[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. VII. THE OXIDATION OF HYDROQUINONE BY CERIC SULFATE

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Introduction

A number of uses of ceric sulfate in volumetric analysis have recently been described in previous papers of this series,[1] and in those of other investigators.[2] In this communication we present a study of the direct volumetric determination of hydroquinone with standard ceric sulfate, both by the potentiometric method and with diphenylamine or methyl red as color indicator. We have compared this new method with methods which have been described previously.

Valeur,[3] Sörensen and Linderström–Lang[4] and Kolthoff[5] have studied the iodimetric determination of hydroquinone. Our experience is in accord with that of Kolthoff, who suggested that the iodimetric method is best applied by adding an excess of iodine, then bringing the hydrogen-ion concentration of the solution below 5×10^{-6}, in order that the oxidation of the hydroquinone to quinone shall be quantitative. The excess of iodine is then determined with standard arsenite solution, rather than with thiosulfate, as Sörensen and Linderström–Lang suggested.

Kolthoff[5] also studied the reaction between hydroquinone and dichromate in strong acid solution; he found that the oxidation was quantitative and that the end-point may be determined potentiometrically with a platinum gauze as indicator electrode; the gauze is heated to redness before each titration. The end-point may also be determined by using diphenylamine as an internal indicator.

We have found that the reaction

$$2Ce(SO_4)_2 + C_6H_4(OH)_2 = C_6H_4O_2 + H_2SO_4 + Ce_2(SO_4)_3, \text{ or}$$
$$2Ce^{++++} + C_6H_4(OH)_2 = C_6H_4O_2 + 2H^+ + 2Ce^{+++}$$

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[1] Furman, THIS JOURNAL, **50**, 755, 1676 (1928); Furman and Evans, *ibid.*, **51**, 1128 (1929); Furman and Wallace, *ibid.*, **51**, 1449 (1929).

[2] Martin, *ibid.*, **49**, 2133 (1927); Willard and Young, *ibid.*, **50**, 1322, 1334, 1368, 1372, 1379 (1928); *Ind. Eng. Chem.*, **20**, 972 (1928); THIS JOURNAL, **51**, 139, 149 (1929); I. A. Atanasiu, *Bull. Soc. Roum. Chem.*, **30**, 1 (1928); Atanasiu and V. Stefanescu, *Ber.*, **61**, 1343 (1928); Rathsberg, *ibid.*, **61**, 1664 (1928); Someya, *Z. anorg. allgem. Chem.*, **181**, 183 (1929); Soule, THIS JOURNAL, **51**, 2117 (1929); Berry, *Analyst*, **54**, 461 (1929).

[3] Valeur, *Bull. soc. chim.*, **23**, 58 (1900).

[4] Sörensen and Linderström–Lang, *Compt. rend. trav. lab. Carlsberg*, **14**, No. 14 (1921).

[5] Kolthoff, *Rec. trav. chim.*, **45**, 745 (1926).

is not only quantitative, but is superior in many respects to the other reactions which have been used for the quantitative determination of hydroquinone. The reaction is rapid at room temperature, and the titrations may be made directly. The potentiometric and diphenylamine end-points are much sharper than is the case when dichromate is used. A bright platinum wire serves as indicator electrode, and we failed to detect electrode poisoning in the ceric sulfate reaction. Methyl red[6] also serves as an indicator if it is added near the end-point. The red color is destroyed by a slight excess of ceric sulfate. Our observations have been made with solutions of hydroquinone which contained various concentrations of sulfuric or hydrochloric acid.

Experimental

The apparatus has been described in previous papers of this series; a bright platinum wire and a normal calomel half-cell made up the electrode system.

The ceric sulfate solutions were prepared by dissolving commercial rare earth oxides in enough dilute sulfuric acid to make the solution 1 *N* in acid when diluted until 0.1 *N* in oxidizing powder. After standing until clear (a week or more), the solutions were filtered and were found to be stable. The ceric solutions were standardized potentiometrically against pure sodium oxalate or pure arsenious oxide. In the latter case iodine monochloride was used as a catalyst.[7]

Hydroquinone solutions were prepared by dissolving pure hydroquinone in water containing 10 cc. of 6 *N* sulfuric acid and diluting to a liter. They were kept in smooth bottles of amber glass and were found to be stable over a period of at least eight hours. The solutions were standardized by adding an excess of standard iodine, and titrating back with standard arsenite solution, using starch as an indicator. The sodium bicarbonate was added after an excess of iodine had been added to the hydroquinone solution.

Diphenylamine was used in 1% solution in sulfuric acid. The methyl red solution contained 0.2 g. of methyl red in 100 cc. of 1.2 *N* sulfuric acid.

Titration of Hydroquinone with Ceric Sulfate. (a) Potentiometric.—Measured portions of hydroquinone solutions were diluted to 100 cc. after adding acid. The nature and concentration of the acid and the rate of addition of the ceric sulfate were not found to be important factors. All titrations were made at room temperature. The results are summarized in Tables I and II.

The potentiometric titration gives a curve rising regularly and gradually from a value between 0.2 and 0.3 volt (Pt *vs.* N calomel electrode) to be-

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[6] Rathsberg, Ref. 2, used methyl red as indicator in the oxidation of trivalent antimony with ceric sulfate.

[7] Willard and Young, THIS JOURNAL, 50, 1368 (1928).

TABLE I

POTENTIOMETRIC TITRATION OF 0.09357 N HYDROQUINONE WITH 0.1179 N CERIC SULFATE

Concn. due to acid added		None	0.75 N H_2SO_4	1.5 N H_2SO_4	0.5 N HCl	1.5 N HCl	2 N H_2SO_4
Hydroquinone, cc.		25	25	25	25	25	50
Ceric sulfate	Calcd., cc.	22.66	22.66	22.66	22.66	22.66	45.32
	Found, cc.	22.65	22.63	22.66	22.65	22.67	45.28
	Error, cc.	−0.01	−0.03	±0.00	−0.01	+0.01	−0.04

TABLE II

POTENTIOMETRIC TITRATION OF 0.0914 N HYDROQUINONE WITH 0.1095 N CERIC SULFATE

Concn. of acid added		None	None	None	1 N H_2SO_4	2 N H_2SO_4	1 N HCl	2.5 N HCl
Hydroquinone, cc.		10	25	50	10	10	10	25
Ceric sulfate	Calcd., cc.	8.35	20.88	41.76	8.35	8.35	8.35	20.88
	Found, cc.	8.34	20.91	41.79	8.35	8.37	8.35	20.88
	Error, cc.	−0.01	+0.03	+0.03	−0.02	+0.02	±0.00	±0.00

tween 0.4 and 0.5 volt as the end-point is approached. The voltage rise at the end-point is of the order of 0.25–0.35 volt per drop (0.05 cc.) of ceric sulfate. The following are some typical values for a titration

Cc. ceric soln.	0.00	20.00	40.00	44.00	45.50	44.57	44.61	44.65
E. m. f.	0.285	0.371	0.404	0.435	0.459	0.583	0.848	0.900

There is an obvious maximum between 44.57 and 44.61 cc. of reagent. The reaction proceeded rapidly at all concentrations of acids that were used and the potential became steady almost immediately.

The reaction was tested further by using pure recrystallized hydroquinone as a standard substance both for ceric sulfate and for iodine. The general conditions were analogous to those which have been described (Tables I and II).

Ceric sulfate was standardized against pure sodium oxalate: found, 0.1073 N, average of 0.1072, 0.1074, 0.1073 N. Hydroquinone was then used as a standard substance.

Hydroquinone, g.	0.2638	0.2539	0.2056	0.1863	0.2570	0.2196
Ceric soln., cc	44.55	43.01	34.81	31.55	43.53	37.23
Normality	0.1076	0.1073	0.1074	0.1073	0.1073	0.1072

These determinations, if interpreted as analyses of hydroquinone with 0.1073 N ceric sulfate, give 99.7, 100.01, 99.95, 99.98, 100.00 and 100.09% of hydroquinone, respectively.

Iodine solutions were standardized directly against weighed samples of pure arsenious oxide (U. S. Bureau of Standards), and then against hydroquinone by adding an excess of the iodine solution and titrating back with standard arsenite, prepared from the pure arsenious oxide.

Iodine Solution I, Normality

Against As_2O_3......	0.1002, 0.1001, 0.0999, 0.1002, 0.1001, 0.1002	Av. 0.1001
Hydroquinone.....	0.1002, 0.1002, 0.1001, 0.0999, 0.1002	Av. 0.1001

Iodine Solution II, Normality

Against As_2O_3......	0.0996, 0.0998, 0.0996, 0.0997, 0.0997	Av. 0.0997
Hydroquinone.....	0.0998, 0.0999, 0.0996, 0.0999 0.0996, 0.0998, 0.0997	Av. 0.0998

The foregoing determinations appear to have established the quantitative nature of the reaction between hydroquinone and ceric sulfate. The use of diphenylamine or methyl red as indicators was then tried, and the potentiometric values were assumed to be correct.

(b) **Diphenylamine as Indicator.**—If 0.05 cc. of a 1% solution of diphenylamine in sulfuric acid is added to the hydroquinone solution, the end of the oxidation of the latter is indicated by the sudden appearance of the blue oxidation product of the diphenylamine. We have found that a correction of 0.05 cc. is to be subtracted from the volume of ceric solution to bring the results into agreement with the potentiometric values, as shown in Table III.

TABLE III

TITRATION OF HYDROQUINONE USING DIPHENYLAMINE AS INDICATOR

Initial volume	100	100	100	200	150	50
Concn. of acid added	None	1 *N* H_2SO_4	2 *N* H_2SO_4	1 *N* HCl	2 *N* HCl	None
Cc. of hydroquinone	25	25	25	25	25	25
Ceric soln. used (uncorr.), cc.	20.96	20.95	20.97	20.96	20.98	20.96

The average of three potentiometric determinations gave 20.92 cc. of ceric solution equivalent to 25 cc. of the hydroquinone.

(c) **Methyl Red as Indicator.**—We have found that methyl red may be used successfully as an indicator in this reaction. As soon as the hydroquinone has been oxidized, the ceric sulfate destroys the red color of the indicator. Because of the color of the quinone that is formed, the end-point change is from deep orange to yellow. It is well to add the methyl red within about a cubic centimeter of the end of the titration. Two drops of 0.2% solution are necessary for a good color change. We have found that methyl red is a less satisfactory indicator in this titration than diphenylamine.

Some results are presented in Table IV. In each case 25 cc. of hydro-

TABLE IV

TITRATION OF HYDROQUINONE USING METHYL RED AS INDICATOR

Initial volume, cc.	50	75	100	150	200
Concn. of acid added	None	1.5 *N* H_2SO_4	1 *N* HCl	1 *N* H_2SO_4	2 *N* HCl
Ceric sulfate used, cc. (uncorr.)	20.93	20.94	20.95	20.93	20.92

quinone was titrated and the average requirement was 20.92 cc. of ceric sulfate by the potentiometric method.

It is evident that there is practically no correction required in this case (0.1 *N* ceric solution).

The Reverse Titration.—A brief study was made of the titration of ceric sulfate with hydroquinone. The general procedure was as has been described, and the end-point was determined potentiometrically. It was first found potentiometrically that 25 cc. of hydroquinone solution was equivalent to 25.91 cc. of ceric sulfate (average of several titrations with ceric sulfate). The results are presented in Table V.

TABLE V

TITRATION OF CERIC SULFATE WITH HYDROQUINONE

Initial concn. of H_2SO_4		0.75 *N*	1 *N*	1.2 *N*	1.5 *N*	2.5 *N*
Ceric solution, cc.		25	50	25	25	25
Hydroquinone	Calcd., cc.	24.13	48.26	24.13	24.13	24.13
	Found, cc.	24.12	48.24	24.15	24.14	24.14
	Error, cc.	−0.01	−0.02	+0.02	+0.01	+0.01

These results indicate that the titration is fully as exact as the reverse process and that, in strong contrast with permanganate, a moderate excess of ceric sulfate does not attack quinone.

A few experiments proved that the isomers of hydroquinone, namely, resorcinol and catechol were oxidized farther than their quinone stages; the reactions proceeded so sluggishly at room temperature that it was not possible to find a definite end-point.

In experiments not detailed here, we found that the determination of hydroquinone with dichromate was much less convenient than that with ceric sulfate, either by the potentiometric or diphenylamine method.

Summary

The reaction between 0.1 *N* solutions of hydroquinone and ceric sulfate has been shown to be stoichiometric, rapid and convenient, as contrasted with other volumetric methods which have been proposed for the determination of hydroquinone.

The titration may be made with either solution as reagent, using the potentiometric method of determining end-points.

When a standard solution of ceric sulfate is used, either diphenylamine or methyl red may be used as an internal indicator. In the former case the customary correction for ceric solution required to oxidize the diphenylamine must be deducted; with methyl red the correction is practically negligible. The diphenylamine color change is more satisfactory than that with methyl red.

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