367. *Separation of the Lanthanons with the Aid of Ethylenediamine-NNN'N'-tetra-acetic Acid.*

By J. K. MARSH.

A preliminary survey of the possibility of separating the lanthanons by fractional precipitation of oxalates or other insoluble salts on breaking their complexes with ammonium or alkali salts of ethylenediaminetetra-acetic acid shows that valuable results are achieved. By this mode of fractionation, yttrium comes close to dysprosium in the lanthanon series, and is separated very rapidly from erbium and the ytterbium earths. A rapid separation of all the heaviest earths, which form the firmest complexes, is also indicated. The method is recommended as being superior to double alkali-sulphate precipitation for an initial separation.

THE recent trend in the chemistry of the lanthanons has been to recognise the limitations of older fractionation processes for separating members of the group in purely cationic form, and to use less fully exploited physical processes such as solvent extraction, or chemical processes involving formation of more or less stable anionic complexes. In this way it has been found possible to utilize differences in the stability of complexes. The most notable example is the success achieved in the use of ammonium citrate and citric acid solution to form a complex with and elute the cations held in an ion-exchange resin such as " Dowex 50." As a micro-method this process is excellent, but the large quantities of reagents and water required detract seriously from its merits as a production process. Even many of the older classical fractionation processes are based upon weak complex formation, as found in the so-called double salts, *e.g.*, with alkali sulphates, ammonium oxalate, ammonium nitrate, and magnesium nitrate. The strong co-ordinating power of citrates and tartrates has long been known but was not successfully utilised until the advent of the ion-exchange technique. Strong complexes are formed by the " Komplexones " developed by Schwarzenbach and his school (*Helv. Chim. Acta*, 1945, **28**, *et seq.*), and Beck (*ibid.*, 1946, **29**, 357; *Mikrochem.*, 1947, **33**, 344; *Anal. Chim. Acta*, 1949, **3**, 41) has shown that ammonium and alkali salts of nitrilotriacetic acid, $N(CH_2 \cdot CO_2H)_3$, " trilo," are very successful in effecting semimicro-scale separations. He dissolved the oxalates in weakly alkaline " trilo " solutions, and reprecipitated them by acidification, or addition of an uncomplexed lanthanon salt or cupric salt solution. This he called the " exchange method," since the copper or the more weakly basic lanthanons combined with the " trilo," displacing the stronger bases which were then precipitated as oxalate; for instance, from a 90% La_2O_3 preparation a 75% yield of pure La_2O_3 was obtained in one operation by acidifying the trilo-complexed oxalate solution with acetic acid.

Of the numerous substances of similar chemical constitution (*i.e.*, having one or more secondary or tertiary amino-groups, and two or more acetate radicals so disposed as to give rise to chelate structures), trilo and ethylenediaminetetra-acetic acid, $[\cdot CH_2 \cdot N(CH_2 \cdot CO_2H)_2]_2$, " H_4 enta," were the most powerful co-ordinating agents found by Schwarzenbach *et al.* for the alkaline earths until they recently prepared 1 : 2-diamino*cyclo*hexane-*NNN'N'*-tetra-acetic acid (*Helv. Chim. Acta*, 1949, **32**, 1682). They have derived a constant whereby the power of the

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various substances can be compared for bivalent metals, by combining the acidity constants for the substance with the equilibrium constants for the reaction between metal ions and complex, yielding metal complex and hydrogen ions (*ibid.*, pp. 1543, 1682; *Nature*, 1949, **163**, 723). The values of the constant for calcium, log K_{Ca}, are for trilo, enta, and the 1 : 2-*cyclo*hexane compound, respectively, 6·41, 10·5, and 12·5. The bivalent elements, it is found, can be arranged in order of co-ordinating tendency irrespective of the agent used, with only minor exceptions. Similarly, the values of the complex-formation constants show that in general each agent has a characteristic degree of efficiency relative to the others; *e.g.*, it may be expected that enta will exceed trilo in the stability of its lanthanon complexes. However, when we change from a bivalent to a tervalent element, a new disturbing condition arises to upset any prediction, but it has been found that enta behaves similarly with bivalent metals and with lanthanum and cerium (*Helv. Chim. Acta*, 1948, **31**, 459). The ions H enta³⁻, H₂ enta²⁻, and H₃ enta¹⁻ thus appear to build complexes with these two elements just as with bivalent elements, but aluminium, ferric iron, and chromium behaved differently and formed hydroxo-complexes, *e.g.*, [Al enta(OH)]²⁻, or held a water molecule.

Since H₄ enta is manufactured in quantity for textile processing, it is freely available for separation of lanthanons. Its low solubility in cold water (0·03 g./100 g.; Bird, *J. Soc. Dyers Col.*, 1939, **55**, 560; **56**, 473) enables it to be recovered by acidification after use.

As a first step for the separation of a crude lanthanon mixture, the application of enta is found to be superior to the classical alkali double sulphate precipitation. The latter process has usually been limited to one or two applications only, owing, not to any inefficiency *per se*, but to the large amount of labour involved in decomposing the double sulphates with alkali and washing the hydroxides free from alkali. Introduction of silica by the alkali also causes much trouble. A partial solution of the difficulty is to roast the double sulphates till anhydrous (Marsh, *Nature*, 1949, **168**, 998). After being ground, all can be brought into solution easily with iced water provided that not too much terbium earths are present; or the yttrium earth solution may be decanted and the insoluble terbium earth residue centrifuged. The efficiency of a single double sodium sulphate precipitation of the crude earths from a quantity of Norwegian gadolinite can be seen from Table I. The precipitates of double sulphate were collected, and the derived oxides analysed spectrophotometrically as far as possible.

TABLE I.

Double sodium sulphate precipitates from crude (Ce-free) gadolinite earths.

Fraction no.	1	2	3	4	5	6	7	8	9
% of total	10	10	6	21	6	14	20	11	2
Apparent at. wt. ...	137	124	114	107	102	97	102	107	127
Oxides, % :									
Pr	8·3	2·5	0·8	—	—	—	—	—	—
Nd	32·4	12·3	3·6	—	—	—	—	—	—
Sm	24·8	12·2	6·2	2·4	—	—	—	—	—
Dy	—	10	13·8	11·0	8·3	6·2	3·9	1·0	—
Ho	—	1·7	2·0	2·1	1·9	1·7	1·6	0·8	0·1
Er	—	—	—	5·5	6·1	6·3	7·5	6·8	4·3
Yb	—	—	—	—	—	—	—	8·0	32·6

TABLE II.

Fractions 1 and 2 of Table I refractionated with " enta."

Fraction no.	1	2	3	4	5	6	7
% of total	22	12	28	17	10	7	4
Oxides, % :							
Pr	10·4	9·3	5·0	0·5	—	—	—
Nd	44·0	43·0	29·0	4·8	0·4	—	—
Sm	10·0	12·0	18·5	7·5	1·5	—	—
Dy	—	—	—	17·6	18·2	16·1	11·7
Ho	—	—	—	1·4	2·4	3·1	4·4
Er	—	—	—	—	4·0	7·3	20·0
Yb	—	—	—	—	—	0	10·0

The first two double sulphate fractions represented in Table I formed the starting material used to ascertain the separational effect brought about by enta, and represented in Table II. The two oxides were united and dissolved in nitric acid, and nine-tenths of the solution precipitated as oxalate. To this was added just sufficient ammonia and ammonium enta solution to cause all the oxalate to dissolve when hot to a solution smelling faintly of ammonia. The reserved

tenth part of nitrate solution was then run in while the oxalate solution was stirred mechanically at its boiling point. Thus there resulted fraction 1 of Table II, since the amount of enta was unable to co-ordinate with the whole of the lanthanon now present, and some material forming the least stable complexes (*viz.*, lanthanum and the cerium earths) was precipitated as oxalate. Subsequent precipitates 2, 3, 4, and 5 were formed by running 10% oxalic acid solution into the hot, stirred complex solution, but solid oxalic acid was used for fractions 6 and 7. The whole of the lanthanon was then seen to be precipitated, and the solution contained nearly 10% of oxalic acid. It was thus nearly saturated when cold. From it, much the greater part of the H_4 enta was recovered next day.

On comparing Tables I and II the following deductions can be made. (1) The concentration of neodymium is at least as effective by enta as by double sulphates. (2) Dysprosium collects by double sulphates in the early middle fractions, whereas by enta it is spread more evenly throughout the yttrium fractions : this is further exemplified in Table III*b*. Conversely, yttrium precipitated in presence of enta is collected at or close to the position of dysprosium in the lanthanon series, whereas by double sulphates it is collected just above the position of erbium, and a considerable Y–Dy separation results. (3) This leads also to the observation that erbium and ytterbium are collected much better in the tail fractions by enta than by double sulphates. It should be noted that Tables I and II represent the separation of the cerium and the yttrium group too sharply. Each group can only be determined satisfactorily in the absence of the other; *e.g.*, erbium cannot be assayed in presence of neodymium. Thus the erbium represented in Table II could not be determined in fractions 1 and 2 of Table I from which all of Table II is derived. Also estimates of samarium are made at a short wave-length and are apt to be high owing to traces of Ce(IV) or Fe(III), etc. This appears to have caused higher estimates in Table I than are found in Table II. The great advantage of enta, however, is not any superiority which it can give in one fractional precipitation, but the fact that it always yields oxalates which require little processing before again being fractionated. Thus the enta fractionation can be carried on continuously without the labour involved each time double sulphates have to be brought again into solution.

TABLE III.

Fraction no.		(a). Tb-free yttrium earths, % :				(b). Dy-rich yttrium earths, % :			
	%.	Dy_2O_3.	Ho_2O_3.	Er_2O_3.	Yb_2O_3.	%.	Dy_2O_3.	Ho_2O_3.	Er_2O_3.
1	16	1·5	·6	3·6	—	42	26·0	1·7	1·3
2	19	1·5	2·7	4·0	—	13	22·6	1·4	0·7
3	34	1·8	2·0	7·7	—	12	27·6	1·8	1·1
4	10	1·8	3·6	6·7	—	9	31·4	2·5	2·3
5	9	2·8	1·8	10·2	6·2	16	30·8	3·7	3·8
6	8	0·7	1·8	18·9	15·7	6	23·4	6·4	11·2
7	4	0·0	0·8	14·5	50·0	2	26·7	7·9	25·3

TABLE IV.

Input of mixed oxides : (*a*), Nd, 85% + Pr, 15%; (*b*), (*c*), (*d*), and (*e*), La, 12·5% + Pr, 87·5%.

Col. (*a*) : NH₄ salt of " enta " Pr and Nd oxalates, and oxalic acid.
,, (*b*) : Na ,, ,, La ,, Pr ,, ,,
,, (*c*) : Na ,, ,, La ,, Pr succinates, and Cu acetate.
,, (*d*) : K ,, ,, La ,, Pr ,, ,,
,, (*e*) : NH₄ double citrates of La and Pr, and oxalate ion.

Fraction.	(a) %.	Pr_6O_{11}, %.	(b) %.	La_2O_3, %.	(c) %.	La_2O_3, %.	(d) %.	La_2O_3, %.	(e) %.	La_2O_3, %.
1	27	16·2	2	25	43	19·6	36	20·3	11	13·2
2	10	16·5	11	23	39	8·5	15	15·6	40	16·0
3	26	16·5	22	15·5	18	4·6	26	11·3	16	13·2
4	23	13·0	10	17	—	—	13	6·0	24	11·2
5	11	9·4	12	13	—	—	7	2·4	7	9·5
6	3	7·2	33	7	—	—	3	16·3 *	2	9·2
7	—	—	10	2·7	—	—	—	—	—	—

* A small final precipitate obtained by oxalic acid and obviously containing potassium oxalate.

Table III*a* shows the result of operating with a concentrated solution of crude yttrium oxide of apparent molecular weight of 250, which had been freed from terbium and earlier earths in the series, and partly fractionated as basic nitrates till considered too poor in coloured earths to repay further extraction. A similar run was done at ten times the dilution, and showed only a

slight improvement in separation. Thus erbia rose in fraction 6 from 19 to 23%, and ytterbia from 50 to 56%, and it was not found at all in fraction 5 of the dilute solution. The effect of dilution is thus of minor importance and is overridden by considerations of convenience. It should be noted that second and third quantities of yttrium nitrate solution together with ammonium oxalate were added to the original enta–oxalate solution, so that not much change in composition of fractions 1—3 of Table III*a* was to be expected. 0·4 Mol. of oxide (100 g.) was here processed in 600—800 ml., though not more than 40 g. were in solution at any one time. It appears that even more (0·6—0·8 mol.) might still have given satisfactory results.

Table III*b* shows the result of operating with a mixture rich in dysprosium. Very little change in dysprosium content relative to yttrium took place. Holmium, however, is seen more clearly than in Table III*a* to be collecting at the tail.

Table IV*a* presents praseodymium contents of fractions obtained by operating with a mixture 85% Nd_2O_3 + 15% Pr_6O_{11}. Further systematic fractionation would be required to enable an assessment of the utility of enta for separating these two oxides, but the prospect is not unfavourable. It may be noted that in Table II the Pr : Nd ratio is seen to change from 1 : 4 in fraction 1 to 1 : 6 in fraction 3.

Table IV *b*, *c*, *d*, and *e* illustrates the change in lanthanum content of fractions obtained under various conditions by precipitating the same mixture of Pr_6O_{11}, 87·5% + La_2O_3, 12·5%. Table IV*b* shows the outcome of using the sodium salt of enta on the oxalates. The ammonium salt was also used, but not all the fractions were analysed. The first and second small precipitates contained 14% and 18% of La_2O_3, respectively. At various times it has been found that poor separation was shown by the first precipitate. This is thought to have been due to working at too high a pH, with solutions containing metastable hydroxide. Values over 8·5 seem undesirable. Precipitates from basic solution were always fine or even unfilterable, though easily centrifuged. The last fraction from the ammonium salt (32%) contained 3·9% of La_2O_3. The amount of lanthanum therefore does not appear to be appreciably different from the content of the tail fractions from the sodium salt.

Table IV*c* and *d* shows the results of co-ordination of succinates with the sodium and potassium salts of enta respectively. The complexes were then broken by adding cupric acetate. The copper took the place of the lanthanon, which was precipitated as succinate. By this method little change in pH occurred during the fractionation.

Table IV*e* gives the effect of formation of a complex with ammonium citrate and then reprecipitation by addition of first ammonium oxalate and then oxalic acid. Large amounts of the latter were required before quantitative precipitation could be brought about. The separation achieved is seen to be much inferior to any of the enta series. Whereas these gave La_2O_3 between 25 and 3%, the citrate series varied only between 16 and 9%.

The effect of conditions on the degree of separation achieved by means of breaking the complex in enta solutions of the lanthanons appears to be small. Displacement of lanthanon by copper at constant pH in place of displacement of enta by oxalic acid by lowering the pH, or use of co-ordinated succinates in place of oxalates are all without any large effects upon the degree of separation brought about. Oxalate seems slightly superior, and its use is easier and cheaper.

It has been found that 1 mol. of enta will cause solution of 1 g.-atom of a lanthanon. The simple salts of lanthanon–enta are insoluble, and have the formula LnH (enta) (Brintzinger, Thiele, and Muller, *Z. anorg. Chem.*, 1943, **251**, 285), and it seems likely that $(NH_4)_3 \left[Ln \begin{array}{c} (enta) \\ C_2O_4 \end{array} \right]$ the highly soluble alkali or ammonium oxalate complexes, which, however, may be obtained crystalline, must have a formula like that inset.

The use of ethylenediaminetetra-acetic acid or future improved co-ordinating agents of similar type gives promise of effecting revolutionary simplification of the purification of the lanthanons, except dysprosium and those in the series near to it. The reagent appears to be most efficient for the four heaviest lanthanons, but it is likely to be of use also with the lightest.

EXPERIMENTAL.

Precipitation of Crude Gadolinite Earths (Table II).—The oxides used (Fractions 1 and 2 of Table I) varied in molecular weight from 318 to 292 and contained very little cerium. A stock ammonium enta solution was prepared by dissolving H_4 enta in sufficient ammonia to give $H_2(NH_4)_2$ enta equivalent to 250 g./l. of H_4 enta. 24 G. of oxalate were formed into a complex with sufficient of this solution (60 ml.) with added ammonia to give a clear solution at the b. p. To this was added a quantity of nitrate solution. The precipitation of the oxalates has already been described, and with slight modifications was in accordance with the procedure generally adopted in all the experiments here reported. The volume of solution was 500—700 ml., and the total oxide 10 g.

Separation of Yttrium Earths, and Determination of the Enta Requirement for Complex Formation (Table IIIa).—25 G. of impure yttrium oxide (*M*, 250; 0·10 mol.) were converted into oxalate. This required 250 ml. (0·214 mol.) of the above stock enta solution, thus demonstrating a 1 : 1 ratio between enta and lanthanon in the complex. The later oxalate precipitates were coarse and appeared to be mixtures.

The precipitation of H₄ enta even at the b. p. will occur when a lanthanon solution of good working concentration is progressively acidified with oxalic acid. Mixed precipitates of oxalate and H₄ enta, or possibly acid or normal lanthanon enta salts or mixed enta–oxalato-salts, are then encountered. When rich in oxalates, the precipitates may most conveniently be ignited, but when rich in enta, the whole of the lanthanon can be removed by boiling the precipitate with a quantity of water, filtering the solution hot, and allowing it to stand overnight. The lanthanon passes into solution at the b. p., but is precipitated as oxalate together with a little H₄ enta or its normal salt, etc., on cooling. The mother-liquor is again boiled with the H₄ enta, and the process repeated so long as lanthanon continues to be extracted. Two or three repetitions give a clean separation of lanthanon, and recovery in a pure state of the bulk of the enta at the lutecium end of the series. Since oxalic acid is sufficiently strong to displace H₄ enta, the final working solution when containing about 8% of oxalic acid at room temperature contains very little enta, and so has little co-ordinating power. The excess of oxalic acid ensures full precipitation of the lanthanon. This has been proved by evaporation to dryness, and ignition of the residue from 100 ml. of solution. No trace of lanthanon was found in it after working on a material rich in ytterbium and lutecium. The last traces of lanthanon oxalate, however, are precipitated only after several days, and may be contaminated with iron.

The Normal Lanthanon–Enta Salts.—Brintzinger *et al.* (*loc. cit.*) have found NdH enta and LaH enta to be insoluble or even highly insoluble salts. By direct union of the oxides of gadolinium and ytterbium and H₄ enta, the author has found that slightly soluble salts result. The solubility of the series appears to increase from lanthanum to lutecium. In an attempt to prepare the oxalate of ytterbium, an insoluble salt containing enta was obtained. However, on precipitation of sufficiently dilute ytterbium-enta solution pure oxalate was obtained. Enta salts will fuse and behave quite differently from oxalates when ignited. The possibility is being explored of fractionating the ytterbium group earths with little or no univalent metal present.

An ammonium–yttrium–enta salt has been prepared as short needles, but it is too soluble and sluggish in crystallisation to afford a means of fractionation.

Dysprosium Fraction (Table IIIb).—5 G. of oxide were used of which half was converted into a complex as oxalate and half then added as nitrate. The initial solution was very alkaline, and the poor separation obtained in the first fraction is believed to be due to this. The experiment was carried out as before with a final volume of about 400 ml.

Separation of Neodymium and Praseodymium (Table IVa).—The oxide used (10 g.) consisted of Nd₂O₃, 85% + Pr₆O₁₁, 15%. 7·5 G. of oxide were formed into a complex with oxalate, and 2·5 g. added as nitrate to a solution of pH 8·5. Subsequent additions of oxalic acid were made. The final precipitate was crystalline and appeared free from H₄ enta, yet on ignition it behaved differently from a pure oxalate, so it is possible that it was a double enta–oxalate salt.

Separation of Lanthanum and Praseodymium (Table IVb, c, and d).—Tests were made with both ammonium and sodium as univalent cation, but no pronounced difference resulted. Succinates were also tried, both sodium and potassium being used as cations. The precipitation by cupric acetate was apt to be delayed and then sudden. The pH was about 7 and the precipitates required to be centrifuged. When the pH was lowered, not all the succinate would precipitate. No advantages were gained by the use of succinates.

Separation of Citrate (Table IVe).—Ammonium citrate was added to a praseodymium nitrate solution, but only a partial precipitation occurred. Enough was then added again to clear the hot solution. Two precipitates were obtained by adding ammonium oxalate, but further precipitates were only obtainable by using oxalic acid.