

335. *Separation of Yttrium and Erbium with the Aid of Ethylenediaminetetra-acetic Acid ("Enta Acid").*

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Yttrium-erbium oxalate is dissolved in diammonium dihydrogen enta and ammonia to give a somewhat acid solution, and is then fractionally precipitated by acidification. Rapid concentration of yttrium occurs in the precipitate. With excess of enta present, oxalate crops can be obtained by cooling hot saturated solutions. After initial spreading, crops are ignited and the oxides dissolved in appropriate mother-liquors, thus stabilising the pH for conducting a continuous fractionation. Erbium is obtained free from yttrium without difficulty, and is separable from enta acid without appreciable loss.

THE main object of this work has been to establish a practicable procedure for the use of "enta" in separating the lanthanons. The wide range of stability of the complexes formed by various earths probably makes a number of individual modifications necessary, but it is important to be able to recover the lanthanons at will. Owing to the complex-forming power of enta, this is unusually difficult, since oxalate or hydroxide precipitation, though normally acting quantitatively, here breaks down.

The separation of yttrium and erbium was chosen for particular study since erbium gives the more stable complexes and is strongly coloured. Its detection by eye or spectroscope is therefore easy, and risk of loss in rejected products is small.

In a previous paper (*J.*, 1950, 1819) the fractional precipitation of a batch of earths as oxalate in presence of enta was reported. A rather different procedure is now described. The precipitation of lanthanon oxalate may occur under widely varying conditions, *e.g.*, (1) from neutral solutions of simple ionic salts, from which precipitation is immediate and only slightly selective; (2) from complex alkaline or neutral solutions holding oxalate to capacity for the amount of complex-forming agent present, from which addition of a simple lanthanon salt solution causes precipitation of oxalate with moderate selectivity of the stronger bases; (3) from solutions highly charged with complex-forming agent (alkali enta), precipitation from which is best brought about by sufficient acid to cause partial decomposition of the soluble complex with production of free Ln^{+++} and oxalate ions up to the concentration permitted by the solubility product for lanthanon oxalate. The complex stability is affected primarily by pH and the nature of the lanthanon. Hence, for a pair of lanthanons of different basic strength, the weaker base will give the more stable complex, and the most suitable pH for selective precipitation of the stronger base will be that at which the stabilities differ most widely. In too alkaline a solution both components may be nearly fully converted into complexes, and precipitation occurs through inability of the complex-forming agent to hold oxalate in solution as in (2) above. In the acid range there is preferential decomposition of the complex of the stronger base.

For yttrium-erbium mixtures, it is best to use solutions at a pH not much higher than that at which enta acid will be precipitated. Half a given supply of lanthanon oxalates is dissolved in ammoniacal enta to give a neutral solution, and then precipitated fractionally at the boil by addition of enta, oxalic, or hydrochloric acid. Addition of enta acid will lower the pH without at first producing an oxalate precipitate. Its use at this stage allows of an adjustment of pH to a suitable value. Oxalic acid brings about precipitation without a sharp change in pH as the lanthanon passes from anionic to cationic binding. Much buffering may also take place by formation of acid ammonium oxalates; thus a point comes when addition of oxalic acid precipitates only a little oxalate. At this stage the liquor is sufficiently acid to dissolve a quantity of fresh lanthanon oxide. This is derived from the reserved half of the original batch of oxalates, and may be converted into complex in two or three portions as shown in the Table,

Initial separation of yttrium-erbium oxide (53% erbium).

Crop.	Wt., g.	Analysis of oxide.		pH of mother-liquor.	Remarks.
		Er_2O_3 , %.			
1	37	27.6		4.56	—
2	38	36.0		4.70	—
3	71	59.0		4.10	45 G. of fresh oxide dissolved in mother-liquor.
4	26	35.2		4.00	26 G. " " "
5	38	38.6		3.82	—
6	35	45.0		3.66	—
7	48	54.0		—	Contained enta acid.
8	35	75.4		—	—
9	82	89.5		—	About 60% of free enta acid.
10	55	97.6		—	" 80% " "
11	57	96.5		—	Contained ammonium tetroxalate and only a little erbium oxalate.

producing a rise in pH of the solution and permitting further oxalate crops to be obtained. The last stage of the precipitation is best carried out by addition of hydrochloric acid. This effectively decomposes the complex, and precipitates a mixture of lanthanon oxalate and free enta acid. The resolution of this mixture is described in the Experimental section.

The initial oxalate crops are separately converted into complex with fresh ammonium enta solution, and partly reprecipitated with oxalic acid. The resulting oxalate crops are ignited to oxide, and dissolved in the appropriate mother-liquors to be submitted to a fractionation on 6—8 fractions at a pH of 4—6.

There is a region of enta/oxalate ratio where a difference of oxalate solubility with temperature arises. This varies with different earths, being higher in the cerium group than with erbium. Thus it comes about that, in the more highly acid ranges of solutions, precipitation of oxalates can be brought about either by the addition of oxalic or hydrochloric acid to the boiling solution till a crop is obtained, or by addition till precipitation is only incipient, and the oxalate crop is formed on cooling. There is not much difference in separational effectiveness of the two methods.

The cooling method gives crops of enta acid at an earlier stage or an ammonium oxalate according to conditions, and so is less satisfactory in the higher acid ranges.

Complete elimination of yttrium from erbium has been obtained on a small sample, but the comparative merits of enta and the ferricyanide method (Marsh, *J.*, 1947, 118) for purifying erbium cannot yet be assessed. Holmium and yttrium are not separated efficiently by the use of enta, but are by ferricyanide. A mixture of yttrium and erbium containing a little holmium should therefore yield pure erbium more efficiently by use of enta than by ferricyanide.

EXPERIMENTAL.

The material used consisted of mixed yttrium and erbium oxides containing 53% by weight of the latter, and free from other lanthanons. Half of the oxide (71 g., 0.25 mol.) was converted into oxalate and dissolved in the necessary minimum of ammoniacal enta (= 125 g. of enta acid) to give an approximately neutral solution. This was diluted to 2 l., and enta acid added at the b. p. till precipitation of oxalate was incipient. The solution was then left to cool overnight. Crop 1 (see table) of oxalate was then collected, the filtrate re-boiled, and oxalic acid added till precipitation of oxalate was again incipient. After crop 3 the solution, which was now becoming acid, was treated with $(Y, Er)_2O_3$ run in as a thin cream as long as it dissolved readily upon being boiled for a few minutes. Cropping of oxalate then proceeded as before, but the solution became too acid after crop 6, and crop 7 contained free enta acid. Crop 8 was taken by adding sufficient oxalic acid to obtain an oxalate crop near the b. p. This was collected without cooling, and was free from enta acid. However, crops 9 and 10, taken similarly, again contained enta acid. On cooling, crop 11 consisted chiefly of an ammonium oxalate. The mother-liquor from crop 11 was divided, and part treated with oxalic acid and part with hydrochloric acid. The hydrochloric acid at once precipitated the remaining erbium, which however was very little. It was evident that hydrochloric acid was preferable to an excess of oxalic acid and was used subsequently.

Successful working of the process depends upon the separation of oxalate and enta acid. The latter is only slightly soluble in cold water, but readily gives hot supersaturated solutions. When the reaction liquor first shows signs of depositing enta acid near the b. p., it is useful to dilute it several-fold. Further acidification with hydrochloric acid is then made just so long as oxalate continues to be precipitated thereby. This oxalate is collected at once, and the liquor left to cool and for 1–2 days. It deposits enta acid mixed with a little oxalate. The mother-liquor then contains only a trace of erbium and very little enta acid; if further acidification and standing produce no further crop, the liquid can be rejected safely.

The procedure described results in crops of nearly pure oxalate which are ignited without difficulty, and a crop of enta acid with some oxalate. When this crop is treated with successive small amounts of cold dilute ammonia, the oxalate forms a complex and passes into solution. It is filtered off, leaving much the greater part of the enta acid pure, as may be proved by bringing it into solution with alkali and examining it for erbium absorption bands. The erbium which has passed into solution is reprecipitated as oxalate as before.

Further working of the crops thus obtained was done by the fractional process already described. The oxalates sometimes contained a little enta, and upon ignition gave a rather vitreous form of oxide which had to be ground wet before it was redissolved in the acid mother-liquors.

The oxalate-enta complex could be obtained as 10-faced monoclinic crystals having the appearance of truncated octahedra of 3–4 mm. diameter, but on long storage one solution deposited prismatic crystals 1 cm. or more long of radiating habit.

The analyses of erbium oxides were made spectrophotometrically on perchlorate solutions, as recommended by Moeller and Brantley (*Anal. Chem.*, 1950, **22**, 433), but even so readings were found to increase by up to 10% on ageing.

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