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PREPARATION OF PURE CERIUM SALTS AND THE COLOR OF CERIUM OXIDE.[1]

BY ARTHUR C. NEISH.

Received February 25, 1909.

The close relationship of the analytical behavior of the elements in the cerium group offers great difficulty in preparing pure cerium salts. The lack of delicate tests for the elements, other than cerium, makes the problem more difficult, so that at present the spark spectrum is the only sure test for purity. The color of pure cerium oxide (CeO_2) has been much disputed, since many of the supposed pure cerium preparations were not pure; the different colors given this oxide, as found in the literature, offers a suggestion for research as well as the preparation of pure cerium salts.

From a review of the different methods proposed for the preparation of pure cerium salts, it was decided to make the process of purification in steps, using the best method for the elimination of each element usually found in the starting material, and repeating these to insure complete purification. Methods involving lengthy crystallizations were omitted. The starting material was the crude oxalate obtained from the Welsbach Company, and it was assumed to contain as impurities all the rare earths found in monazite sands, together with iron, aluminium, calcium and magnesium. Didymium and iron were easily recognized impurities, the absorption bands were very marked.

The method finally adopted consisted of six distinct steps:

1. *Hydrochloric Acid Treatment* to remove iron, calcium, etc.—The crude oxalate (150 grams, 50 grams in each of three beakers) was warmed

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[1] Read at the Toronto meeting of the American Chemical Society, June, 1907.

for an hour on the water bath with 750 cc. of 1 per cent. hydrochloric acid, and washed by decantation and on a Büchner funnel with 1 per cent. hydrochloric acid and hot water. This was repeated successively with 350 cc. of 0.5 per cent. and 350 cc. of 0.2 per cent. hydrochloric acid and washed as before until the color test for iron, with solid ammonium thiocyanate and amyl alcohol, was no greater than that for a blank test.

2. *Ammonium Oxalate Treatment* to remove thorium, zirconium and yttrium.—The oxalate from the above treatment was removed from the funnel, a third placed in each beaker, and a hot solution of ammonium oxalate, saturated in the cold, was added. The beakers were heated on the water bath with frequent stirring for an hour, and allowed to settle. The oxalate settled rapidly, and changed from a fine powder to a distinct crystalline condition; it was filtered through a Büchner funnel, washed with 500 cc. of ammonium oxalate solution, and well with cold water. This treatment was repeated three times, and, on account of the tendency for the oxalate to form lumps, it was found advisable to grind it up in a mortar with ammonium oxalate solution to a thick cream before transferring it to the beakers for the successive treatments.

3. *Potassium Hydroxide Treatment* to remove aluminium, etc.—The oxalate was transferred to a mortar, made into a cream with water and transferred one-third to each beaker; 75 grams of stick potassium hydroxide (purified by alcohol) were added to each beaker and water added to about 500 cc. They were then heated with constant stirring to boiling, then on the water bath for half an hour, diluted to the capacity of the beaker, allowed to settle, filtered through a Büchner funnel, and well washed with about three liters of hot water. The oxalate soon changed to hydroxide, the change was marked by the flocculent appearance of the precipitate as compared with the crystalline and heavy nature of the oxalate; the color changed from pure white to a grayish white, but on dilution with much water the color changed to drab, and when placed in the funnel, especially when the potassium hydroxide was removed and the washing commenced, the surface turned a deeper drab and gradually turned so throughout the mass. On longer exposure to the air the surface turned purple, then reddish brown, and finally canary-yellow; the yellow was undoubtedly due to a ceric condition, and the other colors to intermediate stages of oxidation.

4. *Sulphuric Acid and Potassium Sulphate Treatment* to remove yttrium, ytterbium, erbium and samarium.—Many experiments were tried on a small scale as to whether dilute or strong acid effected solution best. The stronger acid was considered to be the more effective, but in both dilute and strong acid the precipitate could not be all dissolved by boiling, as cerous sulphate was more insoluble in the hot than in the cold. Jolin

states that 100 parts of water at 0° dissolve 16 parts of anhydrous sulphate, while at 100° only 2 parts dissolve. The supernatant liquid had an opalescent appearance suggesting a basic salt; the addition of 10–20 cc. of hydrogen peroxide to each beaker of solution caused the solution to clear up on boiling and more sulphate went into solution. About one third of the hydroxide was transferred to each beaker, 300 cc. of water added, 30 cc. of 50 per cent. sulphuric acid added at intervals and heated to boiling. The peculiar color of the hydroxide soon disappeared and instead a white crystalline salt was deposited. A little more acid was added and boiled, a little hydrogen peroxide (10–20 cc.) added, again boiled until all peroxide was decomposed, allowed to stand and the clear supernatant liquid was poured off. The complete removal of the peroxide was determined by making some of the solution ammoniacal and if any peroxide remained a yellow color or precipitate appeared; a white precipitate indicated complete removal. The volume in each beaker was then made up to about 600 cc., cooled to about 10° in order to dissolve as much as possible, the supernatant liquid poured off, more water and a little acid added, boiled, a little hydrogen peroxide added, boiled, cooled, and treated in this manner until all went into solution. In all the volume was about three liters, and about 90 cc. of 50 per cent. sulphuric acid were used. During solution a brisk evolution of gas was noticed. This was carbon dioxide and oxygen from the decomposition of the carbonate and ceric salt.

This solution was placed in a large evaporating dish, and 100 g. of potassium sulphate dissolved in 500 cc. of boiling water added; crystals deposited immediately. It was allowed to stand over night, heated, and 50 g. more of potassium sulphate, as solution, added and allowed to cool. If no more crystals form enough has been added. It was thought to be advantageous to heat after the addition of potassium sulphate, the potassium sulphate being more soluble, the cerous sulphate less soluble, so that the formation of the double salt was a slow one and the crystals attained a larger size. When the cool supernatant liquid was poured off, the crystals were washed with warm water to dissolve out the excess of potassium salt. Some of the double sulphate was ignited and gave an oxide with a pink tint.

5. *Potassium Hydroxide and Chlorine* to remove lanthanum and didymium.—The crystals of double sulphate were transferred to the three beakers, water added to about three-quarters full, 20 cc. of concentrated hydrochloric acid added, digested on the water bath for half an hour, and the supernatant liquid poured into an evaporating dish. This was continued until all went into solution; a total of 250 cc. of concentrated hydrochloric acid were used. To this solution stick potassium hydroxide was added in excess, and heated until all the cerium was pre-

cipitated as hydroxide, and the filtrate gave no test for cerium after acidifying and adding hydrogen peroxide and ammonia. It was then filtered through a Büchner funnel and well washed with hot water to remove the excess of alkali and potassium salts. The precipitate of hydroxide was transferred to a tall cylinder, capacity about 2300 cc., water added to about 2100 cc., and then 200 g. of potassium hydroxide. An electric stirring apparatus was used to keep the hydroxide well mixed, a stream of chlorine added very slowly, a bubble at a time, until completely saturated (20 hours), and allowed to settle. The supernatant liquid was siphoned off, water added and stirred for 15 minutes, allowed to settle, siphoned, and repeated twice, making three washings with water. The color of the ignited oxide from this treatment was a little improvement over the oxide made from the original sample, showing the presence of a considerable amount of didymium. It was thought that a stronger potassium hydroxide solution would be better; to accomplish this the precipitate, yellow hydrated ceric oxide, was transferred to a Büchner funnel and washed with hot water. The precipitate was transferred to a large evaporating dish, treated with 1500 cc. of water and 150–200 cc. of concentrated hydrochloric acid. The yellow peroxide did not dissolve completely in the acid, but on the addition of a little hydrogen peroxide it quickly dissolved to a clear colorless, cerous solution. The cerous chloride was treated with potassium hydroxide as before, boiled, filtered and washed on the funnel. The moist hydroxide was transferred to the cylinder, 1000 g. of potassium hydroxide added and the volume made up to about a liter and a half, chlorine run in until completely saturated, allowed to settle and the supernatant liquid siphoned off. A liter of potassium hypochlorite solution (20 per cent. KOH) was added, stirred for five hours and the clear liquid siphoned off. The cylinder was again filled with water, 25 g. of potassium hydroxide added and chlorine run in to saturation, allowed to settle and the clear liquid siphoned off, filled with water, stirred, filtered and well washed with water. The yellow precipitate was treated as before with water and hydrochloric acid, the solution was cleared and reduced with hydrogen peroxide, and the cerium precipitated as hydroxide, filtered, washed and transferred to the cylinder. About 2000 cc. of water were added and 1000 g. of potassium hydroxide, chlorine run in quickly at first and slowly to complete saturation. The precipitate was allowed to settle, the supernatant liquid siphoned off, water added, stirred and this run off; the whole was transferred to the funnel and well washed with water to remove potassium salts.

6. *Hydrochloric Acid and Oxalic Acid* to remove iron, etc.—The yellow precipitate was transferred to a large evaporating dish, about 1500 cc. of water and 150 cc. of concentrated hydrochloric acid added and boiled.

After most of the precipitate had dissolved, hydrogen peroxide was added to take all into solution and reduce the ceric to the cerous condition. To the cerous chloride solution 500 cc. of concentrated hydrochloric acid were added and heated almost to boiling; then 1000 cc. of oxalic acid solution (saturated in the cold) added; this gave no precipitate while hot but on cooling crystalline oxalate of cerium separated; this was called "first crop." The first crop of crystals was filtered through a Büchner funnel and well washed with hot water, and dried between filter papers in the air. This cerium oxalate was considered pure. To the mother liquor 1000 cc. of oxalic acid solution were added and allowed to crystallize, about the same yield was obtained, this was filtered, well washed and dried in the air and called "second crop." The oxide obtained on ignition from "first crop" was free from a red tinge due to iron and didymium but had a yellow tint, the color of chamois leather. The oxide from "second crop" had the same color.

When some of the oxalate, first crop, was heated in an atmosphere of pure dry hydrogen it charred brown, and became black on continued heating, and stayed so when cooled in an atmosphere of hydrogen. When this black compound was heated in an atmosphere of pure oxygen a glow ran over the powder, and a precipitate was produced by leading the products into lime-water. The powder turned a canary-yellow, and on higher heating to an orange, on cooling in an atmosphere of oxygen it assumed a light yellow, the color of chamois leather. Another sample of first crop was heated in air free from carbon dioxide and moisture, the oxalate changed to a canary-yellow oxide, a narrow black band preceded the change to yellow; and in the deeper parts it glowed. When these two oxides were heated in hydrogen, they turned a dirty green, a little the color of graphite, and on cooling them in hydrogen both turned a yellow-brown. On heating both in pure oxygen they turned pale yellow, deeper in color at higher temperatures, and when cooled in air they turned light yellow, the same color as mentioned above.

This work was carried out in the autumn of 1903, but on account of the inability to have a spark spectrum analysis made it was abandoned. Through the kindness of Professor J. S. Ames and Mr. Frank L. Cooper, of Johns Hopkins University, a careful analysis of the two crops was made with the following results:

"Sample A (first crop) contains a trace of lanthanum and the merest trace of yttrium." "The same is true of sample B (second crop)." From this one was justified in calling the products pure; the trace of lanthanum indicated that more thorough treatment with chlorine was necessary, the precipitate should have been more thoroughly washed, dissolved and reprecipitated each time before the addition of the alkali and chlorine. The presence of the trace of yttrium was undoubtedly due to the separation by the double sulphate, although yttrium is soluble as well as thorium in ammonium oxalate. The cause of contamination with yttrium was not due to lack of resolution and reprecipitation, although this would have undoubtedly improved it, but to the error in heating the sulphate solution after the addition of potassium sulphate, causing the yttrium sulphate and cerium sulphate, which are more insoluble in the hot than the cold, to separate out, or perhaps to hydrolysis, a property very marked in the cerium earths.

With the following additional operations the method gives a pure product. In 4, the sulphuric acid and potassium sulphate treatment, do not heat the solution after the potassium sulphate has been added but add it to the cold solution. Dissolve this double sulphate with potassium hydroxide and reprecipitate the double sulphate. This should remove this mere trace of yttrium.

In 5, the treatment with potassium hydroxide and chlorine, more thorough washing by decantation and on the filter was needed; the precipitate of peroxide should have been dissolved in acid, etc., after each oxidation with chlorine, reprecipitated with alkali and chlorine added, instead of adding fresh alkali to the peroxide and adding chlorine. This modification should remove the trace of lanthanum.

The finished product showed such marked purity that a spectrum analysis of the starting material was to have been made by Professor Ames, but due to the carelessness of the express company the only sample was lost. I was unable to get more of the same lot from the Welsbach Company, although they said the crude oxalate was of constant composition. A sample from another lot, about the same date of manufacture, was obtained and this as well as the original sample revealed the presence of didymium in considerable quantities, by the absorption spectrum. A sample of the new crude oxalate was sent to Professor Ames and Dr. Cooper and after an unavoidable delay Dr. Cooper reports: "The crude oxalate was very impure and contained a large amount of neodymium, praseodymium, lanthanum, yttrium, thorium, besides calcium, etc., also tantalum." Columbites and tantalites are often found in monazite sands, accounting for the presence of the last-named impurity.

Summary.

The method herein stated, with the slight additional precautions mentioned, offers a good method for preparing pure cerium salts from crude oxalate. In case the starting material were a sand or mineral, the method for solution and precipitation of the rare earths as oxalates, see This Journal, **26**, 780 (1904).

The color of ceric oxide is a pale chamois color; colors of a reddish or pink indicate the presence of colored oxides; a very pale or almost white oxide indicates the presence of white oxides as impurities.

The color of pure ceric oxide is not due to the presence of nitrogen from the air, since the color is the same if ignited in pure oxygen.

The author wishes to thank Mr. H. S. Miner and Mr. M. C. Whitaker, of the Welsbach Company, for samples of material and advice, and especially to thank Professor Ames and Dr. Frank L. Cooper for the time spent and interest taken in establishing the purity of the products, and the impurity of the starting material.

The purity of the finished product is further established by the work of Metzger in this issue; the sample is named by him "4."

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 163.]

A RAPID AND ACCURATE VOLUMETRIC METHOD FOR THE DETERMINATION OF CERIUM IN THE PRESENCE OF OTHER RARE EARTHS.

BY F. J. METZGER.

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The basis for the method described in this communication may be briefly stated as follows: cerous sulphate, in sulphuric acid solution, is converted quantitatively to ceric sulphate by means of sodium bismuthate. The excess of sodium bismuthate is then removed by filtration, a known excess of ferrous sulphate added to reduce the ceric compound, the excess of ferrous sulphate being then titrated with potassium permanganate.

The oxidation and subsequent reduction of the cerium may be represented thus:

$$Ce^{+++} \longrightarrow Ce^{++++} \longrightarrow Ce^{+++}$$

from which it is apparent that to secure accurate results, the ferrous sulphate and permanganate solutions should be dilute.

Solutions Required.—A potassium permanganate solution approximately $N/40$.

A solution containing 10 grams of Mohr's salt and 50 cc. of concentrated sulphuric acid per liter. The value of the permanganate in terms of iron multiplied by 3.08415 gives its value in terms of CeO_2 (1909 at. wts.).

Experimental.—Solutions of five different cerium salts were prepared and carefully standardized for combined rare earth oxides by precipitating as oxalate, igniting and weighing.[1]

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[1] The author is indebted to Messrs. M. C. Whitaker and H. S. Miner, of the Welsbach Light Co., for samples Nos. 1, 2, and 3 indicated in the table below, and to A. C. Neish, for samples Nos. 4 and 5.