835. *Separation of the Lanthanons by Ion Exchange. A Comparison of Eluants.*

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A comparison has been made of the efficiencies of various aliphatic carboxylic acids as eluants in separation of the lanthanons by ion-exchange techniques. This comparison indicates that determinations of stability constants for lanthanon complexes can be used to predict the value of the complex-forming agent in ion-exchange separations. Further, when the exchange resin is in the ammonium form, and when high pH values and low flow rates are employed, ethylenediaminetetra-acetic acid at low concentrations gives separations of the lanthanons which are better than those obtained under comparable conditions by any of the other eluants studied, including citrate solutions. The use of bivalent ions as separating elements in elutions with ethylenediaminetetra-acetic acid has been examined, and with manganese as the separating element this technique has yielded excellent separations of neodymium and praseodymium. Attention is also directed to the necessity of considering molar rather than weight concentrations when comparing eluant efficiencies.

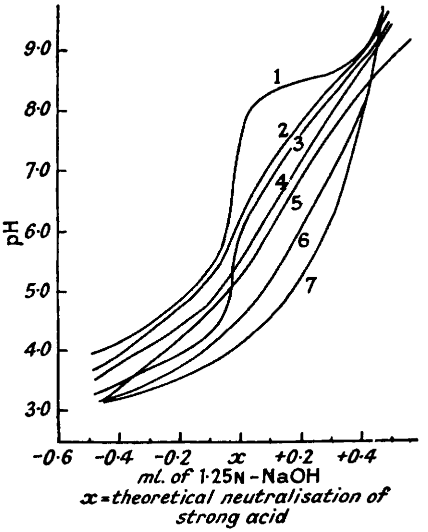
The increasing application of ion-exchange techniques to the separation of the lanthanons and other closely similar cations has led to several fundamental studies on the kinetics of ion exchange. In studies on the lanthanons, however, less attention has been paid to the function of the eluant in these separations. Scattered through the literature are reports on separations obtained with different resins and one or two different eluants but, apart from the studies by Spedding *et al.* on citrate eluants (*J. Amer. Chem. Soc.*, 1947, **69**, 2769, etc.), little systematic work has been done with regard to eluant composition.

Comparison of the efficiencies of eluants in resin exchange systems may be made in the light of formation and disruption of complexes. Thus the replacement of hydrogen on resins by lanthanons indicates that the lanthanon–resin complexes are more stable than are the hydrogen–resin complexes. Similarly, in the system complex-forming resin–lanthanon ion–complex-forming eluant, the partition of the lanthanon between the resin and the eluant will be proportional to the stabilities of the Ln–resin and Ln–eluant complexes. If the ratio of the stability of a Ln–eluant complex to that of the corresponding Ln–resin complex is denoted by the coefficient A, then the optimum separation of two lanthanon ions will occur when the difference between the two values of A is at its maximum. This is only reached, however, when the system is in equilibrium, *i.e.*, at very slow eluant flow rates. At flow rates employed in practice equilibrium is not attained, but the ratio of coefficients of a lanthanon complex of different eluants may be considered as a measure of their efficiencies at a given approach to equilibrium. This means that an eluant which forms complexes of high stability with the eluted ions will, when employed at a high flow rate, be approximately as efficient in separation as an eluant affording a low stability, employed at a low flow rate.

Bjerrum has shown (*e.g.*, *Chem. Reviews*, 1950, **46**, 381) that the formation of complex compounds may be treated mathematically so as to yield integrals denoting the overall stabilities of the complexes. However, the nature of the lanthanon complexes with the eluants considered here has not yet been elucidated sufficiently to be amenable to such treatment and the nature of the resin complex systems is even more obscure. But, since it may be accepted that the higher the stability of a complex, the lower the pH at which it can exist, qualitative indications of complex formation and stability may readily be obtained by acid–base titrations of lanthanon systems.

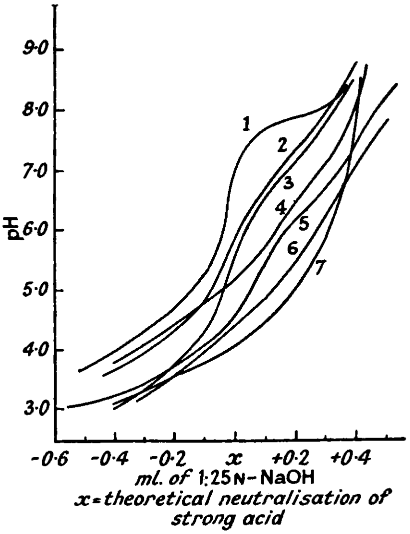
Seven carboxylic acids have been studied for their value as eluants, *viz.*, acetic, malic, tartaric, citric, aminoacetic (glycine), nitrilotriacetic (" trilo "), and ethylenediamine tetra-acetic (" enta "). The pH titration curves for these acids in lanthanon systems are given in Figs. 1 and 2, from which is seen an increasing complex stability through the series as listed.

FIG. 1. *Titrations of* La-*carboxylic acid systems.*



1. Acetic acid.
2. Malic acid.
3. Tartaric acid.
4. Citric acid.
5. Glycine.
6. " Trilo."
7. " Enta."

FIG. 2. *Titrations of* Y-*carboxylic acid systems.*



1. Acetic acid.
2. Malic acid.
3. Tartaric acid.
4. Citric acid.
5. Glycine.
6. " Trilo."
7. " Enta."

The influence on ion-exchange separations of such factors as eluant flow rate, resin bed depth, resin grain size, etc., have been fully studied by Spedding *et al.* (*loc. cit.*; *Discuss. Faraday Soc.*, No. 7, 1949; U.S.P. 2,539,282/1951). The main variables with different eluants are the exchanging ion, and pH and concentration of eluant. These have been examined for the seven carboxylic acids mentioned above, the cation being ammonium in each case.

Spedding (*loc. cit.*) indicated that, in lanthanon separation by ion exchange, the use of eluants at low concentration and high pH values is of more value, for practical purposes, than at high concentrations and low pH values. Since citrate eluants have been well studied it was decided to consider separations with this as standard. Excellent separations of the lanthanons having been obtained by Spedding using 0·1% citrate solutions at pH 6·0, this eluant concentration was initially employed in these studies but, with each eluant, runs were made in two pH ranges, and with both light and heavy lanthanons adsorbed on Dowex-50 resin.

Typical elution curves have been examined for the eluants studied, all at similar concentrations, pH values, and flow rates; those for acetate, citrate, " trilo," and " enta " are given in Figs. 3 and 4. It was immediately evident that (*a*) the efficiency of separation increases with progression through the series to citrate eluants and then decreases, (*b*) higher pH values give best separation of the light lanthanons, and low pH values best of the heavy lanthanons. The latter observation is to be expected from the titration curves of the lanthanon complexes of these acids which show greater difference of the stabilities of the light lanthanon complex series at low pH values. The rise and fall in efficiency of the eluants can be explained on the basis of the argument made above, *viz.*, the lower carboxylic acids, forming lanthanon complexes with stabilities lower than those of the citrate complexes, require a closer approach to equilibrium, *i.e.*, a slower flow rate, in order to approach the efficiency of citrate eluant at the standard flow rate and degree of equilibrium. Similarly, the amino-acids require a faster flow rate as the stabilities of their lanthanon complexes increase.

The elutions with all the acids except " trilo " and " enta " progressed normally, but when these were employed they crystallised in the resin bed when the resin was in its hydrogen form. This was to be expected from the reactions at the adsorption band front :

(*a*) $\mathrm{LnCl_3 + 3HX_{resin} \longrightarrow LnX_{3\,resin} + 3HCl}$

(*b*) $\mathrm{4HCl + (NH_4)_4}$"enta" $\longrightarrow \mathrm{4NH_4Cl + H_4}$"enta" (insoluble)

or (*b*) $\mathrm{3HCl + (NH_4)_3}$"trilo" $\longrightarrow \mathrm{3NH_4Cl + H_3}$"trilo" (insoluble)

The deposition of $\mathrm{H_4}$" enta " in resin columns was noted by Taylor (Univ. Illinois, Thesis, 1950) and by Higgins and Baldwin (ORNL 894, 1951); Taylor reported that " enta " possessed no advantages over citrate as eluant for lanthanons adsorbed on Dowex-50 resin, and considered it to be of value only for " stripping " of the column. Initially, the deposition of $\mathrm{H_4}$" enta " is of value in following the progress of the ion-exchange front, but this front soon outstrips visual observation of the crystallisation. As the concentration of $\mathrm{H_4}$"enta" crystals in the resin bed increases, progressive diminution in eluant flow rate occurs until the adsorption tail passes, thereby making available eluant at a sufficiently high pH for redissolution of the $\mathrm{H_4}$" enta " crystals. The early deposition of $\mathrm{H_4}$" enta " impoverishes the eluant and leads to the falling-off of separation efficiency noted by Taylor. If high concentrations of " enta " are employed in the eluant, operations will eventually be stopped by blocking of the resin column by the deposited crystals.

The deposition of $\mathrm{H_4}$" enta " or $\mathrm{H_3}$" trilo " in the resin bed may, however, be avoided by using a resin giving on exchange Na, K, $\mathrm{NH_4}$, or Th, rather than H, ions. However, the elution curves obtained by Ketelle and Boyd (*J. Amer. Chem. Soc.*, 1947, **69**, 2808) show Na to be eluted with the heavy lanthanons; this precludes the use of an exchange resin in the sodium form. On the other hand, thorium would be expected to be too firmly held by the resin to be replaced by lanthanons (Duncan and Lister, *Quart. Reviews*, 1948, **2**, 307). For the separations recorded for " enta " and " trilo " elutions, Dowex-50 in the ammonium form was therefore employed. During progress of this work it was noted that Fitch and Russell (*Canad. J. Chem.*, 1951, **29**, 363) employed resins in the ammonium form during elution of adsorbed lanthanons with " trilo," having also experienced the deposition of the acid in a hydrogen-resin bed.

To confirm the relation of complex stabilities and flow rates, further runs were made with acetate, glycine, and " enta " eluants. The acetate elution was made at a flow rate one-fourth of that of the citrate standard, the glycine elution at a rate 50% higher, and the " enta " elution 100% higher, than the citrate. These runs were made only on a light lanthanon mixture at the higher pH values previously used. Although the acetate elution did not attain the efficiency of the citrate runs, all three eluants showed highly significant increases in efficiencies, particularly the amino-acid eluants which demonstrated a much improved separation over the citrate. The variation in efficiencies is the more significant as the flow rates of the eluants were chosen quite arbitrarily.

Hitherto, in the literature, statements of eluant concentration have been given as a percentage on a w/v basis. In comparing eluant efficiencies, however, this is insufficient, and concentrations should be expressed as molar concentrations. The need for this is

FIG. 3.

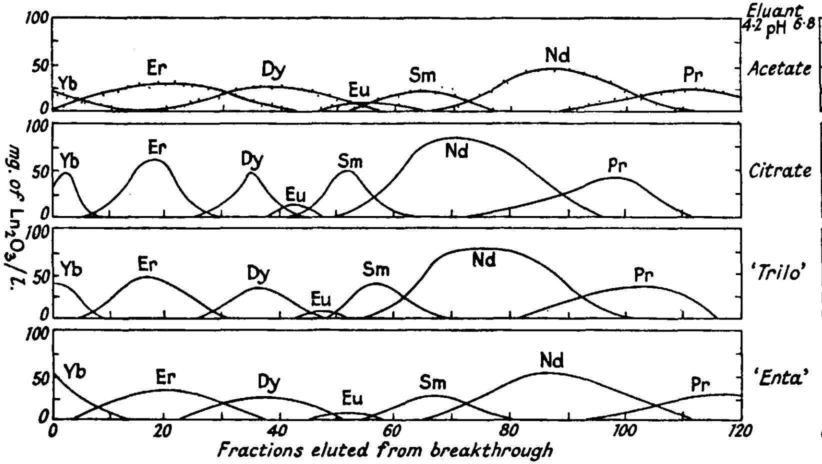
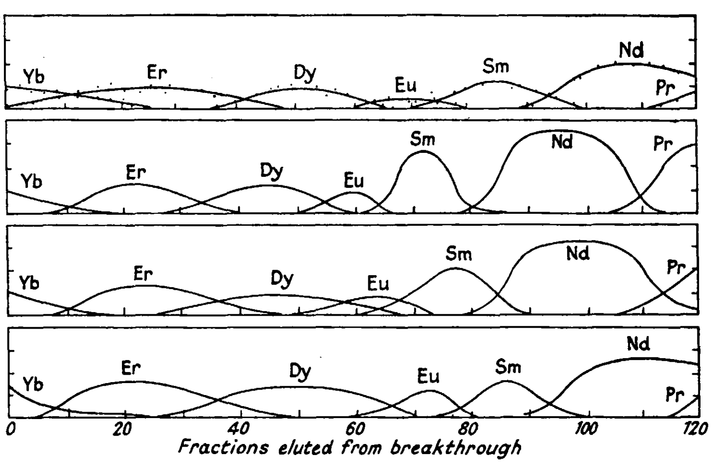


FIG. 4.



Elution of mixed lanthanons from Dowex-50 resin by carboxylate solutions at pH *values* 4·2 *and* 6·8.

FIGS. 5 & 6. *Elution of light lanthanons by " enta " at higher concentration and flow rate.*

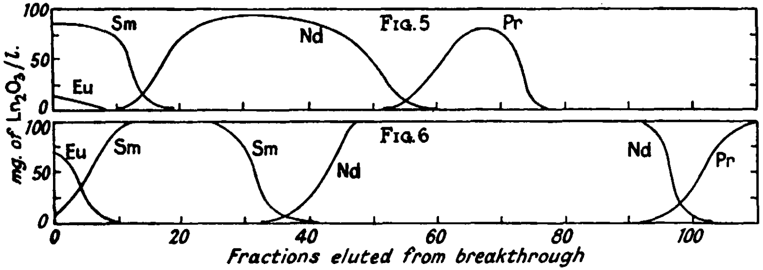


FIG. 5. *Enta* (5·2 × 10^{-3} *mol.*%), *eluant at* 750 *ml./hr.* FIG. 6. *Enta* (5·2 × 10^{-3} *mol.*%), *eluant at* 1·5 *l./hr.*

apparent when it is realised that, in complex formation, acetic acid is monodentate, glycine is bidentate, citric acid tridentate, " trilo " quadridentate, and " enta " sexidentate. Concentrations of these eluants at 0·1% w/v represent molar concentrations of $1\cdot67 \times 10^{-2}$, $1\cdot3 \times 10^{-2}$, $5\cdot2 \times 10^{-3}$, $5\cdot23 \times 10^{-3}$, and $3\cdot4 \times 10^{-3}$%, respectively. The close similarity of the molar concentrations of citric acid and " trilo " obviated the necessity for further comparison of these eluants on a concentration basis. The higher molar concentrations of acetate and glycine coupled with their low efficiencies as eluants indicate that, in spite of the great influence of altered flow rate on their effectiveness in separation of the lanthanons, these eluants cannot compete with citrate on the basis of molar efficiency—at least, when Dowex-50 is the exchanging resin. The greatly enhanced separations obtained with " enta " at high flow rates at a lower molar concentration than citrate rendered necessary a further run for comparison of the two at similar molar concentrations. Figs. 5 and 6 show the elutions obtained with " enta " at $5\cdot2 \times 10^{-3}$ mol.% (*i.e.*, 0·152 w/v) at the citrate standard flow rate and 100% higher. The increase in efficiency shown by these elutions does not appear to confirm the generalisation by Spedding *et al.* (*loc. cit.*) that better separations are obtained with more dilute eluants. Instead, there appears to be a relation, not only between the stabilities of the complexes and flow rate as previously indicated, but also between the stabilities and eluant concentration effect when this latter is based on % w/v.

In elutions of the lanthanons from an Amberlite resin with " trilo," Fitch and Russell (*loc. cit.*) found that cadmium could be introduced into the exchanging system with a beneficial effect on the samarium–neodymium separation. This would suggest that the Cd–" trilo " complex has a stability intermediate between those of the Sm– and the Nd–" trilo " complex. However, Schwarzenbach and Freitag (*Helv. Chim. Acta*, 1951, **34**, 1942) found the overall stability constant (log $\overline{K}$) for " trilo " complexes with cadmium to be 9·54 compared with 10·37 for lanthanum, *i.e.*, the cadmium–" trilo " complex has a lower stability than has the lanthanum complex. The interpolation of cadmium between neodymium and samarium cannot be attributed to ionic sizes (0·97, 1·15, and 1·13 Å, respectively), so the reason for the difference between the elution series and the stability series is obscure unless the complexes formed in the resin column are different from those formed in the system studied by Schwarzenbach and Freitag. However, Fitch and Russell did not apparently consider the influence of molecular ratios when including cadmium in their elutions.

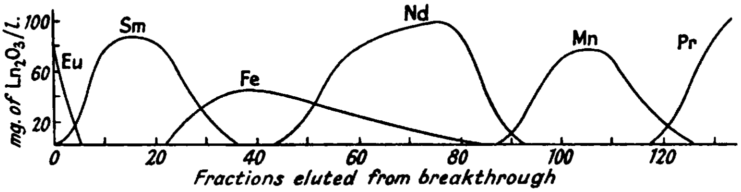
The log $\overline{K}$ values of lanthanon complexes with " enta " have recently been given by the author (*J.*, 1952, 1895); Schwarzenbach and Freitag (*loc. cit.*, p. 1503) have also reported the constants for several bivalent metal complexes with " enta." Consideration of these values, given in the table, shows two groups of interpolations : cobalt, zinc, and cadmium between cerium and praseodymium, and lead, copper, and nickel between erbium and ytterbium. The interpolation of copper at about the region of thulium is interesting because Marsh (*J.*, 1950, 1819) used cupric acetate in exchange separations of the lighter lanthanons but did not extend its use to separation of the heavier earths. It was understood, however, that copper salts would completely remove the lanthanons from an " enta " complex solution. This affords an example similar to that of Fitch and Russell, that overall stability constants of bivalent ions determined in acid–base titration systems appear to be somewhat increased when those bivalent ions are present in a predominantly tervalent-ion system. Confirmation of this was found in two further elutions with " enta," one of light, and the other of heavy lanthanons. Cobalt, zinc, and cadmium chlorides were added to the light lanthanon chloride solution, and copper and nickel chlorides to the heavy

Overall stability constants for " enta " complexed ions.

Ion	log $\overline{K}$	Ion	log $\overline{K}$	Ion	log $\overline{K}$	Ion	log $\overline{K}$
Mn^{2+}	13·47	Zn^{2+}	16·15	Sm^{3+}	17·2	Pb^{2+}	18·2
Fe^{2+}	14·22	Cd^{2+}	16·48	Gd^{3+}	17·2	Cu^{2+}	18·38
La^{3+}	15·3	Pr^{3+}	16·55	Y^{3+}	18·0	Ni^{2+}	18·45
Ce^{3+}	16·05	Nd^{3+}	16·75	Er^{3+}	18·15	Yb^{3+}	18·70
Co^{2+}	16·1						

lanthanon solution before adsorption and elution. Elutions were carried out with " enta " eluant at pH values of 6·8 and 4·2 respectively, with an " enta " concentration of $5{\cdot}2 \times 10^{-3}$ mol.% and a flow rate of 1250 ml./hour. The elution curves showed the Co–Zn–Cd interpolation to spread itself into the Sm–Eu–Gd region whilst the Cu–Ni interpolation disappeared altogether, the bivalent ions being completely eluted before the lanthanons. The direction of the displacement effect referred to above focused attention on manganese and iron. The " enta " complexes with these two metals are placed somewhat lower in the stability series than any of the lanthanons, and it was of interest to determine the degree to which complexes of these ions would be displaced on elution. An elution of light lanthanon chlorides with added ferrous and manganese chlorides was carried out, " enta " being used under the conditions given above. The elution curves obtained are shown in Fig. 7. The degree of separation of praseodymium and neodymium by manganese interpolation is striking; the elution of iron with, and before, neodymium is interesting and is ascribed to a certain extent to oxidation to the tervalent state during elution. Subsequent elutions employing manganese ions as the only addition to a 27% Pr_2O_3 + 72% Nd_2O_3 mixture yielded praseodymium of 98% purity and neodymium free from all traces of praseodymium determinable spectrophotometrically, with four intermediate fractions containing manganese and small quantities of lanthanons.

FIG. 7. *Interpolation of* Fe^{2+} *and* Mn^{2+} *ions in light lanthanon elutions with " enta."*



EXPERIMENTAL

The preliminary titrations were carried out with the lanthanons at a concentration of 5×10^{-3}M, and the carboxylic acids at 2×10^{-2}M. Nitric acid was added to give a strong acid concentration of 1×10^{-2}N, and the titrations were made with 1·25N-sodium hydroxide from a microburette. The change in pH was followed through a glass–calomel electrode system, a Marconi–Ekco pH meter being used.

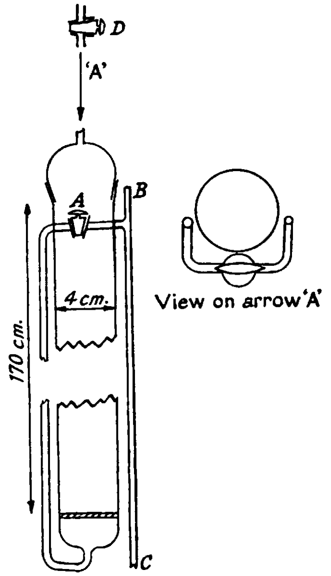
The arrangement in these laboratories of the ion exchange assembly for lanthanon fractionation is briefly as follows: Six or more resin columns are set up in a tubular-steel scaffolding structure carrying, at 8 ft., a platform on which stand six or more 20-l. carboys. Eluant is prepared from demineralised water in a 100-gallon glass-lined vat beneath the carboy platform, and is pumped to each of the carboys *via* a manifold. The use of carboys on the platform instead of another tank is preferable, as it is then possible to keep, say, four columns operating on a standard eluant whilst other columns, fed from different carboys, are being used to evaluate different complexing agents as eluants. In the latter instances the eluant is prepared in a smaller tank at ground level and pumped to the appropriate carboy *via* the manifold.

The construction of the resin columns shows some modification from that of previous workers and is shown diagrammatically in Fig. 8. After passage through the resin bed, the eluant has to rise to the stopcock *A*; this ensures that the resin bed is always covered with liquid, syphoning being avoided by the provision of an air port at *B*. Backwashing for removal of fines and air bubbles is accomplished by attachment of the water inflow to *C* and blocking *B* with a small rubber stopper. With the tap *D* fully open, the flow rate is controlled by tap *A*; when the flow rate has been correctly adjusted, tap *A* is no longer touched, any temporary cessation of operation being effected by closing *D*.

The resin employed for these studies was Dowex-50 of 30—50-mesh grain size. The resin was pretreated in the usual way, finishing in the acid form. For elutions with the resin in the ammonium form, the acid resin was given a final wash of 30 l. of 3% ammonia solution.

The lanthanon mixture generally employed was a combination of light lanthanons *ex* monazite (minus cerium) and heavy lanthanons *ex* yttrotitanite. Some yttrium had been removed from these by ferricyanide fractionation. The light lanthanon mixture employed in later runs had been derived from monazite; cerium had been removed, and the remaining earths subjected to a series of fractional fusions with ammonium nitrate which removed much of the lanthanum at the head (Vickery, *J.*, 1949, 2508). Three tail fractions were combined to give the oxide mixture used here. Analyses of these original oxides and of the eluted fractions were made spectrophotometrically in a Beckman DU quartz spectrophotometer, Moeller and Brantley's extinction coefficients (*Anal. Chem.*, 1950, **22**, 433) being used. Yttrium contents were determined initially by difference and then confirmed by average atomic weight determinations. The two original oxides gave the following analyses. Light lanthanons: Pr_2O_3, 5·7; Nd_2O_3, 45·7; Sm_2O_3, 14·5; Eu_2O_3, 1·0; Gd_2O_3, 5%. Mixed lanthanons: Pr_2O_3, 9·5; Nd_2O_3, 20·6; Sm_2O_3, 10·2; Eu_2O_3, 1·5; Dy_2O_3, 6·2; Er_2O_3, 9·7; Yb_2O_3, 4·0%.

FIG. 8.



10-G. quantities of oxides were adsorbed on the resin beds from chloride solutions, and the beds then washed with the demineralised water until the runnings were free from chloride. Unless otherwise indicated in the figures, elution was carried out at a flow rate of 750 ml./hour, the eluate being collected in 5-l. fractions up to the breakthrough and thereafter in 750-ml. fractions. The lanthanons in the eluate were precipitated as oxalates, filtered off, ignited, weighed, and analysed as indicated above.

Separation of the lanthanons from the ions used as interpolants presented little difficulty in the dilute solutions involved, two oxalate precipitations being sufficient to remove all but traces of the alien metals. Determinations of iron, manganese, cobalt, etc., were carried out by the usual methods—generally ending gravimetrically—on the eluted solutions after removal of lanthanons with oxalic acid and evaporation to dryness to remove organic matter. Absolute accuracy in these determinations was not aimed at, it being sufficient to appreciate where the alien ions were eluted.

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[*Received, April* 10*th*, 1952.]