

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

THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. VI. THE DETERMINATION OF IRON USING BASIC MERCURIC BROMATE

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Introduction

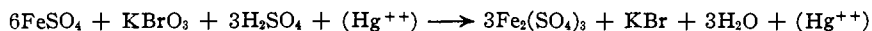
The determination of iron using potassium permanganate in hydrochloric or sulfuric acid solution has been practically universally employed. Permanganate serves as its own indicator. Its standardization using sodium oxalate as reference standard is accurate and convenient. It is probably the most frequently and generally applied of all oxidizing agents. Objections to its use are that because of essential impurities, potassium permanganate is not a reference standard, its solutions are not satisfactorily permanent in oxidizing value and the presence of organic matter interferes.

Potassium dichromate is often substituted for permanganate in determining iron. Dichromate is a reference standard of oxidimetry and its solutions are permanent in oxidizing value.

It has been recently proposed to determine iron using potassium iodate.¹ The reaction in strong hydrochloric acid solution results in the formation of iodine monochloride and has the advantage that organic matter present does not interfere. Iodate solutions can be prepared by weight and are permanent. The iodate determination of iron involves the use of excess of iodate and back titration.

The present paper proposes the use of bromate as a substitute for the above oxidizing agents in the determination of iron. All the advantages of the methods mentioned are provided by the new method with none of the disadvantages. Particularly the method is a direct titration in which the presence of organic matter does not interfere.

Previous Studies.—Ferrous sulfate has been employed successfully in the standardization of sulfuric acid solutions of bromic acid in the presence of mercuric mercury² according to the following reaction:



The oxidation of the iron required three minutes and the excess of ferrous sulfate was finally determined using permanganate. Excellent results were obtained. Fenwick³ in proposing the determination of iron in hydrochloric acid solution electrometrically using potassium bromate describes the process as follows. "The oxidation of ferrous ion with bromate is slow but in the presence of a small amount of cupric salt the velocity is in-

¹ Heisig, *THIS JOURNAL*, 50, 1687 (1928).

² Smith, *ibid.*, 45, 1666 (1923).

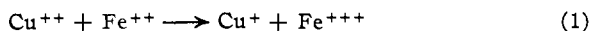
³ Fenwick, "Dissertation," University of Michigan, 1922.

creased to such an extent that an excellent end-point is obtained. A high concentration of hydrochloric acid is necessary, about 15–20% of the concentrated acid gives ideal results." No quantitative data were given since the electrometric character of the end-point above was studied. Collenberg and Sandved⁴ also studied the potentiometric determination of iron using potassium bromate. The following conclusions were drawn: (a) ferric chloride should be reduced using a slight excess of stannous chloride. (b) The hydrochloric acid concentration should be 10–20% by volume (sp. gr. 1.19). (c) Five cc. of 6% cobaltous chloride per 100 cc. volume should be used as catalyst to avoid the necessity for heating the solutions in its absence. The error was 0.25%.

By the process to be described using organic indicators a visual end-point can be obtained. The choice of several possible indicators is provided by reference to the fifth paper of the present series.⁵

Preliminary Considerations.—From a survey of the literature previously given,^{2,3,4} the following method of attack was indicated: the use of hydrochloric acid solution in preference to sulfuric acid to increase the speed of the reaction. The customary use of methyl orange and indigo sulfonate as indicators is not feasible because of the production of premature end-points using potassium bromate as standard solution. Substitution of basic mercuric bromate (HgOHBrO_3)⁶ is known to be a material improvement. The use of stannous chloride as reducing agent would be predicted to give desirable results provided mercuric chloride could be used to remove the excess, avoiding the necessity of the double determination of the reducing agents present as in the method of Collenberg and Sandved.⁴ The use of a cupric ion as catalyst was chosen for a practical study. The determination of iron in the presence of organic matter, together with the selection of an improved dyestuff indicator⁵ for the reaction, completes this study.

The Influence of Cupric Sulfate as Catalyst in the Oxidation of Ferrous Iron with Basic Mercuric Bromate.—The mechanism of the catalytic oxidation of ferrous iron (by bromic acid) in acid solution is indicated by the following two reactions



Reaction 1 indicates the increased speed of oxidation of iron by the bromic acid since the cuprous ion formed is more readily oxidizable than the ferrous ion. Since the oxygen of reaction 2 can be supplied by either atmospheric oxygen or the oxidizing action of the bromic acid employed, low results would be predicted unless the reaction is to be carried out in an

⁴ Collenberg and Sandved, *Z. anorg. allgem. Chem.*, **149**, 191 (1925).

⁵ Smith and Bliss, *THIS JOURNAL*, **53**, 2091 (1931).

⁶ Smith, *ibid.*, **46**, 1577 (1924).

inert atmosphere. The latter expedient is undesirable and means to alter conditions to avoid this were studied.

To study the influence of atmospheric oxygen on reactions (1) and (2) above, solutions were made using known concentrations of ferrous iron plus a small amount of cupric sulfate at a definite concentration of sulfuric acid and a stream of air was passed through the solutions at ordinary temperatures for varying periods of time. The unoxidized iron was then determined by titration with permanganate. The results are shown in Table I.

TABLE I

THE ATMOSPHERIC OXIDATION OF FERROUS SULFATE IN SULFURIC ACID SOLUTION IN PRESENCE OF COPPER SULFATE

Theoretical volume of KMnO_4 required, 17.60 cc.					
Air passage time, hrs.	First Series KMnO_4 required, cc.	Ferrous iron remaining, %	Air passage time, hrs.	Second Series KMnO_4 required, cc.	Ferrous iron remaining, %
0.25	13.90	79.4	2.0	9.60	54.8
.5	13.10	74.8	2.5	7.40	42.2
.75	9.15	52.3	3.0	4.25	24.2
1.0	7.95	45.4	3.5	3.60	20.6
1.25	7.75	44.3	4.0	5.02	28.6
1.50	5.70	32.5	4.75	3.22	18.3

The conclusions to be drawn from the data of Table I substantiated the predictions of reactions (1) and (2). The rate of flow of air was not uniform for the two series, which accounts for the failure in the two to give comparable percentage oxidation in a given time and fluctuations in the air stream account for the absence of more consistent results in each series. The plot of the data using as coördinates the time interval and the logarithm of the percentage oxidation, respectively, indicate that the atmospheric oxidation is a logarithmic function of the time. The reactions would undoubtedly be faster in the presence of hydrochloric acid.

Solutions similar to those of Table I were treated with a stream of acetylene followed by the rapid addition of an excess of ammonium hydroxide. Heavy precipitates of copper acetylides were obtained. Similar tests applied to the cupric sulfate and ferrous sulfate solutions separately gave negative results.

Elimination of the Atmospheric Oxidation of Cuprous Copper.—To prevent the atmospheric oxidation of the cuprous ion produced by the action of the copper sulfate catalyst, which is essential if the use of an inert atmosphere for the titration of ferrous iron is to be prevented, a reagent was sought which would oxidize the copper and leave a reduction compound not affected by atmospheric oxidation. In turn such an addition reagent must be oxidized by bromic acid under the same conditions which prevail for the simultaneous oxidation of iron. Such a reagent is arsenic acid added in the form of ammonium arsenate. The cuprous ion produced in

the presence of ferrous ion is oxidized by the arsenate with the formation of arsenite. The arsenite is in turn not oxidized in acid solution by atmospheric oxygen but is oxidized by bromate under the same conditions as with ferrous iron. A study was made, therefore, of variations in the following reagent concentrations: copper sulfate, ammonium arsenate, hydrochloric acid and phosphoric acid. The indicator to be employed is a final variable to be studied. Fuchsin⁷ was employed as indicator in the preliminary tests following. The effect of the variation of cupric ion concentration is shown in Table II. The ferric sulfate solution was reduced by a slight excess of stannous chloride in hydrochloric acid solution using mercuric chloride to remove the excess.

TABLE II

THE DETERMINATION OF IRON USING BASIC MERCURIC BROMATE IN PRESENCE OF VARIABLE AMOUNTS OF COPPER SULFATE

1 cc. of $\text{Fe}_2(\text{SO}_4)_3 \approx 1.726$ cc. of HgOHBrO_3 . Ferric iron solution approximately $N/10$. 1 g. of $(\text{NH}_4)_3\text{AsO}_4$, 20 cc. of HCl (sp. gr. 1.19) and 10 cc. of 85% H_3PO_4 per 100 cc. of titrating solution at room temperature: $\text{Fe}_2(\text{SO}_4)_3$ solution used, 20 cc.

Titration	Cu ⁺⁺ added, mg.	HgOHBrO ₃ , cc.	HgOHBrO ₃ , calcd.	Difference, cc. of HgOHBrO ₃	Error, g. of Fe
1	1	34.58	34.52	+0.06	+0.0003
2	6	34.54	34.52	+ .02	+ .0001
3	8	34.50	34.52	- .02	- .0001
4	10	34.48	34.52	- .04	- .0002
5	20	34.50	34.52	- .02	- .0001
6	25	34.60	34.52	+ .08	+ .0004
7	30	34.30	34.52	- .22	- .0012
8	40	34.15	34.52	- .37	- .0021

From the examination of Table II the maximum permissible concentration of cupric ion concentration is 20 mg. per 100 cc. of solution titrated. Very small concentrations of cupric ion are sufficient. Too high concentrations of copper give low results.

The effect of variations in the concentration of ammonium arsenate is shown in Table III. Conditions for the data of Table III are the same as

TABLE III

THE DETERMINATION OF IRON USING BASIC MERCURIC BROMATE IN PRESENCE OF VARIABLE AMOUNTS OF AMMONIUM ARSENATE

Titration	$(\text{NH}_4)_3\text{AsO}_4$, g.	AsO_4^{--} , mg./cc.	Ratio, $\text{AsO}_4^{--}/\text{Cu}^{++}$	HgOHBrO_3 , cc.	Error	
					HgOHBrO_3 , cc.	Iron, g.
9	0.0	0.0	..	34.44	-0.08	-0.0004
10	.0	.0	..	34.43	- .09	- .0005
11	.2	1.46	9	34.30	- .22	- .0012
12	.4	2.92	18	34.40	- .12	- .0006
13	.6	4.38	27	34.47	- .05	- .0002
14	.8	5.84	36	34.50	- .02	- .0001
15	1.5	10.95	67.5	34.50	- .02	- .0001

⁷ Society of Dyers and Colourists, "Colour Index," Dye number 678c ($\text{C}_{22}\text{H}_{24}\text{N}_4\text{Cl}$).

for Table II except that the cupric-ion concentration was maintained at 10 mg. per 100 cc. of titrating solution.

From an examination of Table III the most favorable concentration of ammonium arsenate is between 0.6 and 1.5 g. per 100 cc. Concentrations in excess of the higher value produce an unfavorable buffer reaction.

With the use of 10 mg. of cupric ion and 1 g. of ammonium arsenate per 100 cc. by experiments similar to those of Tables II and III, the minimum satisfactory concentrations of phosphoric acid and hydrochloric acid were found to be 5 cc. of 85% H_3PO_4 and 10 cc. of HCl (sp. gr. 1.19) per 100 cc. of solution titrated.

Detailed Procedure for the Determination of Iron

The solution of ferric salt containing 10 cc. of concentrated hydrochloric acid in 25 to 50 cc. volume is heated almost to the boiling temperature and reduced in the hot solution by the dropwise addition of stannous chloride solution until the ferric ion color just disappears and one drop excess of stannous chloride is added. The solution thus obtained is diluted to 80 cc. with cold water and cooled to room temperature. The excess stannous chloride is then removed by the addition of 10 cc. of 10% solution of mercuric chloride. Up to this point the procedure is the same as that employed for the determination of iron using permanganate. For the bromate titration at this point, as also with the permanganate oxidation, 10 cc. of a titrating solution is added and after the addition of a few drops of the indicator the titration with *N*/10 basic mercuric bromate is carried out at room temperature until the first drop excess of oxidizing agent destroys the indicator.

The titration solution used is made by the addition of 4.0 g. of hydrated copper sulfate ($CuSO_4 \cdot 5H_2O$) and 100 g. of ammonium arsenate to a solution of 500 cc. of 85% phosphoric acid diluted to 100 cc.

In addition to the use of the indicator fuchsin already described,⁷ three other indicators were found satisfactory, as is indicated by the results recorded in Table IV.

TABLE IV
THE DETERMINATION OF IRON USING BASIC MERCURIC BROMATE AND VARIOUS INDICATORS

Titration	Indicator	Color index number ⁷	<i>N</i> /10 HgOHBrO ₃ required		Error in Fe value	
			Calcd., cc.	Actual, cc.	Bromate, cc.	Iron, g.
16	Chrysoidine R	21	17.26	17.22	-0.04	-0.0002
17	Chrysoidine R	..	17.26	17.25	- .01	- .0001
18	Bordeaux	88	17.26	17.20	- .06	- .0003
19	Bordeaux	..	17.26	17.26	.00	.0000
20	Naphthol Blue-Black	246	34.52	34.47	- .05	- .0003
21	Naphthol Blue-Black	..	34.52	34.48	- .04	- .0002

From an examination of the data of Table IV, three organic dyes in addition to fuchsin, the indicator employed in obtaining the data for Tables I, II and III and the remaining data of this paper, are made available for the bromate determination of iron. The data of Reference 5 should be examined in connection with the study of available indicators and their characteristics as applied to the present case.

The Determination of Iron by Use of Basic Mercuric Bromate in Presence of Organic Matter.—Preliminary tests indicated that organic matter in a quite general way did not interfere with the determination of iron by bromate under the conditions already described. Among the organic materials examined there were the following: oxalic acid, succinic, citric and tartaric acids, methyl and ethyl alcohols, acetone, formic acid and sucrose. The latter three materials interfere even in low concentration. The qualitative examination of the relationships involved was followed by a quantitative determination of iron in the presence of the various organic reagents and the results are recorded in Table V. Conditions followed in connection with the data obtained in the case of Table IV were duplicated in Table V with the organic material present in addition. The reduction of the ferric sulfate using stannous chloride was carried out in the presence of the organic matter.

• TABLE V

THE DETERMINATION OF IRON IN PRESENCE OF ORGANIC MATTER

Compound added	Amount, g.	HgOHBrO ₃ required, cc.	HgOHBrO ₃ calcd., cc.	Error bromate cc. N/10
Tartaric acid	4	17.28	17.26	-0.02
Citric acid	4	17.19	17.26	- .07
Succinic acid	5	17.20	17.26	- .06
Acetic acid	20	17.28	17.26	+ .02
Oxalic acid	1	17.12	17.26	- .14
Oxalic acid	2	17.16	17.26	- .10
Oxalic acid	4	17.52	17.26	+ .26
Methanol	10 cc.	17.58	17.26	+ .32
Ethanol	10 cc.	17.66	17.26	+ .40
Ethanol	20 cc.	18.52	17.26	+1.26

From the examination of the data of Table V it is observed that for all but excessively large amounts of the products of column one the bromate determination of iron as described is satisfactory. In the case of the presence of alcohol the elimination of interfering large amounts is easily provided for by evaporation. The case of oxalic acid is interesting in connection with the fact that it may be used in sulfuric acid solution at higher temperatures as a quantitative reducing agent² for basic mercuric bromate. A study of various additional organic materials which may be encountered will probably greatly extend the permissible list studied in connection with Table V.

The Preparation of Basic Mercuric Bromate for Use in the Determination of Iron.—Basic mercuric bromate (HgOHBrO₃) is an easily prepared reagent following the descriptive method given by one of us.⁶ Measures are being taken whereby this material can be supplied by the general laboratory chemical reagent supply houses by the time the present paper is available in print. In subsequent papers of the present series the use of

basic mercuric bromate as a standard reference material for use in iodimetry and oxidimetry as well as precipitometry and neutralization reactions will be described. It may thus be said to be an unusual standard of reference. This reagent is stable at 130–140° and acid or neutral solutions of it are perfectly stable for long periods of time. The necessity for making this product available from the usual channels is recognized as a prerequisite to the popularization of its use as a general quantitative reagent. Potassium bromate used as a substitute for basic mercuric bromate in the present work gave small but consistently low values for the determination of iron. The influence of mercuric mercury in the reactions involved is thus indicated as previously discussed.²

Summary

1. A study of the use of bromate in the quantitative oxidation of iron in hydrochloric acid solution has been carried out and the various governing factors have been studied.
2. The conditions employed parallel closely those for the similar determination of iron in hydrochloric acid solution following stannous chloride reduction of the iron and oxidation with potassium permanganate in the presence of mercuric chloride.
3. The titration solution added just prior to the determination of iron by bromate consists of phosphoric acid to which is added copper sulfate and ammonium arsenate. The copper sulfate serves as catalyst for the iron oxidation and the ammonium arsenate prevents interference from atmospheric oxidation caused by the production of appreciable cuprous ion concentrations. The phosphoric acid serves to decolorize the solution when the reduced iron is oxidized by the bromic acid.
4. Four organic internal indicators are described for use in the bromate determination of iron.
5. Advantages of the bromate determination of iron as described make its use favorable as compared to the use of potassium permanganate, dichromate or iodate and particular emphasis is directed to the fact that many organic materials if present do not interfere with the application of the method.

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