Lanthanon Complexes with Ethylenediaminetetra-acetic Acid. Part IV.*

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The displacement of lanthanons from anionic complexes with ethylenediaminetetra-acetic acid (H_4enta) by added cationic lanthanons has been studied spectrophotometrically. The displacement proceeds in order of decreasing atomic number and stability constant of the lanthanon complex; *i.e.*, the cation of a lanthanon of higher atomic number and higher stability constant will displace from anionic " enta " complex a lanthanon of lower atomic number and lower stability constant.

This principle of displacement has been applied to lanthanon separation, pure [Ln enta]$^-$ complexes being progressively converted into cationic form by the addition of calculated quantities of cationic lanthanon. The lanthanon displaced from anionic complex is then extracted from solution by a cation-exchange resin. Good separations of many of the lanthanons have thus been achieved although the pairs praseodymium–neodymium and dysprosium–holmium and the triad samarium–europium–gadolinium remain recalcitrant. Lanthanum, samarium, thulium, ytterbium, and lutetium are readily prepared in good purity by this technique, and satisfactory concentrations of terbium and dysprosium are readily achieved.

All the lanthanons form with ethylenediaminetetra-acetic acid (H_4enta) anionic complexes of the type [Ln enta]$^-$. In spite of the comparatively narrow range of the overall stability constant values for these complexes (log $\bar{K}_{\text{La}}$ 15·3, log $\bar{K}_{\text{Yb}}$ 18·7; Part III *), attempts have been made to use the differences in stability of the individual complexes as a basis for improved method of lanthanon separation. Except, however, in the isolated instances of lanthanum (Vickery, *J.*, 1951, 1817), praseodymium and neodymium (*idem, J.*, 1952, 4357), and in the gross separation of light and heavy lanthanons (Marsh, *J.*, 1951, 3057; 1952, 4804), only mediocre separations have been achieved although even these have shown many improvements upon classical methods of lanthanon fractionation.

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* Part III, *J.*, 1952, 1895.

The formation of anionic lanthanon complexes exerts a profound effect upon the absorption spectra of the coloured lanthanons (Vickery, Part II, *J.*, 1952, 421), consisting of a splitting of the absorption bands and a considerable increase in their extinction coefficients. Exchange of lanthanons between anionic and cationic forms has therefore been studied by noting the effect on extinction coefficients of the absorption spectra of enta-complexed lanthanons by the addition of other lanthanons in cationic form. Figs. 1 and 2 show the progress of such exchanges with increasing quantities of added lanthanon cations, although the materials upon which the experiments are based were not necessarily in equilibrium. One of the more significant features of these figures lies in the further evidence they give of the formation only of complexes at 1 : 1 molar ratios of Ln : enta. No diminution of extinction coefficient occurs until an equivalent of cationic lanthanon is present, whereupon a sharp fall is observed to the usual value of the extinction coefficient of the cationic lanthanon initially present in anionic complex (Fig. 1). If two coloured lanthanons are present in the same system *e.g.*, $[\text{Pr enta}]^- + \text{Nd}^{3+}$, the spectra of complexed praseodymium and simple neodymium ions coexist (Fig. 2) until sufficient neodymium is present fully to displace the praseodymium from the enta complex. Then the nature of the spectra is reversed and the picture is one of complex neodymium and simple praseodymium ions. If a complex of any ratio other than 1 : 1 existed, the variation in extinction coefficient and nature of the spectra would be a more gradual one and discontinuities would be expected in the extinction coefficient graphs at ratios of Ln : enta corresponding to the formation of different complexes.

FIG. 1.

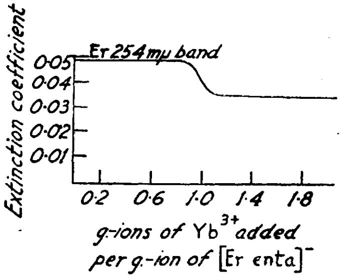
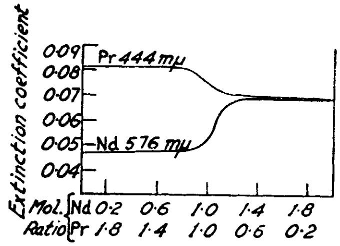


FIG. 2.



The abrupt fall in extinction coefficient indicates also that the rate of exchange is quite rapid. Further measurements showed that the exchange reaction

$$[\text{Ln}_\text{A}\ \text{enta}]^- + \text{Ln}_\text{B}^{3+} \longrightarrow \text{Ln}_\text{A}^{3+} + [\text{Ln}_\text{B}\ \text{enta}]^-$$

proceeds according to the relative stabilities of the Ln_A and Ln_B complexes, *i.e.*, at a rate determined by $\log \bar{K}(\text{Ln}_\text{B})/\log \bar{K}(\text{Ln}_\text{A})$, becoming infinitely fast when Ln_B = ytterbium and Ln_A = lanthanum.

This exchange of anionic and cationic lanthanon forms postulates the rule that the displacement series is that of decreasing atomic number, *i.e.*, *the cation of a lanthanon of higher atomic number will displace from anionic complex a lanthanon of lower atomic number.* The anionic and cationic mixture then resulting can easily be separated by treatment with an ion-exchange resin.

On this displacement and resolution of ionic forms has been founded a method of lanthanon separation. Consider the system $[(\frac{1}{3}\text{Pr}, \frac{1}{3}\text{Nd}, \frac{1}{3}\text{Sm})(\text{enta})]^-$. If, to the solution of such a system be added an additional $(\frac{1}{3}\text{Nd}^{3+})$, *i.e.*, an equivalent of the praseodymium content, the following exchange may be considered to take place :

$$[(\tfrac{1}{3}\text{Pr}, \tfrac{1}{3}\text{Nd}, \tfrac{1}{3}\text{Sm})(\text{enta})]^- + (\tfrac{1}{3}\text{Nd}^{3+}) \longrightarrow [(\tfrac{2}{3}\text{Nd}, \tfrac{1}{3}\text{Sm})(\text{enta})]^- + (\tfrac{1}{3}\text{Pr}^{3+})$$

and the cationic praseodymium can readily be removed from the system by passage through a cation-exchange resin or by batch-wise extraction with such a resin.

Marsh (*loc. cit.*) introduced a technique of lanthanon separation by fractionally precipitating the lanthanons as alkali double sulphates in the presence of enta. The efficacy of this technique depends upon the partition of lanthanons between their simple cationic forms and their anionic, enta, complexes, the cationic fraction being progressively precipitated by sodium sulphate.

This present mode of separation could of course be applied to lanthanon mixtures in bulk, but is limited by the requirement of increasing quantities of lanthanons with increasing stability of the complexes, and this increase roughly parallels the increase in rarity. Thus, in a complete separation of all the lanthanons by this system, sufficient lutetium would have to be available to displace all the preceding lanthanons. With most of the heavy lanthanons available only in little more than gram quantities, this technique therefore has been applied only to more conservative systems in which the component lanthanons have undergone a certain prior degree of fractionation and concentration. The preliminary requirements of this technique are: (i) accurate determination of the composition of the mixture to be resolved, (ii) preparation of the pure enta complex of the mixture so that no extra-complexing effects occur owing to the presence of excess of enta, (iii) the use of dilute solutions, (iv) the use of ion-exchange resins in the sodium form. The necessity of this last requisite is clear when it is realised that hydrogen resins will decrease the pH of the anionic lanthanon solution with consequent disruption of the complexes. On the other hand, the increasing sodium chloride content of the solutions must introduce variations in the stability constants of the lanthanon–enta complexes (cf. Martell *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 5745; *J. Phys. Chem.*, 1952, **56**, 993) and this may be one of the side reactions which prevent the exchange and separation being 100% effective. Replacement of the sodium resin by one in the potassium or ammonium form has an even greater adverse effect on the separations achieved.

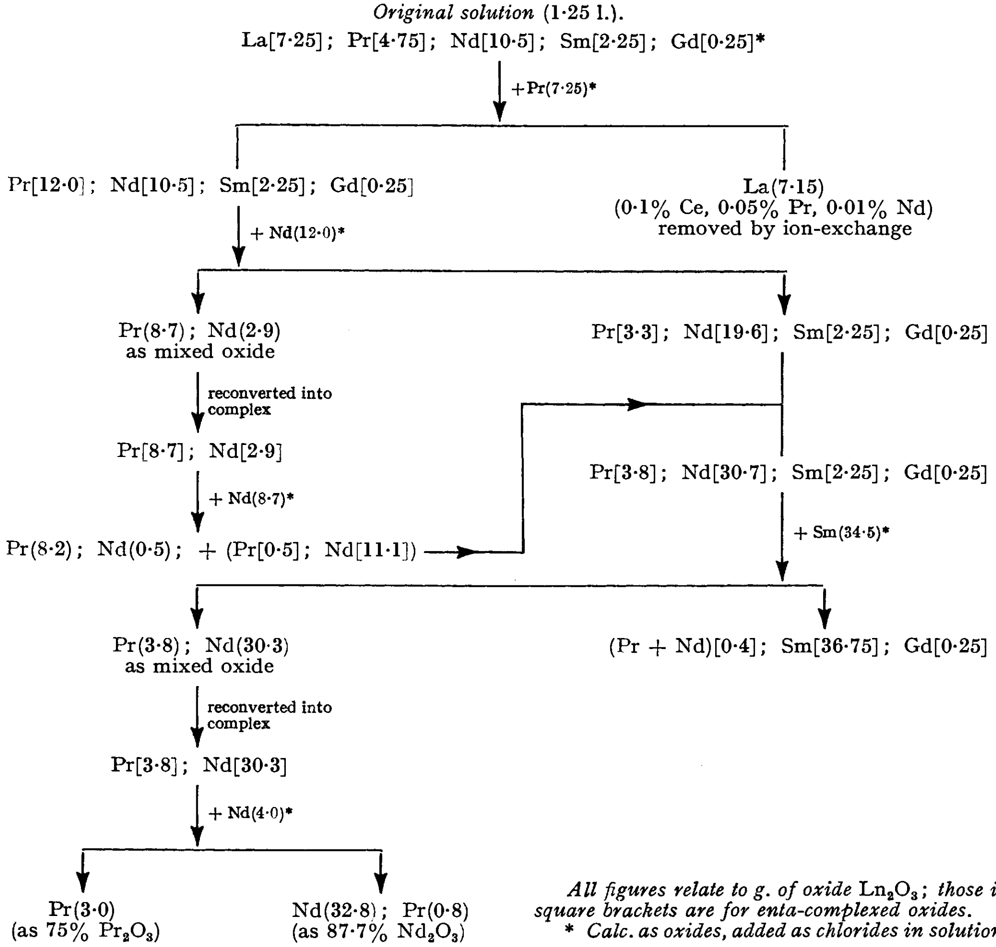
Separation of Light Lanthanons.—From a mixture of light lanthanons, lanthanum can easily be removed in high yield and purity (see Table 1); indeed, by virtue of its significantly lower tendency to complex formation than any of the other lanthanons, lanthanum is probably the most easily separated of all the lanthanons by this technique. There is a difference of 0·75 log $\bar{K}$ unit between the stability constants of lanthanum and cerium enta complexes—a much greater difference than between any other two consecutive lanthanons (average difference, *ca.* 0·30 unit). With cerium removed from the system by the conventional oxidation–hydrolysis procedures, this difference becomes 1·25 log $\bar{K}$ units (between lanthanum and praseodymium), increasing immeasurably the ease with which displacement of lanthanum from anionic complex and its subsequent removal can be effected.

The mutual separation of praseodymium and neodymium by this exchange technique is incomplete. The enta complexes of these two elements differ in their stability constant values by only 0·2 unit, and this appears to approach the limit of resolution by this technique. Part of the difficulty encountered in separating this pair may lie in the degree to which each affects the spectrophotometric determination of the other. Analytical error, however, cannot wholly account for the lack of complete discrimination between neodymium and praseodymium. It will introduce inaccuracy in the quantity of cationic neodymium required to displace the anionic praseodymium, but the contamination of praseodymium by neodymium and *vice versa* is not a fractional effect. No better separation is achieved when cationic neodymium is added fractionally to the system. However, the 3—4-fold increase in praseodymium concentration in one operation, and 4—5-fold increase in two, is not insignificant (see Table 1).

Interpolation of manganese between praseodymium and neodymium was a notable feature of previously reported ion-exchange separations (*loc. cit.*), but this separating effect was not manifest in the exchange system now studied. Addition of Mn^{2+} to the system even in excessive quantities produced no disintegration of the [Pr enta]$^-$ complex. It was quite evident that the present system was not to be compared with those previously studied in which the exchange resin played a dynamic part in the separation as distinct from its now more passive role of collector. Although it had been shown (Vickery, *Nature*, 1952, **170**, 665) that elution series, *i.e.*, complex degradation series, could vary according to the ratio of bi- to ter-valent ions, it was still not possible in this system to interpolate any element between praseodymium and neodymium.

An intensive study of the neodymium–samarium separation was unnecessary because of the excellent reduction methods available for the separation and purification of samarium. Since, however, there is a minimum concentration of samarium below which reduction techniques are relatively inefficient (Vickery, "The Chemistry of the Lanthanons," Butterworth, London, 1953), determination of the extent of samarium separation was important. With 0·45 unit difference in the stability constants of neodymium enta and samarium enta complexes an appreciable degree of separation might be expected by the displacement technique, although an efficiency as high as that of the lanthanum–praseodymium separation would be unlikely. The confirmation obtained of this is shown in Table 1. Separation of neodymium (plus residual praseodymium) from the heavier lanthanons may be considered complete in three fractionations, and concentration of samarium to that adequate for reduction purposes, in one operation.

TABLE 1. *Displacement separation of light lanthanon complexes.*



All figures relate to g. of oxide Ln_2O_3; *those in square brackets are for enta-complexed oxides.*
* *Calc. as oxides, added as chlorides in solution.*

Separation of "Middle" Lanthanons.—The term "middle" lanthanons is retained from older nomenclature to indicate samarium, europium, gadolinium, terbium, and dysprosium. The first three have proved most difficult to separate by ion-exchange techniques (*e.g.*, Ketelle and Boyd, *J. Amer. Chem. Soc.*, **1947**, **69**, **2811**) and the apparent identity of the stabilities of samarium- and gadolinium-enta complexes—log $K_{\mathrm{SmGd}} = 17{\cdot}2$—did not augur well for the application of the displacement technique to the separation of this triad. The reduction methods available for separation and purification of samarium and europium rendered a close study of the samarium–europium–gadolinium system superfluous and it was immediately obvious that no separation of this triad was likely to be achieved by the displacement technique.

Insufficient terbium and dysprosium were available to study the disruption of gadolinium and terbium complexes, so the effect of fractional addition of Y^{3+} was examined. The stability constant of the yttrium–enta complex is 18·0, placing the element at about the position of holmium in the lanthanon series. Yttrium should therefore displace (samarium–europium–gadolinium), terbium, and dysprosium from solution *en bloc.* The extent to which this gross displacement can be converted into a fractional one is seen in Table 2. No separation of the samarium–europium–gadolinium triad is evident, but

TABLE 2. *Displacement separation of middle lanthanon complexes.*

Initial solution : 1 l. containing [4·0 g. Sm, 0·6 g. Eu, 10·0 g. Gd, 0·8 g. Tb, 2·0 g. Dy, 0·2 g. (max.) Ho, 2·4 g. Y].*

17·6 g. of Y_2O_3 (as chloride solution) added fractionally. Fractions 1—7, 9—13 were cationic extracts, fractions 8 and 14 were anionic eluates.

Fr.	1	2	3	4	5	6	7	8
Wt., g.	3·80	3·80	3·32	2·44	2·15	2·07	2·07	17·7
Sm, %	37·4	27·6	23·0	19·3	8·8	4·35	2·42	—
Eu, %	8·43	4·75	2·4	0·41	—	—	—	—
Gd, %	54·0	65·3	65·5	59·5	43·5	20·8	10·2	0·85
Tb, %	0·25	2·1	5·1	9·85	8·8	4·35	1·00	—
Dy, %	—	—	—	0·41	4·16	11·6	20·5	7·00
Ho, %	—	—	—	—	0·45	0·97	1·00	0·62
Y, %	—	0·25	4·0	10·83	34·29	57·93	64·88	91·53

Frs. 4—8 re-" complexed " and treated serially with YCl_3 (75% theoretical requirement).

Y_2O_3 added, g.			Wt., g.	Sm, %	Eu, %	Gd, %	Tb, %	Dy, %	Ho, %	Y, %
1·63	→ Fr. 4 →	Fr. 9	1·74	25·8	0·6	63·2	10·7	—	—	—
	↓ Fr. 5									
1·40	→	Fr. 10	1·50	11·3	—	76·5	12·0	—	—	—
	↓ Fr. 6									
0·91	→	Fr. 11	0·88	11·4	—	62·5	15·9	10·2	—	—
	↓ Fr. 7									
0·71	→	Fr. 12	0·68	8·8	—	33·8	6·9	50·0	1·5	—
	↓ Fr. 8									
1·40	→	Fr. 13	1·71	—	—	8·8	—	80·1	4·1	7·0
	→	Fr. 14	26·0	—	—	—	—	0·8	0·3	98·9

* Unless otherwise indicated, figures given are in terms of "Ln_2O_3;" Y_2O_3 was determined by difference.

some concentration of terbium occurs in the middle of the eight fractions made. Dysprosium is clearly concentrated at the tail of the series. A second row of fractionations on Fraction 4—8 greatly increased the terbium concentration and doubled the dysprosium concentration.

No stability constant has been determined for the [Tb enta]$^-$ complex but since the separation of terbium–dysprosium is apparently more easily achieved than that of praseodymium–neodymium (see p. 1182), the difference in log $\bar{K}$ values between the terbium and dysprosium complexes must be somewhat greater than 0·2 unit. Similarly, to account for the greater separation of terbium from dysprosium than from gadolinium, the stability constant for the terbium complex must be closer to the value for the gadolinium complex (17·2) than to that of the dysprosium complex (17·75). The evidence therefore indicates the [Tb enta]$^-$ complex to have a stability constant value between 17·4 and 17·6 log $\bar{K}$ units.

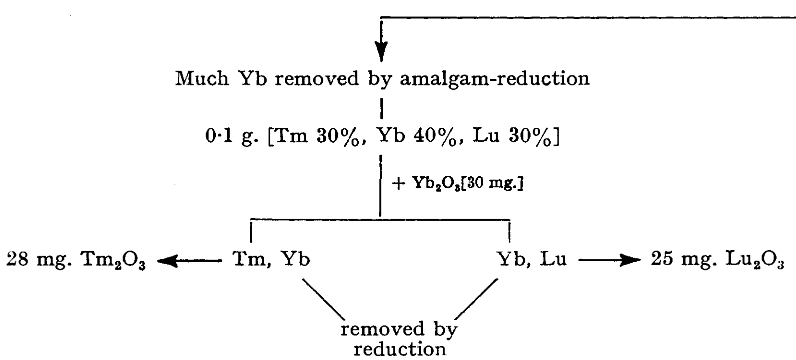
Separation of Heavy Lanthanons.—The heavy lanthanon mixture used contained insufficient holmium, thulium, or lutetium for their reported separations to have much significance. One feature of especial interest, however, was the possible separation of yttrium and erbium; the complexes of these elements differ only by 0·15 unit in their stability constant values so that little if any separation of these two elements could be expected by this displacement technique. Preferential disruption of the yttrium complex by the addition of erbium cations certainly did not effect any noticeable separation, and the fractional addition of Yb^{3+} did not give very different results (Table 3). In the double row of fractionations made, a noticeable feature is the concentration of holmium (and residual dysprosium) at the head of the series with yttrium interpolated between holmium and erbium. This indicates that the stability constant value for the [Ho enta]$^-$ complex lies between 18·0 and 17·75. Because of this, little differentiation can be expected between dysprosium and holmium. This fractional disruption of the complexes with cationic ytterbium gave some separation of yttrium and erbium but was not so effective as separation by ferricyanide precipitation. The separation of erbium from ytterbium is achieved without difficulty (0·55 unit difference in log $\bar{K}$ values). The tendency for the small amount of thulium present to remain with the ytterbium indicated that the stability of the [Tm enta]$^-$ complex is closer to that of the ytterbium than of the erbium complex.

TABLE 3. *Displacement separation of heavy lanthanon complexes.*

Initial solution : 500 ml. containing [0·9 g. Dy, 0·1 g. Ho, 2·9 g. Y, 3·8 g. Er, 0·05 g. Tm, 2·2 g. Yb, 0·05 g. Lu].

The sequence employed was that outlined in Table 2. In the first row of the series 7 g. of Yb_2O_3 as chloride were added fractionally to the initial solution to give 8 fractions (1—7 cationic, 8 anionic). These were re-complexed and each fraction again treated with $YbCl_3$. For convenience, analyses of the first row are omitted.

	9	10	11	12	13	14	15	16	17
Wt., g.	0·65	0·91	1·42	1·61	1·86	1·91	1·97	1·92	11·86
Dy, %	80·0	58·0	17·0	9·4	3·0	—	—	—	—
Ho, %	8·5	8·0	3·0	0·5	—	—	—	—	—
Y, %	8·5	24·0	57·0	58·6	40·1	24·5	9·3	3·7	—
Er, %	3·0	10·0	23·0	31·5	41·4	27·2	11·0	4·1	—
Tm, %	—	—	—	—	—	—	0·5	0·5	0·25
Yb, %	—	—	—	—	15·5	45·5	78·7	91·2	99·50
Lu, %	—	—	—	—	—	—	0·5	0·5	0·25



No lutetium being available for the study of the displacement of thulium or ytterbium complexes, the removal of ytterbium from these heaviest lanthanons was effected by the amalgam reduction technique, leaving a small quantity of a thulium–lutetium concentrate. This was converted into the anionic enta complex, and sufficient Yb^{3+} again added to displace the thulium. Complete separation of thulium from lutetium was thus obtained, the thulium being concentrated some 5—6 fold in the cationic fraction with some ytterbium. Ytterbium being again removed from the thulium–ytterbium and ytterbium–lutetium fractions by reduction, small amounts of thulium and lutetium of good purity were obtained.

EXPERIMENTAL

The mixed lanthanon oxides used had accrued from previous separations of lanthanons derived from monazite (N.S.W.) and davidite (S.A.). These oxides had previously undergone differentiation by fractional crystallisation or basicity techniques and, to some extent, by crude ion-exchange fractionation. Their constitution, and those of the fractions obtained, were determined spectrophotometrically by means of the Beckman DU instrument utilising the extinction coefficients, etc., given by Moeller and Brantley (*Analyt. Chem.*, 1950, **22**, 433) and Wylie (*J. Soc. Chem. Ind.*, 1950, **69**, 143). Terbium was determined by the " active oxygen " method (Barthauer and Pearce, *Ind. Eng. Chem. Anal.*, 1946, **18**, 479).

The individual lanthanon oxides (of neodymium, praseodymium, samarium, erbium, etc.) were all of high purity (*ca.* 99·8%) and had been extracted and purified from the above sources by conventional methods and ion-exchange techniques. Again, all spectrophotometric studies on the displacement of anionic complexes by cations were conducted by use of the Beckman DU instrument. Throughout this study, the spectrophotometric evidence of complex displacement, and the inability of the separation technique to differentiate between complexes differing by less than *ca.* 0·2 unit in stability-constant values, were noteworthy. Much of this must be attributable to the limit of selectivity of the resin. Some degree of anionic take-up always occurs with cationic resins and *vice versa.*

The successful operation of this mode of separation depends upon two features: correct preparation of the initial complex, and correct preliminary treatment of the exchange resin. The avoidance of excess of enta, or the presence of sodium enta in the initial complex is essential. Consider the system: $[(\frac{1}{3}\mathrm{Pr}, \frac{1}{3}\mathrm{Nd}, \frac{1}{3}\mathrm{Sm})(\mathrm{enta})]^- + \mathrm{Na}_4(\mathrm{enta}) + (\frac{1}{3}\mathrm{Nd}^{3+})$. It is clear that interaction of the sodium enta and the neodymium cations will occur preferentially to the displacement of praseodymium from the complex, or, if the cationic neodymium *did* displace praseodymium from its anionic complex, the liberated Pr^{3+} would form a complex with the excess of sodium enta and not be removed by the exchange resin. The use of a gross excess of cationic neodymium could overcome this " extra " complexing effect but, unless the excess of sodium enta were accurately known and corrected for, this excess of neodymium would be extracted together with the liberated praseodymium and thus afford little or no separation of the lanthanons. In the preparation of the complexes used in this study care was always taken to employ a slight excess of lanthanon oxide and slight deficiency of sodium hydroxide, otherwise the method was that of Marsh (*loc. cit.*). The solution of the complex was evaporated to as small a bulk as possible before crystallisation in order to minimise the volume of mother-liquor and to reduce the separation which would occur by fractional crystallisation of the complex. The solid salt prepared was filtered off, washed once with ice-water, and dried by suction, a portion of the solid then being taken for complete analysis of its lanthanon content, to check the composition of the complex and to provide for displacement by the correct quantity of cationic lanthanon.

Correct appreciation of the function of the resin is also necessary. Data given by Duncan and Lister (*Quart. Reviews*, 1948, **2**, 307) give the maximum capacity of Dowex 50 resin as 4·92 m.-equiv./g. of dry resin, *i.e.*, 0·046 g. of $\mathrm{La_2O_3}$ or 0·058 g. of $\mathrm{Yb_2O_3}$ will saturate 1 g. of dry resin. We have found this maximum capacity to decrease with increasing pH, and the figures now obtained are somewhat higher than those given by these workers (0·075 g. $\mathrm{La_2O_3}$, 0·086 g. $\mathrm{Yb_2O_3}$ at pH 1·4; 0·052 g. $\mathrm{La_2O_3}$, 0·066 g. $\mathrm{Yb_2O_3}$ at pH 6·6). In order to avoid take up of oppositely charged ions by the resin, it is probably preferable to convert into cationic form rather more anionic lanthanon than can be held by the amount of resin taken, but this must be considered in the light of the degree of separation desired, since any cationic lanthanon remaining unextracted will adulterate the following fraction and nullify to an increasing extent the displacement achieved.

In the separations recorded here, 25-g. amounts of resin were considered to take up 1·5—2·0 g. of $\mathrm{Ln_2O_3}$. The time necessary for this take-up is also of importance: equilibrium should be established as closely as possible; with the light lanthanons shaking for as long as 12 hr. at room temperature has been necessary, but the heavier lanthanons attain equilibrium more readily, *ca.* 30 min. being sometimes sufficient.

Complete conversion of the resin into its sodium form must be ensured. Lack of attention to this will leave hydrogen ions on the resin and these, on displacement by Ln^{3+}, will reduce the pH of the complex solution with resultant partial disruption of the complex and precipitation of H_4enta. The complex solution should have a pH of 6·8—7·2 and the added lanthanon chloride solution should approach as near to neutrality as possible.

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