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The Separation of Rare Earths by Ion Exchange.[1,2] II. Neodymium and Praseodymium

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I. Introduction

The use of Amberlite IR-1 resin as an ion exchanger for cerium and yttrium and has been described in an earlier publication.[3] The separation was effected by eluting the adsorbed material with a citric acid–ammonium citrate solution. It was pointed out that the process involves small differences in the basicities of the trivalent rare earth ions. These differences account for variations in the stability of the citrate ion complexes of the various rare earths which lead to their separation. The basicities of the rare earths decrease with an increase in atomic number, the difference between any two adjacent rare earths being small. Certain properties of yttrium, including basicity, are intermediate between europium and gadolinium. In the case of cerium and yttrium, which are relatively far apart in basicity, it was found that the degree of separation was dependent upon a number of factors.

The present paper deals with a preliminary study of these factors in order to determine favorable conditions for the separation of adjacent rare earths such as neodymium and praseodymium. The variables considered are (1) the *p*H of the eluant, (2) the weight of sample, (3) the length and diameter of the column, (4) the flow rate and (5) the composition of the starting sample. The particle size of the resin and the original concentration of citric acid in the eluant were kept constant.

The work establishing the separation of neighboring rare earths was performed during the period January–April, 1945, with the objective of determining whether macro amounts of adjacent rare earths could be separated by adsorption on Amberlite resins and elution with the citric acid–ammonium citrate solution at controlled *p*H. During the period of April–September, 1945, further work was done establishing more favorable conditions for the separation. Due to the pressure on war work it was not possible to carry out a thorough systematic investigation of all the variables involved. Such studies are now in progress and will be reported in subsequent papers. However, sufficient work has been done to demonstrate that the phenomena involved are complex. The discussion of various theories and mechanisms will be reserved until such a time as adequate supporting data are available.

II. Materials and Methods

Commercial didymium was used as the source of the rare earths. Analysis with a Beckmann Quartz Spectrophotometer showed 78% Nd, 18% Pr and about 2.5% Sm; the remainder consisted of small amounts of Ce and La with traces of other rare earths. A spectrographic analysis utilizing its emission spectra showed the Sm content to be about 5%; however, the reliability of this method has not been clearly established for quantities of this magnitude. In the spectrophotometric analysis of a mixture allowance has not been made for a possible influence of one component on the other. Rodden[4] has noted that such interference is sometimes appreciable with the rare earths. However, with solutions containing known amounts of Nd and Sm, no appreciable difference was found between the spectrophotometric analysis and the theoretical. These results indicate that ion interference did not account for the discrepancies in the analysis for the Sm and that the spectrophotometric method did give results consistent with the actual weight of Sm. In all subsequent discussion the spectrophotometric procedure is used as standard for determining quantities greater than 1%. However, detailed studies are in progress to compare the two procedures and to explain any discrepancies in results.

In order to put the spectrophotometric analyses on a quantitative basis, the molar extinction coefficients for various absorption peaks were determined for the chloride solutions of pure Nd, Pr and Sm. The complete spectrum from 340 mμ to 1,000 mμ for each one of these salts was investigated. In choosing the proper band to be used in the analysis of mixtures of these rare earths, care was exercised in using only those bands which were isolated from any background absorption of light by any of the other components. It was also necessary that the band be of sufficient intensity to be detectable in low concentrations. These bands were at 795 and 740 mμ for Nd, 444 mμ for Pr, and 401 mμ for Sm. The corresponding extinction coefficients were 8.1 and 6.13 for Nd (4 mμ band width), 6.20 for Pr (1 mμ band width), and 3.38 for Sm (using a 1 mμ band width).

In analyzing a mixture, the total concentration of the solution was in the range of 8–12 mg. (as

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[1] This work was, in part, supported by a grant from the Manhattan District, U. S. Corps of Engineers.

[2] The essential material in this paper was presented before the Manhattan Project Council, Chicago, Illinois, on April 15, 1945; and before the Chicago Section of the American Chemical Society in November, 1945.

[3] F. H. Spedding, A. F. Voigt, E. M. Gladrow and N. R. Sleight, THIS JOURNAL, **69**, 2777 (1947).

[4] C. J. Rodden, *J. Research Natl. Bur. Standards*, **26**, 517 (1941).

oxide) per ml. The Sm could be detected in amounts down to 1%, and the lower limit for detecting Nd and Pr was 0.3%. For the detection of smaller quantities, recourse was made to quantitative spectrographic analyses.

The chemical steps involved in the analysis of a sample of eluate consisted in precipitating the rare earths from the citrate solution as oxalates by adding oxalic acid (10 g./liter of eluant). The precipitates were allowed to settle, filtered, and ignited to the oxides. The oxides were then dissolved in dilute hydrochloric acid (0.5 *N*) to make the resulting solution of the concentration mentioned above.

The per cent. of the rare earths in each sample eluted was determined by measuring the log I_0/I value for each peak, and dividing by the extinction coefficient which gave the concentration of that component in the solution. This was done for each component; the sum represents the total concentration, and the per cent. was determined from this total. This procedure was valid since no ion species other than detectable rare earths were present in the material. The total elution curve was obtained by plotting grams of R_2O_3 per unit volume against volume of eluate. The elution curve for an individual rare earth was obtained by multiplying the ordinate of the total elution curve by the per cent. of the element present and plotting these values against volume of eluate.

The results were plotted in a different manner to further emphasize the extent of separation. This was done by measuring the areas under the Nd and Pr elution curves, from the point of breakthrough[5] to any given volume, converting these areas to milligrams of oxide and dividing by the total milligrams of R_2O_3 eluted to that volume which is similarly determined from the total elution curve. These values are plotted against the per cent. of the total eluted at that point. A typical graph is given in Fig. 1. Similar graphs for the other component, Pr, were not considered necessary since a good separation of Nd would preclude a good separation of Pr.

The general procedures for preparation and operation of the Amberlite IR-1 columns have been given previously.[3]

III. Experimental

1. **Effect of *p*H.**—It was shown clearly in the experiments with Ce and Y[3] that the *p*H of the eluant was an important factor in effecting a separation. Similar studies were made with Pr and Nd. The columns used in the experiments were 16 mm. in diameter and had a resin bed length of 175 cm. The flow rate of the eluant was maintained at 5–6 cm./min. throughout the entire set of experiments.

In series I, the *p*H of eluant was 2.53 for one column and 2.75 for the other. The weights of the starting samples were 0.65 g./sq. cm. (as oxide) and analyzed 21% Pr, the remainder being Nd. In series II the *p*H values were 2.55 and 2.65; the weight of starting material was 0.5 g./sq. cm. and analyzed 43.4% Pr. All the other variables were maintained at constant values. The pertinent data are presented in Table I. The purity curves, given in Fig. 1, show the separation of the Nd and Pr for each of the experiments.

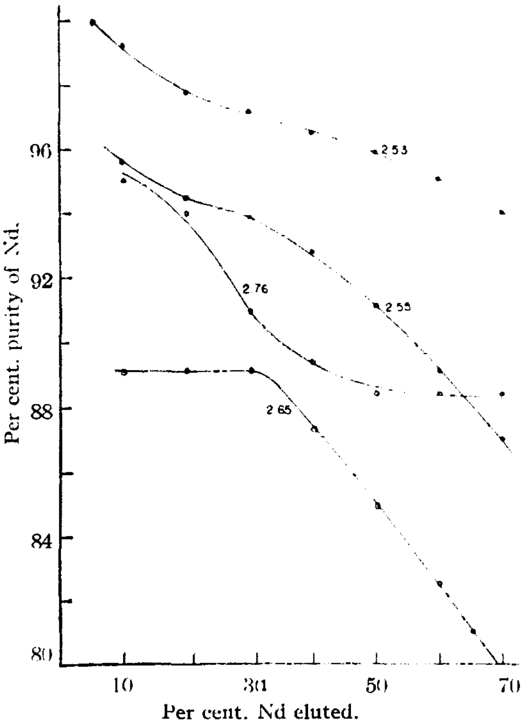

Fig. 1.—The effect of *p*H on the separation: column dimensions, 16 mm. × 175 cm.; flow rate 5–6 cm./min.; composition of starting material, 79% Nd, 21% Pr for the 2.53 and 2.76 experiments and 57% Nd, 43% Pr for the 2.55 and 2.65 experiments.

TABLE I

EFFECT OF *p*H ON SEPARATION OF NEODYMIUM FROM PRASEODYMIUM

% Nd eluted	Series I % Purity of eluted Nd *p*H 2.53	 *p*H 2.75	Series II % Purity of eluted Nd *p*H 2.55	 *p*H 2.65
10	99.2	95.0	95.6	89.1
20	97.8	93.2	94.5	89.1
30	97.1	91.0	93.9	89.1
40	96.5	89.4	92.8	87.3
50	95.9	88.4	91.1	84.9
60	95.1	88.4	89.1	82.5
70	94.0	88.4	87.0	79.6
80	..	..	84.0	77.8
90	..	..	79.6	..

It is clear from these two sets of experiments that a better separation was effected at the lower *pH* value. Comparisons of data should be made only between those experiments in which the composition of the starting material was the same. The possibility exists that a still lower *pH* would increase the separation; a discussion of this is presented in more detail in a later section.

2. **Effect of Weight of Starting Sample.**—The four columns employed were 16 mm. in diameter with a resin bed length of 170–180 cm. The *p*H of the citrate solution was 2.65 and the flow rate 6 cm./min. The weights of samples adsorbed were 0.238, 0.477, 0.953 and 1.906 g./sq.

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[5] The break-through point is defined as that volume of eluate at which the presence of the given element is evident.

cm. calculated as R_2O_3. The samples contained 83% Nd and 17% Pr and were practically free from Sm.

In order to determine how much of the bed length was used for the adsorption of the original material, some very active Ce^{144} tracer was added to each sample. After adsorbing the sample, the length of the column occupied was determined by measuring that portion containing activity with a portable Eck and Krebs type Geiger-Mueller counter. The actual space taken was in direct proportion to the weight of the sample. The data obtained are given in Table II.

TABLE II

EFFECT OF SAMPLE SIZE ON BED LENGTH USED FOR ADSORPTION

Column	Weight of sample g./sq. cm.	Total bed length, cm.	Length used in adsorption, cm.	Effective bed length, cm.
1	0.238	178	8-9	170
2	0.476	173	19	154
3	0.953	168	35-38	131
4	1.906	168	68-71	100

Since the effective bed length was different in each case, the point of break-through varied. Five liters were necessary for the 0.24 g./sq. cm. sample and 2.8 liters for the 1.906 g./sq. cm. sample. Similarly, the concentration of rare earth in the eluates increased with the sample size. The purity curves are shown in Fig. 2. Examination of these data shows that for a given column length and diameter, there is a maximum amount of material which can be adsorbed without adversely affecting the separation under the conditions employed; this is in agreement with similar experiments with Ce and Y.[3] Comparison between the two smallest samples shows very little difference in the separation factor. The results with the columns containing heavier samples were progressively poorer, as would be expected from the decrease in the effective bed length.

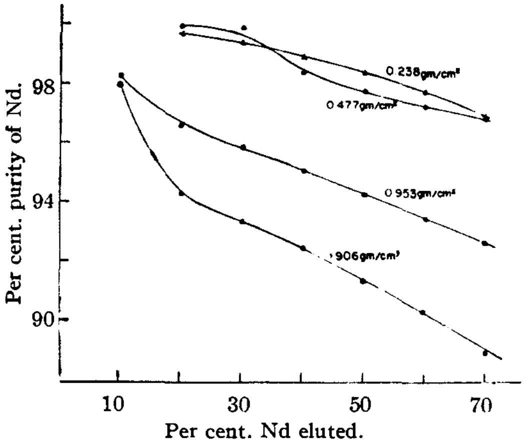

Fig. 2.—The effect of weight of sample on the separation: column dimensions, 16 mm. × 175 cm.; flow rate, 6 cm./min.; pH 2.66; composition of starting material, 83% Nd with 17% Pr.

To establish more firmly the above results on the maximum amount of material which can be used efficiently, four 16-mm. columns were constructed each having a bed length of 350 cm. The amount of material used in the experiments was roughly the same as that used in the experiments with the 175-cm. columns. The flow rate was maintained at 6 cm./min. and the pH at 2.65. The original material analyzed 43.4% Pr, making the detection of the Pr in the early samples more accurate and reliable than in experiments with lower percentages of Pr.

The data obtained at the start of the desorption process are given in Table III. Additional information concerning the break-through points for each column and the concentration of the rare earth in the eluate at the peak of the total weight curve are included in the table. The purity curves are presented in Fig. 3.

TABLE III

EFFECT OF SAMPLE SIZE ON BED LENGTH USED FOR ADSORPTION AND ON BREAK-THROUGH

Column	Wt. of sample, g./sq. cm.	Total bed length, cm.	Effective bed length, cm.	Break-through, liters	R_2O_3 at peak, mg./liter
1	0.254	361	353	22.8	23
2	0.509	354	336	15.1	77
3	1.018	353	315	11.7	199
4	2.036	344	274	9.9	488

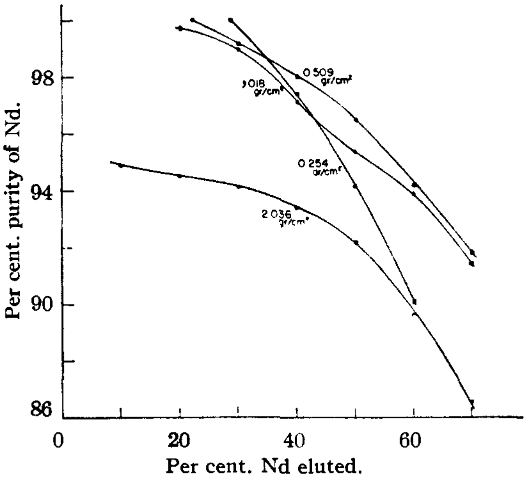

Fig. 3.—The change in separation with change in the weight of sample using longer columns: column dimensions, 16 mm. × 350 cm.; flow rate, 6 cm./min.; pH 2.66; composition of starting material, 56.6% Nd with 43.4% Pr.

The results with the 0.25 g./sq. cm. sample are not too significant since the concentration of the rare earth in the eluate was too low to allow a very accurate determination of the total weight curve. It is to be noted that the break-through for this sample did not occur until 22.8 liters which is far beyond the value predicted from the other samples. This fact and the low concentration would indicate that the material on the column was spread out very thinly, resulting in a decreased separation.

Combining the results obtained with the 175-cm. columns with those obtained with the 350-cm. columns, it is safe to conclude that there is a certain weight of sample for a given column size which will afford the same separation as a smaller sample of the same material, or improve it. Increasing the sample above this weight reduces the degree of separation obtained.

3. Effect of Size of Column

(a) **Length of Column.**—Data are presented in Table IV showing the effect of length of resin bed on the separation of Nd and Pr. In Series I, a 1-g. sample was adsorbed on each of two 16-mm. columns having bed lengths of 175 cm. and 350 cm. The sample in each case analyzed 43.4% Pr and 56.6% Nd; the *p*H was 2.65, and the flow rate 6 cm./min. Series II employed 49-mm. columns with bed lengths of 175 cm. and 850 cm. The sample contained 18% Pr and 2.5% Sm. The sample weight for the smaller column was 9 g. and for the larger column it was 49 g.; the *p*H was 2.65, and the flow rate 5 cm./min. The elution data are given in Table IV. In spite of the fact that both column length and sample size were varied, it is evident that the separation is better for the longer columns.

Table IV

The Effect of Length of Resin Bed on Separation of Nd and Pr

	Series I		Series II	
% Nd eluted	% Purity of eluted Nd 175 cm. column	350 cm. column	% Purity of eluted Nd 175 cm. column	850 cm. column
10	89.1		98.6	99.8
20	89.1	..	98.2	99.5
30	89.0	99.1	97.4	99.1
40	87.3	98.0	96.4	98.6
50	85.1	96.5	95.4	97.9
60	82.7	94.2	94.1	97.0
70	79.5	91.9	92.6	95.7
80	77.8	..	91.8	93.8
% Nd eluted at Pr break-through	3.5	22.5	1.5	5.0

(b) **Diameter of Column.**—It has been shown with columns of the same diameter that the degree of separation is a function of the relative amount of adsorbed material, that is, by the proportionate amount of the column required to adsorb the sample. On this basis one would expect to obtain just as good a separation, all other factors being constant, with columns of larger diameter, if the weights of material used are in the ratio of the cross-sectional areas, providing there are no adverse mechanisms including channeling.

Four columns were tested having bed lengths of about 175 cm. and the diameters 16, 32, 49, and 64 mm. The sample analyzed 20% Pr and 80% Nd and the sample weight on each column corresponded to 0.5 g./sq. cm. The *p*H was 2.65 and the flow rate 6 cm./min. The purity curves are shown in Fig. 4. Altering the diameter made little difference in the separation; the variations observed were within experimental error. Larger samples can be run with large diameter, giving the same separation as smaller columns, providing the linear flow rate is maintained at a constant value.

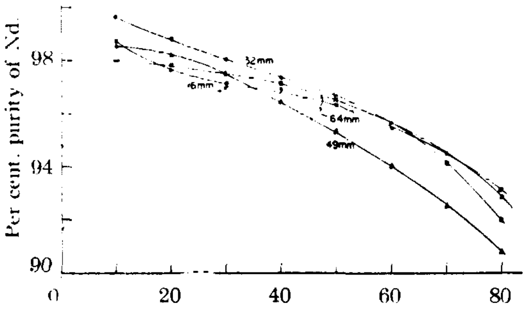

Fig. 4.—The effect of column diameter on the separation: column length 175 cm.: composition of starting material, 80% Nd with 20% Pr; weight of sample, 0.50 g./sq. cm.: flow rate, 6 cm./min.

4. **Effect of Flow Rate.**—Experiments were undertaken in order to determine the optimum flow rate for separation of the elements under consideration. Three identical columns were prepared which were 16 mm. in diameter and 175 cm. in bed length. The same size sample (0.475 g./sq. cm.) was adsorbed on each column and eluted with 5% citrate at a *p*H of 2.65. The original sample analyzed 17% Pr. The flow rates tested were 3, 6, and 12 cm./min.

The break-through occurred in all cases between 3.5 and 4.0 liters. From the total elution curves (Fig. 5) it is readily seen that the concentrations of total rare earth at the peaks in the elution curves differ greatly from one experiment to the next. The maximum concentration increases as the flow rate decreases; that is, 3 cm./min. gives 372 mg./liter at the peak; 6 cm./min., 246 mg./liter; and 12 cm./min., 182 mg./liter. The elution of the Pr appears to be unaffected. The purity curves in Fig. 6 show the improvement in the separation with the slower flow rates. However, the time of the experiment increases with decrease in flow rate, a fact which would be important in large scale operation.

5. **The Effect of the Composition of the Starting Sample.**—The ratio of the components in the starting material represents an important factor in obtaining a pure material. This is inherent in the process since the ratio of the starting materials must vary from one successive experiment to the next if a separation is to be obtained. It is certain, however, that the total amount of pure material obtained in any one experiment is governed by the composition of the starting material, other factors being held constant.

In the *p*H experiments previously described, the column which was operated at a *p*H of 2.53 had a starting sample which contained 21% Pr, while the column operated at a *p*H of 2.55 had a starting sample which contained 43.4% Pr. Since the difference in *p*H is small, its effect on the separation can be neglected. Comparison of the

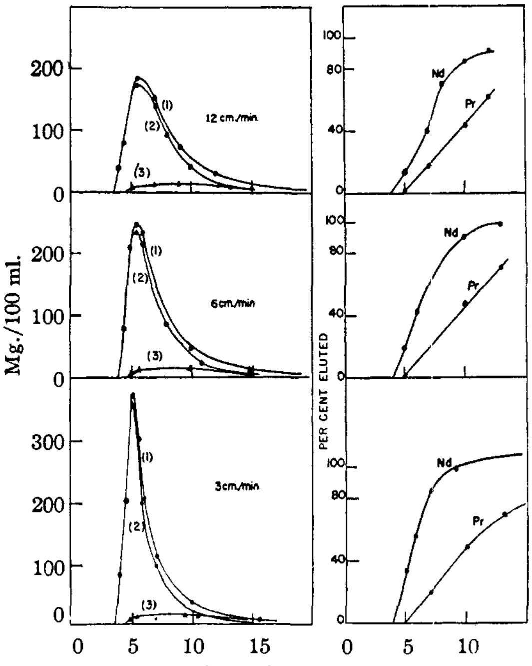

Fig. 5.—The elution curves of Nd and Pr employing different flow rates: column dimensions, 1.6 × 175 cm.; *p*H 2.65; sample wt., 0.476 g./sq. cm.; composition of starting material, 83% Nd with 17% Pr. The separation curve is shown opposite the elution curve for each experiment. Curve 1 in each case represents the total weight curve, while curves 2 and 3 are the elution curves of the Nd and Pr, respectively, drawn after analyses were made.

purity curves in Fig. 1 shows that the separation at *p*H 2.75 for 21% Pr material appears to be as good as that at 2.55 for the 43.4% Pr sample.

The data obtained from the weight of sample experiments could not be used to compare with the length of column experiments due to the fact that there was a large difference in the Pr content of the starting materials; the starting material on the 175 cm. columns contained only 17% Pr while that on the 350 cm. columns contained 43.4% Pr. Comparing the purity curves in Fig. 2 with those in Fig. 3, it is seen that the separation is as good with the 175 cm. column as with the 350 cm. column for each sample weight. Since it has been shown that an increase in column length increases the separation, such anomalous results can only be ascribed to the differences in the composition of the starting materials.

6. Test Under Near Optimum Conditions.—From the foregoing data it was possible to establish a set of more favorable conditions for the separation of Pr and Nd by elution with 5% citrate solution. One factor which has been mentioned but not properly emphasized, was the time necessary to perform a complete experiment. It has been shown that increased separation results when the *p*H and flow rates were lowered, and when the length of the column was increased. All of these results increase the length of time necessary to carry out the elution.

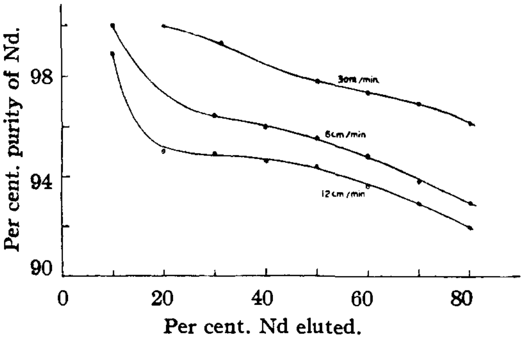

Fig. 6.—Purity curves showing the effect of flow rate on the separation: column dimensions, 16 mm. × 175 cm.; *p*H 2.65; sample wt., 0.476 g./sq. cm.

In compiling this set of conditions, the assumption was made that all of the individual effects on the separation due to each of the variables investigated were additive. By combining the best value for each of the variables and eluting a sample under these conditions, the separation obtained might be expected to represent an approach to the best for these two elements. The conditions are listed below.

(a) ***p*H.**—The best *p*H value for 5% citrate is 2.55. A lower value would retard the elution to such an extent that any separation gain would be offset by the increase in time necessary for the elution. Furthermore, in the case of Ce and Y,[3] an optimum *p*H was obtained; below this value the separation decreased.

(b) **Weight of Sample.**—The sample weight should preferably be between 0.25 and 0.5 g. (as oxide) per sq. cm. of resin bed.

(c) **Flow Rate.**—The separation increased on reducing the flow rate from 12 to 6 to 3 cm./min. An additional increase in the separation may result if the flow rate were further reduced to 1.5 cm./min. At flow rates less than this, particularly with small diameter columns, it becomes increasingly difficult to keep the flow rate accurately adjusted. The elution time and the possibility for back diffusion also increase with decreasing flow rate.

(d) **Size of Column.**—To date, the largest column used has been one with a diameter of 75 mm. In no instance did any single diameter give a separation which differed by more than the experimental error from that obtained from the other size columns, other variables being equal. A bed length of 175 cm. was arbitrarily chosen as standard.

An experiment was performed to test the above set of conditions. A 64 mm. diameter column was used, having a bed length of 175 cm. The sample was 0.25 g./sq. cm. and analyzed 51.7% Pr The flow rate was 1.5 cm./min. and the *p*H

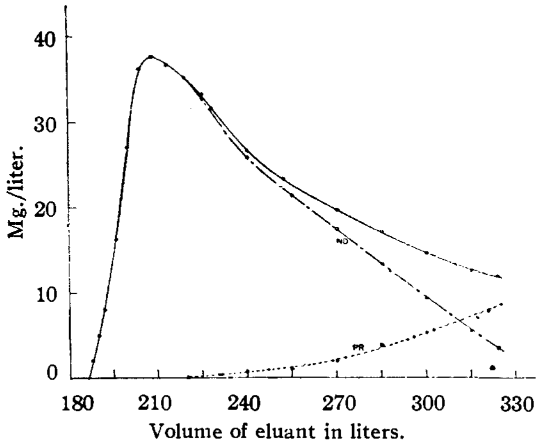

Fig. 7.—Total elution curve under favorable conditions of operation: column dimensions, 6.4 × 175 cm.; composition of starting material, 48.3% Nd with 51.7% Pr.

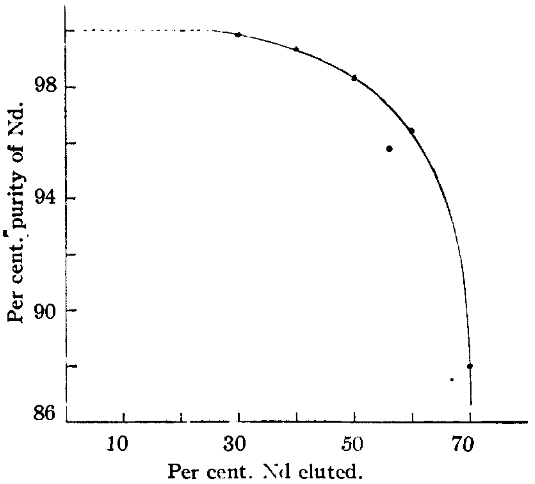

Fig. 8.—Purity curve of the separation of Nd and Pr under favorable conditions: column dimensions, 6.4 cm. × 175 cm.; starting material, 48.3% Nd with 51.7% Pr.

was 2.55. The break-through came at 184 liters which, at this flow rate, was approximately 2.5 days after the start of the elution.

The total elution curve, with the individual elution curves of the Nd and Pr is presented in Fig. 7. The purity curve given in Fig. 8 shows that 22% of the Nd was obtained with spectroscopic purity and more than 50% of the original Nd was eluted with a purity >98% Nd.

7. **Preparation of Pure Pr and Nd.**—As the composition of the starting material exerts a great influence on the degree of separation, it is of interest to determine the per cent. yield of pure Nd from a starting sample containing 98% Nd and eluted under the conditions outlined above.

A total of 1.8 g. of material (as oxide) analyzing 98% Nd was divided into two fractions and adsorbed on two 16 mm. columns, each 175 cm. in length. After eluting under the above conditions and analyzing the samples spectrographically, a total of 1.3 g. of oxide was obtained which analyzed <0.1% Pr. This represents a yield of about 75% in the second passage through the column.

Starting with a 50% Nd-Pr mixture, one passage through the column yielded about 22.5% of the Nd free of Pr, while 50% was >98% pure. By using this 50% and making a second passage through the column, about 75% of this or 37–40% of the original Nd was obtained pure. Thus the yield of pure Nd had been increased by a factor of nearly two by adding a second column. It has not been determined whether a larger over-all yield could have been obtained by a different choice of the intermediate fraction, that is, using in the second column all of that material from the first which was >90% Nd.

In the preparation of the rich Nd fraction in the first column, it may be of advantage to slightly overload it initially and so improve the yield of the material of a specified purity in terms of grams and not of per cent. In this way, the over-all yield of pure Nd in a two column process might be improved.

Several experiments have been performed to prepare pure Pr using the rich Pr fractions coming from the tail end of the Nd elution experiments as starting material. Of 2.8 g. of oxide that contained about 2.0% Nd, greater than 1.3 g. of the eluted material contained <0.1% Nd after a single passage through the column.

Referring to the elution curve in Fig. 7 it is seen that, beyond the peak, the rate at which the Nd is eluted gradually diminishes. It will persist for a long time in all the samples as the Pr content gradually increases in amount. Because of the length of time involved in obtaining very rich Pr samples in a single passage, using 50% Pr as starting material, and because a large portion of the starting material is eluted between the Nd rich and Pr rich fractions, it would be advantageous to strip the column after the bulk of the Nd had been removed and use this fraction on a second column.

The authors wish to thank V. A. Fassel for the many spectroscopic analyses which he performed during the course of this work.

IV. Summary and Conclusions

The research described in this paper was designed to obtain a set of conditions for the efficient separation of the adjacent rare earths Pr and Nd. It has been shown that the method can be applied to the production of relatively large amounts of rare earths of spectroscopic purity and with a relatively small number of operations.

In experiments starting with materials which were nearly pure, high yield of material is obtained in spectroscopically pure form. Thus a series of columns can be used to further purify the rich fractions, leading to larger yields of pure product by two or three passages.

The choice of the length of column is largely arbitrary. Increasing the length of column and decreasing the pH of the eluant and its flow rate have similar effects on the separation. All tend to increase the separation and also the time required for running a given weight of sample through the column. This time increases prohibitively as these factors are changed in the above manner and time becomes a determining factor in any large scale operation. Choices have to be made which depend upon the object of any given experiment. Columns of larger diameter can be operated using correspondingly larger amounts of material without affecting the separation, the length of time involved for an experiment being the same as with smaller columns if the flow rate is adjusted accordingly.

AMES, IOWA RECEIVED JULY 7, 1947

[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

Ion-Exchange as a Separations Method. II. Separations of Several Rare Earths of the Cerium Group (La, Ce, Pr and Nd)[1]

BY DARWIN H. HARRIS AND EDWARD R. TOMPKINS

Introduction

In a previous paper[1a] a method for fractionating rare earth elements by use of ion-exchange columns was described. This method, which depends upon selective elution of cations from a column with complexing agents, was first developed for the separation of curie quantities of the products of uranium fission.[2]

A number of the rare earth elements (*i. e.*, La, Ce, Pr, Nd, 61, Sm, Eu and Gd) appear as fission products.[3] Successful fractionation of several of them, both in trace quantities and in 10-mg. amounts,[1a] using Amberlite resins, IR-1 and IR-100,[4] led to the supposition that complete separation of all the rare earths in one or more adsorption–elution cycles would be possible. It was noted that minor variations in the operating conditions of the columns affected the fractionations rather markedly. Thus, to attain optimum results it seemed imperative that the factors affecting column operation be well understood. Several of these factors have been studied in some detail[5] but the effects of varying a number of others are not so well understood.

F. H. Spedding, *et al.*,[6] using this column method, studied the separation of yttrium from cerium and later of neodymium from praseodymium in gram quantities on large columns. They also studied the effects of several variables on the fractionation efficiency of the column. From the results of these investigations they chose a set of "near optimum conditions" and operating the columns under these conditions they were able to fractionate, from a mixture of equal quantities of neodymium and praseodymium, 22.5% of the neodymium "free of praseodymium."

The work which was being carried out at this laboratory during this time indicated that the fractionation of rare earths with the IR-1 and IR-100 columns could probably be improved somewhat over that obtained by Spedding, *et al.*, if the column operations were better understood, but that there was little hope of achieving complete separation in a single cycle by use of these resins. For this reason, when a new type of ion exchange resin, Dowex 30, was described by Bauman,[7] it was decided that its applicability to this problem should be tested.[8]

A few preliminary experiments comparing the Dowex resins to IR-1 and IR-100 indicated that the Dowex 50 would be far superior to the Amberlite resins for rare earth separations. In these column runs, a mixture of Y and Ce, both in trace concentrations and macroscopic amounts, was eluted from a Dowex 50 column 1 sq. cm. in area by 10 cm. in height with 5%[9] citrate at pH's of 2.75, 3.10, 3.2 and 3.3. As in the previous experiments with IR-1, the degree of separation decreased as the pH was increased, but the separation at any pH was much greater when the Dowex resin was used than that obtained with IR-1. Elution of trace concentrations of these elements from IR-1 columns of this size under similar conditions

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[1] This work was done at Clinton Laboratories, a part of the Plutonium Project, during the period May, 1946, to November, 1946, and is based on work performed under Contract No. W-7405-eng-39 for the Manhattan Project. The information covered herein will appear in Division IV of the Manhattan Project Technical Series as part of the contribution of Clinton Laboratories.

[1a] E. R. Tompkins, J. X. Khym and W. E. Cohn, THIS JOURNAL, **69**, 2769 (1947).

[2] W. E. Cohn, G. W. Parker and E. R. Tompkins, to be published.

[3] J. M. Siegel, THIS JOURNAL, **68**, 2411 (1946).

[4] The Resinous Products and Chemical Co., Philadelphia, Pa.

[5] E. R. Tompkins, *et al.*, to be published.

[6] F. H. Spedding, A. F. Voigt, E. M. Gladrow, *et al.*, THIS JOURNAL, **69**, 2777, 2786 (1947).

[7] W. C. Bauman, *Ind. Eng. Chem.*, **38**, 46 (1946).

[8] Samples of this exchanger and another higher capacity resin, Dowex 50, were obtained from the Dow Chemical Company. The latter exchanger was described by the manufacturer as a "cross-linked aromatic hydrocarbon polymer containing nuclear sulfonic acid groups, belonging to the class of compounds described in U. S. Patent 2,366,007." Because of the high capacity of the Dowex 50, it was chosen for the separations described in this paper.

[9] 5% citrate, as used in this paper, refers to a solution of 50 g. of citric acid monohydrate in a liter of solution, the pH being adjusted with ammonia.