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STANDARDIZATION OF SOLUTIONS USED IN IODIMETRY.[1] II

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Introduction

It is well known that, until recently, rather large discrepancies have existed between results obtained in the standardization of solutions of sodium thiosulfate, using such standards as pure iodine, potassium permanganate and potassium dichromate. The results of Kolthoff,[2] Vosburgh,[3] Hendel[4] and Bray and Miller[5] show that by properly choosing the experimental conditions, these standards may give results agreeing within 0.1%. However, the conditions prescribed by these workers are not in complete agreement among themselves, thus indicating the existence of certain disturbing influences yet unaccounted for. Our experiments also indicate that the thiosulfate-iodine reaction gives equally accurate results in neutral or acid solution, although Vosburgh and Bray and Miller found that accurate results could be obtained only in acid solution.

It is believed that in order for a reaction to be useful as a standard, it should be possible to duplicate its results within 0.05%, rather than merely to obtain values which vary from an average by 0.05% or 0.1%, or even by 0.3% as reported in some cases. This should be true not only for a given method, but also among different methods which are to be used for the same standardization.

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[1] This paper is constructed from the dissertation presented by J. L. Whitman to the Faculty of the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1924.

[2] Kolthoff, *Z. anal. Chem.*, **59**, 401 (1920).

[3] Vosburgh, This Journal, **44**, 2120 (1922).

[4] Hendel, *Z. anal. Chem.*, **63**, 321 (1924).

[5] Bray and Miller, This Journal, **46**, 2204 (1924).

Since in the standardization of a thiosulfate solution by any of the standards mentioned the final results depend upon the reaction between thiosulfate and free iodine, the only value that can reasonably be considered to be correct is that obtained with pure, elementary iodine. It is thus evident that the study of any standard should be based upon a study of the reaction between thiosulfate and iodine, and that no conditions may be chosen for the standardization which are in conflict with the best conditions for that reaction.

By a careful study of the conditions affecting the thiosulfate-iodine reaction, some of which have not before been considered to be of importance, and by the exclusive use throughout the work of the electrometric method of obtaining end-points, we have succeeded in obtaining a maximum variation among results of 0.06%, using pure iodine, potassium permanganate, potassium dichromate and also potassium bromate as standards. The last has not previously been studied critically in this connection.

Part I is a report of the study of the thiosulfate-iodine reaction. Part II contains the results obtained using the various standards mentioned above.

Part I. The Reaction between Sodium Thiosulfate and Iodine

From the time of Du Pasquier,[6] starch has been used almost exclusively as an indicator in iodimetry. Although very sensitive, this, as is true for any reagent giving a color end-point, requires the presence of some excess of the reagent to produce a visible color. The accuracy of the titration also depends to some extent upon the particular starch solution used, and the "personal equation" of the observer. These uncertainties may all be largely eliminated by the use of the electrometric method, and it has been found quite easy to determine the end-point accurately within 0.01 cc.[7] The end-point was determined by interpolation of readings of potential and cubic centimeters of solution obtained immediately preceding and following the end-point. The following data illustrate the method used.

Cc. of reagent	39.86	39.89	39.92	39.95	39.98
E (relative)	0.295	0.283	0.246	0.204	0.194
dE		.012	.037	.042	.010

Since dE at 39.92 is 0.037 while at 39.98 it is 0.010, the end-point is nearer to 39.92 than to 39.95 and 39.93 is taken as the true end-point. If dE

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[6] Du Pasquier, *Ann. chim.*, [3] **73**, 310 (1840).

[7] It is essential that the platinum electrode be cleaned after every titration. This is shown by the following sets of values, the first of which was obtained without cleaning the electrode. The second by cleaning the electrode after every titration. Ordinary "cleaning mixture" has been found to be very satisfactory for this purpose.

I. 1.0635; 1.0649; 1.0639; 1.0618; 1.0608; 1.0631; 1.0634

II. 1.0643; 1.0637; 1.0641; 1.0640; 1.0642; 1.0642; 1.0637 at 39.92 and 39.98 had been reversed, then the true end-point would have been taken at 39.94.

In this work it has been found very convenient to use paired burets, the tips of which are drawn out and bent to one side in such a manner that they may easily be caused to touch the side of a tall beaker. This is desirable when the solution is flowing from the buret, in order that no splashing may occur. The burets thus adjusted were found to deliver about 0.03 cc. per drop.

Materials

Iodine.—C. P., resublimed iodine was again sublimed, once from potassium iodide and twice alone, and kept over phosphorus pentoxide in a greaseless desiccator, although from the work of Foulk and Morris[8] this hardly seems necessary.

Potassium Iodide.—Mallinckrodt's "reagent quality" granular potassium iodide was found to be most satisfactory, no trace of iodine being liberated from an acidified solution that had stood in diffused light for 15 minutes. A solution of the salt showed no alkalinity when tested with phenolphthalein.

Acids.—The best grades of concd. C. P. acids were diluted as needed. No acid was used which gave a test for oxidizing agents, that is, which produced free iodine when mixed with a solution of potassium iodide.

Water.—Redistilled water, or ordinary laboratory distilled water which by comparative experiments gave the same results as the redistilled water, was employed throughout this work.

Iodine Solution.—Sufficient iodine to make a 0.1 N solution, and potassium iodide equivalent to 4% (40 g. per liter) were mixed and triturated with small quantities of water until completely dissolved. This concentrated solution was allowed to stand for some time, at least overnight, in order to insure complete solution of the iodine, and then diluted to the required volume.

Thiosulfate Solution.—About 20 liters of approximately 0.1 N solution was prepared at a time from Baker's C. P. crystallized salt, allowed to stand for at least ten days and the clear solution siphoned into a clean bottle provided with a soda-lime tube. In order to protect such a solution from the light the bottle was painted black. For this purpose a good grade of black automobile enamel has been found to give excellent results and is recommended.

A detailed study has been made of the effect of varying the following factors; dilution, concentration of iodide, kind and concentration of acid, order of mixing the thiosulfate and iodine, time of standing before final titration, and effect of light. Apparently very little work has been done on this phase of the problem. Pickering[9] reports some results but considers that all variations may be explained on the basis of the varying amount of sulfate formed. Vosburgh finds that higher and more accurate results are obtained in a solution containing 0.1 N hydrochloric acid. This point will be discussed later. Kolthoff[10] found that the presence of acid was not essential and by means of buffer mixtures studied the Sörensen (P_H) value at which the formation of sulfate became important.

[8] Foulk and Morris, THIS JOURNAL, **44**, 231 (1922).

[9] Pickering, *J. Chem. Soc.*, **37**, 128 (1880).

[10] Kolthoff, *Z. anal. Chem.*, **60**, 338 (1921).

Effect of Dilution and Concentration of Iodide.—Sufficient water was placed in the titration beaker so that after the addition of about 40 cc. each of the thiosulfate and iodine solutions the final volume would have a predetermined value. The entire time required for a titration was approximately ten minutes. Under these conditions it was found that when the final volume was 400 cc. or greater, the ratio[11] of the volumes used became smaller, indicating a loss of iodine. In this case no iodide is used other than that originally present in the 40 cc. of iodine solution. Thus, when the final volume is 80 cc., the final concentration of iodide is 2%, but with a final volume of 400 cc. the end concentration of iodide is reduced to only 0.4%. These results are summarized in Table I.

TABLE I

EFFECT OF VARIATION OF DILUTION IN THE THIOSULFATE-IODINE REACTION

Series I		Series II	
Final vol., cc.	Ratio	Final vol., cc.	Ratio
80	1.0208	80	1.0223
120	1.0207	120	1.0220
120	1.0209	160	1.0222
160	1.0209	200	1.0218
160	1.0209	280	1.0219
400	1.0183	400	1.0191
400	1.0184	400	1.0180

The loss of iodine may occur in two ways; first, through volatilization when the amount of iodide is as small as 0.4%; second, by hydrolysis, which will result in the formation of iodide and hypo-iodous acid with a consequent loss of free iodine.

Chapin[12] states that at least 4% of iodide must be present to prevent loss of iodine; Popoff and Chambers[13] have found evidence to support this view; and Rice, Kilpatrick and Lemkin[14] believe that 2% is nearly as effective as 4%. Since in the dilution tests described above, the chief factor which might affect the results in the concentration of iodide, further experiments were carried out in which the final volume constant was kept at 160 cc. and the concentration of the iodide varied. It was thus found that no appreciable loss of iodine occurs when the iodide concentration varies from 1 to 8%, except when the solution containing only 1% is allowed to stand for five minutes or more before titration. That the time factor is of importance when the iodide concentration is small is shown by the values in Table II:

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[11] Expressed as cc. of thiosulfate per cc. of iodine. All subsequent volume ratios in this paper are expressed as cc. of thiosulfate per cc. of X, where X is the volume of any standard solution being used.

[12] Chapin, THIS JOURNAL, **41**, 357 (1919).

[13] Popoff and Chambers, *ibid.*, **45**, 1358 (1923).

[14] Rice, Kilpatrick and Lemkin, *ibid.*, **45**, 1361 (1923).

TABLE II

EFFECT OF TIME OF STANDING IN THE THIOSULFATE-IODINE REACTION

Concn. of iodide, %	1		2		3	
Time of standing, min.	0	5	0	5	10	0
Ratio	1.0027	1.0018	1.0025	1.0025	1.0027	1.0030
	1.0027	1.0015	1.0027	1.0027	1.0025	1.0030

This explains certain results of Popoff and Chambers, who found that a higher volume ratio was obtained with 4% iodide than when only 1% was present at the end of the titration, the time of titration being 15 minutes.

Effect of Concentration of Acid.—With the final volume and iodide concentration kept constant at 160 cc. and 1%, respectively, the acidity was varied. A maximum difference of 0.07% in volume ratios was observed using sulfuric acid in concentrations from 0 to 0.4 *M*. Higher concentrations gave somewhat erratic results. Using hydrochloric acid in concentrations varying from 0 to 1.2 *M*, results were obtained which varied by only 0.05%. With acetic acid, results were somewhat less satisfactory but usually checked within 0.1%.

Although it has repeatedly been found that, using the electrometric method, more satisfactory results could be obtained in neutral solution, yet the above results show that in general the presence of acids in concentrations as high as 0.6 *M* does not affect the thiosulfate-iodine reaction. This agrees with the statement of Kolthoff,[10] "that in strongly acid solution the reaction between thiosulfate and iodine proceeds normally, provided one stirs vigorously during the titration."

If free iodine is lost by hydrolysis, this effect should be eliminated or largely reduced by maintaining a sufficiently high concentration of either hydrogen or iodide ion. It should thus be possible to prevent such loss by the addition of either acid or potassium iodide and so obtain correct values even in a large final volume. As stated before, Vosburgh obtained better results in a solution containing 0.2 *M* hydrochloric acid, but it must be remembered that his titrations were made in a final volume of about 400 cc. and in the presence of about 0.5% of iodide. Higher results, with respect to the normality of the thiosulfate solution, would of course be obtained thus in the

TABLE III

EFFECT OF DILUTION AND ACID AND IODIDE CONCENTRATIONS IN THE THIOSULFATE-IODINE REACTION

SERIES I—FINAL VOLUME, 160 CC.			SERIES II—FINAL VOLUME, 400 CC.		
Concn. of iodide, %	Concn. of acid	Ratio	Concn. of iodide, %	Concn. of acid	Ratio
1	0	0.8646	0.4	0	0.8638
1	0	.8650	.4	0	.8635
4	0	.8647	1	0	.8645
4	0	.8649	4	0	.8647
4	0.2 *M* H_2SO_4	.8652	0.4	0.06 *M* HCl	.8646
4	0.2 *M* H_2SO_4	.8651	0.4	0.06 *M* HCl	.8645

acid solution in which hydrolysis of iodine was largely prevented. In Table III are collected a few results, typical of a large number obtained, illustrating the effect of variation of final volume, and iodide and acid concentrations.

Particular attention is called to the fact that here again is found the lower value when large volume and small concentration of iodide are used, but when the iodide is maintained at least at 1% and the titration does not require over ten minutes this difference disappears, as would be expected; further, the difference also disappears in the presence of 0.06 *M* hydrochloric acid, that is, acid equivalent to 1% of iodide, or sulfuric acid up to 0.6 *M*.

Effect of Light.—Most of the authors referred to above at least indicate the necessity of considering the effect of light upon the decomposition of hydrogen iodide. Daubeny[15] in another connection mentions this decomposition, and many others state that the intensity of light is a factor, but in most cases experiments are merely reported as carried out in diffused light. Foulk and Morris[8] found that artificial light gave best results. Sunlight acts as a catalyst to increase the oxidation by the oxygen of the air, of the hydrogen iodide present in an acidified solution of potassium

TABLE IV

EFFECT OF LIGHT ON THE DECOMPOSITION OF HYDROGEN IODIDE

Nos. 1 to 12 were exposed to direct sunlight, Nos. 13 to 23 to diffused light

No.	Concn. of KI, %	Concn. of acid, *M*	Cc. of thiosulfate	Remarks
1	1	0	0	No color after 11 days
2	2	0	0	Faint blue in 11 days
3	4	0	0	Faint blue in 5 hours
4	1	0.2 H_2SO_4	0.1	
5	1	.6 H_2SO_4	.6	
6	1	1.2 H_2SO_4	.9	
7	1	0.2 HAc	0	No color with starch
8	1	.6 HAc	0	No color with starch
9	1	1.2 HAc	0	No color with starch
10	1	0.2 HCl	0.03	
11	1	.6 HCl	.3	
12	1	1.2 HCl	.6	
13	1	0.2 H_2SO_4	0	No color with starch
14	1	.6 H_2SO_4	0.03	
15	1	1.2 H_2SO_4	.1	
16	1	0.2 HCl	0	No color with starch
17	1	.6 HCl	0.03	
18	1	1.2 HCl	.06	
19	4	0.2 HAc	0	Very faint blue in 1 hr.
20	4	.6 HAc	0	
21	4	1.2 HAc	0	
22	4	0.2 H_2SO_4	0.03	
23	4	.2 HCl	.03	

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[15] Daubeny, *J. Chem. Soc.*, **20**, 10 (1867).

iodide; thus, $4HI + O_2 \longrightarrow 2H_2O + 2I_2$. It would therefore be expected that the amounts of iodide and acid which could safely be used together would depend upon the intensity of the light. To test this point the following experiment was performed. A series of 250cc. Erlenmeyer flasks was prepared, each containing in 160 cc. of solution, various amounts of iodide and acid; these flasks were exposed to direct sunlight for 10 to 12 minutes. The amount of thiosulfate required to react with the liberated iodine in each flask was then determined, using starch as an indicator. A similar set was exposed to diffused light for a like period of time.

From these results it is reasonable to conclude that, with solutions containing as much as 4% of iodide, even direct sunlight will have no effect. Likewise, sunlight should have no effect in the presence of acetic acid. Hydrochloric acid or sulfuric acid should not be used in any concentration in direct sunlight, but in diffused light 1% of iodide and 0.2 *M* acids may be used with safety. The correctness of these conclusions is proved by an examination of the data given in Table V.

TABLE V

EFFECT OF LIGHT IN THE THIOSULFATE-IODINE REACTION

Concn. of iodide, %	Concn. of H_2SO_4, *M*	Diffused light	Very bright	Sunlight
		Series I		
1	0	1.0640	1.0638	
2	0	1.0648	1.0642	
2	0.25	1.0648	1.0670	1.0725
		Series II		
1	0			0.8566
4	0		0.8566	
4	0.25	0.8568		

A large number of determinations were made under various light conditions and it has often been observed that results obtained on a bright day differ from and are not so uniform as those obtained on a dark, cloudy day, and that there is often a difference between results obtained in the forenoon and in the afternoon in a room having only east windows. For this reason a means of darkening the room was provided and care was taken that, for any series of results to be compared, the light conditions were similar.

In some of the results here reported it may appear that the light conditions as deduced from Table IV have not always been observed, but it must be remembered that in such cases a relatively large amount of free iodine is already present, and thus the amount of iodine liberated by the influence of light in the course of a titration would then be very much reduced. A consideration of certain data in Tables IV and V shows the truth of this statement. No. 22 in Table IV shows that 0.2 *M* sulfuric acid and 4% iodide in diffused light liberate an amount of iodine equivalent to 0.03 cc. of thiosulfate. Table V shows that under the same conditions but in the presence of 40 cc. of iodine solution no iodine is liberated, as is proved by the fact that the same volume ratio, within the experimental limits, is obtained as in the neutral solution.

Order of Mixing the Solutions.—There is some evidence to indicate that when only 1% of iodide is used slightly higher volume ratios are obtained in neutral solution by adding iodine to thiosulfate than by adding thiosulfate to iodine. However, since more than 1% of iodide is ordinarily used and since iodine cannot be added to thiosulfate when an acid solution is used, this point is not of great importance in this work.

Part II. The Standardization of Sodium Thiosulfate Solution

In Part I were presented the experimental results which led to the selection of certain specified conditions for the reaction between sodium thiosulfate and iodine. In this part will be given the results of a critical study of various methods used in the accurate standardization of thiosulfate solutions. The following substances have been examined as standards: iodine, potassium permanganate, potassium dichromate and potassium bromate. As already pointed out, all of the methods depend finally upon the reaction between thiosulfate and iodine and, therefore, values obtained with the various standards must be compared with that obtained using pure iodine.

Standardization of Sodium Thiosulfate Solution by Iodine

Procedure.—Sufficient iodine to react with about 40 cc. of 0.1 *N* thiosulfate solution was weighed out and dissolved in enough 50% potassium iodide solution to produce a 2% potassium iodide solution in a final volume of 160 cc. This was then titrated electrometrically with approximately 0.1 *N* thiosulfate solution.

Method of Weighing Iodine.—At first the ordinary method of weighing iodine was tried; potassium iodide solution was placed in a weighing bottle having a ground glass stopper and weighed; the stopper was then removed, the required amount of pure iodine added and the bottle again weighed. It was found to be difficult to obtain results that checked accurately by this method. Numerous experiments have shown that a fairly constant loss of 0.0002 g. occurs every time the stopper is removed from a weighing bottle containing concentrated potassium iodide solution. Special forms of iodine weighing apparatus have been devised from time to time to obviate such difficulties as that mentioned above and the volatility of iodine itself. The following type of weighing bottle was designed and has been found to give very satisfactory results.

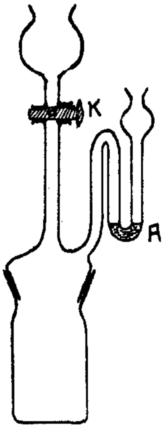

Fig. 1.—Apparatus for weighing iodine.

Into the stopper of an ordinary sized weighing bottle are fused two tubes, one of which is a straight thistle tube carrying a glass stopcock, the other being bent as shown in the diagram and having a small bulb blown in one arm. These tubes are about 3 mm. in internal diameter. Fifty % potassium iodide solution is placed in the bend of the tube as shown at A, and with the cock K open, the apparatus is weighed. The stopper is removed, the necessary amount of iodine is introduced, the stopper replaced, the cock K closed and the whole again weighed. Fifty per cent. potassium iodide solution is then placed in the thistle tube and the cock slowly opened; the solution is allowed to flow in and dissolve the iodine while displaced air passes out through the second tube, any iodine vapor which it carries being retained by the iodide solution in the bend A. The addition of the potassium iodide must be so slow that no liquid is forced out of the second tube, the danger of this being lessened by the small bulb in the tube. After the required amount of potassium iodide has been introduced, water is added until the bottle is nearly filled. The whole apparatus is then placed in the titration beaker which contains enough water to bring the final volume to 160 cc. The stopper is removed and the whole apparatus thoroughly washed, after which the iodine is ready for titration in the usual way. The advantages of this type of bottle are that it does not require between weighings the opening of a vessel containing either solid iodine or a solution of potassium iodide; and the solution of the iodine is accomplished in a closed space.

Results.—Following the results of Part I, 2% of potassium iodide is used since no loss of iodine then occurs, and the final titration is carried out in neutral solution since this gives the same results as an acid solution and the end-point is more satisfactory. The reproducibility of results is shown in Table VI.

TABLE VI

STANDARDIZATION OF THIOSULFATE BY IODINE

	Series I, using ordinary weighing bottle			
Thiosulfate, cc.	37.77	36.27	39.04	41.54
Iodine, g.	0.5655	0.5424	0.5845	0.6207
Thiosulfate, *N*	.11795	.11783	.11796	.11773
	Series II, using special apparatus			
Thiosulfate, cc.	36.87	38.44	39.25	36.50
Iodine, g.	0.5559	0.5759	0.5917	0.5504
Thiosulfate, *N*	.11879	.11882	.11878	.11881

Variation: Series I, 0.18%; Series II, 0.03%.

At another time a series of nine determinations gave an average value of 0.11710, with a maximum variation of 0.06%.

From the data in Table VI it is evident that with a well made apparatus results may continually be checked within 0.05%. It is of interest to compare the values of Table VI, Series II, with results reported by Foulk and Morris and by Vosburgh, which continually differ by 0.2% and sometimes by as much as 0.3%. It is believed that this form of apparatus and the electrometric method constitute a distinct improvement in the manipulation of iodine and iodine solutions.

Standardization of Thiosulfate Solution by Potassium Permanganate

Because of the accuracy with which a permanganate solution may be standardized, this should be an ideal iodimetric standard. The difficulty arises from the fact that the results obtained depend in some degree upon the conditions which prevail during the titration. In discussing the iodide method of standardizing permanganate McBride[16] says, "As a matter of fact, the iodine standardization of permanganate is even more largely affected by conditions than is the oxalate method and none of these influences has been systematically studied."

This method was first suggested by Volhard[17] in 1879, who thought that "for simplicity and rapidity the procedure leaves nothing to be desired." As much cannot apparently be said for its accuracy. The method has been studied by Milobendzki,[18] Schroeder,[19] Bray and McKay,[20] Popoff and Chambers,[13] Vosburgh,[3] Hendel,[4] and by Bray and Miller.[5] An accurate determination involving iodine at a temperature of 50° as used by Schroeder, is doubtful.[21] Variations of as much as 0.5% are found among the various methods proposed.

Standardization of Permanganate.—In order to compare the values of the thiosulfate obtained with pure iodine and permanganate, it was first necessary to prepare and standardize a permanganate solution. McBride's method was selected for this standardization, except that it was thought advisable to try the electrometric method for the end-point instead of the usual colorimetric method. This seemed especially desirable in view of McBride's statement in discussing possible oxidimetric standards, that "such work involves *one uncertainty* which renders the *best results* which could be obtained probably *no more conclusive* than those now at hand. The difficulty is that of *end-points*, for in each case mentioned, the uncertainty in the blank correction required for an end-point is of about the same order as that of the uncertainty in the oxalate values, namely, 0.1% (usually equivalent to 0.05 cc. of 0.1 *N* permanganate solution). We, therefore, at the present time, would assume no greater accuracy for the values obtainable than 0.1%."[22] No great difficulty has been experienced in making this titration electrometrically, as the values shown in Table VII indicate.

TABLE VII

STANDARDIZATION OF PERMANGANATE BY SODIUM OXALATE

Permanganate, cc.	38.82	40.28	39.42	38.74	38.52
Oxalate, g.	0.3061	0.3175	0.3108	0.3055	0.3037
Permanganate, *N*	.11769	.11765	.11768	.11770	.11767
Maximum variation,	0.04%.				

Numerous other experiments have given equally concordant results.

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

[17] Volhard, *Ann.*, **198,** 333 (1879).

[18] Milobendzki, *Z. anal. Chem.*, **46,** 18 (1907).

[19] Schroeder, *Z. öffent. Chem.*, **16,** 270 (1910).

[20] Bray and McKay, THIS JOURNAL, **32,** 1193 (1910).

[21] The results obtained by most of the other authors referred to are summarized and discussed in the article by Bray and Miller and will not be repeated here.

[22] Italics by the authors.

The advantages of the electrometric method are again apparent in this determination. The end-point occurs one drop before the color end-point is obtained. McBride emphasizes the necessity of continually stirring the solution, and of waiting a sufficient length of time after the addition of each drop of permanganate when near the end-point in order for the reaction to reach completion. When an oxidizing agent is added to a reducing agent there is a relatively large increase of potential at the end-point. In this case, when near the end-point, the addition of a drop of permanganate causes an increase in potential which, after a short time, gradually decreases again to a steady value. At the true end-point the large increase of 0.4 to 0.5 v. becomes permanent. Thus the electrometric method affords a means of deciding when sufficient time has elapsed after the addition of a drop of the reagent, and also supports the statement of McBride that the final stage in the reduction of permanganate to divalent manganese is a comparatively slow reaction. In an excess of oxalate the potential readings are very unsteady and any small changes that occur during the first part of the titration are quite irregular. This is likewise true when thiosulfate is titrated with iodine.

Having standardized the thiosulfate with pure iodine and the permanganate with sodium oxalate, it was necessary to determine the conditions under which permanganate would give the same value for the thiosulfate that was found with iodine.

Effect of Iodide and Acid Concentration.—From some preliminary experiments it was found that the volume ratio of thiosulfate to permanganate was quite largely affected by various concentrations of acid and iodide, differences of as much as 0.3% being observed. Table VIII gives a summary of the accurate results which were obtained by varying the factors mentioned above.

TABLE VIII

STANDARDIZATION OF THIOSULFATE BY PERMANGANATE

Effect of Iodide and Acid Concentrations

	Concn. of iodide, %	Concn. of H_2SO_4, *M*	No. of expts.	Av.	Max. var., %
I	1	0.2	8	0.9945	0.12
II	4	.2	6	.9962	.07
III	1	.6	7	.9942	.19

Although the average values of Series I and III are nearly the same, yet the variation within Series III is so great that such results could not be considered accurate. The results within Series II were much more concordant, and it appears that the concentration of iodide is of much more importance than the concentration of the acid. In an extended series of experiments in which the iodide was varied from 1 to 8%, and the acid (sulfuric or hydrochloric) from 0.05 *M* to 0.6 *M*, it was shown that the most constant and reproducible results were obtained in solutions containing 6% of iodide, and acid from 0.05 *M* to 0.2 *M*. In one case 8 runs, all containing 6% of iodide, gave an average ratio of 0.9964 with a maximum variation of only 0.02%.

Effect of Time of Standing.—Numerous experiments have shown that the volume ratio is increased about 0.07% when the mixture is allowed to stand for ten minutes before being titrated. This indicates the use of a larger amount of thiosulfate; that is, more iodine is liberated. This fact and also the necessity of using a high concentration of iodide (6%) are in accord with the findings of Bray, already mentioned, that the reaction occurs in steps, the last being comparatively slow. It might then be expected that in order to bring the reaction to completion a large excess of iodide would be required, and also that standing would favor the complete reaction.

Bray and Miller have suggested that in the work of Popoff and Chambers too high concentrations of acid and iodide were used, resulting in the loss of iodine. They ran blank experiments without the addition of iodine or permanganate and found an oxygen error amounting to 0.5 to 0.7 cc. of 0.01 *N* thiosulfate solution. As has already been shown, this error practically disappears when free iodine is already present. (See Table V.) The following data, however, will show conclusively that no iodine is set free in diffused light even with 6% potassium iodide and 0.1 *M* sulfuric acid.

TABLE IX

EFFECT OF TIME OF STANDING IN ACID SOLUTION IN THE THIOSULFATE-IODINE REACTION

Concentration of iodide, %	2	4	4	4	6	6
Concentration of acid, *M*	0	0.2	0.2	0.2	0.1	0.1
Time of standing, min.	0	0	5	10	0	10
Ratio	1.0022	1.0020	1.0020	1.0020	1.0022	1.0025

Effect of Order of Mixing.—Maintaining the acid and iodide concentrations constant at 0.1 *M* and 6%, respectively, it was found that the volume ratio was always about 0.3% higher when the order of mixing was acid-iodide-permanganate, than when the order was acid-permanganate-iodide. This corresponds with the conclusions of McBride that oxygen is lost when an excess of permanganate is allowed to accumulate in an acid solution. The higher values are probably more nearly correct.

The best conditions then for standardizing thiosulfate with permanganate are as follows: the permanganate should be added to the acidified solution of potassium iodide and allowed to react in the dark for ten minutes before being titrated, and the solution should contain at least 6% of iodide when the titration is complete. Although the concentration of acid and the final volume may be varied somewhat, 0.1 *M* hydrochloric acid and 160 cc. have been found to be very satisfactory. In Table X is a comparison of the results, obtained at different times when the titration was carried out in this way with those obtained when pure iodine was used, as outlined above. Each value is the average of not less than three determinations which differ by not more than 0.05%.

TABLE X

NORMALITY OF THIOSULFATE

By permanganate	0.11820	0.11711	0.11879	0.11859
By iodine	.11814	.11710	.11880	.11857
Difference, %	.050	.008	.008	.017

Standardization of Thiosulfate Solution by Dichromate

Potassium dichromate as a standard in iodimetry was first used by Zulkowsky[23] in 1868. Wagner[24] eliminated the observed errors by using 51.84 for the atomic weight of chromium in place of 52.15, the value then current. This standard has also been studied at various times by Kernot and Pietrafesa,[25] Bruhns,[26] McCrosky,[27] Kolthoff,[2] Hendrixson,[28] Vosburgh,[3] Congdon and Gurley,[29] and by Bray and Miller.[5] McCrosky does not give the concentration of acid and iodide which he used, and makes the final titrations in a volume of 800 cc. He finally explains all remaining errors on the basis of the presence of impurities which cannot be removed by recrystallization. Such an explanation is questionable, since any error in any determination might be explained in the same way. Vosburgh's final titrations were made in a volume of 400 cc. and in the presence of colored chromic ions. In all these investigations the main points of controversy may be placed in three groups: (1) proper concentration of acid and iodide; (2) time required for the reaction to reach completion; (3) effect of dissolved air. As will be shown, the concentrations of acid and iodide are an important factor and comparatively small variations of these may cause quite large differences in results. It is thus quite probable that the various results obtained by different workers are to be explained on the basis of the various amounts of acid and iodide used. It is also quite possible that some have not considered the effect of light, although in many cases this cannot be definitely decided, since no mention of light conditions is made. Preliminary observations showed that the factors of both Groups 1 and 2 have a marked effect upon the results of the standardization.

Certain peculiarities encountered should be mentioned at this point. It was found that when a small concentration of acid was used, 0.1 *M* or

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[23] Zulkowsky, *J. prakt. Chem.*, **103**, 362 (1868).

[24] Wagner, *Z. anorg. Chem.*, **19**, 427 (1899).

[25] Kernot and Pietrafesa, *Rend. accad. sci. Napoli*, **111A**, 275 (1911).

[26] Bruhns, *J. prakt. Chem.*, **93**, 73, 312 (1916); **95**, 37 (1917).

[27] McCrosky, THIS JOURNAL, **40**, 1662 (1918).

[28] Hendrixson, *ibid.*, **43**, 19 (1921).

[29] Congdon and Gurley, *Chem. News*, **128**, 68 (1924).

less, the solution was decidedly blue after the end-point had been reached. When 0.2 *M* or greater concentration was used, the solution then assumed a distinctive green color. Having once been formed, the addition of more acid would not change the blue to green, nor would dilution produce the blue from the green. Again, it was found that the potential readings were unsteady and showed a gradual change with any blue solution, but when green solutions were obtained the readings were very permanent and steady. This slow change in potential similar to that found in the standardization of permanganate with oxalate, again indicates the possibility of a slow reaction. A condition of this kind would probably not be observed when starch was used as an indicator. Because of these facts, very few experiments were performed in which the acid concentration was less than 0.2 *M*.

Effect of Concentration of Acid and Iodide.—An approximately 0.1 *N* dichromate solution was prepared, and volume ratios were determined with thiosulfate. Two well-known brands of dichromate were used. The first was recrystallized twice, the second four times. Both were dried at 160°. In general, better results were obtained with the second sample.

TABLE XI

STANDARDIZATION OF THIOSULFATE SOLUTION BY DICHROMATE

Effect of Acid and Iodide Concentrations

SERIES I			SERIES II		
Concn. of acid	Concn. of KI, %	Ratio	Concn. of HCl, *M*	Concn. of KI, %	Ratio
0.1 H_2SO_4	1	1.0000	0.2	1	1.0012
.2 H_2SO_4	1	1.0000	.2	1	1.0015
.2 HCl	1	1.0000	.6	1	1.0052
.6 HCl	1	1.0082	.6	1	1.0054
.05 H_2SO_4	4	1.0042	.2	4	1.0074
.2 H_2SO_4	4	1.0079	.2	4	1.0074

The data in Table XI show that an increase of either acid or iodide results in the liberation of more iodine, as indicated by the increase in the volume ratio. Further experiments showed that in solutions containing 0.6 *M* hydrochloric acid and 1% iodide the volume ratio decreased about 0.6% when the solution had stood for only five minutes before titration, but that in solutions containing 0.2 *M* acid and 4% iodide the ratio decreased 0.3% after ten minutes and then became constant.

The method finally adopted as most satisfactory was to weigh out about 25 g. of dichromate solution of such strength (the percentage by weight being known) that the amount used would be approximately equivalent to 40 cc. of 0.1 *N* thiosulfate solution. The mixture to be titrated contained 0.2 *M* hydrochloric acid and 2% of iodide, and was allowed to stand in the dark for ten minutes before final titration. Under these conditions the values given in Table XII were obtained; they are here compared with the values obtained with pure iodine and in two cases with permanganate also.

TABLE XII

NORMALITY OF THIOSULFATE SOLUTION

By dichromate	0.11862	0.11809	0.11863
By iodine	.11857	.11815	.11857
By permanganate		.11813	.11859
Maximum difference, %	.04	.05	.05

As before, each value represents the average of not less than three determinations that differ by not more than 0.05%.

The fact that an increase of either acid or iodide increases the amount of iodine liberated indicates that they are of about equal importance in causing the reaction to run to completion. In order to correspond to the proper conditions for the titration of iodine with thiosulfate solution as found in Part I, the iodide should be at least 2% and the correct amount of acid to be used with this is shown to be about 0.2 *M*. This practically agrees with Kolthoff's results, who found that when about 0.3 *M* acid was used with an amount of iodide slightly less than 2% and the mixture allowed to stand for 10 to 15 minutes, nearly the calculated results were obtained. If the starch end-point can be accurately determined in a large volume and in the presence of the color of chromic ions, these results agree fairly well with the conditions prescribed by Vosburgh.

Standardization of Thiosulfate Solution by Potassium Bromate

Because of the ease with which potassium bromate can be purified by recrystallization, Wagner pointed out the value of this substance as an iodimetric standard. While it has often been used as an iodimetric standard (for example, in the determination of tin) apparently no attempt has been made to determine the conditions under which it gives the same results as pure iodine for the standardization of thiosulfate solution. Peters[30] states that potassium iodate and potassium bi-iodate give the same results as pure iodine but does not mention the use of bromate. A few experiments were carried out to determine the value of bromate for this purpose.

TABLE XIII

STANDARDIZATION OF THIOSULFATE SOLUTION BY POTASSIUM BROMATE

Effect of Acid and Iodide Concentrations

Concn. of HCl, *M*	Concn. of KI, %	Thiosulfate, *N*, 25°	Thiosulfate, *N*, 22°
0.1	2	0.11828	0.11840
.1	2	.11826	.11838
.6	2	.11812	.11824
.6	2	.11818	.11830
.1	4	.11797	.11809
.2	4	.11796	.11808
.1	6	.11783	.11795
.2	6	.11788	.11800

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[30] Peters, THIS JOURNAL, **34**, 422 (1912).

A solution containing 0.5255% of bromate was prepared from the pure, recrystallized salt. Approximately 25g. samples of this solution were weighed out, acidified, mixed with iodide and used to standardize the thiosulfate solution. Table XIII shows the final values obtained after some preliminary runs had indicated the general effect of variation of conditions.

Increase in concentration of iodide causes the liberation of more iodine in a given length of time. The acid concentration has much less effect, 0.1 *M* acid with 6% iodide being sufficient to allow the titration to begin immediately. The measurements recorded in Col. 3 of Table XIII were made at a temperature of 25°, while the thiosulfate had previously been compared with permanganate at 22°, using the method described in this article, the normality being found to be 0.11795. Col. 4 shows the normality of the thiosulfate as determined by bromate, corrected to a temperature of 22°. It is thus evident that the correct value is obtained by using 0.1 *M* acid and 6% of iodide and titrating immediately after mixing. The value of the bromate as an iodimetric standard is thus established.

The following values are recorded for comparison.

Normality of thiosulfate by permanganate	0.11795
Normality of thiosulfate by bromate	.11797
Difference, %	.017

Summary and Conclusions

The factors affecting the reaction between sodium thiosulfate and iodine, as indicated by the change in volume ratio of the two solutions, have been studied using the electrometric method of obtaining end-points. The effect of varying the following factors has been investigated; dilution, concentration of iodide, kind and concentration of acid, loss of iodine on standing and action of light. It is shown that the volume ratio of thiosulfate to iodine depends upon the dilution. When a large volume and small concentration of iodide are used, this ratio is too low. This error may be corrected by maintaining 2% or more of iodide or an equivalent amount of acid. This explains the results of certain authors who have obtained better values in acid than in neutral solution. High concentrations of iodide may be used in neutral solution. No loss of iodine occurs in the course of 15 minutes when a concentration of at least 2% of iodide is maintained. Only diffused light should be used when titrations are made in acid solution.

Pure iodine, permanganate and dichromate have at various times been used with various degrees of success, for the purpose of standardizing a solution of sodium thiosulfate. In this paper it has been shown that by properly choosing the conditions, most of the difficulties may be eliminated and that the values obtained with all these standards, and also with potassium bromate, agree within 0.05%. In order to make any of the reactions concerned run to completion, the proper equilibrium conditions must be chosen, and any change in these conditions will affect the completeness of the reaction. Such conditions cannot be predicted beforehand but must be subjected to careful experimental determination.

The best conditions for the standardization of a thiosulfate solution, using the various standards studied, may be summarized as follows.

Pure Iodine.—The sample is weighed in a special weighing bottle and titrated in a neutral solution containing 2% of iodide at the end-point.

Permanganate.—The permanganate is added to an acidified solution of potassium iodide, the mixture allowed to stand in the dark for ten minutes and the titration completed: final acidity, 0.1 *M* hydrochloric acid; final concentration of iodide, 6%.

Dichromate.—The dichromate is added to an acidified solution of potassium iodide, the mixture allowed to stand in the dark for ten minutes and the titration completed; final acidity, 0.2 *M* hydrochloric acid; final concentration of iodide, 2%.

Bromate.—The bromate is added to an acidified solution of potassium iodide, and the mixture titrated immediately; final acidity, 0.1 *M* hydrochloric acid; final concentration of iodide, 6%.

In all cases an amount of the substance equivalent to 40 cc. of 0.1 *N* solution and a final volume of 160 cc., have been found very convenient.

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[Contribution from the Chemical Laboratory of Stanford University]

THE PREPARATION OF PHOSGENO SALTS

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The properties of solutions of aluminum chloride in liquid phosgene can best be interpreted by regarding the solution as containing an acid, $COAl_2Cl_8$, in which the carbonyl group takes the place of hydrogen in the well-known acids.[1] This acid is capable of reacting with metals to yield salts and carbon monoxide, or with metallic chlorides, which are to be regarded as bases typical of this system, to yield salts and phosgene, as set forth in the equations:

$$COAl_2Cl_8 + Ca \longrightarrow CaAl_2Cl_8 + CO \qquad (1)$$
$$COAl_2Cl_8 + CaCl_2 \longrightarrow CaAl_2Cl_8 + COCl_2 \qquad (2)$$

The further study of this group of salts made it essential to develop a general method for their preparation in very pure form, and in relatively large amounts. Because of the intolerable odor of phosgene, its high vapor tension, and the readiness with which all of the reacting materials react with water, this had to be done in a closed system, where the internal pressure might attain 2 atmospheres. Reaction 1 would increase this pressure,

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[1] Germann, *Science*, 61, 71 (1925).