[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA]

VOLUMETRIC DETERMINATION OF FERROUS ION BY MEANS OF POTASSIUM IODATE

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Volumetric solutions of potassium iodate are prepared by dissolving the calculated quantity of pure, dry reagent in water. The solution requires no further standardization, and is permanent. Jamieson[1] reports that a solution of potassium iodate has been kept for ten years without a change of strength. These properties make the reagent particularly valuable to the chemist who makes only an occasional quantitative analysis. Jamieson and others have worked out methods for determining copper, arsenic, antimony, molybdenum, mercury, zinc, tin, hydrazine, hydrogen peroxide, dichromate, tetrathionate, sulfite, thiosulfate and iodide ions. They found that many organic substances did not affect the titrations.

Andrews,[2] in a paper in which he suggests the use of potassium iodate as a volumetric reagent, states that the determination of ferrous ion was unsatisfactory on account of the difficulty of determining the end-point and because iodine was liberated when the solution was allowed to stand. Since no mention is made of the determination of ferrous ion in Jamieson's book, it seemed worth while to investigate the possibility of a satisfactory method for determining ferrous ion, especially since all the solutions needed were available from other work being done in the writer's laboratory.

A preliminary determination was made at the close of a day and it was found that 10 cc. of a solution of ferrous ammonium sulfate, containing 0.0273 g. of ferrous ion as determined by titration with potassium permanganate, required 9.8 cc. of 0.05 N potassium iodate, corresponding to 0.0274 g. of ferrous ion. The end-point was sharp and permanent.

Later, when experiments were started to work out the details, the results were extremely variable, but all were lower than the calculated values as determined by potassium permanganate titration. The reagents were added in the usual order—concentrated hydrochloric acid, iodine chloride, carbon tetrachloride and potassium iodate—to a solution of ferrous ammonium sulfate containing a little sulfuric acid. Inasmuch as the ferrous ion is known to be much less stable in a hydrochloric acid solution than in a sulfuric acid solution,[3] it occurred to the writer that the difference in results might be accounted for by the partial oxidation of the ferrous ion

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[1] George S. Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., Inc., New York, **1926**.

[2] Andrews, *Z. anorg. Chem.*, **36**, 83 (1903); THIS JOURNAL, **25**, 761 (1903).

[3] Sutton, "Volumetric Analysis," eleventh ed., Blakiston and Sons Co., Philadelphia, Pa., **1924**, p. 238.

before the addition of the iodine chloride. If this was the case the iodine chloride should be added before the hydrochloric acid. The ferrous ion would then be oxidized by the iodine chloride rather than by the oxygen in the air. When this change was made in the order of adding iodine chloride and hydrochloric acid, the results checked those obtained with a standard solution of potassium permanganate. The end-point was sharp, and permanent—even after standing overnight.

In order to determine whether or not the increase in the iodine liberated was due to the hydrolysis of the iodine chloride solution before the acid was added, the iodine chloride was mixed with the concentrated hydrochloric acid and the mixture was added to the solution containing the ferrous ion. The results checked those obtained by using potassium permanganate.

To substantiate the theory that the ferrous ion in a concentrated solution of hydrochloric acid was oxidized by the oxygen of the air, carbon dioxide was passed into the flask containing the sample of ferrous ion until the air was displaced. While the stream of carbon dioxide was still passing, concentrated hydrochloric acid was added. The tube through which the carbon dioxide was passing was removed, and the iodine chloride solution and the carbon tetrachloride were added. The amount of ferrous ion which was found was almost the same as that previously determined by titration with potassium permanganate.

To further substantiate this theory, two samples of a solution of ferrous ion, which had been previously standardized with both potassium permanganate and potassium iodate, were placed in similar containers. To one concentrated hydrochloric acid was added, while dilute sulfuric acid (1:5) was added to the other. The containers were covered with filter paper and were allowed to stand for two days with occasional agitation. The sample containing the concentrated hydrochloric acid was titrated with potassium iodate, while the one containing sulfuric acid was titrated with potassium permanganate; 0.65 cc. of 0.1 N potassium iodate was required to titrate the solution containing the hydrochloric acid, whereas 9.83 cc. was required at the beginning of the experiment; 16.3 cc. of 0.0601 N potassium permanganate was required to titrate the solution containing the sulfuric acid; 16.4 cc. was required before exposing to the air.

These results seem to indicate clearly that the ferrous ion must be in a dilute solution of sulfuric acid and not in concentrated hydrochloric acid if the iron is to be maintained in the ferrous condition.

The experimental data showing the effect of changing the order of adding the reagents, etc., are given in Table I.

The procedure finally adopted was to place the sample to be titrated in a glass-stoppered Erlenmeyer flask. Six cc. of the iodine chloride solution and 6 cc. of carbon tetrachloride are added and finally sufficient hydro-

TABLE I

EFFECT OF THE ORDER OF ADDITION OF REAGENTS

Order of adding reagents to the sample		Grams of iron	
First	Second	Taken	Found
HCl	ICl	0.0683	0.0661, 0.0669, 0.0655
ICl	HCl	.0679	.0679
HCl + ICl		.0679	.0676
ICl	HCl	.0273	.0272, 0.0272
HCl	ICl	.0273	.0254, 0.0264
ICl + HCl		.0271	.0272
CO_2, then HCl	ICl	.0554	.0550, 0.0550

chloric acid so that the final volume of the mixture contains at least 12% of hydrogen chloride. This corresponds to 50% of concentrated hydrochloric acid by volume. After cooling the mixture, standard potassium iodate solution is added and the contents of the flask are thoroughly agitated after each addition of the reagent. Both $N/10$ and $N/20$ solutions were used in this work. The titration is complete when the violet color of the carbon tetrachloride disappears, showing that the iodine which was liberated has been oxidized to iodine chloride. The end-point is accompanied by a change of the orange color of the aqueous layer to a lemon yellow. If the end-point is exceeded, the excess potassium iodate may be determined by a potassium iodide solution which has been standardized with potassium iodate. The potassium iodate used in this investigation was "Merck's Purified" which had been recrystallized twice from hot water and dried at 120–140° for an hour. Since the iodine in the potassium iodate gains four electrons when it forms iodine chloride, a 0.1 N solution is prepared by dissolving 1/40 of a gram molecular weight in sufficient water to make a liter of solution. The iodine chloride solution was prepared by the method of Jamieson.[4] Ten g. of pure potassium iodide and 6.44 g. of pure potassium iodate were dissolved in 75 cc. of water, and 75 cc. of concd. hydrochloric acid and 5 cc. of carbon tetrachloride were added. If the carbon tetrachloride did not have a faint pink color after shaking vigorously, a potassium iodide solution was added until the presence of a little iodine was noted in the carbon tetrachloride. On the other hand, if the carbon tetrachloride was more than a faint pink, potassium iodate was added to convert some of the iodine into iodine chloride.

The reactions involved in the titration of ferrous iron are

$$2Fe^{++} + 2ICl + HCl \longrightarrow I_2 + 2Fe^{+++} + 2Cl^- + HCl \qquad (1)$$

$$2I_2 + 1KIO_3 + 6HCl \longrightarrow 1KCl + 5ICl + 3H_2O \qquad (2)$$

The solution to be titrated with potassium iodate must contain sufficient hydrochloric acid to prevent the hydrolysis of the iodine chloride which is formed. At least 12% of hydrogen chloride must be present at the end of the titration.

Table II shows the results obtained by these directions.

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[4] Ref. 1, p. 8.

TABLE II

RESULTS OF ANALYSES USING THE STANDARD METHOD

Iron taken, g.	Found, g.	Iron taken, g.	Found, g.
0.0557	0.0556	0.0271	0.0272
	.0556		.0271
.1393	.1393	.0679	.0676
	.1391		.0679
.0273	.0272	.0728	.0728
	.0273	.1077	.1077
	.0272		.1075

Ferrous ion can also be determined by adding an excess of potassium iodate to a solution of ferrous ion in dilute sulfuric acid (2 cc. of concd. sulfuric acid per 500 cc. of solution), then adding the hydrochloric acid and carbon tetrachloride and titrating the excess iodate with a solution of potassium iodide whose normality has been determined by titration with potassium iodate. If the hydrochloric acid is added first, and then the excess of potassium iodate, low values for ferrous ion are obtained. The equations for the reactions are

$$4Fe^{++} + 1KIO_3 + 6HCl \longrightarrow 4Fe^{+++} + 1KCl + ICl + 4Cl^- + 3H_2O$$
$$1KIO_3 + 2KI + 6HCl \longrightarrow 3KCl + 3ICl + 3H_2O$$

The results are summarized in Table III.

TABLE III

RESULTS OF ANALYSES USING AN EXCESS OF POTASSIUM IODATE

First	Second	Iron taken, g.	Found, g.
KIO_3 (excess)	HCl	0.0554	0.0553
			.0555
HCl	KIO_3 (excess)	.0554	.0547

In order to determine the effect of organic material, ferrous ion was titrated in the presence of acetic acid, succinic acid, tartaric acid, filter paper, ethyl alcohol and formaldehyde. The procedure adopted was to pipet the sample, which contained 10% of sulfuric acid by volume, into a glass-stoppered flask, add the organic material and about 0.5 g. of pure magnesium to reduce the ferric ion. The mixture was allowed to stand until the magnesium had completely reacted and then the titration was carried out according to the standard iodate method used above. The results obtained are given in Table IV.

TABLE IV

TITRATION IN THE PRESENCE OF ORGANIC MATERIAL

Organic material	Iron taken, g.	Found, g.
Acetic acid, 5 cc.	0.0577	0.0578
Succinic acid, 3 g.	.0577	.0577
Tartaric acid, 3 g.	.0577	.0576
Formalin, 6 cc.	.0577	.0578
Ethyl alcohol, 5 cc.	.0577	.0578
Filter paper	.0577	.0575

The fact that iron can be reduced to the ferrous condition and also titrated in the presence of some organic material greatly increases the usefulness and possibilities of the method.

Summary

1. The ferrous ion is oxidized quantitatively to the ferric ion by iodine chloride and the iodine liberated can be titrated with a standard solution of potassium iodate after adding enough concentrated hydrochloric acid so that the final solution will contain 50% of hydrochloric acid by volume.

2. The ferrous ion can also be determined by adding an excess of standard potassium iodate to a dilute sulfuric acid solution of ferrous ion, and then adding concentrated hydrochloric acid and titrating with a standard potassium iodide solution.

3. The presence of many organic compounds such as acetic acid, succinic acid, tartaric acid, ethyl alcohol, filter paper or formalin does not affect the titration.

4. The method is of especial interest to chemists who are called upon to make occasional analyses, for iodate solutions require no standardization and do not change in strength on keeping.

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THE DETERMINATION OF FERROUS IRON IN SILICATE ROCKS.

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BY BYRON A. SOULE

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The exact determination of ferrous iron in rocks has been conceded to be the most difficult and least satisfactory of all usual determinations in rock analyses.[1]

The Cooke method[2] as modified by Pratt,[3] Barnebey[4] and others, is probably the one most commonly used.

This method involves decomposition of the crushed rock sample by boiling with hydrofluoric and sulfuric acids in a capacious platinum crucible, transfer of the solution to a beaker containing boric acid and titration of the resulting mixture with standardized potassium permanganate.[5]

There are three obvious objections to the method: (*a*) the need for a fairly large (and therefore expensive) platinum crucible, (*b*) the impossibil-

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[1] (a) Hillebrand, U. S. Geol. Survey, *Bull.*, **700**, p. 207; (b) Washington, "The Chemical Analysis of Rocks," John Wiley and Sons, Inc., New York, 3d ed., **1919**, p. 183.

[2] Cooke, *Am. J. Sci.*, [2] **44**, 347 (1867).

[3] Pratt, *ibid.*, [3] **48**, 149 (1894).

[4] Barnebey, THIS JOURNAL, **37**, 1481 (1915).

[5] For details see Washington, ref. 1b, pp. 186–191.