not interfere in the least with the aminocaproic acid test. Ammonium sulfide has[1] also been recently shown to be an exceedingly sensitive reagent for copper, but the large number of metals which interfere materially limits its usefulness. At the present time the cost of *n*-aminocaproic acid greatly exceeds that of the other reagents, but it is believed that its great usefulness will serve to cheapen it considerably. It is moreover a simple matter to recover the acid from waste solutions; so that the same supply can be used repeatedly.

Experiments are now in progress in this laboratory to determine the behavior of the rarer elements with *n*-aminocaproic acid and also the conditions under which the reagent may be applied as a specific test for zinc. The use of this reagent for the purposes of quantitative analysis is also under consideration.

Summary.

1. It has been shown that an aqueous solution of normal aminocaproic acid is an exceedingly sensitive reagent for the detection of copper. With this reagent 0.004 mg. of copper may be detected with certainty.

2. Mercury and zinc are the only other common metals which yield, under the conditions specified, a precipitate with the reagent. The interference of the former may be overcome by the addition of sodium chloride, the latter may be prevented from precipitating by adjusting the acidity of the solution.

3. Procedures have been given for the detection of small amounts of copper in the presence of relatively large quantities of foreign metals.

4. The reagent is more specific for copper than any of the other reagents heretofore proposed; and possesses an advantage over the ferrocyanide test in that small quantities of iron do not interfere with its use.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF FLUORIDES—THE ANALYSIS OF SILICATES AND CARBONATES FOR THEIR FERROUS IRON CONTENT.[2]

BY O. L. BARNEBEY.

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The permanganate titration of ferrous iron in the presence of chlorides has attracted attention for a considerable period of time because of the economic importance of the determination of iron, the ease with which iron ores dissolve in hydrochloric acid and the rapidity of conducting the permanganate titration. While the titration of iron with permanganate in hydrochloric acid solution has been studied by many inves-

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[1] THIS JOURNAL, 35, 168 (1913).

[2] Read at the New Orleans Meeting of the American Chemical Society.

tigators,[1] the titration of iron in hydrofluoric acid solution has not received the attention which it merits, expecially considering that this titration has been the source of much solicitude to the geologist, petrographer and chemist for many years. Hydrofluoric acid is the most efficient reagent known at present for the decomposition of a silicate. A permanganate solution is one of the most convenient oxidizing solutions available for oxidation. However, it is generally recognized that when ferrous iron is titrated with permanganate in hydrofluoric acid solution the end point is fleeting and the result high or worthless. Consequently any procedure which increases the accuracy of the titration of ferrous iron with permanganate in fluoride solution has direct application to a very important method of analysis. This study has for its object an improved determination of ferrous iron in fluoride solution and its application to the analysis of silicates and carbonates for their ferrous iron content.

Mitscherlich[2] proposed to decompose the mineral by heating with strong sulfuric acid in a closed tube for a considerable length of time, thus yielding ferrous sulfate, which was subsequently titrated with permanganate. Hillebrand and Stokes[3] as well as de Koninck[4] have shown that this method may give erroneous results in the presence of sulfides which cause the reduction of ferric to ferrous iron, which is later titrated, thus yielding a high percentage. Vogt[5] mentions a similar reducing action of sulfides, Cu_2S being the specific reference.

J. P. Cooke, Jr.,[6] first used sulfuric and hydrofluoric acids for the decomposition and analysis of silicates for their ferrous iron content. The method as proposed by him is in general use to-day. This method, in brief, consists in the decomposition of the silicate with sulfuric and hydrofluoric acids in an atmosphere free from oxygen and titration with permanganate. The air must be excluded to prevent the oxidation of the iron during solution. Cooke passed carbon dioxide through the so-called "Cooke water bath" with inverted funnel cover to exclude the air, added the acid, heated the water in the bath to boiling, shut off the flow of carbon dioxide, allowing the steam to keep the air away from the sample undergoing attack, waited until the silicate was thoroughly decomposed, then passed cold water through the bath to cool the solution, meanwhile passing carbon dioxide, diluted and then titrated the ferrous iron with permanganate.

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[1] See Barnebey, THIS JOURNAL, **36**, 1429 (1914).

[2] *J. prakt. Chem.*, 81, 108, 116 (1860); **83**, 455 (1862).

[3] THIS JOURNAL, **22**, 625 (1900); *Z. anorg. Chem.*, **25**, 326 (1900); Stokes, *Bull. U. S. Geol. Survey*, **186** (1901); *Am. J. Sci.*, [4] 12, 414 (1901).

[4] *Ann. Soc. Geol. Belgique*, **10**, 101 (1883); *Z. anorg. Chem.*, **26**, 123 (1900).

[5] *Z. prakt. geol.*, **1899**, p. 250.

[6] *Am. J. Sci.*, [2] **44**, 347 (1867); see also Avery, *Chem. News*, **19**, 270 (1869); Wilber and Whittlesey, *Ibid.*, **22**, 2 (1870).

This method has several faults: (1), rigid care must be exercised to prevent partial oxidation of the dissolving ferrous iron during the decomposition period; (2), the end point may be more or less indefinite or fleeting; (3), certain naturally occurring substances must be absent or the results are vitiated.

Pratt[1] has attempted to obviate the first-mentioned difficulty by avoiding the use of the water bath and heating the platinum crucible containing the sulfuric and hydrofluoric acids directly, conducting carbon dioxide into the crucible by means of a platinum tube. By the direct heating process he was able to diminish the time of heating to about ten minutes. However, too great concentration of solution was found detrimental, as the strong, hot sulfuric acid had a tendency to oxidize ferrous sulfate. Hillebrand[2] obtained good results by this method.

Hillebrand[2] gives an excellent discussion of the detrimental influence of sulfides, vanadium and organic matter, stating that the titration is "entirely unreliable in the presence of organic matter." This author has also studied the effect of grinding upon the ferrous content of minerals, finding that fine pulverization decreases the quantity of ferrous iron found, which he attributes to the heat effect.

Gage[3] seeks to improve the titration of the iron by the addition of calcium phosphate to precipitate the fluorine as calcium fluoride. Fromme[4] adds a large amount of finely divided silicic acid, thus converting the hydrofluoric acid into fluosilicic acid. Dittrich[5] used potassium sulfate with silicic acid to remove influence of the fluorine. Dittrich and Leonhard[6] studied the use of the three previously mentioned reagents, recommending the use of 10 g. of finely divided silicic acid and 20–25 g. of potassium sulfate in a volume of 100 cc. which contained also 2 cc. of sulfuric acid. Deussen[7] mentions that manganous sulfate, to a certain degree, does away with the source of error. However, this use of manganous sulfate has been shown to be not only of no value but of great detriment by several authors.[8] Hillebrand[8] states that

> "It is possible to titrate ferrous iron in the presence of sulfuric acid, and as much as 5 to 7 cc. of 40% hydrofluoric acid in a total volume of 200 to 400 cc., almost if not quite as exactly as in sulfuric acid alone, provided the iron solution is diluted with air-free water and the titration made immediately after adding the hydrofluoric acid

[1] *Am. J. Sci.*, [3] **48**, 149 (1894).

[2] Hillebrand, "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Survey, *Bull.* **422** (1910).

[3] THIS JOURNAL, **31**, 381 (1909).

[4] *Tschermak's mineralog. u. petrogr. Mitteil.*, **28**, 329 (1909).

[5] "3 Versammlung in Bad Dürkheim," am 29 März, 1910, II Teil, S 92–3; *Ber. Versam. Oberrhein. geol. Ver.*, **2**, 92; *Chem. Abst.*, **5**, 846 (1911).

[6] *Z. anorg. Chem.*, **74**, 21 (1912).

[7] *Ibid.*, **44**, 425 (1905).

[8] Hillebrand, Gage, Dittrich and Leonhard, *Loc. cit.*

and with all possible dispatch." He says further, "in the presence of little ferrous iron, up to, say, 2 centigrams, and 5 to 7 cc. of 40% hydrofluoric acid the color produced by a drop of permanganate lasts some time, but is very evanescent as the ferrous iron, and consequently the manganese salt formed, increases."

In the following pages is outlined a systematic study of various types of agents which suggested themselves as interesting in regard to their effect on the titration of ferrous iron in the presence of fluorides. The effect of each agent is studied under varying conditions of concentration of that agent. Each series of experiments contains the results of a number of titrations with permanganate of measured volumes of standard ferrous sulfate in the presence of measured volumes of hydrofluoric acid and the agent being studied. The total volume in each case was 200 cc. preceding titration unless otherwise designated. Usually, after the end-point reading had been taken and recorded, 0.10 cc. of permanganate was added in excess, the solution then stirred and allowed to stand until the color bleached out. This procedure was adopted as a test on the stability of the end point. Ceresin beakers and hard rubber stirring rods were used.

TABLE I.—SULFURIC ACID AS PREVENTIVE.

1 cc. $KMnO_4$ = 0.009186 g. Fe.[1]

1 cc. $FeSO_4$ = 0.006151 g. Fe.[2]

	Normality.		Iron—Gram.			Time 0.10 cc. $KMnO_4$ lasted. Seconds.
	H_2SO_4.	HF.	Present.	Found.	Error.	
1.......	...	1.0	0.1538	0.1543	+0.0005	10
2.......	0.05	1.0	0.1538	0.1543	+0.0005	10
3.......	0.10	1.0	0.1538	0.1545	+0.0007	15
4.......	0.15	1.0	0.1538	0.1552	+0.0014	25
5.......	0.25	1.0	0.1538	0.1543	+0.0005	40
6.......	0.50	1.0	0.1538	0.1545	+0.0007	70
7.......	0.75	1.0	0.1538	0.1543	+0.0005	120
8.......	1.0	1.0	0.1538	0.1543	+0.0005	140
9.......	2.0	1.0	0.1538	0.1540	+0.0002	130
10.......	4.0	1.0	0.1538	0.1543	+0.0005	120
11.......	5.0	1.0	0.1538	0.1543	+0.0005	120
12.......	8.0	1.0	0.1538	0.1542	+0.0004	30
13.......	12.0	1.0	0.1538	0.1556	+0.0018	3-4
14.......	16.0	1.0	0.1538	0.16+	....	..
15.......	1.0	1.5	0.1538	0.1545	+0.0007	30
16.......	1.0	2.5	0.1538	0.1550	+0.0012	12
17.......	1.0	5.0	0.1538	No end point		..
18.......	5.0	5.0	0.1538	No end point		..

[1] The iron value of this and other permanganate solutions used in this investigation is the average value obtained by checking against sodium oxalate, ferrous ammonium sulfate and electrolytic iron.

[2] Approximately 240 g. of $FeSO_4.7H_2O$ were dissolved in water containing 20 cc. of conc. sulfuric acid (sp. gr. 1.84) and diluted to 8 l. This solution was titrated with the permanganate at the time of using and its value computed from the iron value of the permanganate.

Table I shows the effect of varying concentrations of sulfuric acid on this titration in presence of fluorides.

Experiments 6 to 11 inclusive show that ferrous iron can be titrated at room temperature with moderate accuracy in solutions normal in hydrofluoric acid and normal to 5 *N* sulfuric acid. However, considerably less, or more, sulfuric acid lessens the stability of the end point.

Titration in phosphoric acid solution of all concentrations between 0.1 *N* and 0.125 *N* with normal hydrofluoric acid present gives very fugitive end points. The use of solutions of the acid phosphates of the alkalies also gives very fleeting and indefinite end points. Hence phosphoric acid can not be substituted for sulfuric acid in this titration.

The influence of insoluble phosphates was tried to ascertain if they would give prevention of the indefiniteness of the fluoride end point. Phosphates of zinc, calcium,[1] magnesium, iron and aluminum were used. (See Table II.)

TABLE II.—PREVENTION BY PHOSPHATES INSOLUBLE IN WATER.

1 cc. $KMnO_4$ = 0.005068 g. Fe.
1 cc. $FeSO_4$ = 0.005822 g. Fe.

	Normality.			Phosphate added.	Iron—Grams.			0.10 cc. $KMnO_4$ lasted Seconds.
	H_2SO_4.	H_3PO_4.	HF.		Present.	Found.	Error.	
1	..	..	1.0	$Ca_3(PO_4)_2$[2]	0.1456	0.1343	−0.0113	Fleeting
2	..	..	1.0	$Ca_3(PO_4)_2$[2]	0.1456	0.1368	−0.0088	Fleeting
3	0.75	..	1.0	$Ca_3(PO_4)_2$[2]	0.1456	0.1456	0.0000	Fleeting
4	..	..	1.0	5 g. "	0.1456	0.1389	−0.0067	Fleeting
5	..	..	1.0	10 g. "	0.1456	0.1363	−0.0093	Fleeting
6	..	..	1.0	20 g. "	0.1456	0.1360	−0.0096	Fleeting
7	..	..	1.0	50 g. "	0.1456	0.1302	−0.0154	Fleeting
8	0.60	..	1.0	20 g. "	0.1456	0.1457	+0.0001	40
9	..	0.75	1.0	20 g. "	0.1456	0.1409	−0.0047	Fleeting
10	..	1.5	1.0	20 g. "	0.1456	0.1429	−0.0027	Fleeting
11	..	3.0	1.0	20 g. "	0.1456	0.1455	−0.0001	Fleeting
12	..	..	1.0	$FePO_4$[2]	0.1456	No end point		Fleeting
13	..	..	1.0	$FePO_4$[2]	0.1456	No end point		Fleeting
14	..	..	1.0	$AlPO_4$[2]	0.1456	0.1461	+0.0005	20
15	0.50	..	1.0	$AlPO_4$[2]	0.1456	0.1470	+0.0014	20
16	..	..	1.0	$Zn_3(PO_4)_2$[2]	0.1456	0.1464	+0.0008	5
17	..	..	1.0	$Zn_3(PO_4)_2$[2]	0.1456	0.1470	+0.0014	5
18	..	..	1.0	$Mg_3(PO_4)_2$[2]	0.1456	0.1368	−0.0088	7
19	0.50	..	1.0	$Mg_3(PO_4)_2$[2]	0.1456	0.1414	−0.0042	25
20	0.50	..	1.0	$Mg_3(PO_4)_2$[2]	0.1456	0.1427	−0.0029	30
21	1.0	..	1.0	$Mg_3(PO_4)_2$[2]	0.1456	0.1449	−0.0007	30
22	2.0	..	1.0	$Mg_3(PO_4)_2$[2]	0.1456	0.1455	−0.0001	..

Experiments 1, 2, 4, 5, 6, 7, 18, 19 and 20 gave low results because of precipitation of ferrous phosphate, which consequently was not completely

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[1] Gage, *Loc. cit.*

[2] Added solid in excess.

oxidized by the permanganate. In 19 the phosphate was added before the sulfuric acid, in 20 the acid before the phosphate, which accounts for a higher result in 20. Experiments 8, 11 and 22 indicate that good results may be obtained when the proper adjustment is obtained between phosphate of calcium or magnesium and acid. However, with calcium phosphate and phosphoric acid the end points were fleeting and with magnesium phosphate and sulfuric acid the time test of 0.10 cc. of permanganate was not as favorable as when titrating in sulfuric acid solution without the phosphate (Table I). The results with calcium phosphate do not confirm the work of Gage. Ferric, aluminum and zinc phosphates gave poor results, those with the zinc salt being the best, but the end point was extremely fleeting. The phosphates tried seem to have little merit as preventives.

The action of alkali bisulfates is similar to the action of sulfuric acid, but the neutral alkali sulfates have but a slight tendency to prevent the fluoride influence.

The influence of a number of bivalent neutral sulfates was tried, among such being zinc, magnesium, calcium, mercury, cadmium and manganese sulfates. Zinc, cadmium and mercury sulfates give unstable end points which lack reliability. Calcium sulfate added as a solid in excess gives end points which are but slightly more stable. Magnesium sulfate is much more effective. (See Table III.)

TABLE III.—MAGNESIUM SULFATE AS PREVENTIVE.

1 cc. $KMnO_4$ = 0.009208 g. Fe.
1 cc. $FeSO_4$ = 0.006151 g. Fe.

	Normality. HF.	50% $MgSO_4.7H_2O$. Cc.	Volume. Cc.	Iron—Gram. Present.	Found.	Error.	0.10 cc. $KMnO_4$ lasts.
1	1.0	10	200	0.1538	0.1532	−0.0006	30 sec.
2	1.0	20	200	0.1538	0.1535	−0.0003	40 sec.
3	1.0	40	200	0.1538	0.1537	−0.0001	110 sec.
4	1.0	80	200	0.1538	0.1539	+0.0001	180 sec.
5	1.0	160	200	0.1538	0.1532	−0.0006	20 min.
6	1.8	160	225	0.1538	0.1539	+0.0001	4 min.
7	3.0	180	265	0.1538	0.1535	−0.0003	90 sec.
8	3.0	210	335	0.1538	0.1548	+0.0010	80 sec.

When the hydrofluoric acid is added to a solution containing magnesium or vice versa, a very light precipitate forms. The amount of precipitate increases progressively with the concentration of the acid and magnesium. In Experiment 8 the precipitate was very heavy—probably fluoride of magnesium. The prevention of the fluorine influence is very marked, surprisingly so in view of the comparatively poor prevention of zinc sulfate.

The detrimental influence of manganese salts is shown in Table IV.

TABLE IV.—MANGANESE SULFATE AS PREVENTIVE.

1 cc. $KMnO_4$ = 0.007866 g. Fe.

1 cc. $FeSO_4$ = 0.006151 g. Fe.

Manganese Solution I contains 80 g. $MnSO_4.4H_2O$, 150 cc. H_2SO_4 (sp. gr. 1.84) and 150 cc. H_3PO_4 (sp. gr. 1.7) per liter.

Manganese Solution II = 500 g. $MnSO_4.4H_2O$ per liter.

	Normality. HF.	Mn soln. I. Cc.	Mn soln. II. Cc.	Iron—Gram. Present.	Found.	Error.	Remarks on end point.
1.....	1.0	1	..	0.1538	0.1544	+0.0006	Fleeting
2.....	1.0	5	..	0.1538	0.1544	+0.0006	Very fleeting
3.....	1.0	20	..	0.1538	No end point		Very fleeting
4.....	1.0	..	1	0.1538	0.1663	+0.0125	Very fleeting
5.....	1.0	..	10	0.1538	0.17+	....	Very fleeting
6.....	1.0	..	20	0.1538	No end point		Very fleeting
7.....	1.0	..	40	0.1538	No end point		Very fleeting
8.....	1.0	..	10 + 20 cc. of ion H_2SO_4	0.1538	No end point		Very fleeting

Manganese salts are thus seen to vitiate results to an enormous extent; when present in any considerable quantity, they absolutely inhibit a good titration.

The effect of a number of trivalent sulfates was tried, and that of ferric sulfate found to be of most interest (Table V).

TABLE V.—FERRIC SULFATE AS PREVENTIVE.

1 cc. $KMnO_4$ = 0.009186 g. Fe.

1 cc. $FeSO_4$ = 0.006136 g. Fe.

$Fe_2(SO_4)_3$ Solution.—500 g. crystallized ferric sulfate + 40 cc. H_2SO_4 (sp. gr. 1.84) per liter.

	Normality. HF.	$Fe_2(SO_4)_3$. Cc.	Iron—Gram. Present.	Found.	Error.	10 cc. $KMnO_4$ lasted.
1............	1.0	10	0.1534	0.1531	—0.0003	2 minutes
2............	1.0	20	0.1534	0.1529	—0.0005	5 minutes
3............	1.0	40	0.1534	0.1529	—0.0005	14 minutes
4............	1.0	80	0.1534	0.1530	—0.0004	Time not taken.
5............	3.0	200	0.1534	0.1516	—0.0018	(Volume, 325 cc.)

Ferric sulfate gives good prevention, but with a large amount of hydrofluoric acid a light pink to lavender color is imparted to the solution which is somewhat troublesome (Experiments 4 and 5). When ferric sulfate is added to hydrofluoric acid solutions, the color of ferric salts disappears practically entirely until an excess of ferric iron has been added. Aluminum sulfate gave some preventive effect, but it was not sufficiently satisfactory to be of especial merit. A few experiments using bismuth sulfate were performed. While this salt seemed to improve the end point the improvement was not of sufficient degree to have any value for the purposes of this work. The effect of cerous sulfate was tried and found to be detrimental rather than beneficial.

Cobalt, chromium, nickel and copper sulfates gave colored solutions when added to hydrofluoric acid solutions and thereby prevented the appearance of good end points.

The effect of a number of oxides was tried to ascertain if they react with the hydrofluoric acid so as to yield undissociated fluorides in solution. Oxides of aluminum, magnesium and zinc are not applicable inasmuch as when added in excess they precipitate hydroxide of iron, thus hindering a good clean-cut reaction. Addition of stannic oxide produced apparently no effect, giving a fleeting end point. The yellow color of tungstic oxide interfered during titration and the end point was not stable.

Table VI gives the tabulated results obtained using molybdic oxide.

TABLE VI.—MOLYBDIC OXIDE AS PREVENTIVE.

Iron and permanganate solutions the same as used in Series V.

	Normality. HF.	Solid MoO_3 in excess.	Iron—Gram. Present.	Found.		10 cc. $KMnO_4$ lasted. Seconds.
1........	1.0	......	0.1534	0.1536*b*	0.1542*p*	15
2........	2.0	......	0.1534	0.1509*b*	0.1547*p*	6
3........	1.0	......	0.1534	0.1538*b*	0.1540*p*	10
4........	1.0	......	0.1534	0.1534*b*	0.1536*p*	16
5........	1.0	......	0.0062	0.0073*b*	0.0073*p*	*
6........	1.0	......	0.0006	0.0010*b*	0.0010*p*	*
7........	0.05	......	0.0006	0.0010*b*	0.0010*p*	*
8........	1.0	$(NH_4)_2MoO_4$	0.1534	0.1534*b*	0.1536*p*	*
9........	1.0	solution	0.1534	0.1532*b*	0.1534*p*	*

* Time not taken, but pink end point was fleeting in each case.

Results designated "*b*" were obtained by noting the volume of permanganate required to cause disappearance of the blue coloration formed by the reduction of the molybdenum by the ferrous iron. Results designated "*p*" are those obtained by utilizing the volume of permanganate required to tinge the solution pink.

Columbic and tantalic oxides apparently produced no effect because of the slow solution of these oxides in hydrofluoric acid. If freshly precipitated undoubtedly this action would be faster.

Titanium dioxide gives excellent prevention (Table VII).

TABLE VII.—TITANIUM DIOXIDE AS PREVENTIVE.

Iron and permanganate solutions the same as used in Series V.

	Normality. HF.	Normality. H_2SO_4.	Solid TiO_2.	Iron—Gram. Present.	Found.	Error.	0.10 $KMnO_4$ lasted.
1........	1.0	..	Excess	0.1534	0.1539	+0.0005	90 min.
2........	2.0	..	Excess	0.1534	0.1534	0.0000	60 min.
3........	5.0	..	Excess	0.1534	0.1533	—0.0001	25 min.
4........	1.0	1.0	Excess	0.1534	0.1534	0.0000	80 min.

Silica and silicic acid were used as preventives. The silicic acid was made in the solution by adding sodium silicate to the acid solution containing ferrous iron and hydrofluoric acid (Table VIII).

TABLE VIII.—SILICIC ACID AS PREVENTIVE.

1 cc. $KMnO_4$ = 0.007814 g. Fe.
1 cc. $FeSO_4$ = 0.006151 g. Fe.
Na_2SiO_3 —

	Normality. HF.	Normality. H_2SO_4.	Cc. Na_2SiO_3.	Iron—Gram.			0.10 cc. lasted.
				Present.	Found.	Error.	
1.........	1.0	0.5	10	0.1230	0.1230	0.0000	80 seconds
2.........	2.0	1.0	25	0.1230	0.1180	−0.0050	40 seconds
3.........	2.0	2.0	20	0.1230	0.1225	−0.0005	60 seconds
4.........	2.0	2.0	..	0.1230	0.1250	+0.0020	20 seconds
5.........	5.0	2.0	..	0.1230	0.1266	+0.0036	Very unstable
6.........	5.0	2.0	25	0.1230	0.1238	+0.0008	60 seconds

Experiments 1, 3 and 6 show that moderately good results can be obtained by using silicic acid as preventive. In Experiment 2 too much silicate was added in proportion to the amount of acid present and some of the ferrous iron was precipitated, hence the low result. Experiments 4 and 5 are included to show the relative values obtained in presence of hydrofluoric acid with sulfuric acid compared with sulfuric acid plus the silicic acid.

Granulated silica, prepared by various chemical manufacturers was tried but it did not work so well. The pink end point of the permanganate was far less stable, giving a tendency toward high results, perhaps owing to the more insoluble nature of the silica, or to slight impurities in the silica, or to both causes.

When boric acid is added to hydrofluoric acid in solution, meta-fluoboric acid, HBF_4, is formed, which does not dissociate appreciably to yield hydrofluoric acid in the presence of boric acid. This is illustrated by the fact that a dilute solution of the same will not attack glass.[1]

Table IX gives the results of a study of the effect of boric acid in removing the influence of the fluorine when titrating ferrous salts.

TABLE IX.—BORIC ACID AS PREVENTIVE.

1 cc. $KMnO_4$ = 0.007866 g. Fe.
1 cc. $FeSO_4$ = 0.006156 g. Fe.

	Normality. HF.	Normality. H_2SO_4.	H_3BO_3 solid.	Iron—Gram.			10 cc. $KMnO_4$ lasted.
				Present.	Found.	Error.	
1.........	0.50	..	Excess	0.1231	0.1234	−0.0003	40 min.
2.........	1.0	..	Excess	0.1231	0.1232	+0.0001	40 min.
3.........	2.0	..	Excess	0.1231	0.1232	+0.0001	20 min.
4.........	5.0	..	Excess	0.1231	0.1230	−0.0001	10 min.
5.........	1.0	0.50	Excess	0.1231	0.1232	+0.0001	15 min.
6.........	0.50	..	Excess	0.2462	0.2460	−0.0002	80 min.

The six experiments of Table IX indicate a very high degree of efficiency for the boric acid. In Experiment 4 considerable heat was evolved when the boric acid was added. The amount of solid added in each case

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[1] See also Moissan, *Traite de Chimie Minerale*, **2**, 166 (1904).

depended upon the consumption of the boric acid by the hydrofluoric acid. This is easily regulated, since an excess of reagent does no harm. In fact the excess seems to facilitate obtaining the end point.

Borax was also tried, adding the solid in excess to the sulfate solution containing HF. Its use produced good end points, but not as excellent as with boric acid. A saturated solution of borax was also used with success. Inasmuch as the use of boric acid affords such good titrations a point of interest arises at once in regard to how much effect it will have in offsetting the detrimental influence of manganese salts. This is of especial importance, inasmuch as manganese salts have such a good preventive action when titrating ferrous iron in the presence of chlorides and bromides (Table X).

TABLE X.—BORIC ACID PREVENTION OF THE MANGANESE EFFECT.

Solutions of iron and permanganate the same as in Series IV.

	Normality. HF.	Normality. HCl.	Mn soln. I. Cc.	Mn soln. II. Cc.	Boric acid.	Iron—Gram.		0.10 cc. $KMnO_4$ lasted.
						Present.	Found.	
1....	1.0	..	1	..	Solid in excess	0.1538	0.1538	Definite; time not noted.
2....	1.0	..	5	..	Solid in excess	0.1538	0.1533	Definite; time not noted.
3....	1.0	..	20	..	Solid in excess	0.1538	0.1539	Definite; time not noted.
4....	1.0	0.03	20	..	Solid in excess	0.1538	0.1536	60 seconds
5....	1.0	0.15	20	..	Solid in excess	0.1538	0.1538	40 seconds
6....	1.0	0.30	20	..	Solid in excess	0.1538	0.1538	35 seconds
7....	1.0	0.60	20	..	Solid in excess	0.1538	0.1542	20 seconds
8....	1.0	0.90	20	..	Solid in excess	0.1538	0.1536	12 seconds
9....	1.0	0.90	30	..	Solid in excess	0.1538	0.1538	20 seconds
10....	1.0	1.5	50	..	Solid in excess	0.1538	0.1551	20 seconds
11....	...	0.60	..	..	Solid in excess	0.1538	0.1571	Not definite.
12....	1.0	...	..	10	Solid in excess	0.1538	0.1533	40 seconds
13....	1.0	...	..	40	Solid in excess	0.1538	0.1543	5 seconds
14....	1.0	0.60	..	10	Solid in excess	0.1538	0.1539	4 seconds
15....	1.0	..	..	..	Solid in excess	0.1538	0.1538	120 seconds

In the experiments of Table X the time listed for disappearance of the pink color of the permanganate is only for the disappearance of the deep pink; a lighter shade of pink remained (except in Expts. 11, 13, 14) for a longer period of time than that designated. In Expt. 11 the odor of liberated chlorine was strong. In Expt. 15 after the 0.10 cc. of $KMnO_4$ added in excess had bleached, 0.10 cc. more of $KMnO_4$ was added and this addition required 18 minutes to bleach, after which 0.10 cc. more of $KMnO_4$ retained its pink color for over three hours. This series of experiments shows that the fluorine influence can be removed in the presence of manganous salts very effectively. Hence, in the presence of fluorides, bromides and chlorides the addition of a manganese salt and boric acid allows ferrous iron to be titrated accurately with permanganate.

Inasmuch as hydrofluoric acid solutions of ferrous iron are readily oxidized by the air, it was decided to study the stability of fluoboric acid solutions of ferrous iron. To measured portions of standard ferrous sulfate were added measured volumes of 10 *N* HF; the solutions were diluted to a definite volume and allowed to stand varying lengths of time after which boric acid was added in excess and the ferrous iron titrated. These results were compared with those obtained by adding an excess of boric acid to the fluoride solution immediately after adding the hydrofluoric acid and allowing to stand an equal time.

TABLE XI.—STABILITY OF FLUOBORIC ACID SOLUTIONS OF FERROUS IRON.

1 cc. $FeSO_4$ = 0.006113 g. Fe.
1 cc. $KMnO_4$ = 0.009184 g. Fe.

	Normality. HF.	Volume.	Time.	Iron—Gram.		Remarks.
				Present.	Found.	
1...	1.33	150	10	0.0611	0.0551	Solid boric acid added after standing.
2...	1.33	150	20	0.0611	0.0543	Solid boric acid added after standing.
3...	1.33	150	40	0.0611	0.0518	Solid boric acid added after standing.
4...	1.33	150	30	0.1223	0.1139	Solid boric acid added after standing.
5...	1.33	150	30	0.3057	0.2948	Solid boric acid added after standing.
6...	1.33	150	10	0.0611	0.0613	Solid boric acid added in excess before standing.
7...	1.33	150	20	0.0611	0.0611	Solid boric acid added in excess before standing.
8...	1.33	150	40	0.0611	0.0613	Solid boric acid added in excess before standing.
9...	1.33	150	30	0.1223	0.1223	Solid boric acid added in excess before standing.
10...	1.33	150	30	0.3057	0.3053	Solid boric acid added in excess before standing.
11...	1.33	100	60	0.1834	0.0743	No boric acid added. Aerated.
12...	1.33	100	60	0.1834	0.1834	Solid boric acid added in excess. Aerated.

The results confirm the observations of others regarding the ease of oxidation of ferrous salts in the presence of hydrofluoric acid. However, the addition of boric acid makes the solution so much more stable that the oxidation is negligible in a moderate length of time. In Expts. 11 and 12 air was bubbled through the solutions at the rate of about three bubbles a second for an hour. A ceresin bottle was used to hold the solutions and the glass tubes used for conducting the air in and out of the vessel were coated with paraffin. In this case more thorough agitation was accomplished and the solution was kept more nearly saturated with air. Even in this case the theoretical result was obtained when boric acid was added before agitating. However, without the addition of boric acid about 57% of the ferrous iron was oxidized by the air.

Boric acid is the best of all the agents studied, since it removes the fluorine influence in the iron titration so effectually, is so easily prepared in a high degree of purity, is inexpensive, and is sparingly soluble in water so that the addition of the solid can be easily regulated according to the amount of hydrofluoric acid present. A number of silicate analyses have been made and the following method has been found applicable (Table XII).

Analysis of Silicate and Carbonate Rocks.

An appropriate sample (0.5 to 5 g.) in a capacious platinum dish is covered with water and placed on a Cooke water bath[1] in which the water has been previously thoroughly boiled to remove dissolved oxygen. Carbon dioxide is passed for several minutes, or steam allowed to escape for several minutes, or both, to remove any air inside of the glass funnel, after which 5 cc. of 1 : 1 H_2SO_4 (HCl can be used) is added by pouring down the platinum stirring rod. If carbonates are present care must be exercised to prevent too violent action. Should soluble sulfides be present the acid is likewise added slowly to expel the H_2S as completely as possible. Strong hydrofluoric acid is then added, 5 cc. to 20 cc. depending upon the size of the sample, pouring down the stirring rod. The bath is maintained at an even temperature, a continuous current of steam being expelled through the funnel until the silicate is thoroughly decomposed. If carbon dioxide is allowed to pass through the bath continuously it should be regulated so that its passage is slow, just sufficient to give direction to the current of escaping gases. Occasionally a little previously boiled water is added to the bath to maintain the water level. For this purpose a flask of boiling water should be kept constantly ready for use.

When decomposition is complete the funnel is lifted from its place and cold (previously boiled) distilled water added immediately to the dish to dilute the solution somewhat, followed immediately by an excess of solid boric acid. The solution is stirred, then lifted from the bath. If solid organic matter is present it should be filtered through an asbestos filter using suction (a carbon funnel with a Witte plate is convenient for this purpose) and the filter washed with previously boiled distilled water. The solution is poured into a glass beaker, diluted to a convenient volume, and titrated with standard permanganate. If the solution has been filtered it is titrated in the suction flask. It is well to add some solid boric acid before titrating to give the same color effect as usual at the end point. When hydrochloric acid is used for the decomposition of the sample, some substance should be added to counteract its influence when the ferrous iron is titrated. Since the hydrofluoric acid has been transposed to fluoboric acid any good preventive[1] is applicable. Ten to twenty cc. of the ordinary preventive solution[2] used in the iron titration (80 g. $MnSO_4.4H_2O$ + 80 cc. H_2SO_4 (sp. gr. 1.84) + 80 cc. H_3PO_4 (sp. gr. 1.7) per liter is effective, or the phosphoric acid may be omitted and 160 cc. of sulfuric acid used instead in preparing this solution.

The above method can be easily adapted to Pratt's[3] scheme of decomposing the silicate, which requires less time because of the application

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[1] Cooke, *Loc. cit.*

[2] Barnebey, *Ibid.*

[3] Pratt, *Ibid.*

of a higher temperature. The sample is placed in a platinum crucible, carbon dioxide is conducted into the crucible by means of a platinum tube, which is inserted under one edge of the cover, acid is added and heat applied directly to the crucible. As soon as steam is evolved copiously the carbon dioxide is shut off, hydrofluoric acid added and the cover fitted snugly to the crucible. When decomposition is complete dilute somewhat with water, add boric acid and proceed as usual.

Notes on the Method.

1. Scrupulous care must be exercised to exclude the air when decomposing the silicate with hydrofluoric acid in order to prevent oxidation. However, after the addition of the boric acid the ferrous solution becomes quite stable.

2. A carbon dioxide generator, after filling with carbonate (marble) and acid, should be allowed to generate carbon dioxide for a considerable period of time to remove the air as completely as possible. (Heating magnesite would probably be a still better method for obtaining carbon dioxide.) Only recently boiled water should be used in the water bath and only recently boiled distilled water added to the sample.

3. Until accustomed to the method of analysis the analyst should always check his procedure by heating measured volumes of standard ferrous iron solution with hydrofluoric acid, and titrating with the same manipulation as in the analysis in order to ascertain if the air is being excluded effectively.

4. Filtration is desirable when solid organic matter is visible after the sample is thoroughly decomposed. Filtration may not remove all the influence of the organic matter, however. The soluble organic matter naturally still has opportunity to give a reducing effect. If the clear solution is slightly colored by the presence of organic matter it should be largely diluted and titrated to the first distinct pink tinge of the solution. The presence of organic matter makes the end point much less stable than in its absence. Another procedure can be substituted for filtration. The sample can be transferred to a volumetric flask, diluted to the mark and the residue allowed to settle, after which portions can be withdrawn with a pipette and titrated.

5. Instead of adding solid boric acid the fluoride solution can be poured directly into an excess of a saturated solution of boric acid.

6. A convenient strength of permanganate for titrating samples low in ferrous iron content is 1 cc. = 0.001 g. FeO.

Samples 1–5, inclusive (Table XII), contained no organic matter and were free from sulfides. The end points were fleeting in analyses *2a*, *3a* and *4a*, especially the last two. Samples 6–8, inclusive, contained considerable organic matter. In analysis *6a* the result is only approximate, as the end point was very fugitive because of the organic matter present. In *6b*, *6c*, *6d*, *6e* the solutions were filtered, as also were the samples *7b* and *7c* as well as *8b* and *8c*. Larger portions could have been used to advantage in Samples 5, 7 and 8. Samples were not analyzed according to procedure "*a*" for 7 and 8 because of the presence of large amounts of organic matter. Naturally filtration of the hydrofluoric acid solution is not advisable on account of the rapidity of oxidation of ferrous iron in such a solution by the air and also because of the action of the solution on glass.

TABLE XII.—ANALYSES OF SILICATES FOR FERROUS IRON.

1 cc. $KMnO_4$ = 0.001 g. FeO.

Number.	Sample. Grams.	Per cent. FeO.				
		a.	*b.*	*c.*	*d.*	*e.*
1	4.0	0.12	0.08	0.10	...	0.08
2	2.0	3.74	3.54	3.48	3.56	3.45
3	1.0	6.94	6.49	6.45	...	6.50
4	0.4	14.70	14.36	14.36 14.48	...	14.42
5	2.0	0.09	0.084	0.085	0.078	0.080
6	1.0	6.20	5.47	5.26 5.46	5.46	5.48
7	2.5	....	0.51	0.51	...	....
8	1.0	....	0.43	0.45	...	....

a. Sulfuric and hydrofluoric acids used for decomposition. No boric acid was added.

b. Decomposed like *a.* Boric acid was added.

c. Hydrofluoric acid used for decomposition. Boric acid was added.

d. Decomposed with hydrochloric and hydrofluoric acids. Manganese sulfate (80 g. $MnSO_4.4H_2O$ per liter) and boric acid were added.

e. Decomposed like *d.* Manganese solution I and boric acid were added.

The results obtained by decomposition methods "*b*," "*c*," "*d*" and "*e*" are somewhat lower than those obtained by "*a*," but they are believed to be more accurate. The author prefers the use of sulfuric acid with hydrofluoric acid for decomposition of a silicate whenever this method of attack is applicable, although hydrochloric acid with hydrofluoric acid or hydrofluoric acid alone can be used satisfactorily. The chlorine influence on the titration must always be removed when hydrochloric acid is utilized.

Naturally, when the above method is applied to the analysis of carbonate rocks, the addition of hydrofluoric acid may be omitted if the sample is thoroughly decomposed by the other acids, or if only the iron existing as carbonate is desired. However, the hydrofluoric acid finds application if considerable siliceous matter is present and the total ferrous iron content of the sample is wanted.

The action of these preventives may be classified as follows: Class (*a*) removes most, if not all, of the active hydrofluoric acid by the presence of another acid through the medium of which the oxidation proceeds by virtue of its greater strength as an acid or by mass action. Sulfuric acid by conductivity measurements is stronger than hydrofluoric acid; phosphoric acid is much weaker. Hence sulfuric acid gives fairly good and phosphoric acid poor prevention. The acid salts found to be of worth are valuable mostly for their acidity, *i. e.*, $NaHSO_4$, $KHSO_4$. (*b*) Certain salts react with the fluorides present, forming undissociated fluorides and salts of other acids than hydrofluoric, through the medium of which the reaction proceeds. Examples of this class of preventives are ferric and magnesium sulfates. Phosphates are not desirable inasmuch as they yield phosphoric acid by interaction with hydrofluoric acid, and phosphoric acid is to be avoided in the titration unless all the hydrofluoric acid is removed. Of the neutral phosphates only those of the alkalies are soluble in water, hence to add metal phosphates either the solids or the phosphate dissolved in phosphoric acid must be added, thus forming acid phosphates in most instances and again bringing the phosphoric acid into predominance. Still another difficulty arises from the use of phosphates; sufficient acidity must be present to prevent ferrous phosphate from precipitating. If the ratio of phosphate to acid does not give sufficient acidity the titration is worthless, being low. Classes (*a*) and (*b*) are so closely related that they could properly be included in one class, but in (*a*) hydrofluoric acid is present and in (*b*) a fluoride. (*c*) Other reagents react with hydrofluoric acid in such a manner as to combine the fluorine in the anion which does not dissociate to yield hydrofluoric acid. Boric and silicic acid are such preventives, forming fluoboric and fluosilicic acids by interaction with hydrofluoric acid.

Of the preventives tried the author prefers boric acid. This acid can be obtained on the market in a high degree of purity and is a cheap commodity. It gives a solution which is clear. The solubility of boric acid in water peculiarly fits it for this purpose, being sufficiently high to allow a rapid reaction with hydrofluoric acid and yet not so high as to cause waste of the chemical when adding the solid in slight excess. The appearance of solid boric acid in excess likewise indicates that sufficient reagent has been added to react with the hydrofluoric acid present. This is a distinct advantage when titrating solutions containing unknown or variable quantities of hydrofluoric acid. Solid boric acid in excess is advantageous rather than detrimental in obtaining the end point. The fluoboric acid solution of ferrous iron oxidizes very slowly in the air, thus removing an undesirable feature of the titration accompanying the usual methods for determining ferrous iron. It gives the best prevention of the hydrofluoric influence during titration.

Summary.

1. This study confirms earlier work which has shown that the permanganate titration of ferrous iron in the presence of fluorides gives an unstable end point, the instability increasing with increased concentrations of iron and hydrofluoric acid.

2. The use of sulfuric acid of normal to 5 *N* concentrations permits a good titration to be made in the presence of normal hydrofluoric acid. Phosphoric acid can not be substituted for sulfuric acid, since the former yields a fugitive end point. Certain acid sulfates accomplish the same result as the free acid.

3. Certain sulfates, *i. e.*, ferric and magnesium sulfates, react with the hydrofluoric acid and check its influence in the titration. Phosphates and acid phosphates are undesirable for prevention of the fluoride influence.

4. Certain oxides also have prevention tendencies, *i. e.*, molybdenum trioxide and titanium dioxide, the titanium dioxide being the better. The hydrofluoric acid may combine with the titanium and molybdenum, forming simple fluorides or fluotitanic and fluomolybdic acids. Boric acid and silicic acid remove the hydrofluoric acid, forming fluoboric and fluosilicic acids. Boric acid is the most effective of all reagents studied.

5. Ferrous iron solutions containing fluoboric acid are quite stable in the presence of air.

6. The prevention of the reagents studied may be classified in three divisions: (1) addition of a stronger acid than hydrofluoric acid for the solution medium, (2) conversion to salts of other acids forming also undissociated or sparingly dissociated fluorides by mass action of the preventer, and (3) conversion of the hydrofluoric acid to a complex acid which when dissociated, gives a complex anion rather than the simple fluorine ion.

7. A modified procedure is given for the analysis of silicate or carbonate rocks for their ferrous iron content, using boric acid to remove the detrimental influence of the hydrofluoric acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

THE PERMANGANATE AND IODIMETRIC DETERMINATION OF IODIDE IN PRESENCE OF CHLORIDE AND BROMIDE.[1]

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The permanganate oxidation of iodide to iodate originated with Pean de Saint Gilles.[2] A large number of modifications of this method have

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[1] Read at the New Orleans meeting of the American Chemical Society.

[2] Pean de Saint Gilles, *Compt. rend.*, **46**, 624 (1858).