190. *The Separation of the Lanthanons with the Aid of Ethylenediamine-tetra-acetic Acid (" Enta Acid "). Part VI.* Ion-exchange Studies of the Heavy and Middle Lanthanons and Yttrium.*

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Hot, shallow beds of fine sulphonated polystyrene cation exchanger are loaded with lanthanons and developed on a bed of mixed copper and hydrogen forms of the resin by elution with ammonium-buffered " enta acid ". Good yields of purified heavy and middle lanthanons are obtained, but the separation of dysprosium from yttrium is exceptionally difficult.

A crude load of 0·6 equivalent of lanthanon per cm.^{2} of column cross-section on a bed 60 cm. deep was separated into ternary mixtures. These, re-run at 0·1—0·15 equiv./cm.^{2}, were resolved satisfactorily on 45- or 60-cm. beds (load vol./development vol. = 1) and recovered in solution of concentrations greater than 0·2 equiv./l. Intermediates between each pair of purified earths amounted to about 0·007 equiv./cm.^{2} or a 3 cm. band on the developed column.

The main factors governing the use of ion-exchange resins for separating elements by complex-forming eluants are well established. Thus, the lanthanons have been successfully separated on columns about 10 cm. long of very fine resin near 100° with tracer loads, or again with resin of commercial grade at air temperature, on columns [1] totalling 25—30 m. and 1000 l. in volume with loads of about 0·8 equiv./cm.^{2}. Large plants of similar design are now in use, but intermediate designs have also been described. Spedding, Powell, and Wheelwright [2] eluted copper and lanthanons successively from 90-cm. columns each with fillings of -80 to $+175$ mesh (British) of sulphonated polystyrene resin, using as eluant 2% enta acid in aqueous ammonia solution at pH of 8—9. French workers at C.N.R.S., Bellevue, used sulphonated polystyrene beads in the hydrogen form, of commercial size, in 6—9 m. of columns and eluted with buffered enta acid solutions at the low concentrations necessitated by the small solubility of the free enta acid which is liberated by complex formation of the lanthanons.[3]

The present work follows most nearly the technique of development with copper, which is combined with that in which the hydrogen bed is used. Fine resins have been used and the temperature was raised so that viscosity was lowered and the rate of exchange raised. The columns may thus be shortened, and the plant and resin requirement kept small for a given output. Scaled up for industrial operation, the short columns would be replaced by broad beds.

For about four months, use of copper development columns gave results at least as good as those of Spedding, Powell, and Wheelwright,[2] but then suddenly a complex copper enta salt of low solubility appeared, and the process became unworkable. Only limited

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* Part V, *J.*, 1955, 451.

[1] Spedding and Powell, *Chem. Eng. Progr. Symp.*, 1954, **50**, 7.

[2] Spedding, Powell, and Wheelwright, *J. Amer. Chem. Soc.*, 1954, **76**, 2557.

[3] Loriers and Quesney, *Compt. rend.*, 1954, **239**, 1643; Berghezan and Hérenguel, *ibid.*, 1955, **240**, 1537; Loriers, *ibid.*, 1956, **242**, 261; see also Topp, *Chem. and Ind.*, 1956, 1320.

supersaturation was thenceforth obtainable. Various additives were tried with the object of maintaining supersaturation; the best was a few per cent. of sucrose. It has been found, however, that a mixed copper and hydrogen developing column allows of smooth working. Analysis of the insoluble copper salt indicates the composition Cu[Cu enta],$5H_2O$, though copper was low and hydrogen high pointing to considerable uptake of the soluble dibasic cupric–enta acid, H_2[Cu enta]. Since H_4 enta is also nearly insoluble it is obvious that the eluate during the development stage should be the above soluble cupric–enta acid. The lanthanon (Ln) being assumed to move as Ln enta^{1-}, this will result from the reaction:

$$\text{Ln enta}^{1-} + \text{CuR}_2 + \text{HR} \longrightarrow \text{LnR}_3 + \text{H}_2\text{Cu enta}$$

In practice a mixture of two parts of copper resin and one part of hydrogen resin was found to be the most satisfactory. However, under working conditions there is a tendency for hydrogen to run off too quickly so that late copper eluates show a deeper colour and higher pH and there is a risk of deposition of Cu[Cu enta] causing a blockage in the outlet or a blurring of the copper–lanthanon boundary. If too much hydrogen is present when the elution of copper finishes trouble may ensue owing to crystallisation of free enta acid.

Yttrium presents a special case in that it has to be interpolated in the lanthanon series without occupying a space of its own. In normal complex elution it comes close to dysprosium, but when very dilute eluants are used it may not run off till after terbium.[4] Loriers and Quesney[3] from material containing 90% of yttrium, using a loading of only 0·03 equiv./cm.^{2}, obtained 25% of the yttrium as the trioxide (over 99·9% pure) in solution of concentration less than 1·5 g./l. Yttrium of 99% purity is comparatively easily prepared by methods other than ion exchange, so that material of this purity was used by us. It was confirmed that load and eluant concentration must be kept low, though after development with a dilute solution it was found possible to recover the yttrium by use of eluant of usual concentration. The ion-exchange purification of dysprosium has not been investigated.

Since the light lanthanons give insoluble octahydrated ammonium lanthanon enta salts, a slight white deposit is often seen at the rear of a heavy lanthanon elution. If there is a considerable light lanthanon content in the load separations are adversely affected.

EXPERIMENTAL

Apparatus.—A glass-fibre insulated hot chamber (controlled by thermostat) above a time-based fraction collector held the loaded resin container and the developing column, usually a standard 2 in. Pyrex industrial pipe, 18 or 24 in. long, fitted at the bottom with a felt pad on a perforated glass plate. Hydrostatic pressures up to 4 m. of water were available. The eluate was warmed by being kept in the chamber for a sufficient time before contact with the resin. A time switch provided predetermined operation of heating and eluant flow. It was often convenient to start the elution automatically during the night; for this a rubber tube in the eluant supply line was pinched shut by the loop end of a small tension spring passing through the shelf on which the tube rested. The spring was stretched by a 1 amp. fuse wire which melted when the time switch operated. If the electricity supply failed, a bar was allowed to fall on the tube, thus stopping the flow of eluant. For the collection of fractions, the eluant passed from the hot chamber by a glass ball joint and thence through a stainless steel spindle, to a delivery arm (1/16 in. bore stainless steel) which revolved above a circular rack (radius 15 in.) of 90 holes (diam. $\frac{7}{8}$ in.) which took test tubes for fractions up to 35 c.c. or small funnels delivering into 12 oz. (340 c.c.) medicine bottles. The delivery arm was driven by an electric clock movement through gears at 8—32 min./hole. The delivery arm terminated in a rubber tube inside a spring to which was attached a flag which made contact with a peg beside each hole, thus keeping the tube over the hole until the rotation caused it to jump to the next one. For large-scale work the outputs from groups of four holes each were delivered into larger

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[4] Spedding, *J. Amer. Chem. Soc.*, 1950, **72**, 5350; Loriers and Quesney, ref. 3.

vessels. The fraction collector has thus a very wide range, but in this work flow rates of 10—20 c.c./min. have been used, and collection of fractions in medicine bottles at 15—24 min. intervals has been most general.

Resin.—Dowex 50, $-250 + 500$ mesh, resin was used. Fine material was removed by extensive fractional sedimentation and the remainder was further graded into four grain sizes. Grade 1, the coarsest 40% of the total resin, was used for loading with the lanthanon charge, and grades 2 (30%) and 3 (20%) for the developing columns. Grade 4 was too fine for general use, and grade 3 was best suited for use in columns not longer than 45 cm. Close grading of the resin leads to even filling of the columns and to high efficiency by reducing the amount of channelling under large hydrostatic heads. Much of grade 1 proved to be over 250 mesh size. An approximate balance was found between mesh size, hydrostatic head, and exchange efficiency. Thus if a 60 cm. column of a resin required a given head for a given flow rate a 30 cm. column of finer resin giving the same flow rate under the same head would give an equally good separation at the same loading per c.c. of development bed (*i.e.*, half the first load). Even with these fine resins and high temperatures approximate equilibrium working is obtained only with flow rates below 0·5 cm./min. If we allow that the eluate in the resin bed occupies 40% of the volume, it will then traverse less that 1·25 cm. of bed/min.

General Operation.—Standard 2 in. Pyrex industrial pipes were used as developing columns, after trials with smaller columns. The lanthanon charge was usually held in a cylinder of 2 l. capacity and 62 cm.^{2} cross section, fitted in the lower conical part with a coarse sintered glass disc (diam. 5 cm.). A 6 l. aspirator bottle of 230 cm.^{2} cross section with 2 in. pipe-end neck was also used as charge container for rough separations of large quantities; good separation required that the volume of lanthanon-charged resin should not exceed the volume of developing resin, but a two-stage separation of a crude material is generally profitable. The first-stage eluates are acidified to 0·5N with hydrochloric acid and the precipitated H_4 enta removed after 2—3 days' standing. The earth contents are then reabsorbed on resin for the second stage of purification. It is best, however, to finish the charging of the resin from a neutral solution. The first stage allows grouping of the elements into products having three main constituents, and the second stages treat these groups separately to give high yields of pure products. Pure materials can be prepared with intermediates amounting to at most 0·4 g./cm.^{2} of column, or a 3 cm. band of developed resin bed. Since the total load is of the order of 6—8 g./cm.^{2}, only small pure crops are obtainable if numerous elements are present, and none for earths constituting less than 6—8% of the mixture.

As stated previously the aim during the development period is to run off H_2Cu enta. If this is not achieved blockages may occur, usually in the delivery arm or at its tip; such crystallisation was avoided by adjusting the pH of the eluate as it left the column by introducing acid or ammonia solution through a hypodermic needle in the rubber gasket below the pipe-end. Good separations are obtained when, during the lanthanon elution, the natural acidity is such that considerable H_4 enta crystallisation occurs on standing, but sometimes a crust forms and stops the flow where evaporation is high at the delivery tip.

Eluants containing 2% of H_4 enta buffered with ammonia to pH 8·8 (thymol-blue capillator test), *i.e.*, corresponding approximately to $(NH_4)_3H$ enta, have been used, generally made up from demineralised Thames water. The eluates have pH $<2·5$ (*i.e.*, in the red range of thymol-blue) if there is no danger of Cu_2 enta formation. Provision was made at the top of the column to permit the escape of gas. Above 70° a slow formation of gas in the resin bed occurred, which caused poor results and limited the desirable duration of a run to 40 hours. Partial degassing of solutions is therefore desirable, but temperatures over 70° were not generally used. The resin changes colour on passing from the copper to the lanthanon form with a sharp horizontal boundary, an advance of which of 3—4 cm./hr. is suitable. Thus a 60 cm. column of copper followed by an equal volume of lanthanon will be eluted in 30—40 hours.

In the following accounts of particular experiments the general conditions were as already indicated unless otherwise specified. All weights are given as the oxides (Ln_2O_3).

Crude Heavy-earth Concentrate derived from Gadolinite.—Much of the yttrium had been eliminated by the basic nitrate process. 5 l. of grade 1 resin, loaded with lanthanons (12 equiv.) to give a bed 18 cm. deep, were separated by a felt diaphragm from a 60 cm. × 21 cm.^{2} column of grade 3 resin, half in the copper and half in the hydrogen form. The whole was eluted with 1·5% of H_4 enta in ammonia solution at pH 8·8 until lanthanons appeared (24 hr.) and then 2% of H_4 enta in ammonia solution at pH 8·8 and 80°. Fractions 1—105 were collected at

16 min intervals, 106—118 at 128 min. intervals. Spectrometry in 1 cm. cells showed Yb in 1—45 (max. 40), Tm in 35—105 (max. 45), Er in 50—111 (max. 85), Ho in 85—118 (max. 113), Dy in 109—118 (max. 115). After 72 hours the charge-bottle was disconnected and the column eluted to completion. The remaining charge (70 g.) was developed subsequently on another column; the first few fractions contained a little holmium but over 10% of dysprosium, dropping to 0·2% at the tail which appeared to contain nearly pure yttrium, with only a small amount of terbium in the last fraction.

In the main experiment gas development was excessive owing to too high a temperature and too prolonged an elution, but four useful concentrates were obtained, *viz.*, (*a*) pre-erbium, (*b*) erbium, (*c*) holmium, and (*d*) dysprosium–yttrium. The crude erbium was re-run first, giving heads and tails to increase (*a*) and (*c*). Most of the ytterbium was removed from the pre-erbium concentrate by the sodium amalgam process before further ion-exchange treatment.

Purification of erbium. 1·25 l. of grade 1 resin in the erbium form in a 62 cm.^{2} bed over a development column (60 cm. × 21 cm.^{2}) of grade 2 resin $\frac{2}{3}$rds. in the copper and $\frac{1}{3}$rd. in the hydrogen form were eluted with a 2% solution of H_4 enta at pH 8·7 at 70—75°. Fractions (250—215 c.c.), collected at 16 min. intervals contained: 1—10, no erbium; 1—17, some Tm; 18—64, pure Er (Er_2O_3, 127 g.); 65—72, Er and Ho; 73, pure Ho. The tail (76) contained 7% of Dy and 37% of Ho.

Purification of holmium. 650 c.c. of grade 1 resin in the holmium form in a 62 cm.^{2} bed over a development column (45 cm. × 21 cm.^{2}) of grade 2 resin as above were eluted with the same solution at 15—65°. About 33 cm. of the development column were eluted cold unintentionally, and the adverse effect on the elution is evident. Fractions contained: 1—4, mainly Cu with some Er; 5, a little Ho; 6—9 (9·7 g.), mainly Ho; 10—13 (10 g.), trace of Er; 14—25 (30 g.) pure Ho; 27, impure (50%) Ho.

Purification of lutetium and thulium. 900 c.c. of grade 1 resin in the mixed lanthanon form over a development column (60 cm. × 21 cm.^{2}) of grade 2 resin as above were eluted with the same solution at 70°, at a rate of 12 c.c./min. Fractions collected at 15 min. intervals contained: 1—14, Lu (25·2 g.) and a trace of Sc (Yb was not detected by arc spectroscopy by Johnson, Matthey and Co. Ltd.); 15—20, Lu + Yb (12·2 g.); 21—24, Yb (8·4 g.); 25—28, Yb + Tm (8·2 g.); 29—56, Tm (52·7 g.) and 0·04% of Yb (Er was not detected by arc spectroscopy as above); 57—62, Tm + Er (11 g.), 63—67, Er (9 g.); 68—72, Er + Ho + Dy (6·5 g.).

Purification of gadolinium. Crude gadolinium was prepared from ore by two double sodium sulphate precipitation (cf. ref. 5, Table 2, fraction 6) (Found: Pr, 1; Nd, 9; Sm, 26; Eu + Gd + Tb, 50; Dy, 5; Y, 9%). This was used to transform grade 1 resin into the lanthanon form, 800 c.c. of which in a 62 cm.^{2} bed over a development column (45 cm. × 21 cm.^{2}) of grade 2 resin as above were eluted with the above solvent at 65—67°. Fractions collected at 19·2 min. intervals contained: 1, Er (13) + Ho (13) + Dy (71) + Y (3%); 2, Dy (94) + Y (6%); 3, Dy (93) + Y (7%); 4, Dy (30) + Y (70%) (total 1—4, 7·6 g.); 5—6, Dy (0·7) + Y (99·3%) (total 3·2 g.); 7—11, Y (7·4 g.); 12—15, Y + Tb + Gd (8·2 g.); 16—32, Gd (40·5 g.); 33, Gd (96) + Eu (4%); 34, Gd (49) + Eu (35) + Sm (16%); 35, Gd (8) + Eu(14) + Sm (18) (total 33—35, 8·5 g.); 36—44, Sm (21·6 g.); 45—49, Sm + Nd (8·8 g.); 50, Nd (1·6 g.); 51—52, Nd + Pr + La (5 g.).

Purification of terbium. 1·1 l. of grade 1 resin in the terbium form in a 62 cm.^{2} bed over a development column (60 cm. × 21 cm.^{2}) as above were eluted with a 2% solution of H_4 enta in ammonia at pH 8·8 (15 l.) at 60—65°, for 21 hr. A total of 10 l. of eluant was collected in 61 fractions at 19·2 min. intervals, and contained: 1—8, white oxides free from Tb, mostly Dy and Y; 9, cream-coloured oxide: 10, ochre oxide; 11—50 (Tb_4O_7, 100 g.), oxides of uniform colour, of which those in 12 and 50 were shown by arc spectroscopy not to contain Dy or Gd (Johnson, Matthey and Co. Ltd.). Terbium was absent from fraction 55, which contained pure Gd.

Purification of yttrium (*from* 99·2%). 550 c.c. of grade 1 resin in the yttrium form in a 62 cm.^{2} bed over a development column (60 cm. × 21 cm.^{2}) as above were eluted for the first 65 cm. with a 1·25% solution (pH 8·4) and thereafter a 2% solution (pH 8·7) of H_4 enta in aqueous ammonia at 68°. Development for 30 hr. consumed 23 l. and was followed by 29 fractions at 24 min. intervals containing in all 45 g. in 7·3 l. or 0·06 equiv./cm.^{2}. Fractions contained: 1, Dy (13·5) + Ho (6·1) + Er (9·7%) (total 0·8 g.); 3, Dy (1·25) + Ho (0·17) + Er (0·06%) (total 1·8 g.); 6, Dy (0·5%); 8—9, Dy (0·1%); 10—11, Dy (0·05%); 12—28, Dy (0%) (total 27 g.). At the low concentrations dysprosium was estimated spectrophotometrically

[6] Marsh, *J.*, 1952, 4804.

through 4 cm. of a solution of Y_2O_3 (250 g./l.) in hydrochloric acid. If Beer's law holds, the sensitivity was 0·01% of Dy_2O_3. With heavier loads in other experiments it was found that the head fractions showed large concentrations of impuriries, and the tails were of high purity, but there was a long central portion which was of approximately the same composition as the input. Even in the last experiment fractions 4—6 showed little change in dysprosium content and were of approximately input composition.

Purification of neodymium. A high yield of high-purity neodymium was obtained from a mixture containing 88% of Nd and 12% of Pr by using, in a single column, 30 cm. of Cu-resin and 15 cm. of Nd-resin, a 50% increase in elution rate, a lower temperature (55°), and the usual 2% enta-acid eluant. The short duration of the elution prevented growth of large insoluble particles in the column.

Purification of praseodymium. Addition of 1% of hydroxyethylethylenediaminetriacetic acid (HEDTA) to the usual 2% enta-acid at the same pH served to delay the formation of insoluble enta salts. A 90 c.c. load (Pr 88; Nd 0·5%) on a 45 cm. × 2·5 cm.^{2} Cu-resin column eluted at 40° contained all the neodymium in the first 4% of the lanthanon runnings. The eluant was then changed to a mixture of 0·65% enta-acid and 1·3% HEDTA at pH 8·8, since the stability constants of the lanthanum and praseodymium complexes [6] indicate the superiority of HEDTA for the separation of this pair. Also HEDTA has the advantage of yielding soluble complexes. A sharp separation of Pr from Ce and La resulted.

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[6] Spedding, Powell, and Wheelwright, *J. Amer. Chem. Soc.*, 1956, **78**, 34.