The separation of rare earths by ion exchange. IV. Further investigations concerning variables involved in the separation of samarium, neodymium and praseodymium

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The separation of rare earths by ion exchange. IV. Further investigations concerning variables involved in the separation of samarium, neodymium and praseodymium

Abstract
Previous papers of this series have dealt with some of the variables concerned with the separation of rare earths by means of ion exchange. It has been apparent from the first that the many variables involved should be investigated more thoroughly in order to improve the degree of separation of certain pairs of the rare earths. It was decided, therefore, to study further the effect of such variables as temperature, pH of eluant, size of resin particles and flow rate.

Disciplines
Chemistry

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Contract No. W-7405 eng 82
F. H. Spedding, Director

THE SEPARATION OF RARE EARTHS BY ION EXCHANGE. IV. FURTHER INVESTIGATIONS CONCERNING VARIABLES INVOLVED IN THE SEPARATION OF SATORIUM, NEODYMIUM AND PRASEODYMIUM

by

F. H. Spedding, E. L. Fulmer, T. A. Butler and J. E. Powell

March 1949

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1. INTRODUCTION

Previous papers\textsuperscript{1,2,3,4} of this series have dealt with some of the variables concerned with the separation of rare earths by means of ion exchange. The first and second papers were concerned with variables involved in the use of 5\% citrate solutions for the elution of the rare earths and the third paper dealt with the use of 0.5\% citrate for the separation of rare earths on a pilot plant scale. Although 0.5\% citric acid solution, buffered to a pH value of 3.90 with ammonium hydroxide, has been used successfully for some time on a pilot plant scale for the elution and separation of various rare earth mixtures, it has been apparent from the first that the many variables involved should be investigated more thoroughly in order to improve the degree of separation of certain pairs of the rare earths. For example, the separation of samarium from neodymium obtained using Amberlite IR-100 resin and 0.5\% citric acid solution at a pH value of 3.90 is excellent, the separation of neodymium from praseodymium is only fair and that of gadolinium or europium from samarium is rather poor. It was decided, therefore, to study further the effect of such variables as temperature, pH of eluant, size of resin

\textsuperscript{4} F. H. Spedding, E. I. Fulmer, Suell Ayers, T. A. Butler, Jack Powell, A. D. Tevebaugh and Robert Thompson, \textit{ibid.}, 70, 1671 (1948).
particles and flow rate. The present communication is concerned with the results of investigations which have been completed to date. From this and previous papers it is evident that the mechanism of separation is complex and the authors feel that it is too early to check or to extend the existing theories of column separation. These matters will be considered in a later paper when more data have been obtained and existing data more fully evaluated.

II. MATERIALS, APPARATUS AND GENERAL PROCEDURE

1. Materials.—The pure samarium, neodymium and praseodymium oxides were prepared in the manner previously described for the pilot plant scale operations. The mixtures employed were prepared by mixing the pure oxides in equimolar ratios.

The Amberlite IR-100 resin was prepared by passing the commercial grade resin over a set of standard screens. The two sizes of resin particles employed will be designated as -30+40 and -60+80. The designation -30+40 means that all of the resin passed a number of 30 U.S. Standard Screen, but was retained by a number 40 U.S. Standard Screen. The average diameter of -30+40 particles is approximately double that of the -60+80 particles.

2. Apparatus.—The columns used in the following experiments were constructed of pyrex glass tubing with an outside diameter of 25 mm. and inside diameter of 22 mm., they were closed near the bottom with coarse fritted glass discs in order to support the resin bed. The columns were drawn down to 8 mm. just below the glass disc. The 8 mm. nipple was
connected by means of a short length of rubber tubing to a piece of 8 mm.
tubing drawn down to a capillary tip. A screw clamp on the rubber tubing
permitted the flow rate to be adjusted carefully. The columns were packed
with resin in the following manner. Each column was filled with distilled
water and then tapped sharply as resin was added at the top. It was dis-
covered that the resin bed shrank somewhat during the regeneration cycle
so that it was necessary to add an excess of resin and then submit the whole
bed to several regeneration cycles with periodic tapping using a rubber
mallet. When no further shrinkage occurred after considerable tapping the
beds were adjusted to the desired height by removing the excess resin.

3. General Procedure.—Prior to each new experiment each column was
regenerated with the following solutions in the order given:—4 liters of
5% citrate solution at a pH value of 5.0, 4 liters of 5% by weight sodium
chloride solution and 4 liters of 5% hydrochloric acid (5 ml. of concentrated
hydrochloric acid per 100 ml. of solution). After removing the excess acid
with a distilled water rinse, a sample, consisting of 0.005 moles of $\text{R}_2\text{O}_3$
'(about 1.70-1.75 grams depending on the rare earths involved), dissolved
in 2.6 ml. of concentrated hydrochloric acid and a liter of distilled
water, was adsorbed on the top of the resin bed at a linear flow rate,
down the column, of about 2 cm. per minute. After another rinse with a
liter of distilled water to remove the acid formed in the adsorption
process, the column was considered ready for elution and was attached by
means of a siphon to a reservoir of the eluant.

4. The Eluting Solution.—The eluant used in this series of experiments
has been designated as 0.5% citrate solution. By 0.5% citrate it is to be understood that the solution was made up with 5 grams of citric acid monohydrate per liter of distilled water and then adjusted to the required pH with concentrated ammonium hydroxide. A Beckman pH meter, Laboratory Model G, was used in adjusting the pH of the solutions; the values thus obtained were probably accurate to ±0.02 of a pH unit. In order to prevent the growth of mold, a gram of phenol was added for each liter of the solution.

5. Recover and Analysis.—The rare earths were recovered from the fractions of eluate as their oxalates and ignited to their oxides for weighing. The fractions were analyzed spectrophotometrically using a Beckman Quartz Spectrophotometer. The solutions for analysis were prepared by dissolving 50 mg. of the oxide in 5 ml. of 10% hydrochloric acid. After the sample was dissolved, the solution was diluted to 10 ml. with 10% hydrochloric acid and this solution used for the spectrophotometric analysis. The 10% acid solution was prepared by diluting 10 ml. of concentrated (sp. gr. 1.18-1.19) hydrochloric acid to 100 ml. with distilled water. The neodymium was measured at 740 m\(\mu\), the samarium at 401 m\(\mu\) and the praseodymium at 444 m\(\mu\)^2. The values for the molar extinction coefficients for neodymium, samarium and praseodymium at the above wavelengths were redetermined using the purest materials on hand; the data in Table I compare the new values with those used in previous experiments.
Table I.

Data Employed in the Spectrophotometric Analysis of the Rare Earths

<table>
<thead>
<tr>
<th>Element</th>
<th>Abs. Band</th>
<th>Band Width</th>
<th>Extinction Coefficient, liters x cm x mol-1 x cm-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>740</td>
<td>10</td>
<td>Old value: 6.27, New value: 6.53</td>
</tr>
<tr>
<td>Sm</td>
<td>401</td>
<td>5</td>
<td>Old value: 3.09, New value: 3.09</td>
</tr>
<tr>
<td>Pr</td>
<td>444</td>
<td>5</td>
<td>Old value: 9.30, New value: 10.07</td>
</tr>
</tbody>
</table>

*The value of 7.30 previously given was due to a typographical error. The extinction coefficient value should have been 9.30 and the band width 5 Å instead of 10 Å.

III. EXPERIMENTAL

1. The Effect of pH on the Solution of Pure Samarium at Two Flow Rates Using 0.5% Citrate Solutions in the pH Range 3.30 to 4.20.

Five columns having 30 x 40 Amberlite IR-100 beds, 120 cm. long and 22 mm. in diameter, were each loaded with 1.744 grams of pure Sm2O3. The solution of the oxides in hydrochloric acid prior to adsorption on the resin bed, as described in the general procedure, is assumed in all subsequent discussions. The samples were eluted at a flow rate of 0.5 cm. per minute down the column using 0.5% citrate solutions at pH values of 4.20, 4.10, 4.00, 3.90 and 3.80.

The five columns were then regenerated and reloaded with identical samarium samples as before. These samples were eluted at a linear flow rate of 2.0 cm. per minute down the column with 0.5% citrate at pH values of 4.20, 4.10, 4.00, 3.90 and 3.80.
The data for this experiment are plotted in Figure 1. The pH value of the eluant is recorded beside the curve with which it is associated. The qualifying letter "A" refers to a linear flow rate down the column of 0.5 cm. per minute and the letter "B" refers to the 2.0 cm. per minute flow rate. The significant results of increased flow rate was to reduce the rare earth concentration in the eluate, thus causing the volume of eluate for complete elution to increase. From the elution curves, it was observed that decreasing the pH of the eluant increased the volume required for the break-through to occur. At pH values of 4.00 and above this effect is small, but at lower pH values the increase becomes more pronounced. Evidence has been given for more than one citrate complex active in the column. It is probable, from the shape of the curves observed, that as the pH of the eluant is changed the relative importance of the various citrate complexes changes in this pH range.

2. The Effect of Temperature on the Elution of Pure Samarium at Two Flow Rates Using 0.5% Citrate Solution at a pH of 3.90.

Three columns having beds of -30+40 Amberlite IR-100 resin, 120 cm. long and 22 mm. in diameter, were each loaded with a sample consisting of 1.744 grams of pure Sm$_2$O$_3$ in the manner described above. Two of the columns were equipped with water jackets. One column of this set was maintained at 0$^\circ$ C. by circulating ice water through its jacket, a second column was maintained at 50$^\circ$ C. by circulating hot water from a constant temperature bath through its jacket, and the third column was allowed to remain at room temperature, about 25$^\circ$ C. The samples were eluted at a linear flow rate of 0.5 cm. per minute with 0.5% citrate solution at a
Fig. 1. - The effect of pH on the elution of 1.744 gram samples of pure Sm$_2$O$_3$ from 2.2 x 120 cm. beds of -30-40 Amberlite IR-100 using 0.5% citrate solutions at linear flow rates of 0.5 cm. per minute and 2.0 cm. per minute: O, 0.5 cm./min.; 0, 2.0 cm./min.
pH of 3.30, observed at 25°C. The quantitative change in pH of the ammonium citrate solutions with temperature is not known, since it is a complicated function of the various equilibrium constants. A detailed study of the relation of pH to temperature is planned for a later date.

After the above experiment was completed the columns were stripped, regenerated and reloaded with pure samarium samples as before. The samples were eluted at a linear flow rate of 2.0 cm. per minute with 0.5% citrate solution at a pH of 3.30. The data for this experiment are given in Figure 2. "A" refers to the slow flow rate and "F" to the faster flow rate.

From the break-through values obtained in these experiments, it appeared that lowering the temperature of the solution has an effect comparable to increasing the pH of the eluant, whereas, raising the temperature of the solution gives the opposite effect. The sharpening of the peaks in the case of the 50°C column at both flow rates could not, however, be accounted for in this manner, since the general effect of lowering the pH of the eluant is to spread out the elution curve and to lower the peak concentration of rare earth in the eluate.

By comparing elution curves at the same temperature, but different flow rates, it was observed that a larger volume of eluant was required at the higher flow rate in order to obtain a break-through. It was also noticed that the elution curves were spread out and the peak concentrations lowered at the faster flow rate. This effect was probably due to a somewhat poorer equilibrium maintained between the samarium in solution and the samarium on the resin particles at
**Fig. 2.** - The effect of temperature on the elution of 1.744 gram samples of pure Sm₂O₃ from 2.2 x 120 cm. beds of -30+40 Amberlite IR-100 using 0.5% citrate solution at a pH value of 3.80 (measured at room temperature) and linear flow rates of 0.5 cm. per minute and 2.0 cm. per minute; 0, 0.5 cm./min.; 0, 2.0 cm./min.
the higher flow rate.

3. The Effect of pH on the Elution of Pure Neodymium at Two Flow Rates Using 0.5% Citrate Solutions in the pH Range 3.80 to 4.20.

Five columns having beds of -30+40 Amberlite IR-100 resin, 120 cm. long and 22 mm. in diameter were loaded with 1.683 grams of pure Nd$_2$O$_3$ per column. The samples were eluted at a linear flow rate of 0.5 cm. per minute using 0.5% citrate solutions at pH values of 4.20, 4.10, 4.00, 3.90 and 3.80.

The columns were reconditioned and reloaded with identical neodymium samples as in the above experiments. The columns were then eluted with the 0.5% citrate solutions at pH values of 4.20, 4.10, 4.00, 3.90 and 3.80 at a flow rate of 2.0 cm. per minute. The elution curves for these runs are given in Figure 3. The pH of the eluant is indicated beside the curve to which it corresponds. "A" refers to the slow flow rate and "B" to the faster flow rate.

The conclusions drawn from these two sets of experiments were essentially the same as for the pure samarium elution under the same conditions of pH and flow rate (Section 1). Attention should be directed toward the elution curves for the pH values 4.00, 3.90 and 3.80. The curve for a pH value of 3.90 shows a nearly symmetrical form while those for pH values of 4.00 and 3.80 are roughly mirror images. These facts might indicate a change in the type of citrate complex and/or a shift in the equilibrium between the neodymium in solution and the neodymium on the resin.

It can be seen from Figures 1 and 3 that the elution curve for neodymium at a given pH is nearly identical to the elution curve obtained for samarium at 0.1 pH unit lower. As an example, the elution curve 4.10A obtained for neodymium in Figure 3 should be compared with the samarium
Fig. 3. — The effect of pH on the elution of 1.683 gm. samples of pure \ text{I}_2\text{O}_3 \text{ from 2.2 x 120 cm. beds of -30+10 Amberlite IR-100 using 0.5% citrate solutions at linear flow rates of 0.5 cm. per minute and 2.0 cm. per minute; } 0, 0.5 \text{ cm./min.; } \circ, 2.0 \text{ cm./min.}
elution curve 4.0OA in Figure 1. This effect may be due to differences in the relative basicities of the two rare earths.

It was observed that at pH values of 4.20 and 4.10 the samarium and neodymium broke through at about the same volume. At lower pH values the difference between individual break-through volumes became progressively larger, suggesting that better separations between samarium and neodymium in mixtures should be obtained at the lower pH values.

4. The Effect of Particle Size of the Resin on the Elution of Pure Neodymium at Two Flow Rates Using 0.5% Citrate Solution at a pH of 3.80.

Two columns having beds of -30+40 and -60+80 Amberlite IR-100 resin, respectively, each 120 cm. long and 22 mm. in diameter were loaded in the usual manner with samples consisting of 1.683 grams of pure Nd$_2$O$_3$. These samples were eluted with 0.5% citrate solution at a pH of 3.80 using a linear flow rate down the column of 0.5 cm. per minute.

Upon completion of the above experiment, the columns were regenerated and again loaded with neodymium samples. The samples were then eluted at a flow rate of 2.0 cm. per minute with 0.5% citrate at a pH of 3.80. The data are plotted in Figure 4. The mesh size of the resin particles used is indicated beside the corresponding curve. The letter "A" refers to a linear flow rate down the column of 0.5 cm. per minute; "B" refers to the 2.0 cm. per minute flow rate.

The elution curves show that the break-through volume was reduced and the peak concentration of neodymium in the eluate was increased when the
Fig. 4. -- The effect of particle size of resin on the elution of 1.663 g\textsuperscript{2} \text{gpm} samples of pure \text{Nd}_2\text{O}_3 from 2.2 x 120 cm. beds of Amberlite IR-100 using 0.5\% citrate solution at a pH of 3.80 and linear flow rates of 0.5 cm. per minute and 2.0 cm. per minute: \textbullet, 0.5 cm./min.; \textcircled{0}, 2.0 cm./min.
finer resin was used. It was also observed that the maximum was obtained more rapidly in the case of the finer resin. These results indicate that equilibrium conditions are more nearly approached with the particles of finer mesh size.

At the higher flow rate the elution curves were spread out more and the maxima were lowered in agreement with the results of the experiments of Section 3. It was noticed that decreasing the particle size of the resin counteracted the effect of increased flow rate to some extent.

5. The effect of pH on the Elution of Equimolar Samarium–Neodymium Mixtures at Two Flow Rates Using 0.5% Citrate Solutions in the pH Range 3.80 to 4.20.

Three columns having beds of -30+40 Amberlite IR-100 resin, 120 cm. long and 22 mm. in diameter, were each loaded with a sample made up to contain 0.872 grams of Sm$_2$O$_3$ and 0.841 grams of Nd$_2$O$_3$. This mixture contained 2.50 millimols each of Sm$_2$O$_3$ and Nd$_2$O$_3$ or a total of 5.00 millimols of R$_2$O$_3$. This total was equivalent to that of the pure Sm$_2$O$_3$ and pure Nd$_2$O$_3$ samples taken for the previous experiments. The mixtures were eluted at a linear flow rate of 0.5 cm. per minute with 0.5% citrate solutions at pH values of 4.20, 4.00 and 3.80. The data for this experiment are plotted in Figure 5.

The above experiment was repeated using a linear flow rate of 2.0 cm. per minute instead of 0.5 cm. per minute and the data plotted in Figure 6.
Fig. 5. - The effect of pH on the elution of 1.713 gram samples of equimolar Sm₂O₃-Nd₂O₃ mixtures from 2.2 x 120 cm. beds of -30+40 Amberlite IR-100 using 0.5% citrate solutions at a linear flow rate of 0.5 cm. per minute: ○, Sm₂O₃; □, mixed fractions; ▲, Nd₂O₃.
Fig. 6 - The effect of pH on the elution of 1.713 gram samples of equimolar Sm$_2$O$_3$ - Nd$_2$O$_3$ mixtures from 2.2 x 120 cm. beds of -30+40 Amberlite IR-100 using 0.5% citrate solutions at a linear flow rate of 2.0 cm. per minute; O, Sm$_2$O$_3$; @, mixed fractions; @, Nd$_2$O$_3$. 
Table 2

Data for the Separation of a 1.713 gm. Equimolar Sm₂O₃ – Nd₂O₃ Mixture with 0.5% Citrate Solutions

<table>
<thead>
<tr>
<th>pH of eluant</th>
<th>Flow Rate</th>
<th>Elution Vol, Liters</th>
<th>Total R₂O₃ Recovered Grams</th>
<th>Percent Obtainable in a Pure State</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.20</td>
<td>0.5</td>
<td>16</td>
<td>1.650</td>
<td>Sm₂O₃ 81 Nd₂O₃ 79</td>
</tr>
<tr>
<td>4.00</td>
<td>0.5</td>
<td>16</td>
<td>1.615</td>
<td>Sm₂O₃ 90 Nd₂O₃ 96</td>
</tr>
<tr>
<td>3.80</td>
<td>0.5</td>
<td>&gt;50</td>
<td>1.579</td>
<td>Sm₂O₃ 96 Nd₂O₃ 96</td>
</tr>
<tr>
<td>4.20</td>
<td>2.0</td>
<td>19</td>
<td>1.630</td>
<td>Sm₂O₃ 95 Nd₂O₃ 93</td>
</tr>
<tr>
<td>4.00</td>
<td>2.0</td>
<td>32</td>
<td>1.681</td>
<td>Sm₂O₃ 95 Nd₂O₃ 96</td>
</tr>
<tr>
<td>3.80</td>
<td>2.0</td>
<td>&gt;50</td>
<td>1.534</td>
<td>Sm₂O₃ 96 Nd₂O₃ 95</td>
</tr>
</tbody>
</table>

The percent of each rare earth oxide recovered in a pure state is given in Table 2. The overall recovery of rare earth oxides decreased with decreasing pH of the eluant. This was to be expected, since larger volumes of eluant were required at the lower pH values. Part of the loss at a pH value of 3.80 was due to the use of 5.0% citrate at a pH of 5.0 for stripping the last of the neodymium from the column. It has been observed that the solubility of neodymium and samarium oxalates, calculated as R₂O₃, is roughly 4 mg. of R₂O₃ per liter, and that the solubility increases with increased citrate concentrations.

In calculating the amounts of Sm₂O₃ and Nd₂O₃ obtainable in a pure state, it was necessary to correct for the losses due to the solubility of the oxalates in order to present a true picture of the separation obtained. It was assumed that this soluble portion could be recovered by an appropriate method, such as evaporation of the
filtrate to dryness and ignition of the residue to the oxide. The limit of impurity in this analysis was set at 0.5%. Any sample of Sm$_2$O$_3$ containing less than this percentage of Nd$_2$O$_3$ or any Nd$_2$O$_3$ sample containing less than this amount of Sm$_2$O$_3$ was, therefore, considered pure. A correction of 4 mg. of R$_2$O$_3$ per liter was applied to those samples in each case in which the neodymium and samarium were not completely separated, as defined above. The amounts of Nd$_2$O$_3$ and Sm$_2$O$_3$ present in this mixed portion was determined by a spectrophotometric analysis. These amounts were subtracted from the amounts of Nd$_2$O$_3$ and Sm$_2$O$_3$ taken for the original sample. The differences were taken as the amounts of pure Nd$_2$O$_3$ and pure Sm$_2$O$_3$ obtainable.

The highest degree of separation was obtained by using a pH value of 3.80 and the poorest separation was obtained at a pH value of 4.20. However, three separations at a pH of 4.20 would yield more pure Sm$_2$O$_3$ and Nd$_2$O$_3$ in a given length of time than one separation at a pH value of 3.80. This may be confirmed by reference to Figures 5 and 6 and Table 2 which show that the volume of eluant required for the elution at a pH of 3.80 was at least three times the volume required at a pH of 4.20, while the degrees of separation were of the same order of magnitude in both cases. The length of time and the volume of eluant required for elution are the chief items of expense in the separation process.

The effect of flow rate upon the separation was found to be almost negligible at a pH of 3.80, but this effect increased with
increase in the pH and was detrimental to the separation at a pH of 4.20. As a consequence of this fact, using a low pH and a fast flow rate might prove as economical as using a slow flow rate and a high pH value.

6. The Effect of pH on the Elution of Equimolar Neodymium–Praseodymium Mixtures at Two Flow Rates Using 0.5% Citrate Solution in the pH Range 3.80 to 4.20.

Seven columns having -30×40 Amberlite IR-100 beds, 120 cm. long and 22 mm. in diameter, were each loaded with samples made up from 1.695 grams of a mixture containing equal amounts of Nd₂O₃ and Pr₂O₃ by weight. This gave an approximately equimolar mixture of neodymium and praseodymium equivalent to the number of moles used for the previous samples. The mixtures were eluted at a flow rate of 0.5 cm. per minute with 0.5% citrate solution at pH values of 4.40, 4.20, 4.10, 4.00, 3.90, 3.80, and 3.70. The data are plotted in Figure 7.

The above experiment was repeated at the pH values 4.20, 4.10, 4.00, 3.90 and 3.80 using a linear flow rate of 2.0 cm. per minute. The data are plotted in Figure 8. The pH value is recorded beside the corresponding curve in both cases.

Figure 9 was obtained by plotting the per cent Nd₂O₃ eluted versus the per cent purity of the eluted Nd₂O₃ for the experiments at the slower flow rate. It was discovered that the highest degree of separation was obtained at 3.80 and 3.90. At a pH value of 3.70 the elution was too slow for practical purposes and the degree of separation decreased. Surprisingly, the poorest separation of all
Fig. 7. -- The effect of pH on the elution of 1.695 gram samples of a mixture containing equal amounts of Nd$_2$O$_3$ and Pr$_6$O$_{11}$ by weight from 2.2 x 120 cm. beds of -30+40 Amberlite IR-100 using 0.5% citrate solutions at a linear flow rate of 0.5 cm. per minute: O, Nd$_2$O$_3$;$, mixed fractions; $\oplus$, Pr$_6$O$_{11}$. 
Fig. 8 -- The effect of pH on the elution of 1.695 gram samples of a mixture containing equal amounts of Nd₂O₃ and Pr₆O₁₁ by weight from 2.2 x 120 cm. beds of -30+40 Amberlite IR-100 using 0.5% citrate solutions at a linear flow rate of 2.0 cm. per minute; 0, Nd₂O₃; o, mixed fractions; * , Pr₆O₁₁.
Fig. 2 — Purity curves showing the effect of pH on the separation of Nd₂O₃ - Pr₂O₃ mixtures using 0.5% citrate solutions at a linear flow rate of 0.5 cm per minute. Data obtained from Fig. 7. Points indicate the purity of Nd₂O₃ eluted at various pH levels: O, pH 4.00; □, pH 4.20; ▲, pH 4.40; △, pH 4.60; ■, pH 4.80; ▼, pH 5.00; ▲, pH 5.20; △, pH 5.40; ■, pH 5.60; ▲, pH 5.80.
was that at a pH value of 4.00. Above a pH of 4.00 the degree of separation increased with increasing pH values. This effect was associated with a drastic change in the shape of the elution curve between the pH values 4.00 and 4.10. It can be seen from Figure 7 that the trend is for the praseodymium break-through to occur later relative to the neodymium break-through as the pH of the eluant is lowered. Between the pH values 4.00 and 4.10, however, the neodymium elution curve changes from a square front type to a more gradually sloping type curve. At a pH of 4.00 the neodymium attains its maximum concentration just at the point where the praseodymium break-through occurs. This is not the case at other pH values in this range. It appears that separations at pH values of 4.2 and 4.4 might prove more economical than those at pH values of 3.80 and 3.90 at a linear flow rate of 0.5 cm. per minute. Total elution volumes and the percentages of the Nd₂O₃ and Pr₆O₁₁ obtainable with purities greater than 99.5% are correlated in Table 3. It should be remembered that the columns must be regenerated after each individual separation run and this factor would tend to reduce the advantage gained in using the higher pH values and a greater number of runs. Increasing the flow rate by a factor of four proved to be detrimental in this separation at all pH values.
Table 3

Data for the Separation of Equinolar Neodymium-Praseodymium Mixtures Using 0.5% Citrate Solution

<table>
<thead>
<tr>
<th>pH of Eluant</th>
<th>Flow Rate</th>
<th>Elution Volume, Liters</th>
<th>Amounts of Oxide Obtainable</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm/min.</td>
<td></td>
<td>99.5% Pure</td>
</tr>
<tr>
<td>3.8</td>
<td>0.5</td>
<td>90</td>
<td>84</td>
</tr>
<tr>
<td>3.9</td>
<td>0.5</td>
<td>50</td>
<td>71</td>
</tr>
<tr>
<td>4.0</td>
<td>0.5</td>
<td>35</td>
<td>55</td>
</tr>
<tr>
<td>4.1</td>
<td>0.5</td>
<td>27</td>
<td>52</td>
</tr>
<tr>
<td>4.2</td>
<td>0.5</td>
<td>20</td>
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<tr>
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<td>13</td>
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<tr>
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IV. SUMMARY

This paper describes some experiments designed to contribute fundamental data concerning the separation of the rare earth pairs Sm, Nd and Nd, Pr using Amberlite IR-100 resin and 0.5% citric acid ammonium citrate solutions as the eluant. Such variables as temperature, pH of eluant, size of resin particles, and flow rate were studied. The rapid change in the shape of the elution curves of pure Sm and Nd with small variations in the pH values of the eluant was shown.

Variations in temperature of the eluting solution over the range 0°C to 50°C caused the shape of the elution curves to change. Lowering the temperature of the solution had an effect comparable to increasing the pH of the eluant, whereas, raising the temperature of the solution gave the opposite effect. At the higher temperature it appeared that the equilibrium between the rare earth citrate complex and the resin
was more nearly attained.

Reducing the particle size of the resin had the effect of allowing equilibrium conditions in the column to be approached.

In general, increasing the flow rate by a factor of four caused the rare earth break-through to be delayed, the elution curves to spread out somewhat and the peak concentration of rare earths to be lower. Any spreading or trailing out of an elution curve for a pure substance is almost certain to be detrimental to the separation obtained when mixtures of two elements are involved.

The best separation of a pair of rare earths using 0.5% citrate solution as eluant was obtained at a linear flow rate of 0.5 cm. per minute and pH value 3.80. It was also found that 0.5 citrate at pH values 4.2 to 4.4 and linear flow rate of 0.5 cm. per minute gave fair separations in about one-third the time required for eluant of pH value 3.8.