[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

STUDIES IN IODIMETRY. IV. POTASSIUM PERMANGANATE AS A STANDARD IN IODIMETRY

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Although in a former article[1] it has been shown that potassium permanganate can be used as an independent standard in iodimetry, there were a number of factors which necessitated further study, especially in view of some helpful suggestions by Dr. W. C. Bray. In the former investigation volume burets were employed and it seemed that differences of 0.05% could well be attributed to experimental errors. Weight burets were used in the present investigation in order to reduce errors to a minimum.

Winther[2] has shown that in acid solution the rate at which oxygen reacts with iodide ion in the dark increases as iodine is liberated and that it proceeds much more rapidly in the light. It is true that the thiosulfate–permanganate ratio in 0.1 *M* sulfuric acid is larger when 6% iodide is used than with 2%. However, when iodine solution is titrated under the same conditions no difference in the thiosulfate–iodine ratio is obtained.[3] This indicates that the difference must be due to some other factors.

Effect of Salts.—Since in the titration of the iodine set free by permanganate there are manganous and potassium salts present, the influence of these salts on the thiosulfate–iodine reaction was studied. Table I shows that manganous sulfate and potassium sulfate in 6% potassium iodide and 0.1 *M* sulfuric acid solution and with ten minutes' standing before titration have no effect on the thiosulfate–iodine reaction. The amount of these salts added was that equivalent to 40 cc. of 0.1 *N* potassium permanganate.

TABLE I

EFFECT OF POTASSIUM AND MANGANOUS SALTS

	Wt. ratio		Wt. ratio
No salts present	1.0701	Salts present	1.0704
No salts present	1.0702	Salts present	1.0702

Effect of Concentration of Iodide, Acid and Light.—It seemed desirable to show that in the thiosulfate–iodine reaction up to 6% potassium iodide and 0.1 *M* sulfuric acid can be used together with ten minutes standing without producing any appreciable change in the thiosulfate–iodine weight ratio, provided, of course, the titrations are carried out in the dark. Table II bears out this statement. In this and subsequent tables the concentrations given are at the end of the titrations. Where

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[1] Popoff and Whitman, THIS JOURNAL, **47**, 2259 (1925).

[2] Winther, *Z. physik. Chem.*, **108**, 236 (1924); **113**, 274 (1924).

[3] See ref. 1, p. 2270.

duplicate results are not given, the values were obtained from two or more determinations in which the maximum variation was 0.05%.

TABLE II

EFFECT OF CONCENTRATION OF IODIDE, ACID AND LIGHT

Potassium iodide, %	2	2	6	
Acid	None	None	0.1 M sulfuric	
Time of standing	None	None	Ten minutes	
Wt. ratio in light	1.0688	1.0686	1.0701	1.0702
Wt. ratio in dark	1.0689	1.0693	1.0690	1.0691

The light used in the experiments with 6% potassium iodide was artificial light from four 100-watt bulbs in a room 18′ × 15′ × 13′. Evidently light from such an electric source cannot be substituted for diffused light. In subsequent experiments red light furnished the necessary illumination.

Winther[2] showed that in the light oxidation of iodide by blowing air through the solution requires a thirty-minute induction period and that the speed of the reaction is increased by the presence of a very small amount of iodine. In our experiments air is not blown through the solutions, there are about 40 cc. of 0.1 N iodine solution present, the time of titration is at most twenty-five minutes and the experiments are performed in the dark. Therefore, the conditions under which Winther performed his experiments are widely different and no appreciable oxidation of the iodide ion takes place under the conditions recommended in our work in iodimetry.

Effect of Rate and Method of Introducing Permanganate.—A study was made of the effect on the thiosulfate–permanganate ratio of introducing the permanganate above and below the surface of the acidified solution of potassium iodide, the acid concentration being 0.1 M sulfuric acid. The stirring during the addition of the permanganate was not done by means of an electric motor as in the experiments (open vessel) given in Table V. The difference between the results given in Tables III and V emphasizes

TABLE III

EFFECT OF RATE AND METHOD OF INTRODUCING PERMANGANATE

% KI	Time of standing	Rate of addition	Method of addition	Thiosul.-perman. wt. ratio
6	None	5 minutes	Above	1.0836
6	None	5 minutes	Above	1.0838
6	10 minutes	5 minutes	Above	1.0836
6	10 minutes	5 minutes	Above	1.0832
6	10 minutes	5 minutes	Below	1.0836
6	10 minutes	5 minutes	Below	1.0838
6	10 minutes	1 minute	Above	1.0836
6	10 minutes	5 minutes	Above	1.0832
2	None	1 minute	Below	1.0817
2	None	1 minute	Below	1.0818
2	None	1 minute	Above	1.0798
2	None	1 minute	Above	1.0800

the necessity of using 6% rather than 2% potassium iodide. The results are given in Table III.

These results show that neither the rate nor mode of addition (within certain limits) of the permanganate has any effect when 6% potassium iodide is used. When 2% iodide is used the weight ratio is greater when the permanganate is added below the surface. Evidently 6% potassium iodide is to be preferred.

In the former paper we quoted incorrectly that Bray and MacKay[4] claimed that the reaction between the permanganate and iodide is slow, hence the necessity of using 6% potassium iodide and ten minutes' standing. This contention, however, must be abandoned in view of the more precise data given in Table III. The former results may be attributed to the failure to exclude light from artificial source (see Table II).

Effect of Alkali.—While it is generally known that the potassium iodide used in most work in iodimetry must be practically free from alkali, yet labels of many analyzed "C. P." samples of potassium iodide do not specify the alkalinity. It is very likely that some of the workers who have recommended the use of acid solutions, when standardizing thiosulfate solutions with iodine, had used slightly alkaline iodide without being aware of the presence of the alkali. Table IV shows the effect of using a "C. P." potassium iodide (analysis of which showed alkali) compared to another not containing alkali.

TABLE IV

EFFECT OF ALKALI IN POTASSIUM IODIDE

% KI	Acid	Thiosulfate–iodine weight ratio Alk. iodide	Non-alk. iodide
2	0.1 M H_2SO_4	1.0695	0.9522
2	0.1 M H_2SO_4	1.0695	.9524
2	No acid	1.0672	.9523
2	No acid	1.0669	.9524

It is recommended that the specifications for potassium iodide given by the Committee on Guaranteed Reagents[5] be followed rigidly.

Effect of Concentration of Potassium Iodide in Closed and Open Vessels.—It was further deemed advisable to study whether or not the large difference in the thiosulfate–permanganate ratios, when using 2 and 6% potassium iodide, is due to the fact that iodine is set free rapidly and that unless 6% iodide is employed iodine is lost by volatilization. In order to determine this, a special apparatus was constructed in which the formation and titration of practically all the iodine were performed in a closed vessel similar to the one previously used for weighing iodine.[6] The end-point was then determined in a beaker. Not more than six drops was re-

[4] Bray and MacKay, THIS JOURNAL, **32**, 1193 (1910).

[5] *Ind. Eng. Chem.*, **19**, 648 (1927).

[6] See ref. 1, p. 2266.

quired to obtain the electrometric end-point. Table V gives the data obtained.

TABLE V

EFFECT OF CONCENTRATION OF POTASSIUM IODIDE IN CLOSED AND OPEN VESSELS

Potassium iodide, %	2	2	6	6
Vessel	Closed	Open	Closed	Open
Thiosul.-perman. wt. ratio	1.2155	1.2148	1.2173	1.2164

It can readily be seen that the difference between using 2 and 6% potassium iodide in the permanganate–iodide reaction is not due to loss of iodine in the former by volatilization. It must probably be attributed to the "loss of oxygen" by the permanganate while in the process of reduction. It is significant to note that the loss of iodine in 2 and 6% potassium iodide (when results in closed and open vessels are compared) is about the same.

The Weight Normality of Potassium Permanganate Solution.—In order to show that 6% potassium iodide must be employed in the permanganate method and no time of standing is necessary, the data of Table VI are presented. The standardization of potassium permanganate with sodium oxalate was carried out as recommended by McBride[7] (except that the end-point was determined electrometrically). In the standardization of the sodium thiosulfate by iodine, 2% potassium iodide was employed, while by potassium permanganate 6% of potassium iodide and 0.1 *M* sulfuric acid. All concentrations are referred to a final volume of 160 cc. About 40 cc. of solution was used and about 20 cc. of water was employed for washing the sides of the vessel just before the end-point.

TABLE VI

THE WEIGHT NORMALITY OF POTASSIUM PERMANGANATE SOLUTION[a]

Normality by sodium oxalate	1.0484
Normality by iodine and wt. ratio of thiosul.-permanganate	1.0483

[a] In all the experiments at least two duplicate determinations were made with a maximum variation of 0.05%.

Summary

1. It has been shown by using weight burets that in the thiosulfate–iodine reaction there is no appreciable oxidation of the iodide ion by the oxygen of the air in a solution containing 6% potassium iodide and 0.1 *M* sulfuric acid, even after standing for ten minutes, provided titrations are made in the dark.
2. Manganous and potassium sulfates in concentrations corresponding to 40 cc. of 0.1 *N* potassium permanganate have no effect under the conditions specified in 1.
3. Potassium iodide used in iodimetry must meet the specifications of the committee on guaranteed reagents in respect to alkalinity.

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[7] McBride, THIS JOURNAL, **34**, 393 (1912).

4. Six per cent. potassium iodide must be employed when sodium thiosulfate solutions are standardized with potassium permanganate. Standing is not necessary. The acid concentration may be 0.1 *M* sulfuric.

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ZIRCONIUM. IV. PRECIPITATION OF ZIRCONIUM BY PHOSPHATES

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This paper is devoted to a study of the completeness of precipitation of zirconium by other phosphates. In testing for completeness of precipitation of potassium by zirconium sulfate it was found that this reagent also gave a precipitate with sodium cobaltic nitrite. Therefore, it became necessary to remove the zirconium before testing for potassium. As phosphates have been used for quantitatively determining zirconium and as Noyes and Bray[1] have shown that phosphates do not interfere with the detection of potassium by sodium cobaltic nitrite, the completeness of removal of zirconium by phosphates prior to testing for potassium was investigated.

The results indicated that a five-fold excess of ammonium phosphate, phosphoric acid or microcosmic salt in the presence of 0.344 molal sulfuric acid were all efficient in removing zirconium but that sodium phosphate was inefficient except when used in forty-fold excess. The presence of added acid was necessary.

Literature

Phosphates.—Sodium phosphate,[2] ammonium phosphate,[3] microcosmic salt[4] and phosphoric acid[5] have been used to determine zirconium quantitatively in the presence of sulfuric acid. Biltz and Mecklenburg[6] recommend the qualitative detection of zirconium by sodium phosphate in the presence of hydrochloric or nitric acid, as sulfuric acid slowed up the reaction.

Conditions for the Precipitation of Zirconium Phosphate.—Marden and Rich[2] recommend "a slight excess of sodium phosphate" in the presence of 10% sulfuric acid. Lundell and Knowles[3] recommend an excess of 10 to 100 times the calculated amount of ammonium phosphate in

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[1] Noyes and Bray, THIS JOURNAL, **31**, 634 (1909).

[2] Marden and Rich, *J. Ind. Eng. Chem.*, **12**, 654 (1920).

[3] Lundell and Knowles, THIS JOURNAL, **41**, 1801 (1919).

[4] Steiger, *J. Washington Academy of Science*, **8**, 637 (1908).

[5] Marden and Rich, Bureau of Mines, Bulletin No. 186, 75–77 (1921).

[6] Biltz and Mecklenburg, *Z. angew. Chem.*, **25**, 2110 (1912).