to layers of molecules parallel to the (100) plane, and these layers are bonded to each other by hydroxyl to carboxyl hydrogen bonds. The

observed cleavage parallel to (100) seems to be satisfactorily explained.

The Separation of Rare Earths by Ion Exchange.[1] IV. Further Investigations Concerning Variables Involved in the Separation of Samarium, Neodymium and Praseodymium

BY F. H. SPEDDING, E. I. FULMER, T. A. BUTLER AND J. E. POWELL

I. Introduction

Variables concerned with the separation of certain rare earth mixtures by elution from synthetic ion exchange resins with 5% citric acid solutions have been studied extensively.[2-10] Lower citric acid concentrations have received very little attention, although 0.5% citrate solutions have been used successfully on a pilot plant scale.[11] The present communication presents systematic studies on the effect of such variables as temperature, pH of eluant, size of resin particles and flow rate using 0.5% citric acid as the eluting agent.

II. Materials, Apparatus and General Procedure

(1) **Materials.**—The pure samarium, neodymium and praseodymium oxides were prepared as previously described[11] for the pilot plant scale operations. The mixtures employed consisted of pure oxides in equimolar ratios. The Amberlite IR-100 resin was prepared by passing commercial grade resin over standard screens. Unless otherwise stated −30 + 40 mesh size particles were used in the columns.

(2) **Apparatus.**—The columns, constructed of 22 mm. i. d. Pyrex glass tubing, were closed near the bottom with coarse fritted glass discs. Each column was filled with distilled water and then tapped as resin was added; the bed was given several regeneration cycles with periodic tapping and then adjusted to the desired height by removing the excess resin. Unless otherwise stated, all resin beds were 120 cm. long.

(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

(1) This work was supported, in part, by a grant from the Atomic Energy Commission.

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

(3) F. H. Spedding, A. F. Voigt, E. M. Gladrow, N. R. Sleight, J. E. Powell, J. M. Wright, T. A. Butler and P. Figard, *ibid.*, **69**, 2786 (1947).

(4) D. H. Harris and E. R. Tompkins, *ibid.*, **69**, 2792 (1947).

(5) B. H. Ketelle and G. E. Boyd, *ibid.*, **69**, 2800 (1947).

(6) E. R. Tompkins, J. X. Khym and W. E. Cohn, *ibid.*, **69**, 2769 (1947).

(7) E. R. Tompkins and S. W. Mayer, *ibid.*, **69**, 2859 (1947).

(8) S. W. Mayer and E. R. Tompkins, *ibid.*, **69**, 2866 (1947).

(9) E. R. Tompkins, D. H. Harris and J. X. Khym, *ibid.*, **71**, 2504 (1949).

(10) G. E. Boyd, J. Schubert and A. W. Adamson, *ibid.*, **69**, 2818 (1947).

(11) F. H. Spedding, E. I. Fulmer, T. A. Butler, E. M. Gladrow, M. Gobush, P. E. Porter, J. E. Powell and J. M. Wright, *ibid.*, **69**, 2812 (1947).

value of 5.0, 4 liters of 5% sodium chloride solution and 4 liters of 5% hydrochloric acid. After removing the excess acid with a distilled water rinse, a sample, consisting of 0.005 mole of R_2O_3 (about 1.70–1.80 g. 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.

(4) **The Eluting Solution.**—The eluant, designated as 0.5% citrate solution, contained 5 g. of citric acid monohydrate per liter of distilled water initially and was adjusted to the required pH with concentrated ammonium hydroxide. In order to prevent the growth of mold, 1 g. of phenol was added per liter of solution.[11]

(5) **Recovery and Analysis.**—The rare earths were recovered from the eluate as oxalates and ignited to the oxides for weighing. The fractions were analyzed with a Beckman Quartz Spectrophotometer. The solutions for analysis were prepared by dissolving 50 mg. of the oxide in 5 ml. of 5% hydrochloric acid and diluting to 10 ml. with the same acid. The Nd was measured at 740 mμ, the Sm at 401 mμ and the Pr at 444 mμ.[3,10] The values for the molar extinction coefficients for Nd, Sm and Pr at the above wave lengths were redetermined using the purest materials on hand; the data in Table I compare the new values with those used previously.[11]

TABLE I

DATA EMPLOYED IN THE SPECTROPHOTOMETRIC ANALYSIS OF THE RARE EARTHS

Element	Abs. band, mμ	Band width, Å.	Extinction coefficient 1. × g. moles^{-1} × cm.$^{-1}$ Old value	New value
Nd	740	10	6.27	6.53
Sm	401	5	3.09	3.09
Pr	444	5	9.80[a]	10.07

[a] The value of 7.30 previously given was due to a typographical error. The extinction coefficient value should have been 9.80 and the band width 5 Å. instead of 10 Å.

III. Experimental

(1) **The Effect of pH on the Elution of Pure Samarium and Neodymium in the Range 3.80 to 4.20.**—Columns were loaded with 1.744 g. each of pure Sm_2O_3. 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 flow rates of 0.5 and 2.0 cm./min. at pH values of 4.20, 4.10, 4.00, 3.90 and 3.80. Another experiment, identical in all respects to that described above, except for the substitution of pure Nd for Sm, was performed.

The data for these experiments are plotted in Figs. 1 and 2. The pH value of the eluant is recorded beside the curve with which it is associated. 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
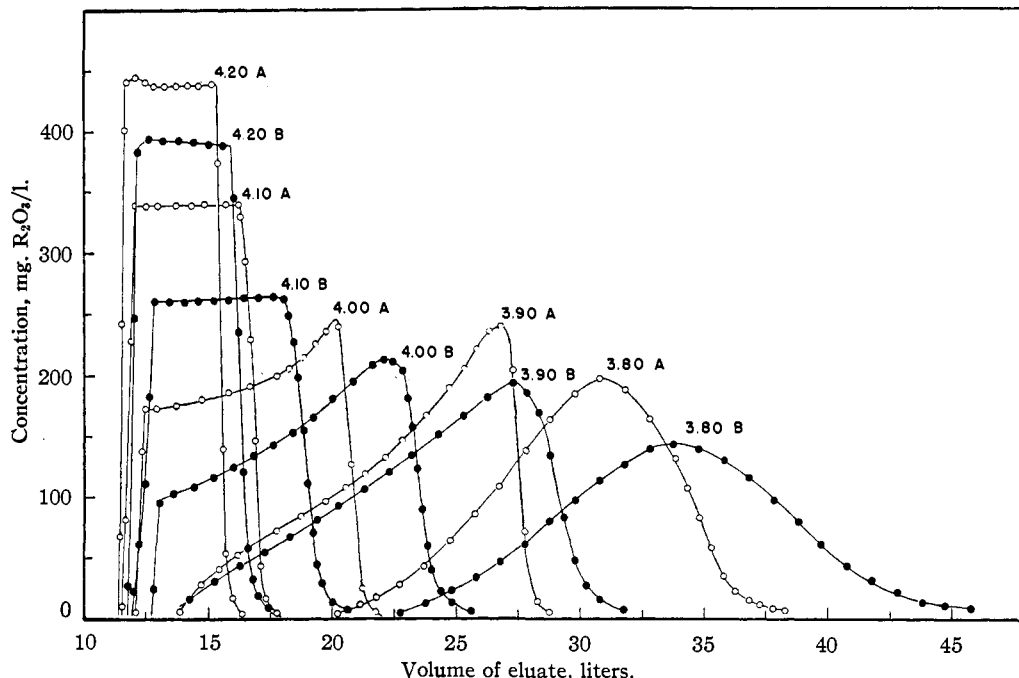
Fig. 1.—The effect of pH on the elution of 1.744-g. samples of pure Sm_2O_3 from 2.2 × 120 cm. beds of −30 + 40 Amberlite IR-100 using 0.5% citrate solutions at linear flow rates of 0.5 cm./min. (A) and 2.0 cm./min. (B).

Fig. 2.—The effect of pH on the elution of 1.683-g. samples of pure Nd_2O_3 from 2.2 × 120 cm. beds of −30 + 40 Amberlite IR-100 using 0.5% citrate solutions at linear flow rates of 0.5 cm./min. (A) and 2.0 cm./min. (B).
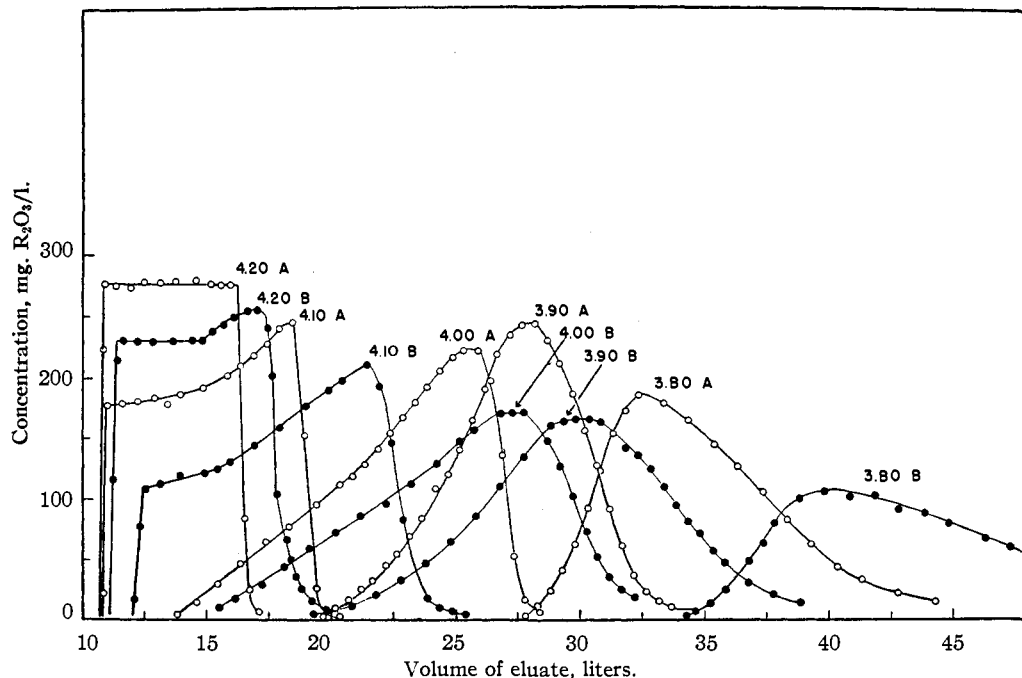
small, but at lower pH values the increase becomes more pronounced. Attention should be directed toward the elution curves for Nd at pH values of 4.00, 3.90 and 3.80. The curve for a pH value of 3.90 shows a nearly symmetrical form while those of pH values of 4.00 and 3.80 are roughly mirror images. These facts might indicate a change in the type of citrate complex and/or a shift in the

equilibrium between the Nd in solution and the Nd on the resin. Evidence has been obtained[12] for more than one citrate complex active in the column.

(12) F. H. Spedding, E. I. Fulmer, Buell Ayers, T. A. Butler, J. E. Powell, A. D. Tevebaugh and R. Q. Thompson, THIS JOURNAL, 70, 1671 (1948).
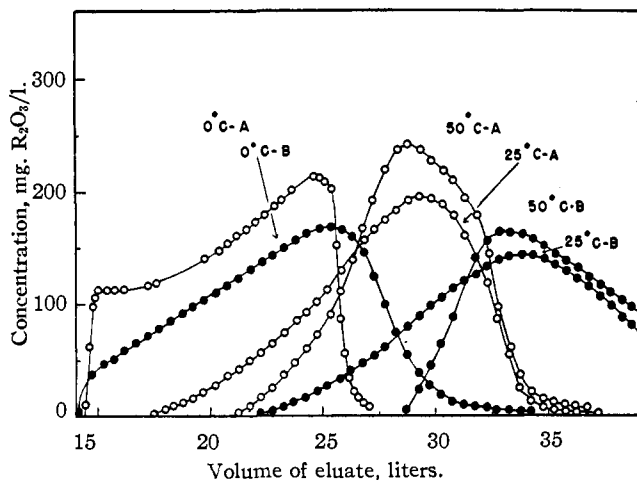
Fig. 3.—The effect of temperature on the elution of 1.744-g. samples of pure Sm_2O_3 from 2.2 × 120 cm. beds of −30 + 40 Amberlite IR-100 using 0.5% citrate solution at a pH value of 3.80 (measured at room temperature) and linear flow rates of 0.5 cm./min. (A) and 2.0 cm./min. (B).

It can be seen from Figs. 1 and 2 that the elution curve for Nd at a given pH is nearly identical to the elution curve obtained for Sm at 0.1 pH unit lower. As an example, the elution curve 4.10A obtained for Nd in Fig. 2 should be compared with the Sm elution curve 4.00A in Fig. 1. This effect may be due to differences in the relative basicities of the two rare earths. At pH values of 4.20 and 4.10 the Sm and Nd 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 Sm and Nd in mixtures should be obtained at the lower pH values.

(2) The Effect of Temperature on the Elution of Pure Samarium at pH 3.80.— Columns were loaded with samples consisting of 1.744 g. of pure Sm_2O_3 in the manner described above. Two of the columns were equipped with water jackets. One column was maintained at 0° by circulating ice water through its jacket; a second column was maintained at 50° by circulating hot water from a constant temperature bath; and the third column was allowed to remain at room temperature, about 25°. The samples were eluted at a linear flow rate of 0.5 and 2.0 cm./min. at a pH of 3.80 measured at 25° (see Fig. 3).

The break-through volumes indicated 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° columns as compared to the lower temperatures could not 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. Ketelle and Boyd[5] have reported that separations can be improved by increasing the temperature when the cation exchanger Dowex 50 is used.

By comparing the 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, except at 0°. Tompkins, Harris and Khym,[9] however, reported that the break-through volume is independent of flow rate when tracer amounts of rare earths are eluted with 5% citrate solution.

(3) The Effect of Resin Particle Size on the Elution of Pure Neodymium at pH 3.80.—Two columns having beds of −30 + 40 and −60 + 80 Amberlite IR-100 resin, were loaded with samples consisting of 1.683 g. of pure Nd_2O_3. These samples were eluted at a pH of 3.80 using a linear flow rate of 0.5 and 2.0 cm./min. The data are plotted in Fig. 4. The mesh size of the resin particles used is indicated beside the corresponding curve.

The elution curves show that the break-through volume was reduced, the peak concentration of neodymium in the eluate was increased and the maximum was obtained more rapidly with the finer resin. These results indicate that equilibrium conditions are more nearly approached with the particles of finer mesh size. These data agree with those of Ketelle and Boyd[5] who demonstrated that decreasing the particle size of Dowex 50 resin improved the separation of various rare earths.

(4) The Effect of pH on the Elution of Equimolar Samarium–Neodymium Mixtures in the Range 3.80 to 4.20.—Three columns were each loaded with a sample containing 0.872 g. of Sm_2O_3 and 0.841 g. of Nd_2O_3. The total weight was equivalent to that of the pure Sm_2O_3 and Nd_2O_3 samples taken for the previous experiments. The mixtures were eluted at a linear flow rate of 0.5 cm./min. at pH values of 4.20, 4.00 and 3.80; the data are plotted in Fig. 5. This experiment was repeated at a flow rate of 2.0 cm./min. The data are compared in Table II. The limit of impurity in the analyses was set at 0.5%, i. e., any sample of Sm_2O_3 containing less than this percentage of Nd_2O_3 or any Nd_2O_3
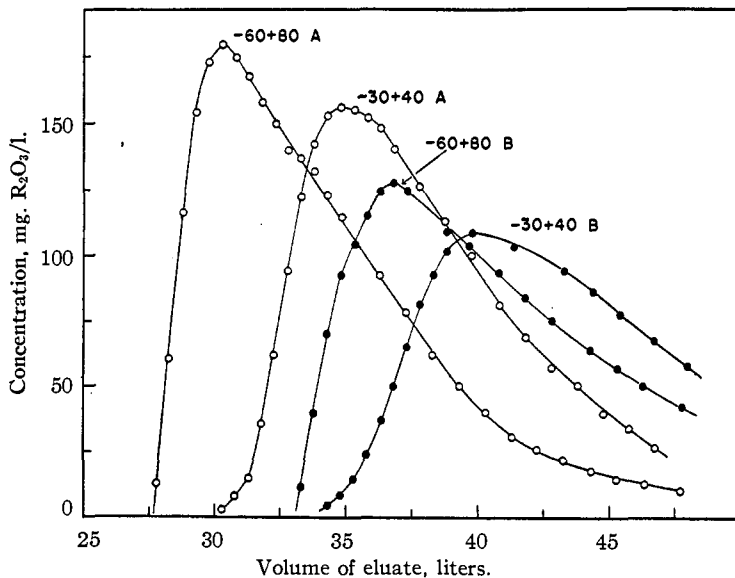

Fig. 4.—The effect of particle size of resin on the elution of 1.683-g. samples of pure Nd_2O_3 from 2.2 × 120 cm. beds of Amberlite IR-100 using 0.5% citrate solution at a pH of 3.80 and linear flow rates of 0.5 cm./min. (A) and 2.0 cm./min. (B).

sample containing less than this amount of Sm_2O_3 was considered pure.

(5) The Effect of pH on the Elution of Equimolar Neodymium–Praseodymium Mixtures in the Range 3.80 to 4.20.—Columns were loaded with samples consisting of 1.695 g. of a mixture of equal amounts of Nd_2O_3 and Pr_6O_{11} by weight; this gave an approximately equimolar mixture
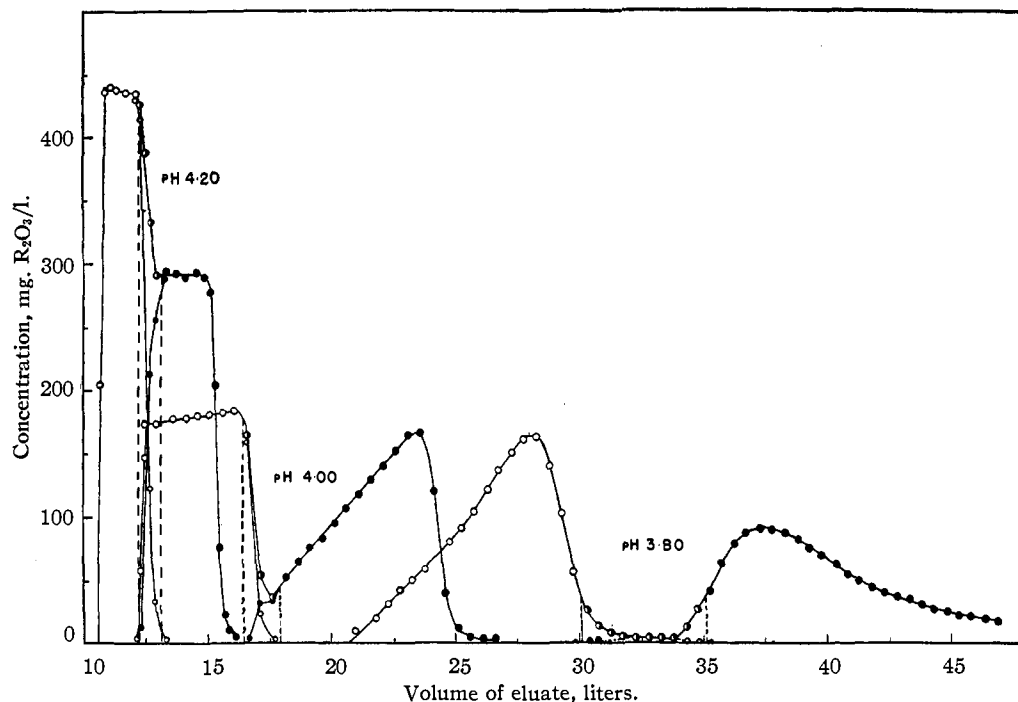
Fig. 5.—The effect of pH on the elution of 1.713-g. samples of equimolar Sm_2O_3–Nd_2O_3 mixtures from 2.2 × 120 cm. beds of −30 + 40 Amberlite IR-100 using 0.5% citrate solutions at a linear flow rate of 0.5 cm./min.; O, Sm_2O_3; ◑, mixed fractions; ●, Nd_2O_3.

TABLE II

DATA FOR THE SEPARATION OF 1.713 G. EQUIMOLAR Sm_2O_3– Nd_2O_3 MIXTURES WITH 0.5% CITRATE SOLUTIONS

pH of eluant	Flow rate, cm./min.	Elution vol., liters	Percentage recovered 99.5% pure	
			Sm_2O_3	Nd_2O_3
4.20	0.5	16	81	79
4.00	0.5	27	90	96
3.80	0.5	50	96	96
4.20	2.0	19	62	76
4.00	2.0	32	95	93
3.80	2.0	50	96	95

of Nd and Pr which is equivalent to the number of moles of R_2O_3 used in the previous experiments. The mixtures were eluted at a flow rate of 0.5 cm./min. at pH values of 4.40, 4.20, 4.10, 4.00, 3.90, 3.80 and 3.70. The data are

TABLE III

DATA FOR THE SEPARATION OF EQUIMOLAR NEODYMIUM–PRASEODYMIUM MIXTURES WITH 0.5% CITRATE SOLUTION

pH of eluant	Flow rate, cm./min.	Elution vol., liters	Percentage recovered 99.5% pure	
			Nd_2O_3	Pr_6O_{11}
3.8	0.5	90	84	82
3.9	.5	50	71	64
4.0	.5	35	55	48
4.1	.5	27	52	64
4.2	.5	20	57	55
4.4	.5	13	70	67
3.8	2.0	90	51	57
3.9	2.0	50	36	51
4.0	2.0	37	38	40
4.1	2.0	26	21	19
4.2	2.0	21	37	22

plotted in Fig. 6. The experiment was repeated at a flow rate of 2.0 cm./min. and the data included in Table III.

The trend is for the Pr break-through to occur later relative to the Nd break-through as the pH of the eluant is lowered. Between the pH values 4.00 and 4.10 the Nd elution curve changed from a vertical front type to a more gradually sloping type curve and a minimum separation occurred at a pH of 4.10. Total elution volumes and the percentages of the Nd_2O_3 and Pr_6O_{11} obtainable with purities greater than 99.5% are compared in Table III.

IV. Summary

Data are presented on 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. The variables studied include pH of eluant, temperature, size of resin particles, and flow rate.

The shape of the elution curves of pure Sm and Nd changed markedly with small variation in the pH values of the eluant. Variations in temperature of the eluting solution over the range 0 to 50° altered the shape of the elution curves; 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 more closely approached. Increasing the flow rate from 0.5 to 2.0 cm./min. caused the rare earth break-through to be de-
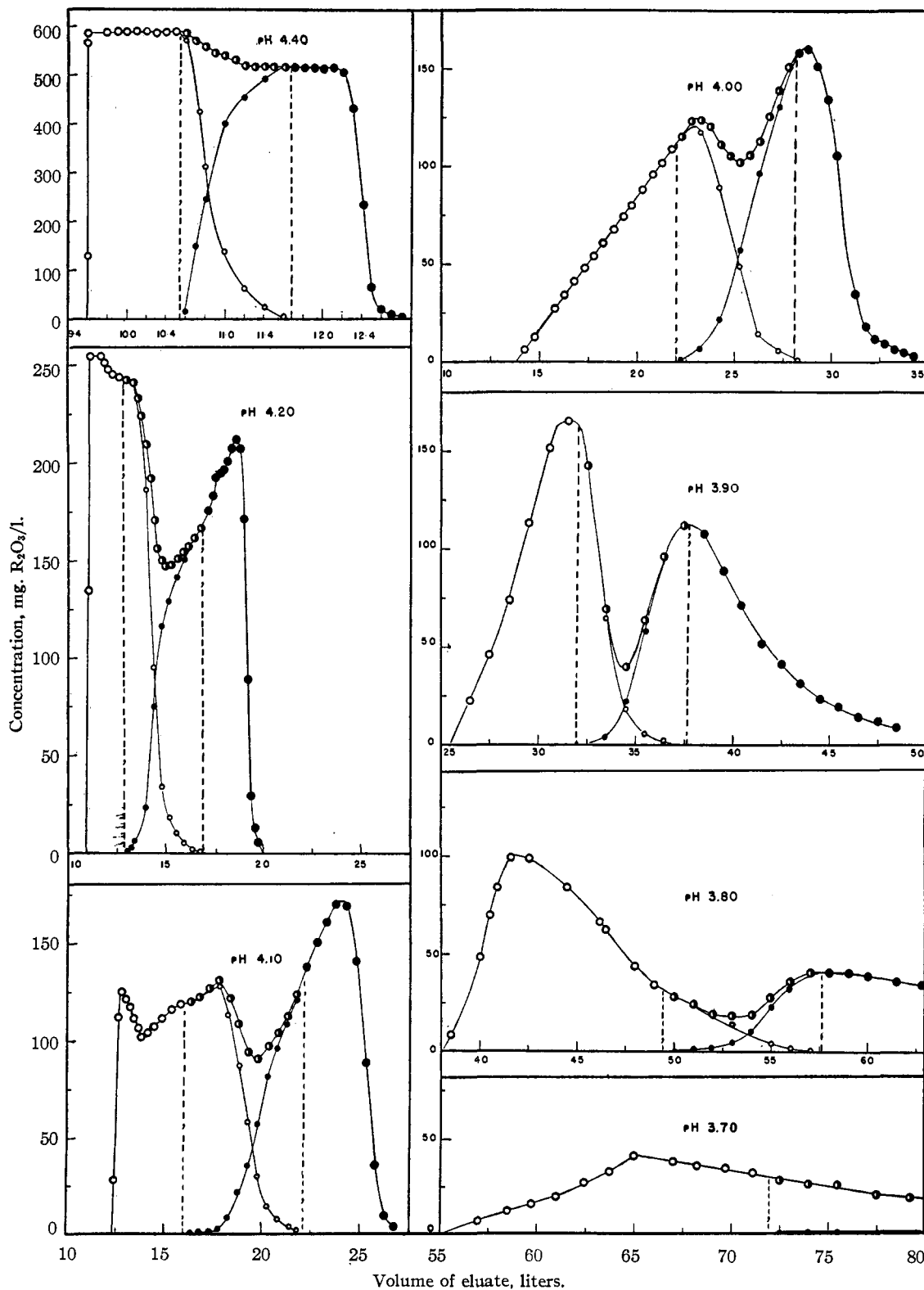
Fig. 6.—The effect of pH on the elution of 1.695-g. samples of a mixture containing equal amounts of Nd_2O_3 and Pr_6O_{11} by weight from 2.2 × 120 cm. beds of −30 + 40 Amberlite IR-100 using 0.5% citrate solutions at a linear flow rate of 0.5 cm./min.: O, Nd_2O_3; ◑, mixed fractions; ●, Pr_6O_{11}.

layed, the elution curves to be spread out and the peak concentration of rare earths to be lowered. This spreading or trailing out of an elution curve for an element tends to be detrimental to the separation obtained when mixtures of two or more elements are involved.

The best separation of the pairs of rare earths tested, using 0.5% citrate solution as eluant, was obtained at a linear flow rate of 0.5 cm./min. and pH value 3.80. It was also found that 0.5 citrate at pH values 4.20 and 4.40 and linear flow rate of 0.5 cm./min. gave fair separations in about one-third the time required for eluant of pH value 3.80.

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The Separation of Rare Earths by Ion Exchange. V. Investigations with One-tenth Per Cent. Citric Acid–Ammonium Citrate Solutions[1]

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

I. Introduction

Variables concerned with the ion-exchange separation of rare earths, using 5% citrate solution as eluant, have been rather extensively studied[2–9] and preliminary investigations have been made in this Laboratory using 0.5%[10,11] and 0.1%[12] citrate. The elution curves with 0.1% citrate were so different, both qualitatively and quantitatively, as to warrant further investigation. It will become evident that the theories[5,8,13] advanced concerning the separation of rare earth elements by ion exchange do not satisfactorily explain all the phenomena observed with 0.1% citrate solutions. It is the opinion of the authors that a general theory, applicable to a wide range of conditions, awaits the obtaining of many more data.

II. Materials, Apparatus and General Procedure

A complete description of materials, apparatus and general procedure is given in a previous paper[11] of this series. Unless otherwise noted the column beds were of $-30 + 40$ Amberlite IR-100

(1) This document is based, in part, on work performed under contract W-7405 eng.-82 for the Atomic Energy Commission.

(2) F. H. Spedding, A. F. Voigt, E. M. Gladrow, N. R. Sleight, J. E. Powell, J. M. Wright, T. A. Butler and P. Figard, This Journal, **69**, 2786 (1947).

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

(4) D. H. Harris and E. R. Tompkins, ibid., **69**, 2792 (1947).

(5) B. H. Ketelle and G. E. Boyd, ibid., **69**, 2800 (1947).

(6) E. R. Tompkins, J. X. Khym and W. E. Cohn, ibid., **69**, 2769 (1947).

(7) E. R. Tompkins and S. W. Mayer, ibid., **69**, 2859 (1947).

(8) S. W. Mayer and E. R. Tompkins, ibid., **69**, 2866 (1947).

(9) E. R. Tompkins, D. H. Harris and J. X. Khym, ibid., **71**, 2504 (1949).

(10) F. H. Spedding, E. I. Fulmer, T. A. Butler, E. M. Gladrow, M. Gobush, P. E. Porter, J. E. Powell and J. M. Wright, ibid., **69**, 2812 (1947).

(11) F. H. Spedding, E. I. Fulmer, T. A. Butler and J. E. Powell, ibid., **72**, 2349 (1950).

(12) F. H. Spedding, E. I. Fulmer, Buell Ayers, T. A. Butler, J. E. Powell, A. D. Tevebaugh and R. Q. Thompson, This Journal, **70**, 1671 (1948).

(13) G. E. Boyd, L. S. Myers, Jr., and A. W. Adamson, ibid., **69**, 2849 (1947).

resin, 120 cm. long and 22 mm. in diameter; the charges consisted of 0.01 mole total rare earth chlorides adsorbed from a liter of aqueous solution. One-tenth per cent. citrate solution was used as eluant in all the experiments described in this paper.

III. Experimental

A. **The Elution of Equimolar Mixtures of Samarium and Neodymium in the pH Range 5.00–6.00.**—Columns were loaded with 1.713 g. of an equimolar mixture of Sm_2O_3 and Nd_2O_3. Elution curves for pH values of 5.00, 5.50 and 6.00, using a linear flow rate of 0.5 cm./min., are given in Fig. 1 and the data shown in Table I.

Table I

Data for the Elution of Equimolar Mixtures of Samarium and Neodymium Using 0.1% Citrate at Several pH Values

pH of eluant	Break-through	Volume in liters Total	Percentage recovered 99.5% pure Sm_2O_3	Nd_2O_3
5.00	38.8	Discontinued at 74.4	99	99
5.50	35.1	47.9	76[a]	83[a]
6.00	29.8	36.4	53[b]	47[b]

[a] The value calculated might have been as much as 10% higher if smaller fractions of eluate had been collected for analysis. [b] The value calculated might have been as much as 20% higher if smaller fractions of eluate had been collected for analysis.

The elution rate increased with increase in pH but the degree of separation decreased. At pH of 5.00 the separation was excellent but the elution rate was too slow for practical purposes. Three separations could be made at a pH of 6.00, or two at 5.50 with the same volume of eluant required to complete one separation at a pH of 5.00. In either case the actual yields of pure rare earths obtained would be greater than those obtained at a pH value of 5.00. The regions of overlap between the Sm and Nd bands were approximately the same width at all pH values investigated. The decrease in separation with increasing pH was due primarily to the increase in concentration of rare earths in this mixed portion of the elution curve.

B. **The Elution of Equimolar Mixtures of Neodymium and Praseodymium at pH Values of 5.00 and 5.50.**—An equimolar mixture of neodymium and praseodymium, made up from 0.841 g. of Nd_2O_3 and 0.854 g. of Pr_6O_{11} was adsorbed on each column and then eluted at a linear flow rate of 0.5 cm./min. The elution curves are given in Fig. 2. The elution at the lower pH was not carried to completion and the fractions were not analyzed, since the elu-