

Summary

1. A volumetric method for chromium, more rapid than any in use, has been developed. The chromium is oxidized with excess ceric salt, three possibilities in procedure being described: (a) oxidation with a measured excess of standard ceric sulfate, the excess being titrated differentially in the presence of chromic acid with standard sodium nitrite or oxalate; (b) oxidation with excess ceric sulfate, addition of nitrite in slight excess to destroy the ceric sulfate, followed by urea to remove all nitrate, after which the chromic acid is titrated with standard ferrous sulfate; (c) oxidation with excess ceric sulfate, the excess being removed with sodium azide, and the chromic acid titrated with standard ferrous sulfate. The excess of nitrite must be small and the time of action short, while with azide a large excess acting for a considerable time has no reducing action on the chromium.

2. Iron does not interfere. If vanadium is present, the sum of the chromium and vanadium is determined.

3. The method is equally applicable and rapid in the presence of large amounts of manganese. Even though some of the latter may precipitate as manganese dioxide during the oxidation, it is readily dissolved by the reducing agent.

4. Diphenylbenzidine or diphenylamine may be used as indicator in method (b) but not in (c).

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CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. IX. PREPARATION AND STABILITY OF SOLUTIONS

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Introduction

The method used by the authors to purify U. S. P. cerous oxalate and to prepare a large supply of ceric sulfate has been described in the first paper in this series.¹ From subsequent work,² especially from that dealing with the determination of vanadium and of chromium, it seemed important to investigate more thoroughly the grades of ceric oxide available in order to find the most convenient and inexpensive materials for use. Information concerning the stability of ceric sulfate solutions has also been obtained.

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

² Willard and Young, *ibid.*, 50, 1334, 1368, 1372, 1379 (1928); 51, 139 (1929); *Ind. Eng. Chem.*, 20, 972 (1928).

Experimental

Solutions were prepared from four samples of ceric oxide kindly furnished by Dr. H. S. Miner of the Welsbach Company of Gloucester, New Jersey. The approximate amount of the oxide required for a liter of 0.1 *N* solution was taken, treated with sufficient sulfuric acid of the density indicated in Table I to make the final solution 0.5 or 1 *M* in sulfuric acid and the paste heated at the proper temperature until the conversion into ceric sulfate appeared complete. This material, when cool, was added to about 500 cc. of water, the liquid heated to 70–80° and filtered. The normality of the solution was determined with standard ferrous sulfate, and from this factor the weight of material required for a liter of 0.1 *N* solution was calculated as well as the cost of the ceric oxide for a liter of such a solution, based on the price per 500 g. In large quantities the cost would be 20–30% less.

TABLE I
PREPARATION AND COST OF CERIC SULFATE SOLUTIONS

Material	Sp. gr. of H ₂ SO ₄ used	H ₂ SO ₄ in the Ce(SO ₄) ₂ soln., molar	G. of oxide per liter of 0.1 <i>N</i> soln.	Cost of oxide per liter of 0.1 <i>N</i> soln. based on price per 500 g.
1 High grade, anhydrous	1.83	0.5	19.2	\$0.17
	1.83	1.0	18.9	.17
2 High grade, hydrated	1.5	0.5	22.5	.15
	1.5	1.0	22.3	.15
	1.3	0.5	24.0	.16
3 Commercial, hydrated	1.5	.5	46.9	.05
	1.3	.5	47.3	.05
4 Commercial, anhydrous	1.5	.5	57.9	.10

With Material 1, a temperature of 150–160° was maintained for a half hour to convert the oxide into sulfate. A small amount of the oxide was not attacked. Sample 2 was converted very rapidly by dilute sulfuric acid into ceric sulfate, a temperature of 130–135° being required with acid of sp. gr. 1.5 and 105–110° with acid of sp. gr. 1.3. The ceric sulfate in the former case dissolved in water to give an almost clear solution; in the latter case there was a small amount of unattacked oxide. Sample 3, when treated with acid of sp. gr. 1.5, was heated to 120–125°, and to 110° if treated with acid of sp. gr. 1.3. Sample 4, the commercial anhydrous material, was not satisfactory. The commercial hydrated oxide contained iron and phosphate and a considerable amount of precipitate settled out in solutions prepared from it. The solution decanted from this precipitate was found entirely satisfactory for chromium determinations² in which an excess of ceric sulfate was used as the oxidizing agent, the excess being destroyed by sodium azide or by sodium nitrite followed by urea² before the titration of the chromic acid with ferrous sulfate. Since the oxide for a liter of such a solution costs only four or five cents,

depending upon whether the price per one-half kilo or per fifty kilos of oxide is used, the cost of the reagent for a single chromium determination is very small. There seems to be no reason why this commercial hydrated material cannot be used in all the methods described by the authors^{1,2} except in the case of the titration of iodide where the ferric salt might cause trouble. Even when the high grade, hydrated oxide is used, the cost of the reagent is not excessive, being only ten to fifteen cents per liter, depending on the quantity of material purchased.

Stability of Ceric Sulfate Solutions

Furman has given data over a period of twelve weeks on the stability of ceric sulfate solutions containing free sulfuric acid.³ Table II contains data over a longer period obtained by the authors on four different solutions.

TABLE II
STABILITY OF CERIC SULFATE SOLUTIONS OVER AN EXTENDED PERIOD

Time, weeks	Normality			
	I	II	III	IV
0	0.09493	0.1043	0.05012	0.09410
10	.09488	.1042	.05009
1604996
20	.09497
27	.09480
33104409400
401042

Solutions I and III were 0.5 *M* in sulfuric acid, II and IV, 1.0 *M*. Twenty liters each of I and II and 2 liters of III were prepared, and the stock bottles were opened a number of times during the periods indicated. Only with Solution IV is the normality expressed in terms of weight normality. The values for this solution are the most accurate indication of the stability of ceric sulfate, for the portion tested after a 33-week interval had been standing during that time in a sealed flask in a well lighted room. These data indicate that ceric sulfate solutions are far more stable than permanganate solutions, the latter oxidizing agent being the only one which is of the same relative oxidizing power as ceric sulfate.

A number of experiments were made to test the stability of ceric sulfate solutions on boiling. In each case 25 cc. of 0.1 *N* solution was diluted with acid and water to a volume of 100 cc. This solution was boiled gently under a reflux condenser for the stated time, cooled to room temperature and titrated electrometrically with standard ferrous sulfate. The values for the normality after such treatment are given in Table III.

These results show that ceric sulfate solutions containing free sulfuric

³ Furman, THIS JOURNAL, 50, 755 (1928).

TABLE III
STABILITY OF CERIC SULFATE TOWARD HEAT

	Acid per 100 cc., cc.	Time of boiling, hours	Normality of $Ce(SO_4)_2$
H_2SO_4 , sp. gr., 1.5	{ 15	0	0.09322
	{ 10	2	.09322
	{ 20	2	.09322
	{ 20	5	.09322
HNO_3 , sp. gr., 1.42	{ 10	1	.09111
	{ 5 + 10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09328
	{ 10 + 10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09288
$HClO_4$, 70%	{ 5 + 10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09322
	{ 10 + 10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09310

acid, or sulfuric acid with moderate amounts of nitric or perchloric acid, are extremely stable toward heat. Such solutions, because of their strong oxidizing power, great stability, utility in a hydrochloric acid solution,¹ ease of preparation and small cost, should find extensive use in analytical work.

Summary

1. The types of ceric oxide available for the preparation of ceric sulfate have been investigated. A high grade, hydrated material supplied by the Welsbach Company meets the most exacting requirements, but the commercial, hydrated product is satisfactory in nearly all cases.

2. The cost of such solutions has been shown to be very small, that of the oxide for a liter of 0.1 *N* solution from the high grade, hydrated material being ten to fifteen cents, and from the commercial, hydrated material four to five cents.

3. The normality of a ceric sulfate solution containing free sulfuric acid has been found to be practically constant over a period of forty weeks. Such a solution is not sensitive to light or air.

4. The normality of a ceric sulfate solution containing free sulfuric acid, or sulfuric acid with a little nitric or perchloric acid, is not changed by boiling the solution for an hour or longer, but the solution loses oxygen if a high concentration of either of the two latter acids is present.

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