

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ARIZONA  
AND NEW HAMPSHIRE COLLEGE.]

## THE CONCENTRATION OF THE ERBIUM EARTHS.

BY PAUL H. M.-P. BRINTON AND C. JAMES.

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An investigation of four different methods for the concentration of the less basic rare earths resulted in the discovery of two of the most rapid procedures for this purpose. The methods examined were (a) formation of basic nitrates; (b) crystallization of chlorides from 1:1 hydrochloric acid; (c) formation of basic chlorides; and (d) formation of basic thio-sulfates. Of these methods (a) and (b) proved to be the best, and the exact manner in which they were carried out is described below.

(a) **Formation of Basic Nitrate.**—When following the old plan involving fusion of the nitrate for separating erbium from yttrium, it has been pointed out from time to time that the best results were obtained when the entire melt went into solution in boiling water, and deposited the basic nitrate in small crystals upon cooling or evaporation. The basic nitrates are more soluble in hot dilute solutions and less soluble in hot concentrated or cold dilute solutions. However, when the mixture consists mainly of the erbium earths, the basic nitrate, if there is much of it, will remain insoluble. The fact that the best results were obtained when the basic nitrate dissolved entirely in the excess of nitrate solution makes it obvious that the same results should be obtained by treating the solution with sodium hydroxide solution.

In order to test this a solution of yttrium nitrate, containing a little erbium, was heated to boiling, treated carefully with a fairly strong solution of sodium hydroxide and thoroughly boiled. The yttrium hydroxide which first precipitated soon dissolved. The addition of the sodium hydroxide solution was continued until minute crystals of the basic nitrate were observed swirling through the liquid. The whole was then set aside to cool. Upon examining the vessel next morning it was found to be lined with a mass of needle-like crystals of the basic nitrate radiating towards the center. These were filtered off, dissolved in the least amount of nitric acid, and the solution heated to boiling and treated with sodium hydroxide solution as described above. The basic nitrate crystals from this solution dissolved in nitric acid giving a rose-red solution showing intense absorption bands of erbium. This, together with a determination of the equivalent, showed that erbium was rapidly collecting in this portion.

The original filtrate was treated several times with sodium hydroxide solution. Although the concentration of the nitrates was kept high, the absorption bands soon began to fade.

Since this method worked so well for the yttrium-erbium mixture, it was next tried out with yttrium, holmium and erbium with good results.

During the fractionation, fractions of the same rare earth content were mixed together. Fractionations of this type are intermittent and do not run so smoothly as the simple crystallization methods. After further work it was noticed that two kinds of basic nitrates were obtained, one as described above, and another which separated from the boiling liquid during evaporation. The former compound readily dissolved in the diluted mother liquor at the boiling point, while the latter did not.

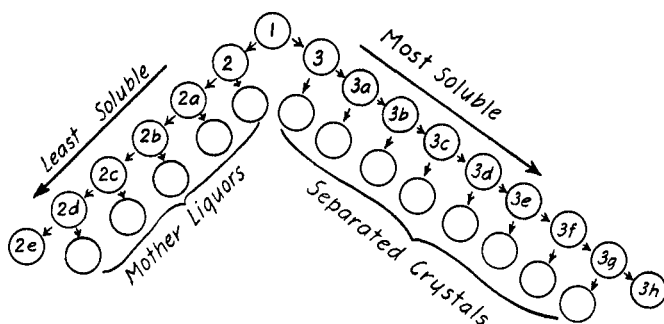
Some of the basic nitrate and a solution of the nitrates which appeared to be of the same rare earth content were next selected. The nitrate solution was diluted somewhat, heated to boiling, the basic nitrate gradually added and the clear solution evaporated to the original volume and allowed to cool. After standing for some time, a quantity of basic nitrate separated out which, when examined in the spectroscope, showed as great an increase in the erbium content as the former sodium hydroxide fractionation or the old classic fusion of the nitrate gave.

It must be admitted that this method when used with the fractional crystallization plan requires much more practice than the crystallization of double nitrates, bromates or ethyl-sulfates. However with a little experience the time saved is very great.

(b) **The Crystallization of the Chlorides.**—For the concentration of the more basic erbium earths, holmium and dysprosium from yttrium, the authors recommend the fractional crystallization of the chloride from constant-boiling hydrochloric acid. The speed of separation was first observed during the preparation of a chloride from an yttrium oxide containing some holmium and dysprosium. The solution of the chlorides was evaporated, cooled in snow and saturated with hydrogen chloride for 20 to 30 minutes. The crystals which formed were removed by suction, the filtrate was again saturated with hydrogen chloride, the crystals were removed, and the whole process was repeated several times. When the final mother liquor was examined it was found to consist of fairly pure yttrium chloride.

The first crystals which were precipitated were then further fractionated by dissolving in water containing a little hydrochloric acid, evaporating until rather thick, cooling by placing the container in snow and saturating with hydrogen chloride. The precipitated crystals were again dissolved in water and the same operations repeated several times. Since the chief interest lay in the least soluble portion, the mother liquors were placed aside each time. The following diagram shows the exact number of fractions that were taken.

Fraction 2e when dissolved in water showed very strong holmium bands while those of erbium could just be distinguished. The solution was precipitated by oxalic acid, the oxalate ignited to oxide and the equivalent determined.



The mother liquor *3h*, which showed only a weak absorption of holmium, etc., was subjected to a double precipitation with oxalic acid. After ignition the equivalent of this fraction was also determined.

No. of Fraction.	I.	II.	Average At. Wt.
<i>2e</i>	126.5	127.9	127.2
<i>3h</i>	90.2	90.1	90.2

Dennis and Dales<sup>1</sup> worked with the hydrogen chloride precipitation method for the fractionation of the yttrium earths. In this case a solution of  $MCl_3$  was concentrated and precipitated in ice-salt freezing mixture by passing in hydrogen chloride for 5 hours. The mother liquor was precipitated by ammonium hydroxide, dissolved in hydrochloric acid and again precipitated by hydrogen chloride. The original solution and the fractions were then compared as to spectra, and no change in the relative intensities of the spectra was observed. On this evidence Dennis and Dales rejected the method.

Since the use of hydrogen chloride is troublesome and unpleasant and moreover since the crystallization occurred mainly where the gas came in contact with the solution, it was thought that crystallization from 1:1 hydrochloric acid would be very much simpler and more effective.

All fractions except *2e* and *3h* from the preceding operations were combined, boiled down to hydrochloric acid of constant boiling point, and fractional crystallization was started. The solutions were evaporated until a scum formed on the surface, when they were allowed to stand for from 15 to 20 hours. Simple decantation was used instead of filtering and washing as was done with the hydrogen chloride method. By the time the tail fraction had become No. 9 the head fraction had become No. 4, owing to the combining of the small head fractions to obtain enough to work with. The atomic weights of these two fractions were then determined, and found to be 92.5 and 124.0, respectively.

<sup>1</sup> Dennis and Dales, *THIS JOURNAL*, 24, 421 (1902).

The crystals and mother liquor from Fraction 7 were next examined in order to find out the speed of separation given by one crystallization. The oxide from the crystals weighed 14.36 g. and the oxide from the mother liquor weighed 39.35. The atomic weight of the oxide from the crystals was found to be 106.1, while that from the mother liquor was 99.8.

After the above tests were made the fractionation was continued for 4 more operations, and the atomic weights of the extremes determined. The head fraction, No. 4, gave 133.70 while the tail fraction, No. 12 gave 91.5.

The absorption spectra were then examined by dissolving 1-g. portions of oxide from various fractions in equal amounts of nitric acid and diluting to the same volume in each case. Fraction 4 gave intense lines of holmium. The crystals from Fraction 7 gave fairly strong lines of holmium, while Fraction 12 gave only very faint lines of this element. Erbium was found to concentrate in the most soluble fractions with the yttrium. This indicated that erbium chloride was more soluble.

To follow the course of the small amount of dysprosium, Fraction 12 was concentrated and more of the solid was added until the holmium spectra in No. 4 and No. 12 were of about the same intensity. By comparing the intensity of the two faint dysprosium bands with that of the middle holmium band, it was estimated that in Fraction 12 the holmium band was 4 times as strong as the dysprosium bands, while in Fraction 4 the holmium was perhaps twice as strong as the two dysprosium bands. This indicated that relatively the dysprosium was twice as concentrated in No. 4 (the least soluble fraction) as it was in No. 12 (the most soluble fraction).

The order of separation in line of decreasing solubility of the chlorides would accordingly run: erbium, yttrium, holmium, dysprosium.

(c) **Basic Chlorides.**—In the case of the basic chloride, the crystals from Fraction 8 of the preceding experiment were dissolved in water, and ammonium hydroxide was added until a fair precipitate was obtained. The mixture was then heated and concentrated until the character of the hydroxide was changed into a granular basic chloride. Five fractions of about equal size were obtained, and of these Fraction 1 gave an atomic weight of 105.6 while Fraction 5 gave 93.4.

(d) **Basic Thiosulfates.**—These precipitates were obtained in the following manner. The boiling chloride solution was treated with very dil. ammonium hydroxide so long as the precipitated hydroxides would dissolve on continued boiling. A solution of sodium thiosulfate was then added, when the basic thiosulfates were immediately precipitated. The precipitate was filtered off, and the whole process repeated. Four fractions were obtained. The head fraction, No. 1, gave an atomic weight of 97.1, while the tail fraction, No. 4, gave 91.0.

### Summary.

The authors highly recommend the basic nitrate method in the two forms herein outlined for the separation of erbium, holmium, dysprosium and the less basic earths from yttrium; and the crystallization of the chlorides from 1:1 hydrochloric acid for the separation of holmium and dysprosium from yttrium.

TUCSON, ARIZ.  
DURHAM, N. H.

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## OXIDATION AND REDUCTION OF HYDROQUINONE AND QUINONE FROM THE STANDPOINT OF ELECTROMOTIVE-FORCE MEASUREMENTS.

BY F. S. GRANGER AND J. M. NELSON.

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Very little work has been done on the study of oxidation and reduction from the standpoint of potential measurements, in the field of organic chemistry, and nearly all of that has been of an empirical character. Bancroft<sup>1</sup> included in a study of a large number of more or less common oxidizing and reducing agents, alkaline solutions of hydroquinone and pyrogallol. The proportions used in making up these solutions were not given, but had they been, they would not have thrown much light upon the composition of the resulting mixtures, since both hydroquinone and pyrogallol are very unstable in alkaline solutions. Furthermore, the potentials were not measured against any standard electrodes, but against other oxidizing and reducing agents. Neumann<sup>2</sup> later put Bancroft's results on a more definite basis by comparing them with a calomel electrode. Baur<sup>3</sup> determined the potentials manifested by solutions made up of definite amounts of hydroquinone and formaldehyde, in aqueous sodium hydroxide. Slaboszewicz<sup>4</sup> made some admittedly rough measurements on aldehyde and alcohol in 2*M* sulfuric acid. Mathews and Bar-meier<sup>5</sup> published some potentials of various photographic developers and Frary and Neitz<sup>6</sup> carried out a more elaborate study along the same lines as those of Mathews and Bar-meier. All of these measurements were determinations of potentials of solutions, made up with definite concen-

<sup>1</sup> Bancroft, *Z. physik. Chem.*, **10**, 387 (1892).

<sup>2</sup> Neumann, *ibid.*, **14**, 193 (1894).

<sup>3</sup> Baur, *Ber.*, **34**, 3732 (1901).

<sup>4</sup> Slaboszewicz, *Z. physik. Chem.*, **42**, 343 (1902).

<sup>5</sup> Mathews and Bar-meier, *Proc. 8th Intern. Congr. Appl. Chem.*, **20**, 189, 193, 179 (1912).

<sup>6</sup> Frary and Neitz, *THIS JOURNAL*, **37**, 2246 (1915).