

[CONTRIBUTION FROM THE EPPLEY LABORATORY]

POTASSIUM DICHROMATE AS A STANDARD IN IODIMETRY AND THE DETERMINATION OF CHROMATES BY THE IODIDE METHOD

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A number of investigators have come to different conclusions with respect to the possibility of using potassium dichromate as a standard in iodimetry. Some¹ have found that the apparent oxidizing capacity of some samples of dichromate was higher than the theoretical. McCrosky¹ showed that the cause of this was connected with the presence of oxygen during the determination and suggested that an impurity in the dichromate catalyzed the reaction between oxygen and iodide ion. Kolthoff² claimed that correct results could be obtained if the concentration of acid during the reaction of dichromate and iodide ions was great enough. He attributed the high results of previous investigators either to the use of too small an acid concentration or to the presence of chromium trioxide as an impurity in the dichromate. Hendrixson,³ by measuring the excess hydriodic acid instead of the iodine liberated, found that dichromate oxidized the theoretically equivalent amount of iodide ion even in the presence of air.

In attempting to determine the oxidizing value of some samples of potassium dichromate by the iodide method a number of different conditions of acidity and procedure, among them those of Kolthoff,² were tried. The results were in all cases appreciably higher than the theoretical. Therefore, a further investigation was undertaken to determine conditions by which chromates could be accurately determined by the iodide method without the complication of the exclusion of air if possible.

Preparation of Materials

Potassium Dichromate.—The various samples of potassium dichromate were prepared by recrystallizing from redistilled water material of c. p. quality. Nos. 1 and 4 were recrystallized once. Nos. 6 and 24 were recrystallized thrice. No. 16 was recrystallized 4 times, the last 2 times in a platinum dish. No. 29 was recrystallized twice, special care being taken in the second crystallization to protect the solution and crystals from dust. Nos. 1, 4, 6, and 16 were dried by heating to constant weight at 180°. No. 24 was heated to constant weight at 160°. No. 29 was dried in a desiccator and the samples fused as described below. About 9 hours' heating at 160° was required to bring air-dried dichromate to constant weight.

Dichromates 4 and 16 and the original material from which No. 24 was prepared were tested for the presence of excess chromium trioxide by the method of Kolthoff.⁴

¹ Wagner, *Z. anorg. Chem.*, **19**, 427 (1899). Bruhns, *J. prakt. Chem.*, **93**, 93 (1916). McCrosky, *THIS JOURNAL*, **40**, 1662 (1918). Meindl, *Z. anal. Chem.*, **58**, 529 (1919).

² Kolthoff, *Z. anal. Chem.*, **59**, 405 (1920).

³ Hendrixson, *THIS JOURNAL*, **43**, 19 (1921).

⁴ Ref. 2, p. 403.

No indication of the presence of this impurity was obtained. The close agreement of No. 29 with several of the others in the experiments of Table IX indicates that drying to constant weight is as efficient as fusing.

Iodine.—The iodine used in standardizing the thiosulfate solutions, originally commercial resublimed iodine, was purified by further resublimation. All samples were ground with potassium iodide and sublimed. No. 1 was resublimed thrice in addition, and No. 2 twice and a third time in the presence of phosphorus pentoxide.⁵ No. 3 was resublimed an additional time from a mixture with potassium iodide, once alone, and once in the presence of phosphorus pentoxide. All samples were kept in a desiccator over calcium chloride.

Thiosulfate Solutions.—Imported sodium thiosulfate purchased several years ago was used.

Potassium Iodide.—A commercial "C. P. Special" potassium iodide was used. Blank determinations showed no trace of iodine liberated under the conditions of the experiments of Table X.

Starch Solution.—A 1% solution of a commercial soluble starch was prepared in the usual manner. Five cc. was used in each titration.

Conditions Affecting the Oxidizing Action of Dichromate

Acid Concentration.—The following experiments show the importance of the acid concentration in the titration of the iodine liberated from hydriodic acid by dichromate.

Solutions were prepared of 200 cc. volume, including 25.00 cc. of a 0.1 *N* potassium dichromate solution, 3 g. of potassium iodide and the amounts of 6 *M* hydrochloric acid shown in Table I. The various substances were mixed in 3 different ways. (1) The dichromate was diluted to 100 cc. and added to 100 cc. of a solution containing the iodide and acid. (2) The dichromate was added to a solution of 175 cc. of the iodide and acid. (3) The iodide dissolved in 15 cc. of water was added to a solution of 185 cc. of the dichromate and acid. The iodine in each case was titrated with a 0.1 *N* thiosulfate solution using starch as the indicator, the titration being made about 1 minute after the preparation of the solution, except when otherwise noted. The agreement of the experiments in which the titration was made after 1 minute with those in which 5 minutes was allowed to elapse before the titration showed that it was unnecessary to wait longer than 1 minute. The results are shown in Table I.

TABLE I
THIOSULFATE REQUIRED TO TITRATE THE IODINE LIBERATED BY DICHROMATE IN SOLUTIONS OF VARIOUS ACID CONCENTRATIONS

6 <i>M</i> HCl, cc.	6.7	8	10	13.4	16.6	20	27	33
Acid, moles per l.	0.2	0.24	0.3	0.4	0.5	0.6	0.8	1.0
Thiosulfate, cc. (1)	{ 25.01	{ 25.00	{ 25.02	{ 25.04	{ 25.04	{ 25.07	{ 25.18	{ 25.22
	{ 25.00 ^a	{ 25.02	{ 25.00 ^a	{ 25.01	{ ...	{ ...	{ ...	{ ...
Thiosulfate, cc. (2)	{ 25.01	{ ...	{ ...	{ 25.02	{ ...	{ 25.09	{ 25.17	{ ...
	{ 25.02	{ ...	{ ...	{ 25.02	{ ...	{ 25.10	{ ...	{ ...
Thiosulfate, cc. (3)	{ 25.00	{ ...	{ ...	{ 25.01	{ ...	{ 25.07	{ ...	{ ...
	{ 25.01	{ ...	{ ...	{ 25.00	{ ...	{ 25.10	{ ...	{ ...

^a The solution was allowed to stand for 5 minutes before the titration was begun.

⁵ McCrosky, Ref. 1, p. 1666, and Foulk and Morris, THIS JOURNAL, 44, 221 (1922), point out the danger of contamination of iodine with water. The latter authors showed that resubliming in the presence of phosphorus pentoxide removed this impurity.

In the experiments of Table I acid concentrations of from 0.2 *M* to 0.4 *M* gave constant results. Concentrations greater than 0.4 *M* gave results higher with respect to thiosulfate required and increasing with the acidity. Similar results were obtained with sulfuric acid, the range over which constant results were obtained being from 0.3 *M* to 0.4 *M*. It is possible that the irregularities in the results obtained by McCrosky¹ in solutions containing dissolved oxygen were due to the use of varying concentrations of acid, some of which were above 0.4 *M*.

The results shown in Table I are not in agreement with the statement of Kolthoff² that an acid concentration equivalent to 0.6 *M* hydrochloric acid is required if the reaction between dichromate and iodide ions is to be sufficiently rapid so that the titration can be made immediately. Preliminary experiments with the acid concentration given as the minimum by Kolthoff and the iodide concentration used in the above experiments gave results 0.4% higher than the theoretical.

Iodide Concentration.—A number of experiments in which the acid concentration was kept constant at 0.3 *M* showed that the volume of the solution could be varied between 100 cc. and 400 cc. without any effect on the result. When 25cc. portions of 0.1 *N* dichromate solution were used, 2 to 3 g. of potassium iodide gave closely agreeing results, but 1 g. and 4 g. or more led to irregular results.

Exclusion of Air.—McCrosky¹ found that determinations carried out with careful exclusion of air gave results in some cases 0.3% lower than those of similar determinations carried out in the presence of air. In the case of one sample of dichromate the presence or absence of air made no difference in results. The contradictory results may have been due to differences in the experimental conditions. The effect of exclusion of air was, therefore, tried in determinations made under the conditions which were shown to give the smallest ratio of thiosulfate to dichromate. In this case a standardized thiosulfate solution and a freshly prepared 0.1000 *N* solution of dichromate No. 6 were used in order to determine what, if any, excess oxidizing action was shown under the conditions so far shown to be the best.

The thiosulfate solution was standardized against pure iodine, Preparations 1 and 2, described below, being used. The procedure was that given by Treadwell.⁶ A weight buret was used and the titrations were made in a stoppered Erlenmeyer flask similar to that used by McCrosky.¹

To standardize the dichromate solution in terms of the thiosulfate solution, 25.00 cc. of the former was diluted to 350 or 400 cc. with a solution containing sufficient hydrochloric acid to bring the acid concentration of the final solution to 0.3 *M*. In the first series of determinations ordinary distilled water was used. In the second series, dissolved air was removed from the dil. acid either by passing carbon dioxide through it for some time, or by boiling and cooling in an atmosphere of carbon dioxide. In the

⁶ Treadwell, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1913, 3rd Ed., vol. 2, p. 646.

TABLE II
STANDARDIZATION OF THIOSULFATE

Iodine G.	Thiosulfate solution		Iodine G.	Thiosulfate solution	
	G.	Wt. normal		G.	Wt. normal
0.1879	14.938	0.09911	0.3059	24.291	0.09922
0.2128	16.926	0.09906	0.4322	34.350	0.09913
0.3394	26.940	0.09926	0.3528	27.992	0.09931
0.2078	16.502	0.09922	0.4803	38.130	0.09925
0.2633	20.882	0.09935	0.2051	16.289	0.09921
0.3208	25.501	0.09912	0.3578	28.456	0.09907
0.3557	28.162	(0.09951)	0.2470	19.620	0.09919
					Av. 0.09919

first series 50 cc. of a 0.3 M potassium iodide solution was added, while in the second 2.5 g. of solid potassium iodide was used. The titrations were made by means of a weight buret. The solutions in the second series were prepared and the titrations made in a stoppered Erlenmeyer flask similar to that used by McCrosky¹ and in an atmosphere of carbon dioxide. In some cases the stopper was removed before the titration was begun, without any noticeable difference in the results.

TABLE III
OXIDIZING ACTION OF A 0.1000 N SOLUTION OF DICHROMATE No. 6 as MEASURED BY MEANS OF A 0.09919 N THIOSULFATE SOLUTION

1. Solution made up and titrated in presence of air		2. Air excluded during the preparation of the solution and the titration	
Thiosulfate, for 25.00 cc. of dichromate		Thiosulfate, for 25.00 cc. of dichromate	
G.	Dichromate Apparent normality	G.	Dichromate Apparent normality
25.270	0.10026	25.242	0.10015
25.270	0.10026	25.230	0.10010
25.248	0.10017	25.255	0.10020
25.258	0.10021	25.237	0.10013
25.290	0.10034	25.248	0.10017
25.293	0.10035	25.285	0.10032
25.255	0.10020	25.268	0.10025
Av. 0.10026		25.232	0.10011
		25.250	0.10018
		Av. 0.10018	

The results in the second series of Table III average nearly 0.1% less than those of the first. Exclusion of air exercises a corrective influence on the apparent excess oxidizing action of dichromate. This effect is not as great in these experiments as that found by McCrosky¹ and the results in the second series are nearly 0.2% too high. A number of more careful experiments with other dichromate preparations agreed well with the average of the second series.

There is a possibility of error in the value of the thiosulfate solution. It is to be noticed that the concordance of the various titrations of the pure iodine is not as great as would be expected from the experimental

conditions. Duplicate determinations frequently disagree by 0.2%. On the other hand the results of the titration of the iodine liberated by dichromate are in general more concordant than this. Impurities in the iodine are not probable in view of the work of Foulk and Morris.⁵ The iodine liberated by dichromate was titrated in an acid solution while the standard iodine was titrated in a neutral solution. The presence of iodate as an impurity in the potassium iodide could not explain the difference,⁷ since tests showed absence of iodate in the iodide used. Topf⁸ found errors of 2 to 4% in the titration of iodine with thiosulfate in a solution containing ammonium carbonate, too little thiosulfate being required. Abel⁹ showed that in alkaline solutions thiosulfate is oxidized to sulfate by iodine. Barneby¹⁰ obtained erratic results when he attempted to titrate iodine with thiosulfate in a sodium hydrogen carbonate solution, although good results were obtained when titrating with an arsenite solution. In the titration of iodine with thiosulfate in a neutral solution the hydroxyl-ion concentration must be dependent on the purity of the potassium iodide and the alkalinity of the thiosulfate solution. It might be such, locally at least, as to cause a small amount of sulfate formation. If this took place the results would be irregular and also too low with respect to the amount of thiosulfate required, and a high value for the strength of the thiosulfate solution would result.

The Titration of Iodine with Thiosulfate

Effect of Acidity.—The above observations suggest that the usual procedure in standardizing thiosulfate solutions by means of iodine is liable to lead to small errors tending to give high results. The following results of the titration of iodine with thiosulfate verify this conclusion.

An iodine solution was prepared of approximately 0.1 *N* strength and containing 25 g. of potassium iodide in a liter and 25.00cc. portions were titrated with a 0.1 *N* thiosulfate solution using starch as the indicator. The sample was added to 375 cc. of a solution containing 1.25 g. of potassium iodide and a little acetic or hydrochloric acid.

TABLE IV
EFFECT OF ACID ON THE TITRATION OF IODINE WITH THIOSULFATE

Acetic acid, moles per l.	0.01	0.1	0.3	
HCl, moles per l.	0.1	0.3	
Thiosulfate, cc.	27.765	27.75	27.79	27.79	27.795	27.805
	27.78	27.78	27.79	27.795	27.785	27.80
	27.73	27.78	27.79	27.77	27.77	27.79
	27.74
	27.77

⁷ Chapin, *THIS JOURNAL*, 41, 357 (1919).

⁸ Topf, *Z. anal. Chem.*, 26, 149 (1887).

⁹ Abel, *Z. anorg. Chem.*, 74, 406 (1912).

¹⁰ Barneby, *THIS JOURNAL*, 38, 331 (1916).

Titrations in acid solutions give more concordant results than titrations in neutral solutions. The 9 titrations in 0.1 *M* and 0.3 *M* acetic acid and 0.1 *M* hydrochloric acid show a maximum variation among themselves of 0.1%. The average of these results is about 0.1% higher with respect to thiosulfate required than the average of the determinations in neutral solutions. This explains the greater part of the apparent excess oxidizing value of dichromate in the experiments of Table III.

Effect of the Presence of Air.—The difference between the results in neutral and acid solutions, respectively, might be explained as due to the action of dissolved air in the latter. Therefore, some titrations were made in dil. acid solutions both in the presence and in the absence of air.

A dil. hydrochloric acid solution was prepared of about 375 cc. volume and such that when diluted to 400 cc. the acid concentration would be that given in the table below. In some of the determinations this solution was boiled and cooled in an atmosphere of carbon dioxide, and the titration made in an atmosphere of carbon dioxide. In all cases 25.00 cc. of a 0.1 *N* iodine solution containing 2.5 g. of potassium iodide, was added and the solution titrated with a 0.1 *N* thiosulfate solution using starch as the indicator.

TABLE V

EFFECT OF EXCLUSION OF AIR ON THE TITRATION OF IODINE WITH THIOSULFATE

HCl, moles per l.	...	0.2	0.2	0.3	0.3	0.4	0.4	0.9
Atmosphere	Air	Air	CO ₂	Air	CO ₂	Air	CO ₂	Air
Thiosulfate, cc.	{ 21.36	21.40	21.38	21.39	21.39	21.43	21.40	21.45
	{ 21.39	21.36	21.385	21.40	...	21.435	21.40	...

II. 0.4 *M* acid, titration in the absence of air gave lower results than titration in the presence of air, and the results were in better agreement with those obtained with more dilute acid. The results in Tables III and IV indicate that this effect of air is appreciable in solutions of hydrogen-ion concentration equivalent to that of 0.3 *M* hydrochloric acid, but is not as great as in the case of 0.4 *M* acid. It evidently decreases with the hydrogen-ion concentration.

Whether or not the effect of air can be explained as due entirely to oxidation of the hydriodic acid was not determined. If so, the amount of oxidation during the titration would depend on the intensity of the light as well as on the hydrogen-ion concentration of the solution. For safety the upper limit of hydrogen-ion concentration for titration in the presence of air should be set at about that of a 0.1 *M* hydrochloric acid solution. Under these conditions, with 2.5 g. of potassium iodide in a volume of 400 cc. and in diffused daylight, longer than 30 minutes was required for the liberation of an appreciable amount of iodine.

The best conditions for the titration of iodine are not the most practical for the reaction of dichromate and iodide ions, which requires a higher acidity in order to take place with sufficient rapidity. Therefore, either the iodine liberated by dichromate must be titrated in an atmosphere

of carbon dioxide, or the solution must be diluted before being titrated.¹¹ Some titrations of iodine liberated by dichromate were made in both ways for comparison and to establish the best conditions for the second method.

Twenty-five-cc. portions of a 0.1 *N* dichromate solution were diluted with 25 cc. of hydrochloric acid of the required concentration and 50 cc. of 0.3 *M* potassium iodide solution was added. After a certain time, as shown in Table VI, the solutions were diluted to 400 cc. and titrated with a 0.1 *N* thiosulfate solution.

Some control experiments under the conditions of the experiments of the second series of Table III required 24.49 cc., 24.50 cc., 24.50 cc. and 24.50 cc. of thiosulfate solution, respectively.

TABLE VI
TITRATION IN SOLUTIONS OF 0.1 *M* ACID OR LESS OF THE IODINE LIBERATED BY DICHROMATE IN MORE CONCENTRATED ACID SOLUTIONS

Acid, moles per l.	0.2	0.2	0.2	0.3	0.4	0.6
Time for reaction, min.	2	3	4	4	2	2
Thiosulfate, cc.....	{ 24.47 ^a	{ 24.50 ^a	{ 24.49	{ 24.49	{ 24.51	{ 24.50 ^b
	{ ...	{ ...	{ 24.49	{ 24.48	{ 24.49	{ 24.50 ^b

^a The color returned after the end-point, showing that the reaction was incomplete before titration.

^b The solutions were diluted to 600 cc. to make the acid concentration 0.1 *M* before titrating.

With this procedure, practically constant results were obtained under all conditions tried, when enough time was allowed for the reaction between the dichromate and iodide. These results, obtained without excluding air, agree with the results of the control experiments in which air was excluded.

The Determination of Chromates under Correct Conditions

From the experiments so far described conditions can be deduced which should allow precise determination of chromates by the iodide method. Table IV shows that iodine should be titrated with thiosulfate only in an acid solution. Atmospheric oxygen need not be excluded. The reaction between the dichromate and iodide ions should take place in a solution of an acidity equivalent to between 0.2 *M* and 0.4 *M* hydrochloric acid and containing 2 to 3 g. of potassium iodide. The reaction should be allowed to proceed in the dark for between 4 and 10 minutes,¹²

¹¹ Treadwell, Ref. 6, p. 649, and Murray, "Standards and Tests for Reagent Chemicals," D. Van Nostrand Company, New York, 1920, p. 259, recommend diluting the solution in this way. The former gives as the reason for so doing the indistinctness of the end-point in concentrated solutions due to the color of the chromic ion. The conditions given by Murray are essentially the same as those found in this investigation to be satisfactory. The use of boiled water for diluting seems unnecessary, however.

¹² At these iodide- and hydrogen-ion concentrations the reaction between dissolved oxygen and iodide ion is appreciable. Blank determinations showed that with 0.4 *M* acid and 2.5 g. of potassium iodide in 100 cc. an appreciable amount of iodine was liberated after 4 minutes in diffused daylight on a bright day and after 10 minutes when the flask containing the mixture was placed in a cupboard after preparation. The danger of considerable oxidation of iodide ion by oxygen in strongly acid solutions is a serious objection to the conditions given by Treadwell, Ref. 6, p. 649.

after which the solution should be diluted¹³ to about 400 cc., bringing the acidity to 0.1 *M* or less and the concentration of chromic ion to such a value that the color will not interfere with the end-point. As a check on these conditions and in order to determine the accuracy of the method a thiosulfate solution was standardized against pure iodine and the chromate content of a number of samples of purified potassium dichromate was determined.

Samples of iodine preparations 2 and 3 were weighed by the method of Treadwell⁶ and added to 400 cc. of 0.1 *M* acetic acid which contained also about 1 g. of potassium iodide. The iodine was then titrated with a 0.1 *N* thiosulfate solution by means of a weight buret using starch as the indicator. Some of the titrations were made in stoppered flasks and some in open flasks, but no difference was noticed between the two sets. The thiosulfate solution had been allowed to age for some time before standardization. It was standardized frequently during the chromate determinations. In Table VII all of the determinations are reported.

TABLE VII
STANDARDIZATION OF THIOSULFATE SOLUTION BY IODINE

No.	Iodine G.	Thiosulfate solution G.	Equivs. Na ₂ S ₂ O ₃ per 1000 g.	Variation from mean Pts. in 1000	Av.
3	0.41105	32.509	0.09962	-0.1	±0.5 ^a
2	0.3037	23.987	0.09975	+1.2	
3	0.2271	17.967	0.09959	-0.4	
3	0.2585	20.455	0.09957	-0.6	
3	0.28605	22.617	0.09965	+0.2	
3	0.36705	29.034	0.09961	-0.2	
2	0.29415	23.268	0.09961	-0.2	
3	0.5815	46.000	0.09960	-0.3	±0.4
2	0.33475	26.463	0.09967	+0.4	
3	0.3566	28.206	0.09961	-0.2	
3	0.24175	19.098	0.09974	+1.1	
3	0.25285	19.994	0.09964	+0.1	
3	0.3655	28.927	0.09955	-0.8	
3	0.24225	19.154	0.09963	±0.0	
3	0.25905	20.484	0.09964	+0.1	±2.9 ^b
3	0.24195	19.059	(0.10002)	(+3.9)	
3	0.2705	21.322	(0.09996)	(+3.3)	
3	0.3269	25.813	(0.09978)	(+1.5)	
			Av.	0.09963	

^a The titrations were carried out in stoppered flasks.

^b The acid was omitted in these determinations. The results are not included in the average.

Table VII confirms the previous conclusion that for greatest accuracy in titrating iodine with thiosulfate the solution should be slightly acid. The last 3 determinations were made in a neutral solution. They vary

¹³ After dilution the solution can be allowed to stand in the dark until it is convenient to titrate it. Blank determinations showed that such a solution could stand for longer than 30 minutes in diffused daylight before an appreciable amount of iodine was set free.

among themselves by more than 2 parts in a thousand and are 3 parts in a thousand higher than the average of the other results. The average variation from the mean in the other results is ± 0.4 parts in a thousand, about half that in the results of Table II.

For the chromate determinations 0.2g. samples of the potassium dichromate preparations described below were weighed out, dissolved in 50 to 60 cc. of water in 750cc. Erlenmeyer flasks and the solutions acidified with 5 cc. of 6 *M* hydrochloric acid. Fifty cc. of a 0.3 *M* potassium iodide solution, containing 2.5 g. of the iodide, was added and the solutions were allowed to stand in the dark for 5 minutes. They were then diluted with 300 cc. of water and titrated by means of a weight buret with the 0.09963 *N* thio-sulfate solution using starch as the indicator. In 3 determinations, as indicated in the table, boiled water was used and carbon dioxide passed into the flask for some time before dissolving the dichromate. Solid potassium iodide was used, 50 cc. of water being added to keep the volume the same as in the other determinations. In two other determinations, as noted, a smaller volume and 1 *M* acid were used for the reaction between the di-

TABLE VIII
DETERMINATION OF CHROMATES BY THE IODIDE METHOD

Dichromate No.	Thiosulfate Solution G.	Potassium dichromate		Diff., Obs. Pts. in 1000	Actual Av.
		Obs. G.	Actual G.		
1	41.009	0.20034	0.20025	+0.4	+0.5
1	40.956	0.20008	0.20005	+0.1	
1	40.969	0.20014	0.19995	+1.0	
4	41.015	0.20037	0.20015	+1.1	+0.4
4	40.968	0.20014	0.2002	-0.3	
4	41.036	0.20047	0.2004	+0.3	
4	41.008	0.20033	0.2002	+0.6	+0.8
6	40.983	0.20021	0.19995	+1.3	
6	40.993	0.20026	0.20015	+0.5	
6	41.022	0.20040	0.2003	+0.5	+0.1
16	40.949	0.20004	0.20005	-0.1	
16	40.959	0.20009	0.2001	-0.1	
16	40.899	0.19980	0.19975	+0.3	+0.8
16 ^a	40.970	0.20015	0.20015	± 0.0	
16 ^a	41.014	0.20036	0.20035	+0.1	
16 ^a	40.998	0.20028	0.20025	+0.1	+0.8
24	40.951	0.20005	0.1998	+1.3	
24	40.974	0.20016	0.2000	+0.8	
24	41.035	0.20046	0.20035	+0.5	+0.8
24 ^b	40.960	0.20010	0.1999	+1.0	
24 ^b	41.080	0.20068	0.20055	+0.6	
29	41.253	0.20152	0.20135	+1.1	+0.8
29	41.068	0.20062	0.2005	+0.6	
29	40.970	0.20015	0.2000	+0.7	
Av. diff., Obs.—Actual				+0.6	
Av. diff. omitting No. 16				+0.7	

^a Air-free water was used in these determinations.

^b During the reaction of the dichromate and iodide ions the solution was 1 *M* with respect to acid and had a volume of 60 cc. It was diluted to 600 cc. before titration.

chromate and iodide. These solutions were diluted to 600 cc. after standing for 1 minute. The samples of dichromate No. 29 were fused in a platinum boat inside a glass tube through which was passed a current of pure dry air. They were then treated as in the other determinations. All determinations made, with the exception of one in which the weight of the sample was uncertain, are reported in Table VIII.

Table VIII shows that chromates can be determined to within 0.1% by the iodide method. There is, however, a small difference between the observed and actual amounts of dichromate, except in the case of Dichromate No. 16. This difference averages 0.07% when the determinations on Dichromate No. 16 are excluded. Impurities other than chlorine and bromine in the standard iodine, and loss of iodine while transferring from the weighing bottle to the solution would tend to make the observed value for the thiosulfate solution too high. The presence of chromium trioxide as an impurity in the dichromate, and slight reduction of chromic ion to the chromous state would give high results in the chromate determinations also. The presence of air is shown to have no effect in the case of Dichromate No. 16. Errors leading to low results are less probable. Of the errors giving high results those affecting the standardization by iodine seem about as probable as those affecting the chromate determination. No basis is at hand for deciding which of the two, iodine or potassium dichromate, is the more reliable standard. The results indicate, however, that both are reliable to 0.1%.

The agreement with the other determinations of those in which the acid concentration was 1 *M* before the solution was diluted shows that there is a fairly wide range of experimental conditions within which correct results should be obtained. The larger acid concentrations, however, while reducing the time required for the reaction, make the danger of oxidation of iodide ion by air greater.

Permanganate as a Standard for Thiosulfate Solutions

Bray and McKay¹⁴ found that standardization of a thiosulfate solution by titrating the iodine liberated from an excess of iodide by permanganate gave a value for the normality which was less than that given by standardization against iodine. The thiosulfate solution the standardization of which is shown in Table II was standardized also by means of a permanganate solution. The permanganate solution, which was standardized by McBride's method,¹⁵ was added to 400 cc. of solution containing 2 to 5 cc. of 6 *M* hydrochloric acid and 2.5 g. of potassium iodide, and the iodine titrated. The results were about 0.4% higher than the value calculated from the data of Table III, assuming potassium dichromate as the standard. The permanganate standardization is evidently unreliable as McBride¹⁶ has observed.

¹⁴ Bray and McKay, *THIS JOURNAL*, **32**, 1198 (1910).

¹⁵ McBride, *ibid.*, **34**, 415 (1912).

¹⁶ Ref. 15, p. 411.

Summary

Titration of iodine with thiosulfate in a dil. acid solution gives results 0.1 to 0.3% higher and more concordant than the results of titration in a neutral solution.

The presence of air affects the titration of iodine with thiosulfate when the acidity of the solution is equivalent to 0.3 *M* hydrochloric acid or greater, causing too much thiosulfate to be required.

An apparent excess of oxidizing action of dichromate is caused by the titration of the iodine in a solution of too high an acid concentration. This can be corrected by exclusion of air, but more easily by dilution to such a hydrogen-ion concentration that the presence of air will not interfere.

Chromates can be determined within 0.1% by the iodide method under the proper conditions.

Potassium dichromate as a standard for thiosulfate solutions agrees with pure iodine within 0.1% but gives a slightly lower value. Errors in the iodine standardization leading to such a difference seem about as probable as errors in the dichromate standardization.

A standard permanganate solution is unreliable as a standard for thiosulfate solutions.

NEWPORT, RHODE ISLAND

[CONTRIBUTION FROM THE PHILADELPHIA WORKS OF E. I. DU PONT DE NEMOURS AND CO.]

THE EFFECT OF VARIATION IN WEIGHT OF THE RIDERS AND PLUMMETS OF THE WESTPHAL BALANCE UPON THE ACCURACY OF SPECIFIC-GRAVITY DETERMINATIONS

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The Westphal balance is largely used in the oil and heavy chemical industries because of the rapidity and ease with which specific-gravity determinations can be made. It is sometimes used to check the accuracy of hydrometers. Obviously for this purpose it is necessary that accurate results be obtained with the instrument, since a variation of ± 0.005 from the true specific gravity in the indicated density of the standardizing liquid will lead to an error in an hydrometer reading ranging from $\pm 2.0^\circ$ to $\pm 0.2^\circ$ Bé. from the true reading, the maximum error being attained when the standardizing liquid has a low specific gravity, (0.60–0.61). The accuracy of specific-gravity determinations with the Westphal balance is dependent upon the exact interrelation of the plummet displacement *P*, the weight of the index weight *W*, the weight of the first decimal rider *R*₁, and the weights of the second, third and fourth decimal riders *R*₂, *R*₃, and *R*₄. It has been found with instruments at present in use that this interrelation is not exact, and that weight variations in the riders