[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. VI. THE VOLUMETRIC DETERMINATION OF CERIUM

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Introduction

The persulfate[2] and bismuthate[3] oxidation methods for cerium have remained probably the most accurate as well as the most generally applicable of the many volumetric procedures proposed for this metal. The former method has been tested by a number of investigators,[4] all of whom found it accurate if the experimental conditions suggested by von Knorre were followed closely. The oxidation with persulfate was carried out in a solution containing just enough acid to prevent the precipitation of basic ceric salts, the reaction being

$$H_2S_2O_8 + Ce_2(SO_4)_3 = 2Ce(SO_4)_2 + H_2SO_4$$

If too much acid was present, the oxidation of the cerous salt was incomplete. In the actual procedure, the persulfate was added in three or four portions, the solution boiled after each addition and finally boiled for about fifteen minutes to destroy excess persulfate. Such experimental technique is, obviously, tedious and inconvenient. The oxidation with persulfate has also been carried out in alkaline solution by Sterba-Boehm and Matula,[5] who dissolved the precipitate in potassium iodide and hydrochloric acid and titrated the iodine with thiosulfate, and by Autié,[6] who used nitric acid to dissolve the precipitate and hydrogen peroxide to determine the ceric salt. Either of these procedures involves a number of steps and consistent results were not obtained in the latter method. From this last paper one might be led to think that there were no accurate methods thus far for cerium, as the author's experimental data from a study of a number of volumetric oxidation methods leave much to be desired. Such, however, is not the case. His statement that the reaction of ceric ion with ferrous sulfate is somewhat reversible and that any method based upon this titration is consequently inaccurate, is absurd if one considers the oxidation-reduction potentials of the two systems involved.

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[1] From a dissertation submitted by Philena Young to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Von Knorre, *Z. angew. Chem.*, **11**, 717 (1897); *Ber.*, **33**, 1924 (1900).

[3] Metzger, THIS JOURNAL, **31**, 523 (1909).

[4] (a) Hintz and Weber, *Z. anal. Chem.*, **37**, 103 (1898); (b) Power and Sheddon, *J. Soc. Chem. Ind.*, **19**, 636 (1900); (c) Marc, *Ber.*, **35**, 2370 (1902); (d) Furman, THIS JOURNAL, **50**, 755 (1928).

[5] Sterba-Boehm and Matula, *Rec. trav. chim.*, **44**, 400 (1925).

[6] Autié, *Bull. soc. chim.*, **41**, 1535 (1927).

Hydrogen peroxide may be used in this particular titration, as he suggests, but certainly has no advantage over ferrous sulfate in accuracy or stability.

In studying the action of oxidizing agents on cerous salts, Barbieri[7] found that silver nitrate catalyzed in an acid solution the oxidation of cerous nitrate or sulfate with persulfate and used this fact for the purification of crude cerium salts. However, he did not test the possibilities of the method quantitatively. Since his publication investigators have continued to use the original von Knorre method.[4d,5,6,8] The present paper describes the much simpler technique which is possible in the presence of silver ion as catalyst.

Experimental

Titration with Ferrous Sulfate.—The approximately 0.05 *N* cerous sulfate was prepared from C. P. material and contained 50 cc. of sulfuric acid, sp. gr. 1.83, per liter. Four analyses of 25cc. portions of this solution, using a bismuthate oxidation followed by electrometric titration of the ceric sulfate with standard ferrous sulfate, gave 0.1858, 0.1863, 0.1861 and 0.1858 g. of cerium. Definite amounts of this solution were taken; water, sulfuric acid and silver nitrate (containing 2.5 g. of silver nitrate per liter) were added to a total volume of 200 cc., followed by solid ammonium persulfate. The liquid was boiled for ten minutes, cooled to room temperature and titrated electrometrically with 0.05 *N* ferrous sulfate which had been standardized against ceric sulfate of known strength. A silver chloride–platinum electrode system was used. The vessel containing the silver chloride electrode in 0.1 *N* potassium chloride was placed directly in the liquid to be titrated. The quantities of the various materials and the results are shown in Table I.

TABLE I

OXIDATION WITH PERSULFATE–SILVER NITRATE AS CATALYST–TITRATION WITH FERROUS SULFATE

Acid, cc.	$(NH_4)_2S_2O_8$, g.	$AgNO_3$, cc.	Ce taken, g.	Ce found, g.
2.5 cc. of H_2SO_4, sp. gr. 1.83	1	5	0.1860	0.1863
2.5 cc. of H_2SO_4, sp. gr. 1.83	0.5	5	.1860	low
2.5 cc. of H_2SO_4, sp. gr. 1.83	1	5	.1116	.1118
2.5 cc. of H_2SO_4, sp. gr. 1.83	3	5	.3720	.3722
2.5 cc. of H_2SO_4, sp. gr. 1.83	2	5	.3720	.3719
10 cc. of H_2SO_4, sp. gr. 1.83	2	10	.1860	.1859
10 cc. of H_2SO_4, sp. gr. 1.83	4	10	.1860	.1860
10 cc. of H_2SO_4, sp. gr. 1.83	5	5	.1860	.1858
10 cc. of H_2SO_4, sp. gr. 1.83	5	2.5	.1860	.1856
5 cc. of H_2SO_4, sp. gr. 1.83	2	2.5	.1860	.1860
5 cc. of H_2SO_4, sp. gr. 1.83	4	2.5	.3720	.3722
5 cc. of HNO_3, sp. gr. 1.42	2	2.5	.1860	.1858
10 cc. of HNO_3, sp. gr. 1.42	4	2.5	.1860	.1849
5 cc. of $HClO_4$ (70–72%)	2	2.5	.1860	low

From the data in Table I it is seen that the correct procedure for determining cerium is to use a sulfate solution containing 2.5–10 cc. of sulfuric acid, sp. gr. 1.83, per 200 cc.,

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[7] Barbieri, *Atti R. Accad. Lincei*, **25**, I, 37 (1916).

[8] Lindeman and Hafstad, *Z. anal. Chem.*, **70**, 433 (1927).

or a nitrate solution with 5 cc. of nitric acid, sp. gr. 1.42, in the same volume, add to this 1–5 g. of solid ammonium persulfate, depending on the amount of acid present, 2–5 cc. of silver nitrate (containing 2.5 g. of silver nitrate per liter), boil for ten minutes, cool to room temperature and titrate electrometrically with standard 0.05 *N* ferrous sulfate.

The silver nitrate caused no interference during the titration, the end-point equilibrium was rapid, never more than a few seconds being required for the voltage to become steady and the break in potential averaged 200–250 mv. per 0.03 cc. of 0.05 *N* ferrous sulfate. A variation in volume between 100 and 300 cc. during the oxidation did not alter the results. The remarkable effect ascribed by Lindeman and Hafstad[8] to the presence of a considerable quantity of magnesium sulfate in the solution at the time of a persulfate oxidation was not apparent when silver nitrate was present. The persulfate procedure with silver ion as catalyst is simple and rapid, and has a certain advantage over the bismuthate method in which not only is a filtration required but also a blank determination on the technical bismuthate usually available.[9] Experiments to test the effect of the presence of other rare earths were not made, as the persulfate method has been shown[2,4a,b] to be applicable in such cases.

Titration with Potassium Iodide.—Since ceric nitrate or sulfate may be accurately titrated electrometrically with potassium iodide,[10] such a titration should be possible after a persulfate oxidation if a blank correction is made for the reaction between the silver nitrate and the iodide. To test this point, 15cc. portions of a ceric sulfate solution were taken, treated with 2.5 cc. of sulfuric acid, sp. gr. 1.83, and water to a volume of 200 cc. The stated amounts of silver nitrate (containing 2.5 g. of silver nitrate per liter) were added and the solution was titrated electrometrically with an approximately 0.05 *N* potassium iodide solution which had been standardized against ceric sulfate of known strength. The results are shown in Table II.

TABLE II

IODIDE TITRATION OF CERIC SULFATE—SILVER NITRATE PRESENT

No.	$AgNO_3$, cc.	NaCl, cc.	KI, 0.05 *N*, cc.	Blank actual	Blank calcd.
1	0	0	24.33–24.32	0.00	0.00
2	1	0	24.61	.28	.27
3	2	0	24.89	.56	.54
4	4	0	25.43	1.10	1.09
5	6	0	25.96	1.63	1.63
6	2	2	24.89	0.56	..
7	2	5	24.88	.55	..

The sodium chloride solution added before the titration in the last two experiments was of the same normality as the silver nitrate solution. The results for these two experiments show that the silver chloride is converted quantitatively into silver iodide during the titration. The values for the calculated blanks were obtained by considering the actual blank in Experiment 5 as correct and taking the proper aliquot portions of this value for the other blanks. The very close agreement between the actual and calculated blanks shows that the correction to be applied is strictly proportional to the amount of silver nitrate in solution.

[9] Someya, *Z. anorg. Chem.*, **168,** 56 (1927), states that a filtration is unnecessary, but he used a very pure grade of bismuthate in his work. He found, however, that he had to wait three to five minutes at the equivalent point for equilibrium to be established.

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

Twenty-five cc. portions of the cerous sulfate used in Table I were diluted with water and acid to 200 cc., the persulfate oxidation was carried out in the presence of a measured amount of silver nitrate and the ceric sulfate and silver nitrate were titrated electrometrically with the same 0.05 *N* potassium iodide used in the experiments in Table II. The weight of cerium present was 0.1860 g. The results are shown in Table III.

TABLE III

OXIDATION WITH PERSULFATE–SILVER NITRATE AS CATALYST—TITRATION WITH POTASSIUM IODIDE

No.	H_2SO_4, sp. gr. 1.83, cc.	$(NH_4)_2S_2O_8$, g.	$AgNO_3$, cc.	KI, 0.05 *N*, cc.	Blank, actual, cc.	Ce, g.
1	2.5	1	2	23.23	0.55	0.1862
2	2.5	1	4	23.78	1.10	.1862
3	2.5	1	1	less than 21 cc.	...	...
4	5 cc. HNO_3, sp. gr. 1.42	2	2	23.21	0.55	.1860

The actual blank correction for the silver nitrate was obtained by considering the difference between the volumes in Experiments 1 and 2, or 0.55 cc. as the volume of potassium iodide required by 2 cc. of silver nitrate solution. The amounts of cerium found in the 25cc. portions of the cerous sulfate solution agree very closely with the results in Table I as well as with the bismuthate analyses. The break in potential amounted to 100–150 mv. per 0.03 cc. of 0.05 *N* potassium iodide.

Titration with Sodium Nitrite.—The possibility of using sodium nitrite as the reducing agent for ceric ion after a persulfate oxidation was investigated. Measured portions of a standard ceric sulfate solution were taken, diluted with water and acid to a volume of 200 cc. and titrated electrometrically with 0.1 *N* sodium nitrite, the greater portion being added from a pipet beneath the surface of the liquid, the remainder in a similar way from a 10cc. buret. The temperature of the solution was 40–45°. The results are shown in Table IV.

TABLE IV

NITRITE TITRATION OF CERIC SULFATE

$Ce(SO_4)_2$, 0.1 *N*, cc.	Acid, cc.	$NaNO_2$, 0.1 *N*, cc.
20	5 cc. of H_2SO_4, sp. gr. 1.83	17.18
20	10 cc. of H_2SO_4, sp. gr. 1.83	17.15
20	20 cc. of H_2SO_4, sp. gr. 1.83	17.23
50	5 cc. of H_2SO_4, sp. gr. 1.83	42.82
20	5 cc. of HNO_3, sp. gr. 1.42	17.12
20	10 cc. of HNO_3, sp. gr. 1.42	17.12
20	15 cc. of HNO_3, sp. gr. 1.42	17.12
50	10 cc. of HNO_3, sp. gr. 1.42	42.82
10	10 cc. of HNO_3, sp. gr. 1.42	8.56

The results were not quantitative in perchloric acid solution. The equilibrium in the region of the end-point was very slow in sulfuric acid solution and slightly more rapid in nitric acid solution. The break in potential averaged 50–100 mv. in the former and 150–200 mv. in the latter cases per 0.03 cc. of 0.1 *N* sodium nitrite. With a temperature of 60°, the equilibrium at the end-point was somewhat more rapid and the values were not altered.

Two procedures were used for standardizing the nitrite solution: that of Busvold[11] depending on the reduction of silver bromate by nitrite and the weighing of the silver bromide formed, and that of Lunge[12] based on the titration of standard permanganate with nitrite. Laird and Simpson[13] tested both of these methods and found the gravimetric procedure accurate. In the volumetric method their results were not so exact, but they state that with sufficient care accurate results could probably be obtained. A series of preliminary titrations of 0.1 *N* potassium permanganate with 0.1 *N* sodium nitrite in solutions containing 10 cc. of sulfuric acid, sp. gr. 1.83, per 200 cc. showed that closely checking duplicates could be obtained and that the volume of nitrite solution varied strictly with the amount of permanganate used, if the precaution of adding the nitrite beneath the surface of the liquid was observed.

An approximately 0.1 *N* sodium nitrite solution was prepared from material containing only 0.002% of chloride. (1) 0.8 g. of silver bromate was dissolved in 200 cc. of water in a 500cc. flask at 80–85°, 100 cc. of the nitrite solution added from a pipet, followed by 30cc. of sulfuric acid, sp. gr. 1.2, the liquid being shaken thoroughly at this time and at frequent intervals to coagulate the silver bromide. After standing for three to four hours on the edge of the hot-plate, the precipitate was filtered, washed thoroughly with hot water and dried to constant weight. The same results were obtained when the silver bromate was dissolved in 2 *N* acetic acid,[11] provided that acetic acid distilled from chromic acid was used. With the ordinary C. P. acetic acid, the results were high, probably due to the presence of formic acid. (2) Fifty cc. portions of 0.06901 *N* permanganate, standardized against sodium oxalate, were treated with 165 cc. of water and 10 cc. of sulfuric acid, sp. gr. 1.83. Twenty-five cc. of nitrite solution was added from a pipet beneath the surface of the liquid; the solution was then heated slowly while the remainder of the nitrite was added in a similar way from a 10cc. buret. The end-point was determined electrometrically and the final temperature was 50–55°. (3) Twenty-five cc. portions of 0.09488 *N* ceric sulfate, standardized against sodium oxalate, were treated with 170 cc. of water and 50 cc. of nitric acid, sp. gr. 1.42, and titrated electrometrically at 40–45° with sodium nitrite, using the technique described above. The results are shown in Table V.

These data indicate that accurate results may be obtained in the titration of permanganate with a reducing agent, a procedure which has been much debated, and the authors intend to investigate the permanganate–nitrite reaction in greater detail.

[11] Busvold, *Chem.-Ztg.*, **38**, 28 (1914).

[12] Lunge, *Ber.*, 10, 1073 (1877).

[13] Laird and Simpson, THIS JOURNAL, **41**, 524 (1919).

TABLE V

STANDARDIZATION OF SODIUM NITRITE SOLUTION

Method of standardization	Normality factor	Average
Gravimetric	0.1064, 0.1061, 0.1062 .1063	0.1062
Titration of standard permanganate	.1064, .1064, .1064	.1064
Titration of standard ceric sulfate	.1064, .1064	.1064

An accurate procedure for nitrite, based upon the addition of the nitrite solution to excess of standard ceric sulfate, followed by titration of the excess of the oxidizing agent with standard ferrous sulfate or potassium iodide, is obvious from the above experimental work.

Determination of Cerium

Twenty-five cc. portions of the cerous sulfate solution used in Table I were diluted with water and 5 cc. of nitric acid, sp. gr. 1.42, to 200 cc., and the persulfate oxidation in the presence of silver nitrate was carried out in the usual way. The ceric sulfate was titrated electrometrically at 40–45° with the sodium nitrite standardized above. Three analyses gave 0.1855, 0.1859, 0.1859 g. of cerium, a close agreement with the average value 0.1860 g. of cerium from bismuthate oxidations.

Attempts to titrate the ceric sulfate with oxalate in hot solution in the presence of silver nitrate after having boiled the liquid for ten minutes to remove excess persulfate were not very satisfactory. The equilibrium was reached very slowly in the region of the end-point and the volume of oxalate required was slightly larger with silver nitrate present, but not proportional to the amount of this latter material. If the ceric sulfate solution was cooled to room temperature, considerable hydrochloric acid and 5 cc. of 0.005 N iodine chloride added, the titration with oxalate seemed to proceed rapidly but no end-point break could be obtained.

A few experiments were made to test the quantitative possibilities of two methods suggested by Barbieri:[7] (1) titration of cerous salt in strong sulfuric acid solution with permanganate, and (2) a similar titration in a dilute acid solution containing phosphoric acid. A visual end-point was impossible in the first method, due to the color of the ceric salt, and very difficult to obtain with even fair accuracy in the second method. A potentiometric end-point was impossible in either case, the slight solubility of the ceric phosphate probably being the source of trouble in the second method.

Summary

1. Cerium may be accurately determined in the presence of the other rare earths by oxidation with persulfate in the presence of silver nitrate as catalyst, followed by electrometric titration with standard ferrous sulfate, potassium iodide or sodium nitrite. Hydrogen peroxide offers no advan-

tages in accuracy or stability of solution. The procedure in this oxidation method is much simpler and more rapid than that required in the original von Knorre persulfate method.

2. With potassium iodide a blank correction must be subtracted from the volume used because of the action between the silver and iodide ions.

3. With sodium nitrite the equilibrium in the region of the end-point is quite slow. The sodium nitrite solution, if practically free from chloride, may be standardized gravimetrically by weighing the silver bromide formed from the action between silver bromate and nitrite in acid solution. An alternative method is the electrometric titration of standard potassium permanganate with the nitrite solution.

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NOTE

An Improved Test for Borates.—A solution suspected of containing a borate is made slightly alkaline with sodium hydroxide and evaporated practically to dryness. The residue is treated with 1 cc. of concentrated sulfuric acid and allowed to cool. Two cc. of methanol is then added and the solution transferred to a test-tube. The latter is fitted with a two-holed rubber stopper through which two glass tubes of about 4 mm. bore are inserted. One of these tubes extends to the bottom of the test-tube, and the external portion of it is bent to an angle convenient to allow its use as a mouthpiece. The other tube serves to conduct the vapors from the test-tube and therefore does not extend far below the rubber stopper. The external portion contains a right angle bend and terminates in a long capillary. This capillary should be at least 3 cm. long and should have a bore not greater than 0.5 mm.

When air from the lungs is blown into the apparatus the bubbles arising through the heated solution convey the volatile methyl borate (if present) out through the capillary tube. The exit stream of vapors is directed into a small, non-luminous Bunsen flame. A characteristic green color will be produced in the Bunsen flame if a borate is present in the original solution.

The long capillary of the exit tube prevents any flame from traveling back into the test-tube and at the same time concentrates the effect in the Bunsen flame.

As little as 0.2 mg. of boric acid has been detected by this test.

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