

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS.

IX. THE STANDARDIZATION OF THIOSULFATE SOLUTIONS. DETERMINATION OF THIOSULFATE

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Introduction

It has been demonstrated that ceric sulfate solutions 0.5–3 *N* in sulfuric acid are stable for long periods of time (at least a year) if prepared from rare earth oxide mixture of suitable grade.¹ Having a standardized ceric sulfate solution available it is desirable to know whether such a solution may be used for checking the normality of a standard thiosulfate solution in the same manner that bichromate or permanganate solution may be used.² Ceric ion is reduced readily and completely by iodide ion, and the equivalent quantity of iodine that is liberated may be titrated with thiosulfate in the usual manner. Several investigators³ have shown that such a process is tedious to carry out experimentally, apparently because the oxidation of hydriodic acid by air is catalyzed by cerous salts. This error may be minimized or eliminated by working with solutions freed from air, in an inert atmosphere (Martin³). We have studied this method of standardization of thiosulfate and have found that the presence of a small quantity of ferric ion in the ceric solution causes an additional error which may be minimized by adding a small quantity of phosphoric acid in order to render the ferric ions inactive. In view of all of these complications, we have studied an alternative method which has proved to be excellent.

This alternative method consists in the titration of a measured volume of the thiosulfate solution with ceric sulfate. Direct titration in the absence of iodide is far from stoichiometric, because of the effect of the acid which must be present in the ceric solution, and probably because of the nature of the reaction between ceric and thiosulfate ions as well.⁴ If a *suitable*

¹ N. H. Furman, *THIS JOURNAL*, **50**, 755 (1928); for other papers of this series, see *ibid.*, **50**, 1675 (1928); **51**, 1128, 1449 (1929); **52**, 1443, 2347 (1930). Willard and Young, *ibid.*, **51**, 149 (1929); for other papers of the series see, *ibid.*, **50**, 1322, 1334, 1368, 1372, 1379 (1928); **51**, 139, 149 (1929); **52**, 36, 132, 553, 557 (1930); *Ind. Eng. Chem.*, **20**, 972 (1928).

² For references on the use of bichromate, cf. I. M. Kolthoff (translated by N. H. Furman), "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1929, Vol. II, p. 369. For permanganate, cf. W. C. Bray and H. E. Miller, *THIS JOURNAL*, **46**, 2204 (1924); S. Popoff and J. L. Whitman, *ibid.*, **47**, 2259 (1925). A bibliography is given in the latter paper.

³ Bunsen, *Lieb. Ann.*, **105**, 40 (1858); Browning, *Z. anorg. allgem. Chem.*, **22**, 297 (1899); Martin, *THIS JOURNAL*, **49**, 2133 (1927).

⁴ Benrath and Ruland found that the direct reaction proceeded approximately according to the equation: $2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{Ce}(\text{SO}_4)_2 = \text{Ce}_2(\text{SO}_4)_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_4\text{O}_6$

amount of iodide is added to the thiosulfate solution, and if the initial volume is made sufficiently large, disturbing effects are eliminated, and the titration may be made rapidly and simply to the starch-iodine end-point. The same method of titration may of course be applied to the determination of thiosulfate.

At the start of the titration there is visible liberation of iodine about the entering drops of ceric sulfate, but the iodine is consumed rapidly by the thiosulfate and the blue starch-iodine color does not appear even temporarily if the solution is well stirred until the concentration of thiosulfate is greatly diminished near the end-point.

The reaction $2\text{Ce}^{++++} + 2\text{I}^- = 2\text{Ce}^{+++} + \text{I}_2$ proceeds almost instantaneously so that the oxidation of the thiosulfate is effected by the normal reaction: $\text{I}_2 + 2\text{S}_2\text{O}_3^{--} = 2\text{I}^- + \text{S}_4\text{O}_6^{--}$. Under these conditions direct interaction of ceric and thiosulfate ions plays a negligible role.

Experimental

The ceric solutions were prepared by dissolving commercial rare earth oxides in sulfuric acid, filtering and diluting to 0.1 *N* oxidizing power and 1–2 *N* sulfuric acid concentration.⁵ The solutions were standardized against Bureau of Standards sodium oxalate, either potentiometrically or by the iodine monochloride catalytic method of Willard and Young.^{5,6}

0.1 *N* Iodine and thiosulfate solutions were prepared in the usual manner and standardized against Bureau of Standards arsenious oxide, and re-sublimed iodine, respectively, using starch indicator.⁷

Use of Standard Ceric Sulfate to Determine the Normality of Thiosulfate

Method 1.—The ceric solution was pipetted into a solution containing an excess of potassium iodide; the iodine was titrated with thiosulfate. When air was not excluded, errors of the following magnitudes were found: cc. of approx. 0.1 *N* thiosulfate calcd., 28.39; cc. found, 28.61–28.81. The end-point was not permanent, nor even moderately stable. If the air is displaced with carbon dioxide, and if no phosphate is present, the error is smaller, but not negligible. For example, we found 28.61, 28.49, 28.51 cc. of thiosulfate; calcd., 28.39 cc. Much better results are obtained if phosphoric acid is added to combine with the iron, the air of course being excluded by carbon dioxide. The solutions were prepared by mixing 60 cc. of potassium iodide solution (20 g. per liter), 25 cc. of sulfuric-phosphoric acid mixture (150 cc. of each of the concentrated acids per liter), and 25 cc. of ceric sulfate, after air had been expelled from the solution: calcd., 23.87 cc.; found, 23.90, 23.92 cc. Under these conditions no ceric phosphate is

[*Z. anorg. allgem. Chem.*, 114, 267 (1920)]. Our experiments indicate a larger consumption of ceric sulfate per mole of thiosulfate.

⁵ Procedure of Willard and Young, *THIS JOURNAL*, 50, 1322 (1928); 51, 149 (1929), and Furman and Evans, *ibid.*, 51, 1128 (1929).

⁶ Furman, *ibid.*, 50, 755 (1928).

⁷ The details given by Kolthoff, "Volumetric Analysis," Vol. II, Chap. XII, were followed carefully.

precipitated. Previous experience of one of us (F.) had shown that with pure ceric solutions no phosphoric acid is necessary: calcd., 16.58 cc.; found, 16.60, 16.60 cc.

Our experience is, therefore, in agreement with that of others in finding the method to be accurate if proper precautions are observed. We believe that it is much more tedious and no more accurate than the following one.

Method 2.—Measured volumes of thiosulfate solution are added to a suitable mixture of potassium iodide, starch solution and water and are titrated directly to the starch-iodine end-point with standard ceric sulfate. If the initial volume of the solution is large enough, the acid and the iron which are present in the ceric sulfate solution do not interfere.

There is a lower limit of iodide concentration for any given set of conditions. For example, with an initial volume of 125 cc., containing 25 cc. of approximately 0.1 *N* thiosulfate and 20 cc. of starch (2 g. starch per liter), the following values were found

KI present, g.....	0.8	0.4	0.16	0.128	0.08	0.08	0.08
Ce(SO ₄) ₂ soln., cc.....	23.42	23.40	23.41	23.43	23.56	23.50	23.55

Correct values (23.41 cc.) were found down to 0.128 g. of potassium iodide. We therefore recommend that at least 0.15 g. of the iodide be present per 125 cc. of initial volume.

Erratic results are obtained if the initial volume of the solution is too small. The summary of results and conditions that is given in Table I will show the magnitude of the errors when the volume is too small.

TABLE I
TITRATION OF THIOSULFATE WITH CERIC SULFATE

	1	2	3	4	5	6	7	8	9
Na ₂ S ₂ O ₃ (0.0956 <i>N</i>), cc.	10	10	10	25	25	25	25	25	25
KI, g.	0.4	1.0	1.0	0.1	0.2	0.2	0.3	0.3	0.5
Initial vol., cc.	50	70	100	50	50	100	100	100	100
Ce(SO ₄) ₂ (0.1086 <i>N</i>), cc.	8.80	8.83	8.80	22.45	22.30	21.99	21.99	22.03	22.03
Ce(SO ₄) ₂ calcd., cc.	8.81	8.81	8.81	22.01	22.01	22.01	22.01	22.01	22.01
Error, cc.	-0.01	0.02	-0.01	+0.44	+0.29	-0.02	-0.02	+0.02	+0.02
		10	11	12	13	14	15	16	17
Na ₂ S ₂ O ₃ soln., cc.	50	50	50	50	60	50	50	50	50
KI, g.	2	1	1	1.6	1.6	1.2	1.6	1.6	1.6
Initial vol., cc.	150	200	300	400	400	500	500	500	500
Ce(SO ₄) ₂ used, cc.	44.48	44.14	44.32	47.37	47.36	47.29	47.26	47.31	47.31
Ce(SO ₄) ₂ calcd., cc.	44.03	44.03	44.03	47.28	47.28	47.28	47.28	47.28	47.28
Error, cc.		+0.45	+0.11	+0.29	+0.09	+0.08	+0.01	-0.02	-0.03

NOTE: Determinations 13-17 were made with different ceric and thiosulfate solutions from the others.

A series of determinations with 25 cc. of thiosulfate and initial volumes of 200-300 cc. gave results of 22.01, 22.00, for the 0.0956 *N* solution, and 25.44, 25.46, 25.47 for another solution for which the calculated value was 25.45 cc. If 25 cc. of thiosulfate is used, accurate results are found with initial volumes of 100-300 cc. Note, however, the large errors that result

when the volume is 50 cc. (Nos. 4 and 5, Table I). When 50 cc. of thiosulfate is used, the initial volume must be about 500 cc. in order to avoid erratic results (Nos. 15-17, Table I). The error disappears somewhere between an initial volume of 400 and one of 500 cc. If the initial volume is as low as 100 cc. with 50 cc. of thiosulfate taken, errors as large as 0.7 to 1.7 cc. may result. We attribute the erratic values to decomposition of thiosulfate by the acid from the ceric solution, followed by oxidation of the sulfurous acid by either iodine or ceric sulfate. It is possible that the ferric iron (about 1 mg. per 25 cc.) which is present in the ceric solution may cause error when the acidity is high (small initial volume), but we have invariably observed the error to be in the opposite direction to that which would be caused by the iron, and in extreme cases to be three or four times as great as the maximum possible effect of the iron. In general, it appears to be wise to make the initial volume at least 10 times the volume of the thiosulfate used.

The correctness of the method was tested in a preliminary fashion by standardizing both iodine and ceric solutions directly against 25-cc. portions of 0.1000 *N* arsenious oxide solution prepared from Bureau of Standards arsenious oxide. The normality of the thiosulfate was then determined by titration with the iodine and ceric solutions, respectively.

Standardization of Ceric Solution.—Twenty-five cc. portions of arsenite required: 22.67, 22.75, 22.75, 22.68, 22.75, 22.73, 22.77 cc.; average 22.73 cc. equivalent to normality of 0.1100.

Iodine Solution.—Twenty-five cc. of arsenite required: 25.57, 25.58, 25.53, 25.52 cc., average 25.55 cc. Normality 0.0978 (4). Normality of thiosulfate, assuming ceric to be correct: 0.0957, 0.0954, 0.0958, 0.0957, average 0.0957. Normality of thiosulfate assuming iodine to be correct: 0.0958, 0.0959, 0.0960, 0.0959, average 0.0959.

The standardization of ceric sulfate against arsenious oxide was made by Willard and Young's procedure.⁸ They found that this procedure gives results about 3 parts per 1000 lower than those found with electrolytic iron or sodium oxalate as a primary standard. Our work was done before the appearance of Swift's paper⁹ in which he states that correct results may be obtained in 4 *N* hydrochloric acid solution with iodine monochloride catalyst. We applied no correction to our results, but if such correction were applied the ceric normality would be 0.1103 and hence the two methods would agree to about 1 part per 1000. Unfortunately, no oxalate standardization of the ceric sulfate solution which we used for this work was made.

A more rigorous check on the fundamental correctness of our method of standardizing thiosulfate was made with weight buret technique. The Friedman and La Mer type of buret was used and found to be eminently satisfactory.¹⁰

⁸ Willard and Young, Ref. 5, p. 1372.

⁹ Swift and Gregory, *THIS JOURNAL*, **52**, 901 (1930).

¹⁰ Friedman and La Mer, *Ind. Eng. Chem., Anal. Ed.*, **2**, 54 (1930).

STANDARDIZATION OF CERIC SULFATE AGAINST BUREAU OF STANDARDS SODIUM OXALATE

	1	2	3	4	5
Na ₂ C ₂ O ₄ , g.	0.2047	0.2471	0.2457	0.2116	0.2744
Ceric soln., g.	31.655	38.189	37.977	32.650	42.409
Weight normality	0.09659	0.09657	0.09657	0.09674	0.09657
				Average, 0.09661 <i>N</i>	

Nos. 1, 2, 4 and 5 were made by the iodine monochloride method of Willard and Young;⁵ No. 3 was titrated in hot solution containing 20 cc. of concd. hydrochloric acid per 100 cc. Nos. 1-3 were separately weighed samples of oxalate, and Nos. 4 and 5 were weighed aliquot portions of a weighed solution of 1.1270 g. of oxalate.

STANDARDIZATION OF THIOSULFATE AGAINST RESUBLIMED IODINE¹¹

	1	2	3	4
Iodine, g.	0.3741	0.6186	0.3379	0.5248
Thiosulfate soln., g.	29.787	49.236	26.879	41.736
Weight normality	0.09895	0.09899	0.09905	0.09907
			Average 0.09901 <i>N</i>	

TITRATION OF THIOSULFATE WITH CERIC SULFATE

	1	2	3	4	5
Initial vol., cc.	300	300	300	300	500
(1) Thiosulfate soln., g.	20.172	21.924	19.455	18.747	40.252
(2) Ceric soln., g.	20.650	22.452	19.903	19.201	41.184
Ratio [(2)/(1)]	1.0237	1.0241	1.0231	1.0242	1.0231
				Average 1.0236	

In Nos. 1-4, 2 g. of potassium iodide, and in No. 5, 4 g. of potassium iodide were present. In each case 20 cc. of 0.2% starch solution was present.

Hence the normality of the thiosulfate found indirectly is $0.09961 \times 1.0236 = 0.09889$ as contrasted with the directly determined value of 0.09901. The method, therefore, appears to be quantitative to better than 2 parts per 1000 (1.2 parts); the discrepancy between the direct and indirect values is of the same order of magnitude as that of the uncertainty regarding the purity of the sodium oxalate (one part per thousand according to the Bureau of Standards).

Potentiometric Method.—A number of experiments were made potentiometrically; these will not be described in detail. It was found that in the presence of iodide a very small jump in potential, Pt *vs.* N calomel electrode (about 0.01 volt per 0.05 cc. of 0.1 *N* ceric sulfate), occurred at the end-point of the reaction. The iodine-starch end-point is much superior in this case.

In the absence of iodide there is no definite potentiometric end-point; no fairly stable high e. m. f. (0.8-0.9 volt, Pt *vs.* N calomel electrode) is

¹¹ The iodine was kept until needed in a stoppered vessel in a desiccator over anhydrous barium perchlorate ("desicchlora"). The lid of the desiccator was not greased.

developed until about a 25% excess of ceric sulfate has been added; the potential is not constant, indicating further reaction. The direct interaction of ceric and thiosulfate ions appears to be rather slow, and the thiosulfate is in part decomposed (by acid) with formation of sulfurous acid (odor of sulfur dioxide).

Determination of Thiosulfate.—It is possible to determine thiosulfate in solutions or in salts by titration with standard ceric solution, if potassium iodide is present.

Recommended Procedure.—If approximately 0.1 *N* ceric solution is used: dissolve 0.5–0.7 g. of crystalline sodium thiosulfate (or an equivalent quantity of any other thiosulfate) in water, add 0.3 to 0.4 g. of potassium iodide, and starch solution (20 cc. of 0.2% solution), dilute to 250 cc. and titrate with ceric sulfate to the starch-iodine end-point.

Eleven students followed a procedure approximately as given in the preceding paragraph, although the importance of the initial volume-concentration relations was not fully realized at the time when this work was done. Working on clear crystals of uneffloresced sodium thiosulfate pentahydrate (Kahlbaum preparation), the following values were found: 63.69, 63.82, 63.90, 63.72, 63.53, 63.82, 63.30, 63.60, 63.61, 63.38, 63.52% $\text{Na}_2\text{S}_2\text{O}_3$ (calcd., 63.71%). In each case the value given is an average of two or more concordant determinations. The majority of the determinations (9 out of 11) are satisfactory.

A number of other possible applications of the use of iodide as a sort of "catalyst with known mechanism" in ceric sulfate oxidations are being studied in this Laboratory. In effect this method makes use of the iodide-iodine system not only as a catalyst but as an oxidation-reduction indicator (with the addition of starch) as well.

Summary

A standard ceric sulfate solution may be used to determine the normality of thiosulfate: (a) by liberating iodine from an iodide and titrating the former with thiosulfate. Air must be excluded, and ferric iron, if present in the ceric solution, must be rendered inactive by means of phosphate, (b) by titration of a mixture of thiosulfate, iodide and starch indicator with ceric sulfate. The initial volume should be ten times that of the thiosulfate used; 0.15 g. of potassium iodide should be present per 125 cc. of initial solution.

The reaction between ceric sulfate and thiosulfate, with intermediate action of iodide, has been shown to be stoichiometric at least to 1.2 part per thousand.

The reaction may be applied to the determination of thiosulfate.