problem in their drying. In emulsions of these, water must be present as an independent liquid, and have nearly its own vapor pressure. Obviously, no salt can form a stable hydrate having a vapor pressure greater than that of its saturated solution, and this is less than the vapor pressure of pure water. Therefore, a salt shaken in such an emulsion will continue to take up water until it is entirely converted into the highest hydrate it can form at the temperature of the experiment, or until all the water is removed from the oil. The choice of the salt to be used would depend simply on its cheapness and the percentage of water when hydrated. Sodium sulfate answers both these requirements, and seems well adapted to drying this class of liquids.

SHEFFIELD CHEMICAL LABORATORY OF YALE UNIV.,
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A NEW METHOD FOR THE SEPARATION OF CERIUM.

BY C. JAMES AND L. A. PRATT.

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Cerium differs from the other elements of the rare earths, in that it forms a series of more highly oxidized compounds. It is a well known fact that many of these ceric compounds very readily undergo hydrolysis, and this property has been made use of for the separation of the element. Cerium material obtained by those methods, which give a precipitate of hydrated ceric oxide, is usually less pure than that obtained from operations giving basic salts. Hitherto, the great disadvantage of precipitating cerium as basic ceric nitrate has been that only a portion of the cerium could be thrown out of solution. The authors have found that potassium bromate is capable of oxidizing cerous nitrate in a faintly acid or neutral solution, so that this element may be entirely separated from the other rare earths.

When a solution of the rare earth nitrates is boiled with potassium bromate in the presence of a lump of marble (saccharoid limestone), the cerium is entirely precipitated as the basic ceric nitrate, with varying amounts of basic ceric bromate. The cerium obtained in this manner is free from other rare earths, if the operation has been carefully conducted.

In working on a large scale with concentrated solutions, it is advisable to use a slight excess of bromate, and to stop the action while a little (about 1 per cent.) cerium remains in the liquid. Under these conditions, a cerium product is obtained which, after washing with a 5 per cent. ammonium nitrate solution, gives a pale straw colored oxide. A saturated solution of the nitrate of this material shows no trace of absorption spectrum when tested with a layer 20 cm. thick.

Experimental Data.

A solution of pure cerium nitrate was prepared and standardized by precipitating with oxalic acid, and igniting to CeO_2. Ten cc. contained 0.4068 gram CeO_2. In a similar manner a solution of didymium nitrate was made, and standardized. Ten cc. contained 0.4109 gram of the oxide.

Many experiments were performed in the endeavor to find an ideal substance with which to keep the liquid neutral. The results obtained are given below.

(*a*) *Lump Marble.*—Ten cc. of each of the standardized solutions, together with 5 grams of potassium bromate, were diluted to 100 cc., a piece of marble added, and the whole boiled. After a few minutes, a yellow precipitate began to form and free bromine was evolved. The precipitate was filtered, washed with a 5 per cent. solution of ammonium nitrate, and dissolved in hydrochloric acid. It was found necessary to dissolve the precipitate in the beaker previously used, owing to the fact that it was impossible to wash all ceric basic nitrate from the sides of the vessel. The hydrochloric acid solution was boiled, cooled and filtered. The clear filtrate was evaporated to remove the excess of acid, then diluted, and the cerium precipitated as the oxalate. Six experiments carried out in this manner, the time of boiling being varied, gave the following results:

No.	Time. Minutes.	Wt. of CeO_2 (Found).	Wt. of CeO_2 (Theoretical).
1	15	0.3896	0.4068
2	20	0.4083	0.4068
3	25	0.4076	0.4068
4	30	0.4102	0.4068
5	35	0.4123	0.4068
6	45	0.4144	0.4068

Ten cc. of the didymium solution free from cerium were boiled with potassium bromate and marble for 30 minutes and in this case no percipitate formed.

(*b*) *Powdered Marble*, lead carbonate, zinc carbonate, zinc oxide, copper carbonate and copper oxide caused the solution to become rapidly alkaline, which hindered the oxidation by the bromate.

(*c*) *Magnesite* proved to be much slower in its action, and owing to the fact that the mineral lacked uniformity in contour, the basic ceric salts entered the crevices and could not be washed out.

(*d*) *Dolomite* would undoubtedly serve the purpose of ordinary marble, if sufficiently pure. The specimens available for our experiments contained iron, and were unsuited for the work.

The important fact, brought out by the above experiments, and others not included, is that lump marble, presenting, as it does, comparatively small surface, is the best material with which to keep the solution in a proper state of acidity for the oxidizing action of the potassium bromate. It should be specially noted that powdered marble is not applicable, as the neutralization is carried so far that the product is contaminated with didymium.

Quantitative Estimation.—Since no satisfactory gravimetric method for the estimation of cerium is known, the authors considered it worth while to attempt to apply this process for quantitative work. In this endeavor, a double precipitation was carried out, using a smooth lump of marble (containing no crevices) so that any adhering precipitate could be easily washed therefrom. The first precipitation was continued until the mother liquor failed to give a test for cerium. This point was determined by withdrawing a small quantity of the supernatant liquid with a pipette, and applying the hydrogen peroxide test. When the liquid was found to be free from cerium, the precipitate was filtered, and washed with a 5 per cent. solution of ammonium nitrate. The filter paper with the precipitate was returned to the beaker, and treated with nitric acid, and a little potassium bromate to oxidize the paper. (It was found absolutely necessary to oxidize all the filter paper, otherwise the cerium could not be precipitated, even after several hours' boiling.) After having boiled the solution to remove the excess of acid, the residue was dissolved in water, and treated as before with potassium bromate and marble. The boiling was continued until the supernatant liquid failed to give a test for cerium. The precipitate was separated on a filter, washed with ammonium nitrate solution, placed in the original beaker, and dissolved in hydrochloric acid. The liquid was then filtered, evaporated to remove the excess of acid, the residue taken up with water, and the cerium precipitated as the oxalate. This was ignited, and the cerium weighed as CeO_2.

The following results were obtained:

	(1)	(2)
CeO_2 found.................	0.4100	0.4094
CeO_2 present..............	0.4068	0.4068

The Purification of Cerium on a Large Scale.—The material used for this work consisted of the monazite earths freed from thorium. The oxides were dissolved in nitric acid, the concentrated solution made nearly neutral, heated to boiling, and potassium bromate added. As soon as red fumes of bromine made their appearance, two or three large pieces of marble were placed in the container and the boiling continued for a few hours. The length of the operation depended upon the amount of cerium in the solution. Small portions were withdrawn at intervals, and as soon as it was ascertained by the hydrogen peroxide test that nearly all the cerium had been thrown out of solution, the boiling was discontinued, The marble was then removed and the precipitate allowed to settle. The clear supernatant liuqid was syphoned off and the precipitate washed upon a Buchner funnel with a 5 per cent. solution of ammonium nitrate. The basic salt was dissolved in hydrochloric acid and the filtered solution treated with oxalic acid. Sometimes, however, it was found more advantageous to precipitate the cerium as the sulfate by gradually adding concentrated sulfuric acid to the chloride solution, and partially evaporating on the water bath. Alcohol was added to the residue, the sulfate separated by filtration, and washed with alcohol. For a final purification, the sulfate was rendered anhydrous, made into a saturated solution in cold water and once again precipitated by heating.

The small amount of cerium remaining with the other earths in the original mother liquor was next precipitated by boiling with potassium bromate and marble until some of the clear liquid no longer gave the hydrogen peroxide test. This precipitate of cerium carrying a little of the other rare earths was dissolved in nitric acid and added to the next batch for preparation of pure cerium.

The precipitate thrown down by this process varies very considerably, depending upon the conditions of the experiment. It was found, when concentrated solutions were used, that very dense precipitates were obtained. This is a very important point, since the light precipitates, obtained from dilute solutions, filtered with great difficulty. It was impossible to wash even the densest precipitates with water, owing to the formation of colloidal solutions. This difficulty was overcome by washing with a 5 per cent. ammonium nitrate solution. When a large excess of bromate was employed, the cerium was obtained chiefly as a basic ceric bromate. Under the best conditions, using only a slight excess of bromate, a basic ceric nitrate was obtained. On dissolving this precipitate in acid only a slight amount of bromine was evolved.

With too small an amount of bromate, the solution became alkaline, the precipitate darkened in color, and was found to contain didymium, etc. Such a precipitate was purified by dissolving in concentrated nitric acid with the help of a *very little* alcohol. The resulting solution, possessing a deep orange-red color, gave a heavy precipitate upon diluting, and boiling with marble. Care must be taken not to allow the solution to become alkaline by boiling too long.

By the bromate method, the authors obtained many kilograms of cerium salts of such a purity that a saturated solution of the nitrate gave no absorption bands, when observed through a layer 20 cm. thick.

With a little experience, the method is easily controlled and the production of large amounts of pure cerium compounds is only a matter of hours. It would seem that this method might well become commercially valuable as potassium bromate can now be obtained quite cheaply.

Once again the authors desire to express their thanks to the Welsbach Company for material, through the courtesy of Dr. H. S. Miner.

DURHAM, N. H.

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NEW RARE EARTH COMPOUNDS.

BY L. A. PRATT AND C. JAMES.

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The salts given in this paper were prepared while searching for some crystallin compounds which might be useful for fractional crystallization of the yttria earths.

Yttrium Methylsulfonate, $Y(CH_3SO_2O)_3.4H_2O$.—In the preparation of this salt, yttrium oxide was dissolved in methylsulfonic acid and the solution evaporated. The residue was taken up in alcohol and precipitated by ether. The compound separated as a viscous mass, which rapidly became crystallin. It was separated from the liquid as far as possible with suction and air-dried. The salt was too soluble to be of value for fractional crystallization.

Calculated: Y, 19.93; S, 21.54. Found: Y, 19.72; S, 21.42.

Yttrium Methenedisulfonate, $Y_2(CH_2(SO_2O)_2)_3.(2^1/_2H_2O?)$.—This compound was prepared by dissolving yttrium oxide in methenedisulfonic acid. The solution was evaporated and treated with absolute alcohol and ether. The resulting precipitate was filtered, washed with ether, and air-dried. The salt is very soluble.

Calculated: Y, 23.87. Found: Y, 23.76.

Yttrium Methinetrisulfonate, $YCH(SO_2O)_3.3^1/_2H_2O$.—This salt was made by dissolving yttrium oxide in methinetrisulfonic acid and evaporating the solution. Upon the addition of alcohol to this liquid, the compound was completely precipitated. It was washed with alcohol with the aid of suction, and air-dried. The salt is insoluble in alcohol and in acetic acid and only slightly soluble in nitric acid.

Calculated: Y, 21.96; S, 23.73. Found: Y, 21.91; S, 24.04.

The methinetrisulfonic acid for this compound was prepared[1] by treating powdered acetanilide with fuming sulfuric acid.

Yttrium Ethylsulfonate, $Y(C_2H_5SO_2O)_3.4H_2O$.—Yttrium oxide was dissolved in ethylsulfonic acid and the solution evaporated. The residue was taken up in alcohol and upon treatment with ether the compound came down in a crystallin form. This was washed on a filter with ether and dried in the air. Like most of the other sulfonates, this compound was very soluble.

Calculated: Y, 18.23. Found: Y, 18.05.

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[1] *J. Chem. Soc.*, **75**, 280.