with Salstrom's data upon activities was obtained in the case of silver bromide in lithium bromide and sodium bromide. In the case of lithium and potassium salts the deviation from ideality seemed slightly greater for the chlorides than for the bromides.

6. The activity coefficients of various salts other than chlorides and bromides might be determined by measurements of e. m. f. in cells otherwise similar to those employed in this research.

7. An interpretation of Günther-Schulze's observations upon the diffusion of silver ion into glass from fused silver halides was offered.

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Ceric Sulfate as a Volumetric Oxidizing Agent. XIV. Indicator Methods for the Standardization and Use of Ceric Sulfate

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Introduction

Accurate methods, already described, for the standardization of ceric sulfate include (1) the titration of sodium oxalate in a hot hydrochloric, sulfuric or perchloric acid solution. The end-point may be determined either potentiometrically[1,2] or visually.[1] If the titration is made in a hydrochloric acid solution at room temperature in the presence of iodine chloride as catalyst, the end-point is determined potentiometrically.[1] (2) The titration of ferrous ion from electrolytic iron in a sulfuric, hydrochloric, or perchloric acid solution. The end-point may be determined potentiometrically,[3] with diphenylamine sulfonic acid as an oxidation-reduction indicator,[4] with diphenylamine or diphenylbenzidine,[3] or with methyl red, erio glaucine, or erio green.[5] *o*-Phenanthroline ferrous complex has been suggested as an oxidation-reduction indicator for this titration[6] and because of its high oxidation potential it is more satisfactory than any of the indicators mentioned above. (3) The titration of arsenious oxide in a hydrochloric acid solution. If bromide or iodide ion or iodine chloride is present, the titration may be carried out at room temperature and the end-point determined potentiometrically[7] or by the use of chloroform if iodine chloride is the catalyst.[8]

[1] Willard and Young, THIS JOURNAL, **50**, 1322 (1928).

[2] Furman, *ibid.*, **50**, 755 (1928).

[3] Willard and Young, *ibid.*, **50**, 1334 (1928).

[4] Willard and Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, 1933, p. 183.

[5] Furman and Wallace, THIS JOURNAL, **52**, 2347 (1930).

[6] Walden, Hammett and Chapman, *ibid.*, **53**, 3908 (1931).

[7] Willard and Young, *ibid.*, **50**, 1372 (1930).

[8] Swift and Gregory, *ibid.*, **52**, 901 (1930).

Of these three primary standards, sodium oxalate and arsenious oxide are the two which are more commonly available, but the only indicator method for either is that using the iodine monochloride end-point in the arsenite titration.[8,9] Indicator methods for the titration of either of these primary reducing agents with ceric sulfate would be especially desirable for the standardization of the latter, and the present study was undertaken both to investigate the possibility of using *o*-phenanthroline ferrous complex as an oxidation–reduction indicator in such titrations and to clear up discrepancies relating to the proper concentration of hydrochloric acid for solutions of sodium arsenite when titrated with ceric sulfate in the presence of iodine chloride as catalyst.[7,8]

Experimental Methods and Results

Reagents and Solutions.—The sodium oxalate and arsenious oxide were from the U. S. Bureau of Standards. A 0.1 N solution of the latter was prepared by dissolving the proper amount of it in sodium hydroxide, adding sufficient hydrochloric acid to this solution to react with the sodium hydroxide used, and following this with 10 g. of sodium bicarbonate. The solution was then diluted to the correct volume.

The ceric sulfate solutions were prepared in two ways: (1) by treatment of high-grade ceric oxide with sufficient concentrated sulfuric acid to cause the solid ceric sulfate formed, when dissolved in water, to give a solution of the desired normality and 0.5 M in sulfuric acid;[10] (2) by dissolving solid ceric ammonium sulfate[11] in water containing sufficient sulfuric acid to make the final solution 0.5 M in sulfuric acid. These solutions were standardized against Bureau of Standards sodium oxalate.[1]

The iodine chloride solution was prepared by dissolving 0.279 g. of potassium iodide and 0.178 g. of potassium iodate in 250 cc. of water and adding at once 250 cc. of concentrated hydrochloric acid.[12] The solution thus obtained was 0.005 M in iodine chloride. It was adjusted potentiometrically by adding dilute potassium iodide or iodate. An alternative method for adjusting such a solution is described by Swift and Gregory.[8]

Since in the action between *o*-phenanthroline and ferrous ion, three molecules of the former combine with one of the latter, a 0.025 M solution of the indicator may be prepared by dissolving the correct amount of *o*-phenanthroline ($C_{12}H_8N_2 \cdot H_2O$) in a 0.025 M aqueous solution of ferrous sulfate. Ordinarily one drop of this indicator solution[6] is sufficient to afford a very sharp color change.

Standardization of Ceric Sulfate against Sodium Oxalate.—Preliminary experiments showed that the reaction of sodium oxalate with ceric sulfate at room temperature in a hydrochloric acid solution containing iodine chloride as catalyst was not rapid enough for the use of *o*-phenanthroline ferrous complex as indicator. When the oxalate solution was heated somewhat, the indicator was not destroyed appreciably

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[9] Since this paper was presented for publication, an article by Walden, Hammett and Chapman has appeared (THIS JOURNAL, **55**, 2649 (1933)) in which the value of *o*-phenanthroline ferrous complex in titrations involving ceric sulfate is shown and a method of obtaining the molar oxidation potential of the indicator is described. These authors give three indirect methods for the standardization of ceric sulfate, none of which is duplicated in the material in this paper.

[10] Willard and Young, THIS JOURNAL, **51**, 149 (1929).

[11] This substance, which is obtainable from O. T. Coffelt, Jackson, Michigan, affords the most convenient method for the preparation of ceric sulfate solutions; see Willard and Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, 1933, p. 183.

[12] G. S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Co., New York, 1926, pp. 8, 9.

and the reaction was much more rapid. A temperature of 50° seemed most satisfactory, for at higher temperatures too much of the indicator was destroyed, while at much lower temperatures the reaction was not sufficiently rapid.

In each experiment listed in Table I, a definite volume of a standard sodium oxalate solution was measured into a 400-cc. beaker. Water, concentrated hydrochloric acid and iodine chloride solution were added, and the solution was heated over a free flame while being stirred constantly with a thermometer until its temperature was 50°. One drop of indicator solution was added and the titration made with ceric sulfate. The solution, if below 45° near the end of the process, was reheated to 50° and the titration completed. The normality of the ceric sulfate from potentiometric standardization against sodium oxalate was 0.08056.

TABLE I

TITRATION OF SODIUM OXALATE WITH CERIC SULFATE, *o*-PHENANTHROLINE FERROUS COMPLEX AS INDICATOR

$Na_2C_2O_4$ 0.1 *N*, cc.	HCl added, sp. gr. 1.18, cc.	ICl, 0.005 *M*, cc.	Initial vol., cc.	Indicator 0.025 *M*, drops	$Ce(SO_4)_2$, cc.	Character of end-point
25	30	5	100	1	0.08067	Slow
25	25	5	100	1	.08059	Satisfactory
25	20	5	100	1	.08052	Satisfactory
25	15	5	100	1	.08059	Satisfactory
25	10	5	100	1	.08059	Satisfactory
25	5	5	100	1	.08064	Not clear
25	15	2.5	100	1	.08054	Satisfactory
25	15	10	100	1	.08059	Satisfactory
25	25	5	150	1	.08043	Satisfactory
25	37	5	150	1	.08051	Satisfactory
25	15	5	75	1	.08056	Satisfactory
10	15	5	100	1	.08049	Satisfactory
50	30	5	100	2	.08061	Slow
50	20	5	75	2	.08056	Slightly slow
50[a]	5	5	100	2	.08070	Slow
25[b]	5	5	100	1	.08060	Satisfactory
25[b]	0	5	100	1	.08063	Satisfactory

[a] Sufficient sodium chloride added to supply chloride ion equivalent to that in 10 cc. of hydrochloric acid, sp. gr. 1.18. [b] Sodium chloride equivalent to 15 cc. of hydrochloric acid, sp. gr. 1.18.

In the solutions of higher acidity, the red color of the indicator was not evident throughout the titration, the solution being quite yellow or brownish yellow. If the titration was interrupted for a moment, the indicator color returned. As the end-point was approached the yellow color became fainter and the red shade more evident. It was possible to titrate rapidly to within 5 or 6 drops of the end-point. As a usual thing, the solution was then reheated to 50° and the titration completed. It was considered that the end-point had been reached when the solution was pale blue in color and when there was no return of any pink color after an interval of one minute. In the solutions of lower acidity, the red color was more in evidence and the yellow color less prominent throughout the titration. The last three experiments indicate that a certain concentration of chloride ion is necessary in this reaction. The indicator color disappeared in the last experiment when the first portion of ceric sulfate was added, but returned as more was added. The free acid in the oxidizing agent was undoubtedly needed to cause the reaction to proceed smoothly.

To check more closely this indicator method of standardizing ceric sulfate, measured volumes of a standard solution of sodium oxalate were titrated with ceric sulfate added from a weight buret. From the weights of ceric sulfate solution used, the number of equivalents of oxidizing agent per 1000 g. of solution were calculated. The results are shown in Table II. For the titrations in column A, 50-cc. portions of 0.1 N sodium oxalate were treated with 15 cc. of hydrochloric acid, sp. gr. 1.18, and 10 cc. of 0.005 M iodine chloride, diluted to 100 cc. and titrated potentiometrically. For the titrations in column B, 10-cc. portions, in C, 25-cc. portions, and in D, 50-cc. portions of the same sodium oxalate solution were treated with 20 cc. of hydrochloric acid, sp. gr. 1.18, and 5 cc. of 0.005 M iodine chloride, diluted to 100 cc., and titrated as already described, with *o*-phenanthroline ferrous complex as indicator.

TABLE II

STANDARDIZATION OF CERIC SULFATE AGAINST SODIUM OXALATE

A	B	C	D
0.07627	0.07627	0.07629	0.07644
.07630	.07625	.07631	.07644
.07629	.07626	.07631	.07638

The reaction at the end-point for each titration in column D was slow. It seemed probable that the higher concentration of sulfuric acid, due to the larger volume of oxidizing agent added in these cases, was the cause of this as it has been shown in earlier work[1,2] that the reaction between oxalate ion and ceric sulfate is slow if much sulfuric acid is present. To check this point more carefully, the character of the reaction at the end-point was studied by titrating 2-cc. portions of 0.01 N sodium oxalate solution with 0.01 N ceric sulfate. The procedure used for the experiments in Table I was followed. One drop of indicator was added for each titration.

TABLE III

EFFECT OF SULFURIC ACID ON THE REACTION BETWEEN SODIUM OXALATE AND CERIC SULFATE

HCl added, sp. gr. 1.18, cc.	ICl, 0.005 M, cc.	H_2SO_4, 0.5 M, cc.	Initial vol. cc.	$Ce(SO_4)_2$ 0.1 N, cc.	Character of end-point
15	10	0	100	2.03[a]	
20	5	0	125	2.07	Satisfactory
20	5	10	125	2.06	Satisfactory
20	5	20	125	2.04	Slightly slow
20	5	30	125	2.00	Slow
20	5	40	125	1.75	Very slow
20	5	50	125	1.72	Very slow
10	5	40	125	2.07	Slightly slow
5	5	40	125	2.06	Slow
10	5	60	125	1.95	Very slow

[a] A potentiometric standardization.

The data in Tables I, II and III show that this indicator method for the standardization of ceric sulfate is very satisfactory. For especially accurate results it is preferable to use not more than 30–35 cc. of ceric sulfate in the titration, although the error introduced by the sulfuric acid in larger volumes of the oxidizing agent is very small. To offset the effect of the sulfuric acid, it might appear desirable to increase the volume of the solution at the time of titration, but by such a step the end-point reaction becomes somewhat slow.

Standardization of Ceric Sulfate against Arsenious Oxide.—Preliminary experiments showed that the reaction of ceric sulfate with sodium arsenite in a hydrochloric acid solution containing iodine chloride as catalyst and *o*-phenanthroline ferrous complex as indicator was sufficiently rapid at room temperature until within a few drops of the end-point. If the solution is heated to 50° before the last few drops of ceric sulfate are added, the end-point reaction is rapid—more rapid than in the case of sodium oxalate.

In each experiment in Table IV a definite volume of standard sodium arsenite was taken, and water, hydrochloric acid, iodine chloride and always one drop of 0.025 *M* *o*-phenanthroline ferrous complex added. When within a few drops of the end-point, the solution was heated to 50° and the titration completed. The normality of the ceric sulfate from potentiometric standardization against sodium oxalate was 0.08056.

TABLE IV

TITRATION OF ARSENIOUS OXIDE WITH CERIC SULFATE, *o*-PHENANTHROLINE FERROUS COMPLEX AS INDICATOR

$NaAsO_2$ 0.1 *N*, cc.	HCl added, sp. gr. 1.18, cc.	ICl, 0.005 *M*, cc.	Initial vol., cc.	$Ce(SO_4)_2$ normality	Character of end-point
25	25	5	100	0.08057	Satisfactory
25	25	10	100	.08062	Satisfactory
25	25	2.5	100	.08059	Satisfactory
25	15	2.5	100	.08057	Satisfactory
25	10	2.5	100	.08059	Satisfactory
25	5	2.5	100	.08062	Slow
25	0	2.5	100	.08062	Not clear
25	35	2.5	100	.08059	Slightly slow
25	30	5	200	.08057	Satisfactory
25	30	2.5	200	.08054	Satisfactory
25[a]	15	2.5	100	.08057	Satisfactory
25[b]	15	2.5	100	.08057	Slightly slow
25[b]	5	2.5	100	.08057	Not clear
10	10	2.5	100	.08061	Satisfactory
10	25	2.5	100	.08061	Satisfactory
50	10	2.5	100	.08062	Satisfactory
50	25	2.5	100	.08063	Satisfactory
25[c]	0	2.5	100	.08059	Satisfactory

[a] 10 cc. of 9 *M* sulfuric acid present in the solution. [b] 20 cc. of 9 *M* sulfuric acid present in the solution. [c] Sufficient sodium chloride added to supply chloride ion equivalent to that in 10 cc. of hydrochloric acid of sp. gr. 1.18.

The end-point reaction in the titration of an arsenite is invariably more rapid than in the titration of an oxalate. The arsenite–ceric sulfate reaction, moreover, is not sensitive to sulfate ion, so that amounts of arsenite requiring larger volumes of ceric sulfate may be used—a decided advantage from the point of view of accuracy. Also arsenite solutions, when properly prepared, are stable over a long period. From the last experiment in Table IV it is seen that the chloride ion is more important than the hydrogen ion in promoting the catalytic action of the iodine chloride.

To check this indicator method for the standardization of ceric sulfate, a series of titrations was made in which the ceric sulfate was added from a weight buret and the number of equivalents of the oxidizing agent per 1000 g. of solution was calculated in each case. In column A of Table V are the data for the potentiometric standardization of ceric sulfate against sodium oxalate in hot hydrochloric acid solution, in B the potentiometric standardization of the same solution against sodium oxalate at room temperature in a hydrochloric acid solution containing iodine chloride, in C the potentiometric standardization against arsenious oxide at room temperature in a hydrochloric acid solution containing iodine chloride, and in D the standardization against arsenious oxide in a hydrochloric acid solution containing iodine chloride and *o*-phenanthroline ferrous complex as indicator.

TABLE V

STANDARDIZATION OF CERIC SULFATE AGAINST SODIUM OXALATE OR ARSENIOUS OXIDE

A	B	C	D
0.05127	0.05121	0.05126	0.05123
.05127	.05119	.05125	.05122
.05125	.05118	.05126	.05125
.05126	.05122	.05126	.05125
	.05125	.05125	.05126

Thus it is evident from the data in Tables II and V that very accurate results may be obtained in the standardization of ceric sulfate solutions against either sodium oxalate or arsenious oxide with *o*-phenanthroline ferrous complex as an oxidation–reduction indicator.

Effect of Hydrochloric Acid on the Potentiometric Standardization of Ceric Sulfate against Arsenious Oxide.—In earlier work[7] the authors found that the normality factor for ceric sulfate from potentiometric standardization against arsenious oxide in a hydrochloric acid solution containing iodine chloride was about three parts in a thousand lower than that against electrolytic iron or oxalate. Swift and Gregory have pointed out[8] more recently that the concentration of hydrochloric acid present at the end of this titration as described in the earlier paper by the present authors was less than 2 *M*, and they recommend a concentration of 4 *M* hydrochloric acid at the end of the titration for quantitative results. The authors have confirmed their own previous work and the statements of Swift and Gregory by measuring out 25-cc. portions of a 0.1 *N* sodium arsenite solution, adding sufficient hydrochloric acid to give the concentration specified in Table VI and 10 cc. of 0.005 *M* iodine chloride, and diluting the solution in each case to 100 cc. The titration was then made with a ceric sulfate solution added from a weight buret. The results obtained are given in Table VI.

TABLE VI

THE EFFECT OF HYDROCHLORIC ACID ON THE POTENTIOMETRIC STANDARDIZATION OF CERIC SULFATE AGAINST ARSENIOUS OXIDE

HCl at end of titr., moles/liter	4.6	4.2	3.4	3.0	2.7	1.9	1.2[b]
Equiv. of ceric sulfate in 1000 g. soln.	0.04877	.04876	0.04878	0.04874	0.04869	0.04865	0.04871
		.04875	.04874	.04875	.04871	.04865	.04871
		.04871	.04875	.04874	.04869	.04872[a]	.04871

[a] In this one titration the ceric sulfate was added very slowly in the region of the end-point. [b] Potassium chloride added in sufficient amount to make the total chloride ion concentration of the solution at the end of the titration 3.4 molar.

With an acidity of 4.6 moles of hydrochloric acid per liter at the end of a titration, the reaction is too slow, both during the main titration and at the end-point; with a final acidity of 3.0–4.2 moles per liter, the end-point reaction is fairly rapid, and with an acidity below 3 molar the end-point reaction is very slow. Therefore the final acidity in hydrochloric acid should be between 3.0 and 4.2 molar, preferably a little above 3 molar as the reaction is somewhat more rapid then.

Previously Jamieson,[12] and Swift and Gregory,[8] have emphasized the importance of maintaining a certain minimum concentration of hydrochloric acid in titrations of arsenite with an oxidizing agent, when the iodine monochloride end-point is used. The last series of results in Table VI indicate clearly that in the arsenite–ceric sulfate titration the concentration of the chloride ion is of far greater importance than the concentration of hydrogen ion. This same fact has been shown to apply to the oxalate–ceric sulfate titration and may hold for other reactions in which iodine monochloride is used.

The arsenite titrations in column C, Table V, were made in solutions 3.4 molar in hydrochloric acid at the end of the titration. A comparison of the values in columns C and A shows that the arsenite–ceric sulfate reaction is quantitative under the proper conditions. On the other hand, a comparison of the values obtained for the normality of ceric sulfate from solutions of final acidity 3.4 and 1.9 molar in hydrochloric acid, as given in Table VI, explains the reason for the authors' statement in an earlier paper concerning this reaction.

The Standardization of 0.01 *N* Ceric Sulfate Solutions.—A 0.01 *N* solution of ceric sulfate is often desirable. The two indicator methods just described have been used to standardize such a solution and the data obtained are given in Table VII.

Thus it is seen that 0.01 *N* solutions of ceric sulfate may be standardized very accurately by these indicator methods, and also that such dilute

TABLE VII

STANDARDIZATION OF 0.01 N SOLUTIONS OF CERIC SULFATE

Time of standing, weeks	Against arsenious oxide		Against sodium oxalate			
	Indicator		Potentiometric		Indicator	
			Soln. A, 0.5 M in H_2SO_4			
0			0.01017	0.01019	0.01020	0.01020
			.01020			
7.5	0.01017	0.01017			.01017	.01017
12	.01017	.01017			.01016	.01014
			Soln. B, 0.25 M in H_2SO_4			
0			0.01117	0.01118	0.01116	0.01117
			.01119		.01116	
3	0.01114	0.01117			.01117	.01116
7.5	.01117	.01117			.01113	.01112
12	.01115	.01115			.01111	.01111

solutions are much more stable than permanganate solutions of the same normality.

Recommended Procedures for the Standardization of Ceric Sulfate Solutions (0.01 to 0.1 N)

A. **Against Arsenious Oxide.**—Measure into a 400-cc. beaker that volume of a standard solution of sodium arsenite which will require from 40–50 cc. of ceric sulfate, or weigh out a suitable amount of arsenious oxide. In the latter case the sample must be dissolved in 15 cc. of water containing 1 g. of sodium hydroxide. Add 15–20 cc. of hydrochloric acid, sp. gr. 1.18, and 2.5 cc. of 0.005 M iodine chloride, and dilute the solution to 100 cc. Add 1 drop of 0.025 M *o*-phenanthroline ferrous complex as indicator and titrate at room temperature with ceric sulfate until the brown color of the indicator returns slowly after the addition of each drop of oxidizing agent. Heat the solution to 50° (use a thermometer as stirring rod) and continue adding ceric sulfate very slowly until there is no return of the brown color of the indicator within a minute.

B. **Against Sodium Oxalate.**—Use that weight of sample or that volume of a standard solution of sodium oxalate which will require 25–35 cc. of ceric sulfate (0.5 M in sulfuric acid) in titration. If the ceric sulfate is 0.25 M in sulfuric acid, 40–50 cc. should be used. Add 10–20 cc. of hydrochloric acid, sp. gr. 1.18, and 5 cc. of 0.005 M iodine chloride, and dilute to 100 cc. After heating the solution to 50° (use a thermometer as stirring rod), add 1 drop of 0.025 M *o*-phenanthroline ferrous complex as indicator and titrate with ceric sulfate until the solution is pale blue in color and there is no return of any pink color after an interval of one minute. If the temperature falls below 45°, reheat the solution to 50°.

Indicator Methods Involving other Uses of Ceric Sulfate.—It was found possible to use ceric sulfate in most of the reactions for which it has already been used potentiometrically. Only experimental conditions which were found satisfactory are recorded in Table VIII.

The titration of a vanadyl salt with ceric sulfate, using this indicator, was not satisfactory. Another application is the titration of uranium in the triple acetate of sodium and zinc or magnesium in the determination of sodium.[13] The experiments in Table VIII as well as those of

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[13] Furman, Caley and Schoonover, THIS JOURNAL, **54**, 1344 (1932); Kolthoff and Lingane, *ibid.*, **55**, 1871 (1933).

TABLE VIII

INDICATOR METHODS INVOLVING OTHER USES OF CERIC SULFATE

Acid added, cc.	ICl, 0.005 *M*, cc.	Initial vol., cc.	Temp., °C.	$Ce(SO_4)_2$ used, 0.08056 *N*, cc.	$Ce(SO_4)_2$ calcd., cc.	
HCl, sp. gr. 1.18				**Potassium Ferrocyanide**		
10	0	200	20–25	68.91	68.90	One drop indicator added at beginning. Reaction rapid at room temp. Color change at end-pt. from a light mustard to a clear yellowish-green; very sharp in soln. contg. HCl and slightly less sharp in soln. contg. H_2SO_4.
5	0	100	20–25	13.81	13.78	
0	0	100	20–25	34.43	34.45	
10	0	100	20–25	34.46	34.45	
H_2SO_4, sp. gr. 1.5						
10	0	100	20–25	34.43	34.45	
HCl, sp. gr. 1.18				**Thallous Sulfate**		
50	5	200	50	12.24	12.24	One drop indicator added at beginning. End-pt. reaction as a rule more rapid than in titrat. of arsenite.
20	5	100	50	12.24	12.24	
40	5	200	50	4.92	4.90	
40	5	200	50	29.40	29.38	
HCl, sp. gr. 1.18				**Antimony**		
10	5	100	50	54.08	54.13	One drop indicator added at beginning. Titration very similar to that of arsenite. In first expt., soln. became opalescent before titrat. completed. No color change at end-pt. if acidity too high. Should have 15 cc. of HCl per initial vol. of 100 cc.
15	5	100	50	51.82	51.83	
30	5	200	50	57.17	57.15	
15	5	100	50	29.16	29.20	
HCl, sp. gr. 1.18				**Hydrogen Peroxide**		
10	0	200	20–25	13.47	13.46	One drop indicator added at beginning. Reaction rapid at room temp.
10	0	200	20–25	67.31	67.30	
30	0	200	20–25	33.64	33.65	
5	0	100	20–25	33.64	33.65	
H_2SO_4, sp. gr. 1.5				**Uranous Sulfate ($U(SO_4)_2$)**		
10	0	200	50	13.09	13.08	One drop indicator added at beginning. Reaction rapid at 50°. Color change from brownish-yellow to clear green at end-pt. sharp.
20	0	200	50	65.40	65.40	
10	0	200	50	32.68	32.70	
				Ceric Sulfate		
				H_2O_2 used, 0.1 *N* cc.	H_2O_2 calcd. cc.	
0	0	200	20–25	55.75	55.71	Indicator (one drop) not added until within 0.2–0.3 cc. of end-pt., when soln. is almost colorless. Otherwise no color development at end-pt. Color change at end-pt. from very pale blue to pink.
0	0	200	20–25	7.42	7.41	
0	0	300	20–25	37.16	37.14	
HNO_3, sp. gr. 1.42				$NaNO_2$ used, 0.1 *N* cc.	$NaNO_2$ calcd. cc.	
5	0	200	50	8.27	8.25	Indicator (one drop) must not be added until within 0.5 cc. or less of end-pt. End-pt. reaction rather slow; therefore the last 5–6 drops of $NaNO_2$ should be added very slowly. Color change from pale bluish-gray to pink.
5	0	200	50	41.23	41.24	
5	0	100	50	20.65	20.62	
10	0	200	50	41.30	41.24	

Walden, Hammett and Chapman,[5] show the possibility of titrating the ceric sulfate formed by a persulfate oxidation[14] in the determination of cerium with ferrous sulfate, hydrogen peroxide, or sodium nitrite, using *o*-phenanthroline ferrous complex as an oxidation-reduction indicator. The authors have checked the use of these three reducing agents in this determination and have found the first two of them to be satisfactory. With the discovery of this valuable indicator, it becomes possible to use the more stable ceric sulfate as conveniently as permanganate for a considerable number of reactions and thus to avail oneself of the advantages it offers over the older and better known oxidizing agents.

Summary

1. Indicator methods for the standardization of ceric sulfate solutions have been described. They are based upon the titration either of sodium oxalate or of arsenious oxide in a hydrochloric acid solution containing iodine chloride as catalyst and *o*-phenanthroline ferrous complex as oxidation-reduction indicator.
2. These methods have been applied also to the standardization of very dilute ceric sulfate solutions, 0.01 *N*, which have been shown to be stable over a considerable period of time.
3. A further study of the potentiometric titration of arsenious oxide with ceric sulfate in a hydrochloric acid solution containing iodine chloride as catalyst has been made and the acidity required for quantitative results has been verified.
4. A number of indicator methods involving the use of ceric sulfate, with *o*-phenahthroline ferrous complex as indictor, have been pointed out: the titration of $Fe(CN)_6^{--}$, Tl^+, Sb^{3+}, U^{4+} and H_2O_2, and the titration of ceric sulfate with H_2O_2 or $NaNO_2$.

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[14] Willard and Young, THIS JOURNAL, **50**, 1379 (1928).