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STUDIES IN IODIMETRY. III. COPPER AS A STANDARD IN IODIMETRY

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The standardization of solutions in iodimetry has been studied extensively by many investigators. It has been shown by Popoff and Whitman[1] that potassium permanganate, potassium dichromate and potassium bromate can be used as independent standards for sodium thiosulfate solutions and that they all give practically the same value (within 0.05%) as that obtained when iodine is used as a standard.

It is usually considered that copper cannot serve as an independent standard for sodium thiosulfate solutions and therefore it is generally recommended that thiosulfate solutions be standardized against metallic copper under identically the same conditions that are to be used subsequently. It has been possible, however, to find conditions which give the same value (within 0.05%) when using copper and iodine as standards for sodium thiosulfate solutions. The foregoing was made possible by the use of an unquestionable, reliable and easily reproducible preliminary standard (iodine), by controlling the factors which influence the reactions so that variations were kept within 0.05%, and finally by the exclusive use of electrometric methods of determining the end-points.

The use of copper as a standard in iodimetry was first mentioned by de Haen[2] in 1854. Since 1854 many investigators have made a study of the causes of variations in the results obtained by standardizing the sodium thiosulfate solution against copper and against pure iodine. The larger deviations have been attributed to various causes.

The object of the present investigation was to determine the factors which influence the reaction between copper solutions and potassium iodide and thus to enable us to place copper as an independent standard in iodimetry.

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

[2] De Haen, *Ann.*, 91, 237 (1854).

Materials

Iodine.—Best quality iodine was resublimed once from potassium iodide and twice alone.

Sodium Thiosulfate.—c. p. quality sodium thiosulfate crystals were placed in a large bottle, through the stopper of which a glass tube was connected to the condenser of an all-glass water still and redistilled water was distilled over into the bottle until the solution was approximately 0.1 *N*. The normality of this solution did not change for over three weeks.

Copper Sulfate.—Analyzed c. p. cupric sulfate was twice recrystallized and a 0.1 *N* solution was prepared using redistilled water.

Copper.—Pure electrolytic copper was employed. This metal was prepared by the method given on p. 1305.

Potassium Iodide.—A solution of Mallinckrodt's reagent quality potassium iodide was employed which gave no color to phenolphthalein and which contained no iodate.

Water.—The ordinary laboratory distilled water was redistilled in the presence of potassium permanganate in an all-glass apparatus.

Experimental Procedure

The easiest approach to the solution of the problem at hand consisted in the study of the various factors which determine the reaction between a copper sulfate solution and potassium iodide. If these were determined beforehand, it would be an easy matter to decide whether or not copper can serve as an independent standard for sodium thiosulfate solutions.

The factors which may determine the extent and kind of reaction are: (1) concentration of potassium iodide, (2) kind and concentration of acid, (3) cuprous iodide, (4) order of addition of reagents, (5) time of standing and (6) the presence of salts.

In order to study the foregoing factors, approximately 0.1 *N* solutions of copper sulfate and sodium thiosulfate were prepared and kept in bottles which were painted with black auto enamel. The reagents were added very slowly (about 15 cc. per minute) and with constant stirring whenever reactions were taking place. The end-point was determined electrometrically. The end-point was calculated by the simple process of interpolation described formerly.

Practically all of the determinations were made by using weight burets. The concentrations of all the solutions are expressed in the final volume, which was 160 cc. in all cases. The total time of each titration was about fifteen minutes. The copper sulfate was added from an especially made weight pipet. In all cases the volumes of the copper sulfate and the sodium thiosulfate solutions employed were about 35 to 38 cc. The numerical values given represent the averages of at least two determinations which did not differ by more than 0.05 of a per cent. Unless otherwise stated the copper sulfate solution was added to the potassium iodide solution.

1. **Effect of the Concentration of Potassium Iodide.**—The concentration of potassium iodide was varied from 2 to 24%. These concentrations do not allow for the iodide ion used up in the reaction. Table I shows the influence of the concentration of potassium iodide in the reaction between copper sulfate and potassium iodide in neutral solution. In all cases the iodide was added to the copper solution. The ratios are weight ratios of sodium thiosulfate solution to copper sulfate solution.

TABLE I

THE EFFECT OF CONCENTRATION OF POTASSIUM IODIDE

Concn. of KI, %	2	4	6	8	12
Weight ratios	1.0926	1.0935	1.0932	1.0928	1.0936

Up to 12% of potassium iodide the effect of increasing the concentration of potassium iodide is negligible. The lowest result obtained when 2% potassium iodide was used is no doubt due to loss of iodine, as in the final volume there was not 2% of potassium iodide present. When sufficient potassium iodide was present to dissolve the cuprous iodide completely, the weight ratio was increased by about 0.2%. The latter may be due to the oxidation of the cuprous ion to cupric by the air with the subsequent liberation of more iodine. It is possible, however, that Bray and MacKay's[3] suggestion that cuprous iodide adsorbs iodine is correct.

2. **Effect of Kind and Concentration of Acid.**—In order to determine the effect of acid on the reaction, the concentration of potassium iodide was kept constant at 4% and the reactions were made in neutral, 0.1 *M* sulfuric acid and 0.4 *M* acetic acid solutions. The reactions were carried out in the dark in order to prevent oxidation of the iodide ion by the air. The results obtained are recorded in Table II.

TABLE II

KIND AND CONCENTRATION OF ACID

Acid	Neutral	0.1 *M* sulfuric	0.4 *M* acetic
Ratios	1.0934	1.0959	1.0942

Evidently acid increases the amount of iodine set free. This may be due either to the oxidation of the iodide ion by the air, or to the oxidation of the cuprous ion to cupric (by the air) with the subsequent reaction with the iodide ion to form iodine. The presence of acid will no doubt increase the above oxidation. Since, however, it has been shown in previous investigations that the former does not take place in diffused light, the increase of the iodine set free may be due entirely to the oxidation of the cuprous ion to the cupric. Cuprous salts, especially the chloride and bromide, are well-known oxygen carriers in acid solutions.

Evidently the hydrogen-ion concentration is a decided factor, as the iodine set free is greater with sulfuric acid than with acetic acid. It is advisable, therefore, to keep the actual acidity as low as possible. The results obtained appear to differ from those reported by others. Bray and MacKay[3] find sulfuric acid objectionable but not acetic acid. Peters[4] finds that a small concentration of sulfuric acid or a large concentration of acetic acid can be employed without any effect.

3. **The Effect of Cuprous Iodide.**—In order to determine the effect

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[3] Bray and MacKay, THIS JOURNAL, **32,** 1199 (1910).

[4] Peters, *ibid.*, **34,** 422 (1912).

of cuprous iodide, it was found necessary to prepare cuprous iodide and observe its effect upon the sodium thiosulfate–iodine reaction. The cuprous iodide was prepared by the addition of copper sulfate solution to potassium iodide solution. The cuprous iodide was washed with dilute potassium iodide solution (making use of the centrifuge) until practically free from iodine. The amount of iodine that remained in the cuprous iodide was determined by electrometric titration with sodium thiosulfate and the volume of thiosulfate required was subtracted from the total volume of thiosulfate in the subsequent titrations. Experiments were performed in which the effect of cuprous iodide on the thiosulfate–iodine reaction in the presence of 4% potassium iodide in neutral and in acid solution was determined. The results are given in Table III.

TABLE III

EFFECT OF CUPROUS IODIDE ON THIOSULFATE–IODINE REACTION

	Neutral, no CuI	Neutral + CuI	0.1 *M* H_2SO_4 + CuI	0.4 *M* HAc + CuI
Series I	0.9916	0.9917	....	....
Series II	.9905	....	0.9945	0.9930

From the foregoing results it may be concluded that cuprous iodide has no effect on the thiosulfate–iodine reaction in neutral solutions containing 4% of potassium iodide. In acid solutions, however, the effect is appreciable. It is advisable, therefore, to keep the solutions in titrations involving cupric salts and iodide ions as nearly neutral as possible. The effect of acetic acid seems to be much greater than that shown in Table II. This may be due to the fact that it was almost physically impossible to duplicate the experimental conditions.

4. **Order of Addition of Reagents.**—It was found that the order of addition of the reagents (when using 4% potassium iodide) made practically no difference, as the values obtained were 1.0935 and 1.0933.

5. **Time of Standing.**—In the dichromate-ion–iodine-ion–hydrogen-ion reaction it is necessary to let the reaction proceed for ten minutes before sodium thiosulfate is added. The effect of time of standing with the cupric-ion–iodide-ion reaction was determined using 4% potassium iodide. Table IV gives the results obtained.

TABLE IV

EFFECT OF TIME OF STANDING

	Weight ratio
Titrated immediately	1.0935
Standing for 10 min. before beginning titration	1.0934
Standing for 10 min. just before the end-point	1.0935

Evidently, under the conditions employed, the reaction between copper sulfate and potassium iodide goes to completion immediately and no time of standing is necessary.

6. **The Presence of Salts.**—The effect of the presence of salts was not determined. According to former investigators, potassium sulfate or salts in general decrease the amount of liberated iodine. It was deemed advisable, therefore, to keep the concentration of salts as small as possible in the standardization of the sodium thiosulfate solution by metallic copper.

The Determination of the Concentration of the Copper Sulfate Solution

From the study of the effect of the various factors in the copper sulfate–potassium iodide reaction, it was found necessary to perform the reaction in a solution which was as nearly neutral as possible and in the absence of salts. In order that these conditions might be rigidly maintained, a 0.1 N solution of copper sulfate was prepared and its concentration determined accurately by electrolysis. Former studies on the electrolytic determination of copper in this Laboratory by Tucker[5] were of special value.

The Electrolytic Determination of Copper.—A rotating platinum anode and copper gauze cathode served as the electrodes. A current of 1.5 amperes was used. The electrolysis was made to proceed until no positive test was obtained by haemotoxylin. The use of haemotoxylin as a test for copper was first introduced by Bradley;[6] however, no specific directions are given by former investigators. The test as finally employed was as follows.

About 2 cc. of the solution (after electrolysis had proceeded for about forty minutes) was placed in a small porcelain crucible. Two or three drops of the haemotoxylin indicator were added and then enough solid sodium carbonate to produce a red color. Finally, a saturated solution of sodium bisulfite was added dropwise until the red color disappeared. If copper were present, a blue color remained. A decided positive test for copper was obtained from a solution which contained 0.06 mg. of copper in 200 cc. of solution. If 0.06 mg. of copper still remained in solution the error would be about 6 parts in 30,000 or 0.02%. In this connection it may be of interest to state that the potassium ferrocyanide spot-plate test, as ordinarily used, is hardly sensitive enough as there can be as much as one mg. of copper without detection. Again, the method[7] of adding more water to the electrolysis solution and observing whether or not any copper is deposited on the freshly exposed platinum surface of the cathode, cannot be considered a sensitive test for copper as we have not been able to observe any deposit of copper when there was 0.5 mg. of copper in 200 cc. of solution. Again, the method employed by Quisumbing and Thomas[7] of withdrawing the cathode is open to very serious objections, as is shown by the following experiments.

Solutions containing varying concentration of acids per 200 cc. were prepared. These were placed in the electrolysis apparatus and the weight of the cathode before and after withdrawal was determined. The current was left on and the cathode was quickly withdrawn and plunged into distilled water. This method will be called the "short cut" in order to contrast it with the "siphon" method, in which the electrolysis solution was continually being siphoned off and distilled water added so as to keep the solution over the cathode. The latter process is continued until the ammeter showed very little or no current (this required about 2 liters of water). Table V gives the results obtained.

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[5] Tucker, Iowa "Thesis," 1924.

[6] Bradley, *Chem. News*, **94**, 189 (1904).

[7] Quisumbing and Thomas, THIS JOURNAL, **43**, 1503 (1921).

TABLE V

LOSS OF COPPER USING THE "SHORT CUT" AND "SIPHON" METHODS OF WITHDRAWING THE CATHODE

Vol. of concd. acids, cc.	2, nitric	0.3, nitric	2, sulfuric	0.3, sulfuric
"Short cut" loss, mg.	1.3	0.3	1.8	0.8
"Siphon" loss, mg.	0	0	0	0

It can be seen readily that even at a concentration of 0.3 cc. of concd. nitric acid there is a loss of 0.3 mg. by the "short cut" method, as compared with no loss by the "siphon" method even when 2 cc. of concd. sulfuric acid were employed.

Strangely enough no one except Fales[8] has considered the solubility of the platinum anode in the electrolytic determination of copper. The solubility of platinum serving as the anode is not negligible and amounts to about 0.2 mg. when 2 cc. of concd. sulfuric acid and 1 cc. of concd. nitric acid per 200 cc. are employed. It must be stated, however, that Fales' suggestion of weighing the cathode after the deposition (not before) is complete, dissolving the cathode deposit and weighing the platinum electrode will hardly allow for the solvent action of the platinum anode. Certainly no platinum is present in the solution just as electrolysis is started. Any platinum that dissolves during the electrolysis will be deposited over the copper and it will be removed on dissolving the copper. It was ascertained that a mixture of nitric and sulfuric acids present to the extent of 0.15 cc. of each or 0.3 cc. of sulfuric acid only, will not exert solvent action on the platinum anode. In subsequent determinations these concentrations of acids were employed.

Although the haemotoxylin test for copper was negative, nevertheless it was deemed necessary to make absolutely certain that no appreciable amount of copper was left in the two liters of the "wash" solution There-fore the entire solution was evaporated to dryness. A few drops of nitric acid was added, the solution neutralized with ammonium hydroxide and then acidified with sulfuric acid. At the same time about two liters of water were evaporated and the residue (if any) treated in similar fashion. Potassium iodide was added to these solutions. Both solutions required only one drop of sodium thiosulfate to pass the electrometric end-point. It is believed that the foregoing tests show conclusively that the deposition of copper, as performed, is practically complete, especially since haemotoxylin gave no test for copper after the "wash" solution was evaporated to about two cubic centimeters.

Table VI gives the results obtained for the concentration of copper in the copper sulfate solution which was employed for the standardization of the sodium thiosulfate solution.

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[8] Fales, "Inorganic Quantitative Analysis," Century Book Co., New York, 1925, p. 342.

Table VI

The Concentration of the Copper Sulfate Solution

Series I. 0.15 cc. of HNO_3 + 0.15 cc. of H_2SO_4

	1	2	3	4
Wt. of $CuSO_4$ soln., g.	54.486	52.417	53.158	49.893
Wt. of Cu deposited, g.	0.3365	0.3235	0.3281	0.3082
Cu per g. of $CuSO_4$ soln., g.	0.006174	0.006171	0.006172	0.006177

Series II. 0.30 cc. of H_2SO_4

	5	6	7
Wt. of $CuSO_4$ soln., g.	50.892	50.655	50.603
Wt. of Cu deposited, g.	0.3141	0.3127	0.3125
Cu per g. of $CuSO_4$ soln., g.	0.006172	0.006173	0.006175

Average of Series I (excluding No. 4) = 0.006172
Average of Series II = 0.006173
Average of all values = 0.006173

The Standardization of Sodium Thiosulfate

Since pure elementary iodine is considered to be the best standard for sodium thiosulfate solutions, the sodium thiosulfate was standardized against pure iodine according to the method of Popoff and Whitman[1] and the results were compared with the values obtained when using the standard copper sulfate solutions and pure copper.

The Iodine Method.—The special apparatus described by Popoff and Whitman was employed. The final volume was 160 cc. and 4% of potassium iodide was used.

The Copper Sulfate Method.—The copper sulfate solution was added to a potassium iodide solution containing 4% of potassium iodide in the final volume of 160 cc.

The Copper Method.—Pure electrolytic copper was prepared and used in this determination. To prepare the pure copper, copper sulfate was recrystallized several times and an acidified solution of this salt was used in the electrolysis. A copper foil was employed as the cathode for the preparation of the electrolytic copper. It was a comparatively easy matter to remove the copper from the copper foil. The attempt to use aluminum foil failed as the electrolytic copper seemed to be contaminated with aluminum.

About 0.24 g. of copper was dissolved in 8 cc. of 6 *M* nitric acid. The solution was evaporated on the steam-bath until on cooling it would completely solidify. The residue was dissolved in about 20 cc. of water and dilute sodium hydroxide solution added until a permanent precipitate was just formed. Now 8 *M* acetic acid was introduced until the precipitate completely dissolved and then about four drops in excess. The solution was diluted to about 100 cc. with water and enough potassium iodide was added so that in the final volume of 160 cc. there would be 4% potassium iodide. If a sufficient amount of acetic acid was added to make the solution 0.4 *M* as directed by Fales, the error was increased by about 0.1%.

In all of the experimental work the potassium iodide was a 50% solution (by volume) and it was added very slowly with constant stirring (by an electric motor).

The copper sulfate solution, as well as the sodium thiosulfate solution, was weighed and the results given in Table VII are calculated on the basis of 1000 g. of sodium thiosulfate solution.

TABLE VII

THE NORMALITY OF THE SODIUM THIOSULFATE SOLUTION

Standard	Series	Normality	Diff. comp. to I_2, %	Series	Normality	Diff. comp. to I_2, %
Iodine	I	0.08880	..	I	0.00880	..
$CuSO_4$	I	0.08881	0.01	II	0.08883	0.03
Cu	I	0.08881	0.01	II	0.08881	0.01

No attempt will be made at this time to explain why previous workers were not able to make the standardization of a thiosulfate solution by copper check with other standards, because an explanation is not possible when all the factors are not known. One may venture stating that the standards and probably the conditions employed by former investigators were not ideal.

Summary

1. (a) From the study of the reaction between copper sulfate and potassium iodide, it was found that a change of concentration of the latter from 4 to 12% in neutral solutions had no effect on the thiosulfate–copper sulfate ratio.

(b) In the presence of 0.1 *M* sulfuric acid and 4% potassium iodide the thiosulfate–copper sulfate ratio is increased by about 0.2% and in the presence of 0.4 *M* acetic acid by 0.08%.

(c) The order of addition of the reagents makes no difference in neutral solutions when 4% potassium iodide is used.

(d) Time of standing (ten minutes) has no effect in the presence of 4% potassium iodide.

2. Cuprous iodide has no effect on the thiosulfate–iodine ratio in the presence of 4% potassium iodide and in neutral solutions. In acid solutions it causes an increase in the ratio.

3. Some glaring errors are pointed out in the electrolytic determination of copper. It is recommended that the concentration of acid be kept low and that practically all of the acid be removed before the copper cathode is taken from the solution. A very sensitive test for copper is used.

4. It is now possible to use either copper sulfate solution or pure copper as an independent standard in iodimetry provided the salt and the acid concentration are kept very small.

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