small amounts of fluoride the accuracy of the method is satisfactory, particularly if the size of sample can be so regulated that the amount of fluoride in the final cell is above 10 mg. per liter.

5. *Application to micro determination.*—As indicated in the tables, the method is suitable for quantitative determination of as little as 1 gamma of fluoride in 5 cc. of solution taken for analysis.

Disadvantages of the Technique

1. *Necessity for an empirical curve.*—Unfortunately it is impossible to relate the e. m. f. of the concentration cell to the amount of fluoride in any way except by an empirical equation. Fortunately, however, it is a straight line relationship in the range studied. Thus for all practical purposes this is no serious disadvantage. All of the measurements given in this paper, using cell 2, were made using the same empirical curve. Since the reagents are perfectly stable, a curve once determined is satisfactory for a year or more if sufficient reagent is made. The amounts suggested in this paper are sufficient for about 15,000 determinations.

2. *Limited to small amounts.*—Because of the very nature of the technique, our procedure is

limited to the determination of small amounts of fluoride. A detailed study has not been made of the application of this technique to larger amounts using a much higher concentration of ferric ion in the reagent. The preliminary titrations indicate that such an application could be made, but the range we have chosen to study should be satisfactory for most of the fluoride determinations necessary.

3. *Accuracy*.—Although, as pointed out above, the accuracy is very good for the small amounts of fluoride determined, it should also be mentioned that the method would not be satisfactory for the accurate determination of fluoride in a substance whose fluoride content is greater than 10%, because in that case a 1% error would be appreciable, whereas for very small amounts of fluoride a 1% error is not important.

4. *Liquid junction*.—It is important to keep the total impurity molarity of the unknown fluoride solution below 0.01 *M*, else an appreciable liquid junction potential will cause fictitious results. In practice this is very easily done, by distilling the sample from impurities if in no other way. The distillate is much lower than 0.01 *M* in foreign ions.

It should be pointed out that the size of sample of an unknown should be adjusted so that the amount of fluoride in the final concentration cell is between 0.1 and 30 mg. per liter, preferably greater than 10 mg. per liter, since the percentage error is smaller for larger amounts of fluoride.

The procedure we have described corresponds

to the "Standard Solution" method for chloride used by Furman and Low.³ An attempt was made to apply the "small excess" method³ to the determination of fluoride, but with no success. The e. m. f. of the cell, with fluoride in both sides, seemed to be dependent upon the difference in fluoride concentration between the two sides rather than the ratio of the two concentrations. Because this "small excess" method offered no promising results, we abandoned a further study of it in favor of the procedure we have given.

The material presented in this paper gives indication that the technique described should be applicable to the determination of a number of other substances, such as aluminum, phosphate, sulfate, citrate or tartrate, by slight modifications of the procedure. It is hoped that further study will confirm this prediction.

Summary

A technique has been described for the determination of fluoride rapidly and accurately by means of a simple concentration cell. Interference of other ions can be eliminated entirely, since the procedure is applicable to the determination of fluoride in the distillate obtained in separating fluoride from all impurities. The range over which the method has been applied is 0.2 to 60 mg. per liter in a 5-cc. sample which is taken for analysis. Results are given showing the method's applicability to water analysis and to the determination of fluoride in phosphate rock.

AMHERST, MASS.

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NOTES

Dibenzyl Sebacate

BY R. E. BURNETT AND J. J. RUSSELL

The new compound dibenzyl sebacate was synthesized recently in this Laboratory for use in another investigation.¹ Sebacic acid was esterified with benzyl alcohol, the crude ester then distilled at 0.5 mm. pressure, and the middle fraction recrystallized several times from its melt. The following are properties of the

(1) Verhoek and Marshall, unpublished results.

pure dibenzyl sebacate.

Temp., °C.	Refractive index <i>n</i> _D (Abbe)	Density <i>d</i> ₄
30.0	1.5171	1.055(6)
35.0	1.5152	1.051(9)
40.0	1.5133	1.048(1)

Colorless plates, practically odorless; melting point (from cooling curve), 28.3°; boiling point (in Claisen flask), 257° (uncorr.) at 4 mm.

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, N. Y.

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