937. *The Separation of the Lanthanons with the Aid of Ethylenediaminetetra-acetic Acid ("Enta Acid"). Part IV.* Sodium Lanthanon Sulphate Precipitation from Sodium Lanthanon Enta Solution.*

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Comparison of precipitation of sodium lanthanon sulphate from ordinary cationic lanthanon solutions, and from solutions of, mainly, sodium lanthanon enta but containing also some cationic lanthanon shows much sharper segregation of individual elements in the case of the enta solutions. The selective action of double sodium sulphate precipitation is augmented by a selective rejection from the enta complex of the more strongly basic elements. Least advantage is gained for the triad dysprosium, holmium, and yttrium, the exact position of the last depending upon experimental conditions.

A salt $4Na[Ln\ enta],H_4enta,24H_2O$ reported in Part III* is in fact $Na[Ln\ enta],6H_2O$.

LITTLE is known of the lanthanon salts of ethylenediaminetetra-acetic acid, but members of three series have been described: (*a*) LnH enta (Ln = La or Nd; Brintzinger *et al.*, *Z. anorg. Chem.*, 1943, **252**, 285); (*b*) Ln_4enta_3 (Ln = Y; *idem, ibid.*, 1948, **256**, 641); (*c*) Na[Ln enta] (Ln = Nd; Moeller and Brantley, *J. Amer. Chem. Soc.*, 1950, **72**, 5447). The salts of (*a*) and (*b*) are described as simple, but coloured salts of type (*b*) give absorption bands having the characteristic sharpening associated with complex salts. The salts of type (*c*) are very stable, and complex stability increases with decreasing lanthanon basicity. Use of the varying stability of the complex lanthanon enta salts in order to augment the separational effect of sodium lanthanon sulphate precipitation is now described. The complex salt involved in the series from lanthanum to holmium is of type (*c*), but from erbium to lutetium its nature is not determined.

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* Part III, *J.*, 1951, 3057.

Five different concentrations of lanthanons covering the whole range of elements were examined for efficiency of separation by double sodium sulphate precipitation in presence of a large proportion of the complex sodium lanthanon enta salt. Since the complex portion of the lanthanons is not precipitable from a reaction mixture of simple and complex salts, only a partial precipitation can be effected in the double sulphate process. Hence, when the reaction stops it can be restarted by supplying more simple salt, or decomposing some complex lanthanon salt by acidification. Both methods are useful in practice, the former at early stages and the latter towards the end of a precipitation operation; alternatively, Beck's exchange method may be applied (*Mikrochem. Acta*, 1948, **33**, 344), another metal giving more stable complexes than the lanthanons being added to wrest the complexing agent from them. Beck used copper sulphate to break down lanthanon nitrilotriacetates in a fractional oxalate precipitation. It can be used similarly to promote double sulphate precipitation with enta solutions, since a soluble sodium copper enta salt and lanthanon sulphate are formed. In this work the sodium lanthanon enta salt has usually been allowed to crystallise out when reasonable quantities of sodium sulphate no longer give much more double sulphate precipitate. A portion was then collected and treated with excess of hydrochloric acid, yielding enta acid and lanthanon chloride. The latter was then returned to the warm reaction mixture, and another crop of double sulphate formed by further heating. When after several repetitions no more enta salt crystallised, only elements giving easily soluble double sodium sulphates remained in solution. These elements do not form insoluble acid enta salts, LnH enta, like the cerium-group elements, so treatment of the solution with mineral acid now yields enta acid, after removal of which double sulphate can again be cropped.

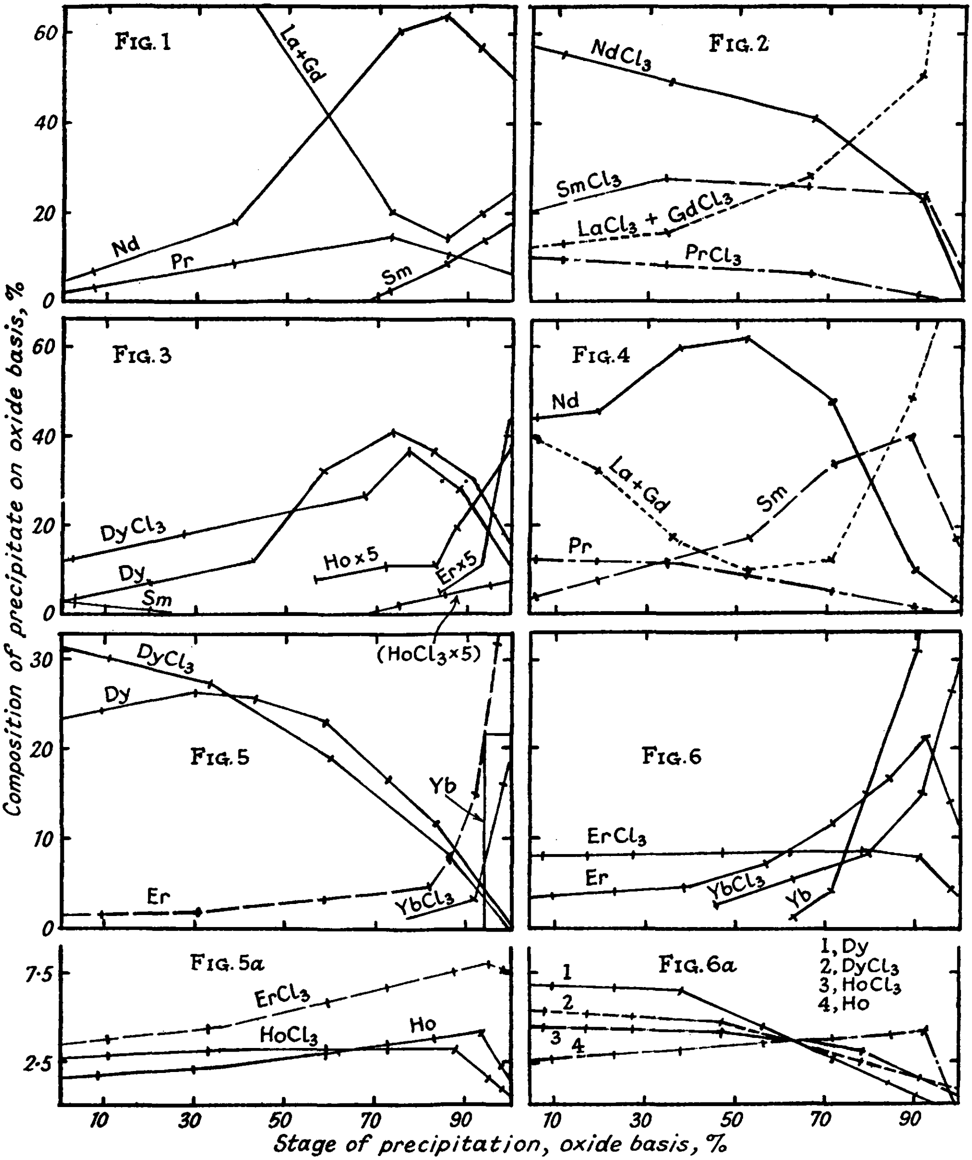
The concentrates examined were (1) a cerium-group mixture similar to that found in monazite after removal of most of the cerium (Fig. 1); (2) a samarium and gadolinium concentrate (Figs. 2 and 4); (3) a gadolinium and dysprosium concentrate with some yttrium (Fig. 3); (4) a dysprosium and yttrium concentrate (Fig. 5); (5) a concentrate of yttrium- and ytterbium-group elements (Fig. 6). Except with the first mixture parallel precipitations for the purpose of comparison were made in each instance by classical procedure on chloride solutions; but since here with the cerium group it is well known that the operation is separationally ineffective, it was omitted. Each concentrate was precipitated in 5—10 fractions as sodium lanthanon sulphate and these were individually converted into oxide and then analysed as far as possible spectrophotometrically in chloride solution. Compositions of precipitates change continuously from start to finish, but each fraction taken covers a certain percentage range. Thus if the first fraction consists of 14% of the whole, its composition is represented at its mid-point in the figures, *i.e.*, 7% on the horizontal scale. The proportion of individual oxides as determined in each oxide fraction is plotted vertically.

Fig. 1 shows the effect of fractionation on mainly sodium lanthanon enta in the cerium group. Neodymium rises from a concentration of 5% at initiation of precipitation to 64% on the oxide basis at the stage of 85% precipitation and then falls to 50% at the finish. Praseodymium is seen to rise and fall comparatively little as it occupies a central position between lanthanum and neodymium, the two main constituents of the mixture, but the Nd/Pr ratio changes significantly. Samarium is concentrated in the last 30% of the precipitate. The two colourless earths are determined by difference, lanthanum concentrating at the head and gadolinium at the tail. Hence, we may conclude that the initial precipitate is about 92% lanthanum. The colourless constituents, after falling to a minimum at 85% precipitation, rise again at the tail as gadolinium collects here. Since it collects even more effectively than samarium we can conclude that there is very little except in the last 15% of precipitate. As already stated, classical procedure would show very little segregation of the earths, except gadolinium at the tail.

Figs. 2 and 4 show effects of precipitating a cerium-group mixture having an enrichment of samarium and gadolinium, and perhaps some yttrium present. Good segregation of gadolinium is seen in Fig. 2 to have been brought about even by classical procedure, but the separation of the other constituents is slight compared with that achieved by use of complexing agents and represented in Fig. 4. The case of samarium is perhaps the most striking. The last 10% of precipitate, mainly gadolinium, being neglected, samarium varies only between 19 and 27% in Fig. 2, but between 3 and 40% in Fig. 4. Two or three

FIGS. 1, 3, 5, *and* 5A. FIGS. 2, 4, 6, *and* 6A.

Fractionation effect of double sodium–lanthanon sulphate precipitation from sodium lanthanon enta (Ln *symbol only*), *or* $LnCl_3$ *solutions.*



Approximate proportions of oxides present in the materials fractionated.

Fig. 1, La 42, Pr 7, Nd 44, Sm 3, Gd 4? %.

Figs. 2 and 4. Pr 7, Nd 44, Sm 22, La + Gd (by diff.) 27%.

Fig. 3, Gd + Tb 55?, Dy 22, Y 13? %.

Fig. 5, Dy 19, Ho 3, Er 6, Yb 2, Gd + Y (by diff.) 70%.

Fig. 6, Dy 3, Ho 3, Er 8, Tm 1·5, Yb 8, Y + Lu (by diff.) 76·5%.

applications of this new double sulphate procedure should enable a very rapid concentration of samarium to be obtained from monazite earths and prove a useful alternative to double magnesium nitrate fractionation for the isolation of crude samarium.

Fig. 3 shows the initial concentration of dysprosium in gadolinium to be about one-quarter as great when enta solution is used as when chloride is used, in the case of the particular mixture of earths studied. This contained about 22% of dysprosium and 55% of gadolinium and terbium, so that a ratio of 1 : 2·5 fell to 1 : 4 in chloride solution and 1 : 16 in enta solution. Holmium and erbium were scarce in the mixture, the precipitation of which is represented in Fig. 3, but it is evident that they have been eliminated more effectively by the use of enta. Their concentrations have been multiplied here 5-fold for clarity in plotting.

Figs. 5 and 6 show holmium concentrating slightly in the tail of a holmium–yttrium mixture, but very little separation is shown when chloride solution is used. By use of the sodium lanthanon enta salt solution the separation of yttrium and erbium is rendered much easier than heretofore. Indeed, all the elements precipitating subsequently to yttrium are found to undergo good segregation. Fig. 6 shows ytterbium absent from early fractions but increasing to 50% at the tail in the enta series on precipitating a crude yttrium material with an initial 8% of ytterbium. After allowance for the presence of at least 10% of lutetium + thulium, the yttrium content cannot be more than 40% at the tail. The Y/Er ratio is then about 2 compared with 20 in the first fractions. The ratio remains around 10 throughout the chloride series. In subsequent larger-scale work considerable improvement even on the foregoing was found (Table 2). In the Fig. 5 series the Y/Er ratio varied between 2·3 and 33 when enta was used, *i.e.*, 14-fold, compared with a 2-fold variation when chlorides were used. Thulium is not shown in Fig. 6. Estimates were rather erratic, but showed that, as was to be expected, it accumulated between erbium and ytterbium. This is confirmed in Table 2. Figs. 5*a* and 6*a*, drawn to double vertical scale between 0 and 10%, make the behaviour of some of the scarcer elements of the Figs. 5 and 6 series clearer.

TABLE 1. *Course of a sodium lanthanon sulphate precipitation with material mainly in the form of sodium lanthanon enta,* Na[Ln enta].

	In			Out	
	Lanthanon or H_2SO_4	Na_2SO_4 or $10H_2O$, kg.	Fraction no.	Double sulphate, kg. (damp)	Colour of oxide
YW 2	23 Moles $LnCl_3$ 2·7 Kg. NaOH 5 Kg. H_4 enta	2 (10)	1	3	Cocoa
	4·5 Moles $LnCl_3$	2 (10)	2	2	,,
	4·5 Moles $LnCl_3$	2·5 (10)	3	2 + 2 Kg. Na[Ln enta], (A)	,,
	(A) $\longrightarrow LnCl_3$	3 (10)	4	1·5	,,
YW 6	6·7 Moles $LnCl_3$		5	1·5	Rust
		1 (0)	6	1·4 + Na[Ln enta], (B)	
	(B) etc. $\longrightarrow LnCl_3$		7	1·1	Light brown
YW 7	7 Moles Na[Ln enta]		8	1·1	
		2 (10)	9	1·0 + 2·5 Kg. Na[Ln enta], (C)	
		2 (10)	10	0·5	
	(C) $\longrightarrow LnCl_3$	0·5 (0)	11	1·4 + 1·5 Kg. Na[Ln enta], (D)	
	(D) $\longrightarrow LnCl_3$	0·75 (0)	12	1·2	
		1 (0)	13	1·4	
	H_2SO_4, 50 ml.		14	0·7	
YW 10	1·5 Kg. $NaLn(SO_4)_2,H_2O$	0·5 (0)	15	1·2	
	,,		16	1·7	
	,,		17	1·0	Pale cream
	,,		18	1·0	
	H_2SO_4, 167 ml.		19	0·4	Pale rose
YW 11	4 Moles $Ln_2(SO_4)_3$	0·5 (0)	20	2·0	
	H_2SO_4, 133 ml.	0·5 (0)	21	0·7	
	,, 300 ,,	0·5 (0)	22	0·6	
	,, 200 ,,		23	1·0	
	,, 150 ,,		24	1·0	Strong rose
	,, 150 ,,		25	0·9	
	,, 150 ,,		26	0·8	White

The experiments leading to Figs. 1, 2, 4, 5, and 6 were each done with 30—40 g. of oxide in a solution volume of under 800 ml. For Fig. 4, the excess of enta was taken up by adding copper sulphate. Fig. 3 represents an experiment on a larger scale with about 550 g. of oxides in 8 l. A still larger operation covering all the elements was subsequently carried out, up to 35 l. of solution and nearly 10 kg. of oxides being used. Results here showed that large-scale working yielded even better results than small-scale, probably because the slower tempo of precipitation led to a greater selectivity. The whole course of the operation is summarised in Table 1 and analyses of oxides from most of the fractions are recorded in Table 2, the maximum concentration of each element being in heavy type. The material worked on in this operation has already been split into eleven fractions (" YW 1 "—" YW 11 ") by classical double sulphate precipitation procedure. Starting with complexed cerium-group elements, double sulphate precipitates were obtained by addition of solutions of simple salts progressively of terbium, yttrium, and ytterbium group elements.

In Part III (*loc. cit.*) a salt 4Na[Ln enta],H_4enta,$24H_2O$ was described. An error arose owing to a systematic use of a molecular weight of 236 instead of 292 for enta acid. The salt in question should therefore be simply Na[Ln enta),$6H_2O$. It is the same salt as is believed to be chiefly involved in bringing about the results described in the present paper.

EXPERIMENTAL

Sodium Lanthanon Sulphate Precipitation from Chloride Solutions.—This followed conventional lines. In the yttrium group, hot solutions were used with addition of sodium chloride to obtain fuller precipitation (Marsh, *Nature*, 1949, **163**, 998). A final precipitate of hydroxide was made. Usually 5—8 fractions were taken.

Fractionation of Sodium Lanthanon Enta Salt Solution.—The pH of a hot solution of the salt Na[Ln enta],$6H_2O$ was adjusted. For the cerium-group precipitation a value of 5·5—6 was found suitable. High values caused the precipitate to be too fine, and with lanthanum and other early members of the series present low values were likely to cause precipitation of the acid salt, LnH enta. This had to be avoided, or loss of selectivity resulted. Control by indicator paper was sufficiently accurate. The stirred solution at about 50° was treated with sodium sulphate, and heating continued cautiously. The sudden precipitation which was often troublesome in precipitating the yttrium-group as double sulphates was less likely to occur from enta solutions. Nevertheless, particularly with the cerium group, slow initiation of precipitation so that not too many nuclei were formed was desirable. Good grain size was thus obtained and selectivity promoted. Precipitation usually occurred at 60—80°. The presence of carbonate was undesirable, but the solution could be acidified sufficiently to boil out carbon dioxide if necessary. Solutions stronger than equivalent to 80 g. of oxide per l. were found inconvenient in the cerium group owing to the tendency of enta salt to crystallise during filtration. Use of a large excess of sodium sulphate was avoided, but when it failed to give further precipitation readily the solution was allowed to cool overnight. Most of the enta salt then crystallised. A suitable portion of it was collected, washed free from sulphate, made into a hot concentrated solution, and treated quickly with excess of hydrochloric acid till the colour became permanent. Slow addition of acid was liable to produce a precipitate of insoluble acid enta salt which was difficult to decompose, but it was not difficult to avoid its formation. A crop of enta acid soon began to separate, and was collected next day. Then the solution was roughly neutralised and returned to the reaction mixture, the pH was adjusted, and the solution heated. Another crop of double sulphate was now obtainable. This cycle of operations was repeated till no more enta salt crystallised. The solution then contained much sodium chloride and some sulphate. Heating by flame of glass vessels containing solid Na[Ln enta] was avoided. The liquor was heated separately from the solid and then dissolved it readily. Finally, the reaction mixture was made either acid or strongly alkaline. The acid solution slowly deposited enta acid and then gave a further double sulphate crop on heating. Oxalic acid brought down a final crop of oxalate. With insufficient alkali the final solution gave on boiling a troublesome hydroxide, but with a large amount of alkali it was readily filterable. It was found possible to precipitate fully as hydroxide all the earths showing visible absorption bands, but a large excess must be used. Acidification and final oxalate precipitation is the preferable method.

Fractionation with the Aid of Copper Sulphate.—A solution of copper and sodium sulphates, each of molar concentration, was used for the fractionation represented in Fig. 4. 100 g. of sodium lanthanon enta in 400 ml. at 80—85° were treated dropwise with 50 ml. of sulphates. Precipitation started slowly and in 15 min. a coarse granular precipitate had formed (=2·3 g. oxide). A second crop was obtained with another 20 ml. of sulphates in 10 min. with a further 10 min. of hot digestion (=5·6 g. oxide). Seven crops were taken in all in this manner. One atomic proportion of Cu per Ln had then been added, but 20 g. of additional sodium sulphate were added for the last precipitation. Enta acid was recovered by addition of hydrochloric acid and excess of ammonia was then found to give only a trace of hydroxide precipitate.

Fig. 3 represents only the latter half of a larger-scale operation than the other experiments. 550 g. of oxides, largely freed from samarium and europium, were made into enta salt and some of the fractions from the Gd–Dy region of the Na[Ln enta],$6H_2O$ fractionation reported in Part III (*loc. cit.*) were successively added in the form of chloride solutions. There were about 8 l. of solution. Twelve fractions amounting to 1300 g. of double sulphate were taken. The first three fractions contained neodymium and up to 7% of samarium, but only 0·7% of dysprosium. Only when no more chloride solutions were available was the series shown in Fig. 3 started, and fractions 13—22 obtained (1440 g.). Terbium was seen by oxide colour to be maximum in fraction 16 and absent in 22. Fractions 18—22 were obtained by adding copper sulphate (320 g.) to the solution when it was found that no more enta salt would crystallise from it.

Large-scale Precipitation (*Tables* 1 *and* 2).—Material from fractions ("YW") 2, 6, 7, 10, and 11 (final) of a double sodium sulphate precipitation of a chloride solution of yttriotungstite (formerly erroneously named thoriotungstite) was available. Spectrophotometric analyses of these fractions expressed as derived oxide percentages were :

YW 2 : Pr 6·4, Nd 23·4, Sm 15·8, La, Ce, Gd, etc. (by diff.) 54%.
YW 6 : Dy 19, Ho 3, Er 6, Yb 2, Gd + Y (by diff.) 70%.
YW 7 : Dy 13·5, Ho 3, Er 5·4, Y, etc. (by diff.) 78%.
YW 10 : Dy 3, Ho 3, Er 8, Tm 1·5, Yb 8, Y, etc. (by diff.) 76·5%.
YW 11 : Ho 0·7, Er 6, Tm 1·6, Yb 16·3, Y, etc. (by diff.) 75·4%.

YW 2 as dried hydroxide was treated with cold 4N-hydrochloric acid. A little dissolution of cerium and liberation of chlorine occurred. Sufficient enta acid (5 kg.) and sodium hydroxide were added to part of the chloride solution (17 mols.) to convert it into Na[Ln enta],$6H_2O$. Cropping of sodium double sulphate was then started. As further lots of YW 2 chloride solution, and then YW 6 and YW 7 chlorides were added, a large amount of sodium chloride accumulated in the reaction liquor. After fractions 3 and 6 of double sulphates had been taken, and the complex salt crystallised, the mother-liquors were acidified, the resulting enta acid collected next day, and then the mother-liquors fully precipitated as double sulphate. This precipitate was converted into sodium lanthanon enta and redissolved together with the main body of the same salt in fresh water. Deposits of Na[Ln enta],$6H_2O$ were at first always obtained overnight, and from time to time some of them were converted into chloride, their content of enta acid being withdrawn; but in the latter half of the operation they were not

TABLE 2. *Analyses of oxides derived from sodium lanthanon sulphate fractions as shown in Table* 1.

						Oxides.						
Fraction	La [1]	Pr	Nd	Sm	Gd [2]	Dy	Ho	Y [3]	Er	Tm	Yb	Lu [4]
1	**64**	8·5	21	7								
2	43	**11·5**	33	13								
3	22	10·6	40	18								
4	3	10·0	**53**	30	4							
5	tr	4·5	34	**30**	31							
6		1·0	9	26	**50**	5		9				
8			2	1·6		23						
9					17	24	1·9	57				
11						23	1·9		1			
12						**24**	3·1		3			
13						19	3·4	74	3·5			
15						11	**3·6**	80	5·5			
17						4	2·0	89	5·1			
19						2	1·7	**92**	4·6			
21						1·3	1·9	87	9	0·9		
22							1·8	86	10	2·3		
23						0·3	1·9	69	19	2·4	6	
24							0·0	28	**28**	6·8	32	5
25								10	17	**6·8**	57	10
26								2	3·5	5·7	**72**	18
27									2·3	3·8	64	**30**

[1] By difference and including Ce. [2] By difference and including Lu and Tb. [3] By difference. Where gadolinium is also likely the figures for both gadolinium and yttrium, if given, are based on apparent atomic weight determinations. [4] By difference, but the apportionment of this difference between Lu and Y is conjectural.

encountered. The fraction YW 10 of crude sodium yttrium sulphate was soluble in ice-water to the extent of 400 g./l., and was therefore added as solution. It was used in four portions. The fraction YW 11 was in the form of crude oxide and was added as such, and the warm reaction mixture treated with sulphuric acid till it remained acid. Dissolution, however, remained only about 50% effective. At this stage acidification produced no insoluble enta salt, and was used directly on the reaction mixture to remove enta acid. At worst, at boiling point a mixed crop of double sulphate and enta acid was produced which was resolvable by leaching out the sulphate with cold water. If not too much mineral acid was added at once, the double sulphate was removable from the hot solution and the enta acid only appeared on cooling overnight (Table 1). The crop weights are for damp filter-cake, $NaLn(SO_4)_2,H_2O$, except for the last few crops which contained much more sodium sulphate, and doubtless approximated to the known salt $Na_5Er(SO_4)_4,3{\cdot}5H_2O$. Precipitation from a brine solution, however, appeared to give the former salt even at the tail end. Early crops were twice washed with hot water, but the more soluble crops could not be so treated satisfactorily. The final liquor (15 l.) contained much sodium hydrogen sulphate. The pH, however, was low enough to precipitate enta acid. When neutralised at the b. p. a crop of sodium sulphate was obtained but it contained no lanthanon. Further alkali precipitated iron which was present. This was removed, and 1·5 g. of Ln_2O_3 recovered from it. The iron-free solution, when made N with respect to sodium hydroxide, gave a precipitate $\equiv$ 10 g. of Ln_2O_3. More alkali gave no further yield. Only a trace of organic matter was found to be present and the liquor was rejected. Addition of limited oxalic acid (about 5 g./l.) gives on storage an easier recovery of remaining lanthanon than the use of alkali.

Spectrophotometry.—The yttrium group oxides were in general made into slightly acid chloride solutions of 50 or 100 g./l. in 4-ml. graduated tubes. Much colourless earth tends to broaden but render less intense the absorption bands of other earths. Estimates of low concentrations therefore tend to be too low, resulting in an apparent increase in the total quantity of a coloured earth when it undergoes good concentration. Thus in Fig. 3 more erbium seems apparent after concentration from enta solution. This source of error may give a slight exaggeration of the superiority of enta. Estimates were made at once after preparation of the solutions. Lower concentrations within the known limits of the validity of Beer's law could be used with the cerium group. Estimates were made with a Beckman D.U. spectrophotometer.

DISCUSSION

The improved separation by double sodium sulphate precipitation described above depends upon the easy establishment of equilibrium in a mixed solution of lanthanons in cationic and complexed forms. Whether the complex compound is molecular or to some extent ionised would not appear to matter; but high stability of the complex appears to be important. The range of stability with different complexing agents would seem to widen in the lanthanon series with an increase of average stability, just as a percentage difference between two numbers will increase in absolute value as the numbers chosen increase. Enta acid forms the most stable soluble complexes of metals in general of any reagent at present in commercial production. It is this property which has led the author to apply it to lanthanon separation in the expectation of producing wider differences between members of the series than are usually encountered.

Lanthanum is both the most insoluble as sodium double sulphate, $NaLa(SO_4)_2,H_2O$, and the least stable as enta complex, $Na[La\ enta],6H_2O$, of all the lanthanons. Hence, in a solution containing both simple and complex lanthanon salts, if equilibrium is established, there will be a greater proportion of lanthanum in the mixture forming the simple salt than in that forming the complex salt. The reverse will be true for lutetium. Now only a simple lanthanon salt will react with sodium sulphate to give a double sulphate, and so it follows that the precipitable portion of mixed simple and complex salts is richer in lanthanum than an average of the whole solution. Clearly, an improved concentration of lanthanum in the first double sulphate precipitates is to be expected from the mixed solution as compared with a similar lanthanon solution purely cationic in form. The improvement will in general be dependent upon the relative proportion of cationic and complexed lanthanon present, but in practice will be limited by diminishing precipitability as the cationic form decreases, fractions smaller than 15% of the material in solution being in general undesirable.

The place of interpolation of yttrium in the lanthanon series was found to vary in different experiments. For instance, the small-scale work illustrated in Figs. 5 and 5*a* shows holmium concentrating at the tail and dysprosium at the head, *i.e.*, they are split apart by yttrium; but in the large-scale work (Table 2) yttrium is interpolated as in classical double sulphate precipitation. Two factors contend to govern the position of yttrium in the enta double sulphate series—its basic strength and the solubility of the double sulphate. Only the latter is operative in the classical process. The slower tempo of the large-scale work has favoured the solubility factor at the expense of the basicity factor. It was noted in Part I (*J.*, 1950, 1819) that in oxalate precipitation from enta solution yttrium came down with or before dysprosium. Here there is little difference in oxalate solubilities and the basicity factor is therefore predominant and places yttrium yet earlier in the series.

The practical operations involved in the use of enta complexes to hold back from precipitation the weak bases in the lanthanon series are rather more troublesome than operations in ordinary double sulphate precipitation, but the increase in separational efficiency, which is general throughout the whole series, renders their use desirable.

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