Material Used.—The sample of pentene-1 was obtained from the Phillips Petroleum Company; it was part of the large batch which had been reported by the National Bureau of Standards to have a purity of 99.34 ± 0.4 mole per cent., based upon freezing point data. It had a normal boiling point of 30.07 ± 0.02°. Before being loaded into the bomb, the material was de-gassed and fractionally distilled under a vacuum at −65°.

The Accuracy Attained.—The compressibility data are believed to be accurate to 0.1 to 0.2% at all temperatures up through 175°. However, at the two highest temperatures, the isotherms are estimated, by an extrapolation of the accurate lower temperature isotherms, to be in error by 0.2 to 1% for the 200° isotherm and by 2% for the 225° isotherm.

The reality of polymerization was demonstrated by an investigation of the vapor pressures. At 175°, with a total specific volume (volume of liquid plus volume of gas divided by the total number of grams of material) of 3.2938 ml./g., the vapor pressure was 27.056 atmospheres, and with a total specific volume of 2.8362 ml./g., the vapor pressure was 27.061 atmospheres; this difference of 0.005 atmospheres is probably due to experimental error and to the presence of a small amount of impurity. However, after these measurements, the temperature was raised to and kept at 195° for several hours and at 200° for several hours. On cooling to 175° and adjusting again to the same total specific volumes as before, the vapor pressures were found to be 27.003 and 27.030 atmospheres, respectively. These vapor pressure values are not only considerably lower, but they show a greater difference for the two total specific volumes. These facts were considered as evidence that the material was no longer pure pentene-1 and that some polymerization had taken place.

The Experimental Data.—The compressibilities are presented in Table I at the various constant temperatures.

Acknowledgment.—This work was made possible, initially, by a grant from the Defense Research Laboratory, The University of Texas, under the sponsorship of the Naval Bureau of Ordnance, Contract NOrd-9195.

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[Contribution No. 124 from the Institute for Atomic Research and the Department of Chemistry, Iowa State College; Work Performed in the Ames Laboratory of the Atomic Energy Commission]

The Separation of Rare Earths by Ion Exchange. VI. Conditions for Effecting Separations with Nalcite HCR and One-tenth Per Cent. Citric Acid–Ammonium Citrate Solutions

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

Procedures have been developed for the successful separation of the rare earths using a high capacity resin, Nalcite HCR, and 0.1% citrate solution. The high capacity resin proved to be definitely superior to a low capacity resin, Amberlite IR-100, for the separation of the heavy rare earths. Gram quantities of Er, Ho and Dy have been obtained in purities greater than 99%. The process proved to be equally efficient when stepped up 50-fold to a pilot plant scale separation of the more abundant rare earths.

I. Introduction

Previous communications from this Laboratory[1–7] have dealt only with the use of the low capacity resins, Amberlite IR-1 and IR-100, for the separation of rare earths by ion exchange on a macro scale. Although Amberlite IR-1 proved to be undesirable due to its relative high solubility, IR-100 was found to give satisfactory separations over a rather wide range of conditions and has been successfully employed for the separation of certain rare earths from their mixtures. Harris and Tompkins[8] have stated that Dowex 50 resin is superior to the Amberlite resins IR-1 and IR-100 for rare earth separations; their comparison appears to be based on experiments performed on yttrium and cerium mixtures, using 5% citrate solutions in the *p*H range 2.75 to 3.3. Recent investigations,[4,6] using 0.1% citrate solutions, resulted in elution curves which differed significantly from those previously reported. The present communication deals with the use of the high capacity resin, Nalcite HCR, with 0.1% citrate solutions.

II. Materials, Apparatus and General Procedures

Unless otherwise noted, the materials, apparatus and procedures are the same as those previously given.[5]

1. **Resin.**—Nalcite High Capacity Resin, a sulfonated copolymer of styrene and divinylbenzene, was used in all experiments described in this paper; according to a private communication from the Dow Chemical Co., the National Aluminate Corporation is licensed to distribute Dowex 50 resin under the trade name Nalcite HCR. Resin particles of −40 + 50 mesh size were used in the 22-mm. and the 40-mm. i.d. columns, and −30 + 40 mesh size in the 6-inch i.d. columns.

2. **Resin Beds.**—Each of the 40-mm. columns contained 450 g. of air-dried resin which gave a bed height of 60 cm. in the NH_4^+ cycle and 63 cm. in the H^+ cycle. Each 6-inch column was loaded with 9 kg. of resin, which gave a bed height of 30 in. in the H^+ cycle. The conditioning of the resin has been previously described.[5]

3. **Eluant.**—The eluting solution was 0.1% citrate, based on anhydrous citric acid; the concentration of the eluant was, therefore, 9.4% greater in citric acid than that used in previous investigations[6] in which the concentration was based on the monohydrate.

4. **Recovery of the Heavy Rare Earths.**—Certain properties of the heavy rare earths make them more difficult to recover than the light rare earths; for example, the complexing action with citrate ions is increased; the oxalates are more soluble; and the rate of precipitation[9] is slower.

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[1] F. H. Spedding, A. F. Voigt, E. M. Gladrow and N. R. Sleight, This Journal, **69**, 2777 (1947).

[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, *ibid.*, **69**, 2786 (1947).

[3] 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).

[4] F. H. Spedding, E. I. Fulmer, B. O. Ayers, T. A. Butler, J. E. Powell, A. D. Tevebaugh and R. Q. Thompson, *ibid.*, **70**, 1671 (1948).

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

[6] F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, *ibid.*, **72**, 2354 (1950).

[7] F. H. Spedding, *Discussions Faraday Soc.*, No. 7, 214 (1949).

[8] D. H. Harris and E. R. Tompkins, This Journal, **69**, 2792 (1947).

[9] D. S. Martin and C. Crouthamel, *ibid.*, **72**, 1382 (1950).

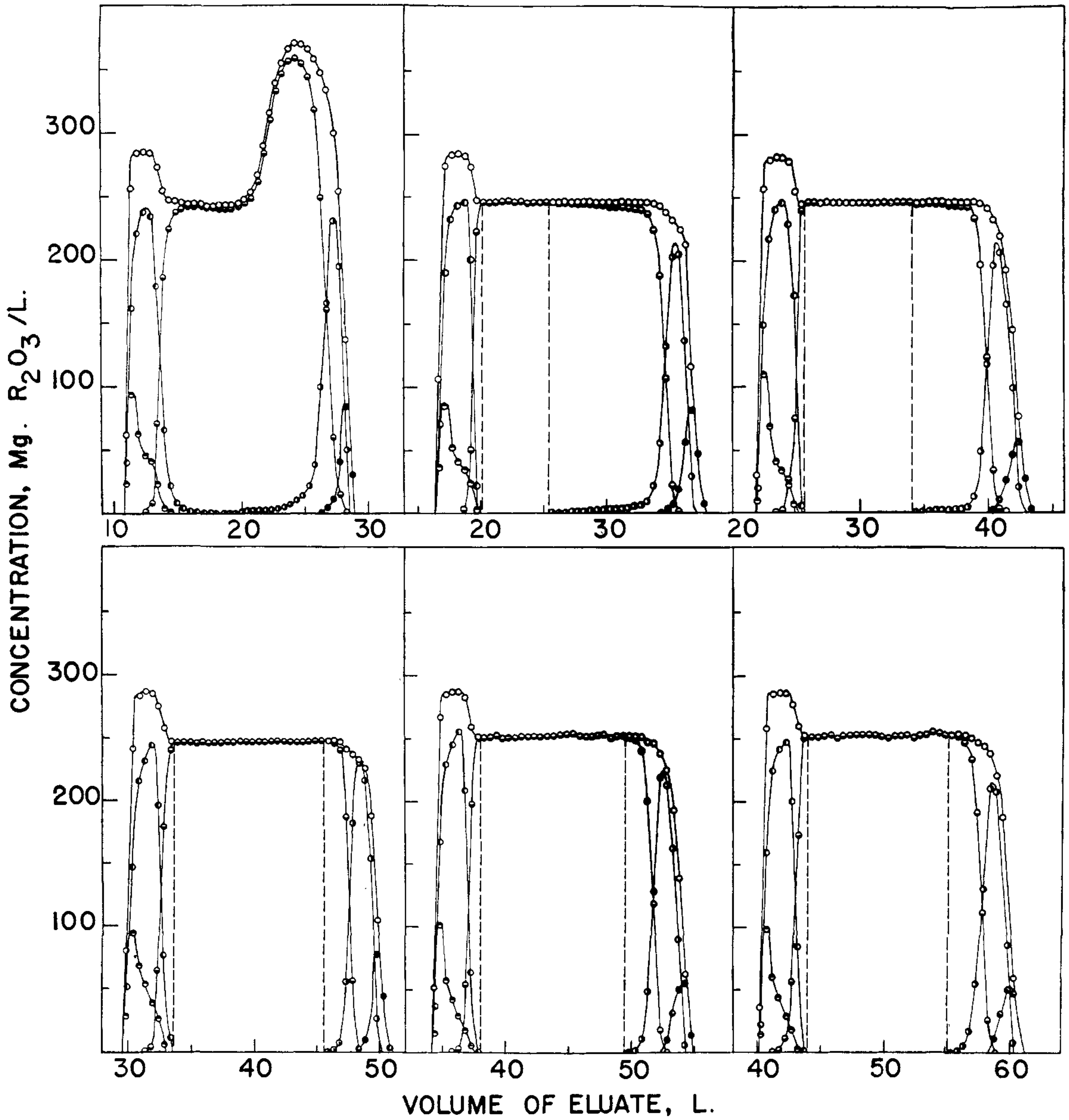

Fig. 1.—The elution of 5-g. samples of 76% Nd_2O_3, 11% Sm_2O_3, 9% Pr_6O_{11} and 4% other R_2O_3 from −40 + 50 Nalcite HCR resin beds, 22 mm. in diameter and 30, 40, 50, 60, 70 and 80 cm. long, with 0.1% citrate solution at a *p*H of 6.15 and a flow rate of 0.5 cm./min.: ◓, heavy R_2O_3; ◐, Sm_2O_3; ◒, Nd_2O_3; ◑, Pr_6O_{11}; ●, La_2O_3 and CeO_2; ○, total mixed R_2O_3; vertical dashed lines indicate Nd fractions 99.9% pure.

Several methods of precipitation were investigated. The method finally used for the recovery of the heavy rare earth oxides, in concentrations of approximately 250 mg. per liter, was a modification of a procedure suggested by Rodden.[10] The solution was heated to 70–80°, and 2 g. of oxalic acid and 200 mg. of tannic acid were added per liter; the resulting *p*H was 1.8–2.0 which was optimum for precipitation. The solution was then boiled for 15–30 min. and allowed to stand 48 hr. at room temperature before filtering; over 95% of the rare earth oxalate precipitated. The rare earths remaining in solution may be recovered by readsorption, stripping and reprecipitation.

TABLE I

DATA USED FOR SPECTROPHOTOMETRIC ANALYSIS OF THE HEAVY RARE EARTHS

Element	Wave length, mμ	Slit width, mm.	Abs. coef. (liters mole^{-1} cm.$^{-1}$)	Interfering elements	Corrections (based on absorbancies)
Er	522	0.02	3.13	Nd[a]	....
Ho	536	.02	4.54	Er	0.02 of Er peak at 522 mμ
Dy	908	.02	2.33	Ho, Yb[a]	0.03 of Ho peak at 536 mμ

[a] As no Yb or Nd was present in the samples analyzed, no corrections were necessary.

5. **Methods of Analysis.**—The spectrophotometric data, used in this Laboratory, for the light rare earths have been previously reported.[5] The data employed for the analyses of the heavy rare earths are listed in Table I. Spectrographic analyses were made according to the methods of Fassel and Wilhelm.[11,12]

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(10) C. J. Rodden, private communication.

(11) V. A. Fassel and H. A. Wilhelm, *J. Opt. Soc. Am.*, **38**, 518 (1948).

(12) V. A. Fassel, *ibid.*, **39**, 187 (1949).

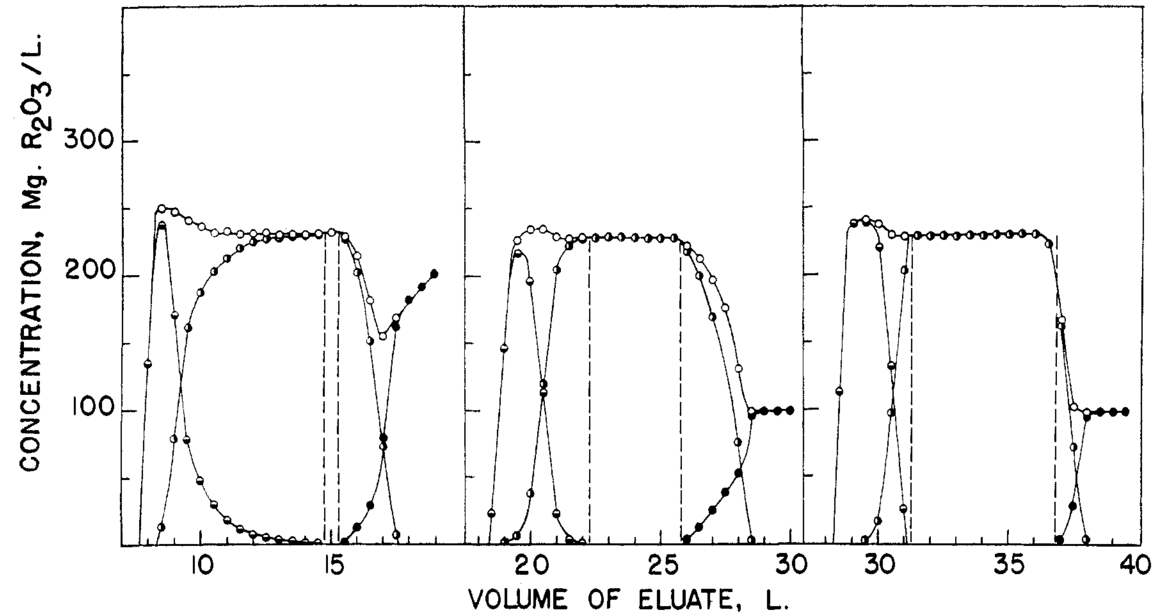

Fig. 2.—The elution of 3.5-g. samples of 43.5% Pr_6O_{11}, 10.2% Nd_2O_3, 46% La_2O_3 and traces of Sm_2O_3 and CeO_2 from −40 + 50 Nalcite HCR resin beds, 22 mm. in diameter and 20, 40 and 60 cm. long with 0.1% citrate solution at a *p*H of 6.15 and a flow rate of 0.5 cm./min.: ◒, Nd_2O_3; ◑, Pr_6O_{11}; ●, La_2O_3; ○, total mixed R_2O_3; vertical dashed lines indicate Pr fractions >99.9% pure.

III. Experimental

1. **The Effect of Increased Column Length with a Constant Weight of Sample.**—Six beds of −40 + 50 mesh size resin, 22 mm. in diameter, were prepared in the acid cycle, rinsed with distilled water and leveled to heights of 30, 40, 50, 60, 70 and 80 cm., respectively. The initial load, per column, was 5 g. of Lindsay Light & Chemical Co. code #630 oxide, consisting of 76% Nd_2O_3, 11% Sm_2O_3, 9% Pr_6O_{11} and 4% other R_2O_3. Elution curves and conditions for this experiment are given in Fig. 1.

In each case the total heavy rare earths was determined by difference and tended to separate and precede the Sm as expected, except for Eu and Gd. The Ce and La concentrated at the rear of the band and were also determined by difference. No Sm or Pr was obtained pure from this mixture in any case due to their low initial concentrations and the overlapping of neighboring bands. Data for the Nd separation are given in Table II. The yield of > 99.9% Nd increased until a column length of 60 cm. was reached and then remained constant within the limits of experimental error. The shapes of the elution curves were identical for all lengths greater than 30 cm. It can readily be seen from Fig. 1 that the lengths required for optimum separation and for attainment of the equilibrium type elution curve for this mixture do not coincide. The same effect was also observed in the separation of a crude Pr oxide which contained 43.5% Pr_6O_{11}, 10.2% Nd_2O_3, 46% La_2O_3 and traces of Sm_2O_3 and CeO_2; the material was obtained from Lindsay Light & Chemical Co. as "praseodymium ammonium nitrate." The elution curves for this mixture and the experimental conditions are given in Fig. 2. Data from this experiment are recorded in Table II.

Table II

The Effect of Column Length on the Separation of Nd and Pr from Crude Concentrates

Sample weight Nd crude, g.	Sample weight Pr crude, g.	Column length, cm.	Amt. obt. > 99.9% pure Nd_2O_3, g.	Amt. obt. > 99.9% pure Pr_6O_{11}, g.	Yield of Nd_2O_3 obt. >99.9% pure, %
5.0		30	0.0000		0.0
5.0		40	1.2269		32.2
5.0		50	1.8397		48.3
5.0		60	2.9654		78.1
5.0		70	2.9041		76.5
5.0		80	2.7822		73.2
	3.5	20		0.1159	7.6
	3.5	40		0.8000	52.6
	3.5	60		1.2604	82.9

2. **The Effect of Proportionate Increase in Column Load and Length.**—In an earlier paper concerning Amberlite IR-100 and 0.1% citrate,[6] it was reported that the separation could be made more efficient by a proportionate increase in load and length. Figure 3 shows that the same effect occurred when Nalcite HCR was used in place of Amberlite IR-100 as the exchange resin. However, the series of separations shown was not based on the optimum load per unit length. The data from these experiments are presented in Table III. The percentage yield dropped off in the case of the 100-cm. column, but this effect was due to poor packing in the bed.

Table III

The Effect of Increasing Length and Load Proportionately on the Separation of Nd from a Concentrate

Bed length, cm.	Column load as R_2O_3, g.	Amt. Nd_2O_3 obt. >99.9% pure, g.	Yield of Nd_2O_3 obt. >99.9% pure, %	Volume of eluant req. l.
20	2.50	0.0000	0.0	18.6
40	5.00	1.1042	29.1	37.8
60	7.50	2.2283	39.1	55.5
80	10.00	4.1316	54.4	74.5
100	12.50	4.9079	51.7	93.0

3. **The Effect of *p*H on the Separation of Various Rare Earth Mixtures.**—The effect of *p*H of 0.1% citrate, using Nalcite HCR, was in good agreement with data reported previously, using Amberlite IR-100.[6] The maximum concentration obtained for an element at a given *p*H was lower with Nalcite than with Amberlite; this effect was probably due to the more acidic nature of Nalcite HCR. The increase in separation with decreased *p*H, previously observed with Amberlite, was not as pronounced when Nalcite was used; in fact, as shown in Fig. 4, the separation of Nd from neighboring rare earths was practically independent of *p*H in the range studied. Figures 5, 7 and 8, and Tables VI and VII illustrate the effect of *p*H on the separation of other rare earth mixtures.

4. **The Effect of Increased Load on Columns of Equal Length.**—Data from a number of pilot plant scale runs illustrate the effect of column load on the total and percent-

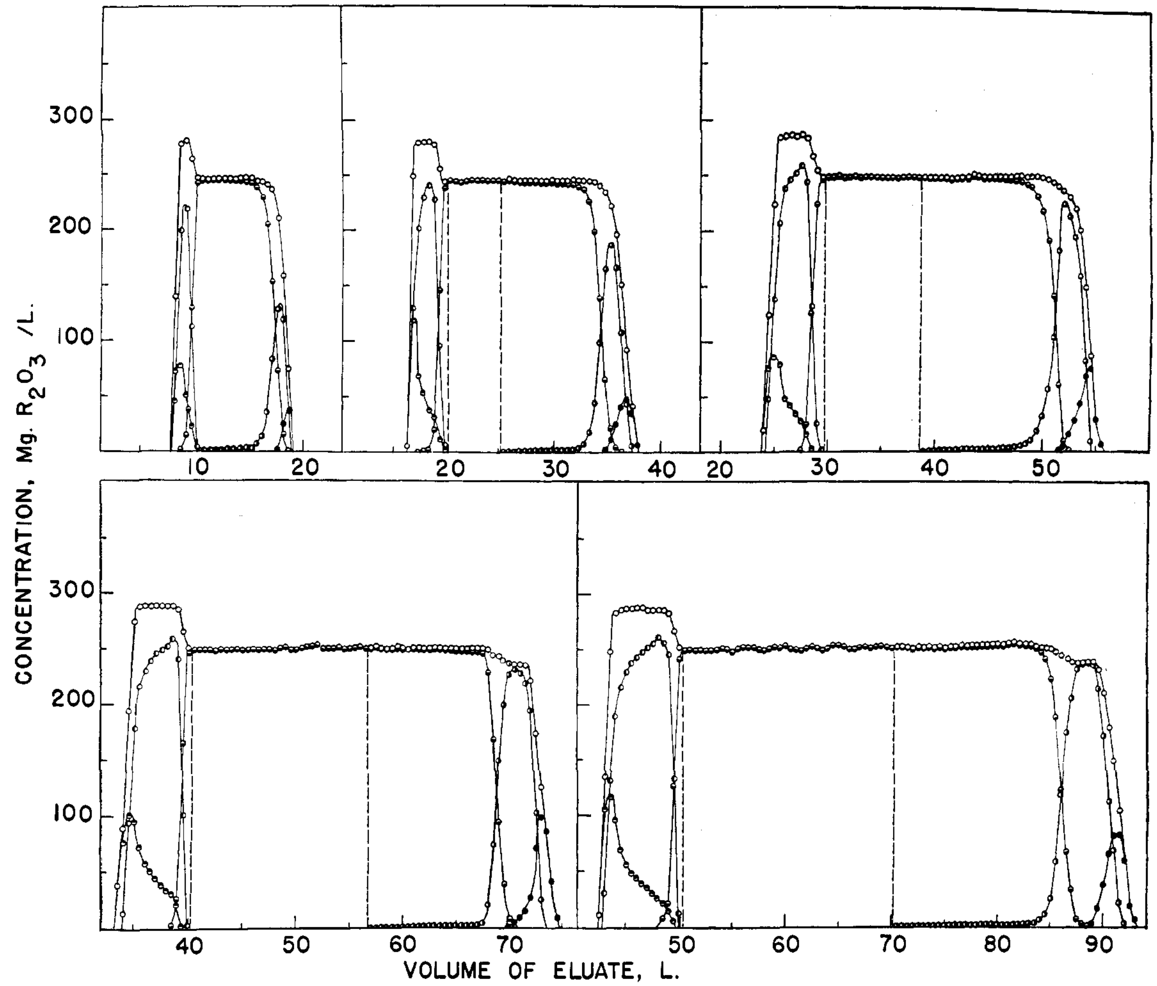

Fig. 3.—The elution 2.5, 5.0, 7.5, 10.0 and 12.5 g. samples of 76% Nd_2O_3 from $-40 + 50$ Nalcite HCR resin beds, 22 mm. in diameter and 20, 40, 60, 80 and 100 cm. long, with 0.1% citrate solution at a *p*H of 6.15 and a flow rate of 0.5 cm./min.: ◓, heavy R_2O_3; ◐, Sm_2O_3; ◒, Nd_2O_3; ◑, Pr_6O_{11}; ●, La_2O_3 and CeO_2; ○ total mixed R_2O_3; vertical dashed lines indicate Nd fractions >99.9% pure.

age yields of spectrographically pure Nd obtained from code #630 oxide. The resin beds were 6 in. in diameter and 30 in. in length. The samples were all eluted with 0.1% citrate at a *p*H of 6.1 and a flow rate of 0.5 cm./min. The average yields per column for different column loads are given in Table IV.

TABLE IV

THE EFFECT OF INCREASED LOAD ON COLUMNS OF EQUAL LENGTH USING CODE #630 OXIDE

Column load as R_2O_3, g.	No. of columns operated	Av. wt. of >99.9% Nd_2O_3 obtained per column, g.	Percentage of available Nd_2O_3 obtained >99.9% pure, %	Total volume of eluant req., l.
250	10	140.2	73.8	3050
300	10	162.0	71.0	3180
325	5	166.2	67.3	3300
375	8	162.2	57.0	3400
450	2	156.4	45.7	3550

For a column of the specified dimensions, the optimum load for this particular crude mixture appears to be approximately 325 g. when the above operating conditions are used. A slight precipitate formed in the resin bed during the elution of the 450-g. loads, but redissolved as elution progressed.

A similar study of the effect of column load was made using the Pr concentrate described in Section 1 and under the conditions given above. The average yields per column for different column loads are given in Table V. The columns were stripped immediately after the Pr was eluted since, under these conditions, La elutes much more slowly than does the Pr and has relatively little value. In every case an insoluble rare earth citrate compound precipitated in the resin bed almost immediately after the elution was begun. This precipitate was found to contain every rare earth component present in the original crude. Although this precipitate dissolved as elution progressed and the last traces completely disappeared before break-through occurred, sufficient bed length had to be provided in order to separate the rare earths in the precipitated portion. The amount of precipitate was observed to increase markedly as the column load increased. Since excessive precipitation blocked the resin bed pores and increased channeling, the optimum load is between 250 and 300 g. for a column of the above dimensions.

TABLE V

THE EFFECT OF INCREASED LOAD ON COLUMNS OF FIXED LENGTH USING A Pr CONCENTRATE

Column load as oxide, g.	No. of columns operated	Av. wt. of >99.9% Pr_6O_{11} obtained per column, g.	Percentage of available Pr_6O_{11} obtained >99.9% pure, %	Total volume of eluant to elute the Pr, l.
225	10	67.6	69.1	2560
250	10	76.5	70.2	2600
300	1	79.6	61.0	2640

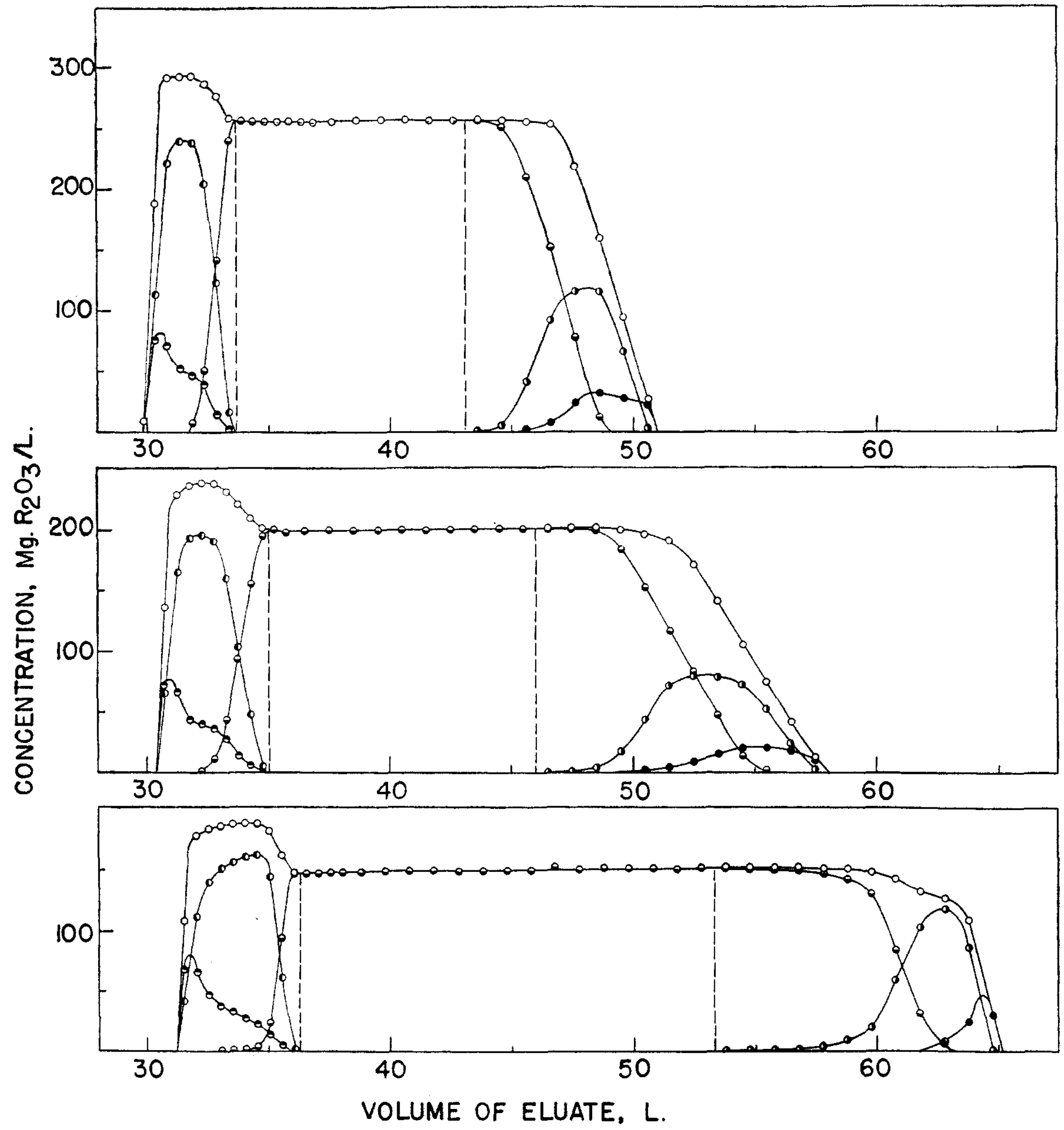

Fig. 4.—The elution of 5-g. samples of 76% Nd_2O_3 from −40 + 50 Nalcite HCR resin beds, 22 mm. in diameter and 60 cm. long, with 0.1% citrate solutions at *p*H values of 6.2, 6.0 and 5.8 and a flow rate of 0.5 cm./min.: ◓, heavy R_2O_3; ◐, Sm_2O_3; ⊖, Nd_2O_3; ◑, Pr_6O_{11}; ●, La_2O_3 and CeO_2; ○, total mixed R_2O_3; vertical dashed lines indicate Nd fractions >99.9% pure.

5. **Purification of Er.**—The analysis of the starting material was 90% Er_2O_3, 8% Ho_2O_3 and 1% Tm_2O_3. Ten grams of the oxide were used for each column. Duplicate columns were eluted with 0.1% citrate solutions at *p*H values of 5.40, 5.70 and 6.00; the duplicate columns checked each other closely. At all three *p*H values, the Ho concentrated toward the rear of the band, and the Tm toward the front, yielding pure Er in between. Figure 5 shows that the latter portion of the Er band contained traces of Ho which could be detected only by spectrographic analysis. Table VI lists the yields of Er_2O_3 obtained at the specified purities.

TABLE VI

YIELDS OF Er_2O_3 OBTAINED AT DIFFERENT *p*H VALUES

*p*H of eluant	Percentage of available Er_2O_3 obtained >99.0% pure	>99.9% pure
5.40	73	36
	76	41
5.70	74	42
	78	52
6.00	66	35
	67	41

TABLE VII

PERCENTAGES OF PURE RARE EARTHS OBTAINED FROM MIXTURES ELUTED AT DIFFERENT *p*H VALUES

*p*H of eluant	Wt. R_2O_3 adsorbed, g.	Percentages of available oxides obtained, >99% pure Er_2O_3	Ho_2O_3	Dy_2O_3
5.40	10	65	75	33
5.70	10	73	50	26
6.00	10	50	60	19
5.70	15	86[a]	70	28

[a] Includes the yield of Er_2O_3 (3.5%) obtained > 99.9% pure.

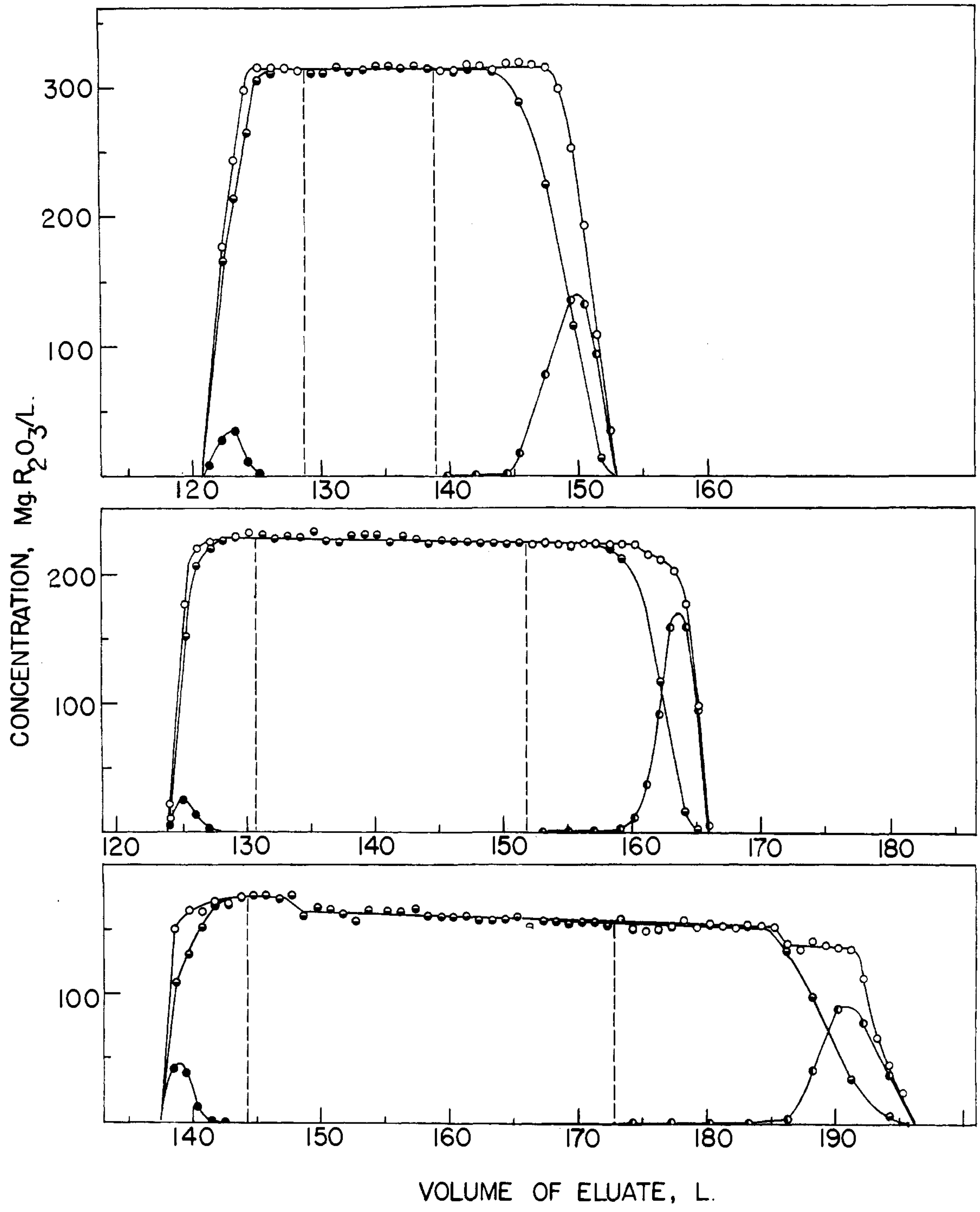

Fig. 5.—The elution of 10-g. samples of 90% Er_2O_3, 8% Ho_2O_3 and 1% Tm_2O_3 from −40 + 50 Nalcite HCR resin beds, 40 mm. in diameter and 80 cm. long, with 0.1% citrate solution at *p*H values of 6.0, 5.7 and 5.4 and a flow rate of 0.5 cm./min.: ●, Tm_2O_3; ⊖, Er_2O_3; ◐, Ho_2O_3; ○, total mixed R_2O_3; vertical dashed lines indicate Er fractions >99.9% pure.

6. Separation of Er, Ho and Dy.—The composition of the starting material was 56% Ho_2O_3, 27% Er_2O_3, 17% Dy_2O_3 and 1% Y_2O_3. Ten grams of the oxide mixture was used for each of three columns and 15.0 g. on a fourth. The 10-g. columns were eluted at *p*H values of 5.40, 5.70 and 6.00, and the 15-g. column at a *p*H of 5.70. A typical elution curve is shown in Fig. 6. Spectrophotometrically pure Er, Ho and Dy were obtained from all columns, as indicated in Table VII, but no spectrographically pure rare earths were obtained, except for a small amount of Er_2O_3 from the 15-g. column. A better Er separation was obtained at a *p*H of 5.70 than at other *p*H values; however, better separations of Ho and Dy were obtained at a *p*H of 5.40. Data in Section 4 indicate that still better separations could be obtained for these column dimensions by using a larger load, although more time would be required for elution.

7. The Separation of Sm, Eu and Gd Mixtures.—Ketelle and Boyd[13] have pointed out that the triad Gd, Eu and Sm constitutes what should be a difficultly separable group of rare earths; in this Laboratory a marked separation of Gd from Sm or Eu from Sm by ion exchange has never been

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(13) B. H. Ketelle and G. E. Boyd, THIS JOURNAL, 69, 2800 (1947).

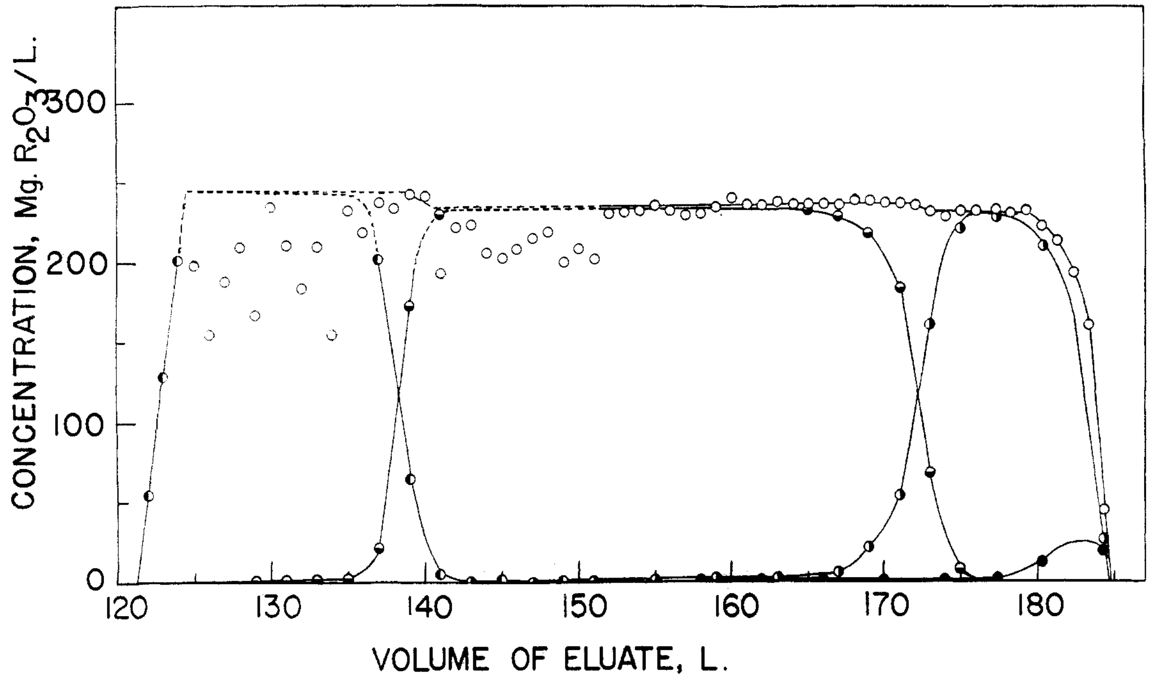

Fig. 6.—The elution of a 15-g. sample of 56% Ho_2O_3, 27% Er_2O_3, 17% Dy_2O_3 and 1% Y_2O_3 from −40 + 50 Nalcite HCR beds, 40 mm. in diameter and 60 cm. long, with 0.1% citrate solution at a *p*H value of 5.7 and a flow rate of 0.5 cm./min.: ◐, Er_2O_3; ⊖, Ho_2O_3; ◑, Dy_2O_3; ●, Y_2O_3; ○, total mixed R_2O_3; erratic total R_2O_3 points at the front of the curve were due to incomplete precipitation of the rate earth oxalates.

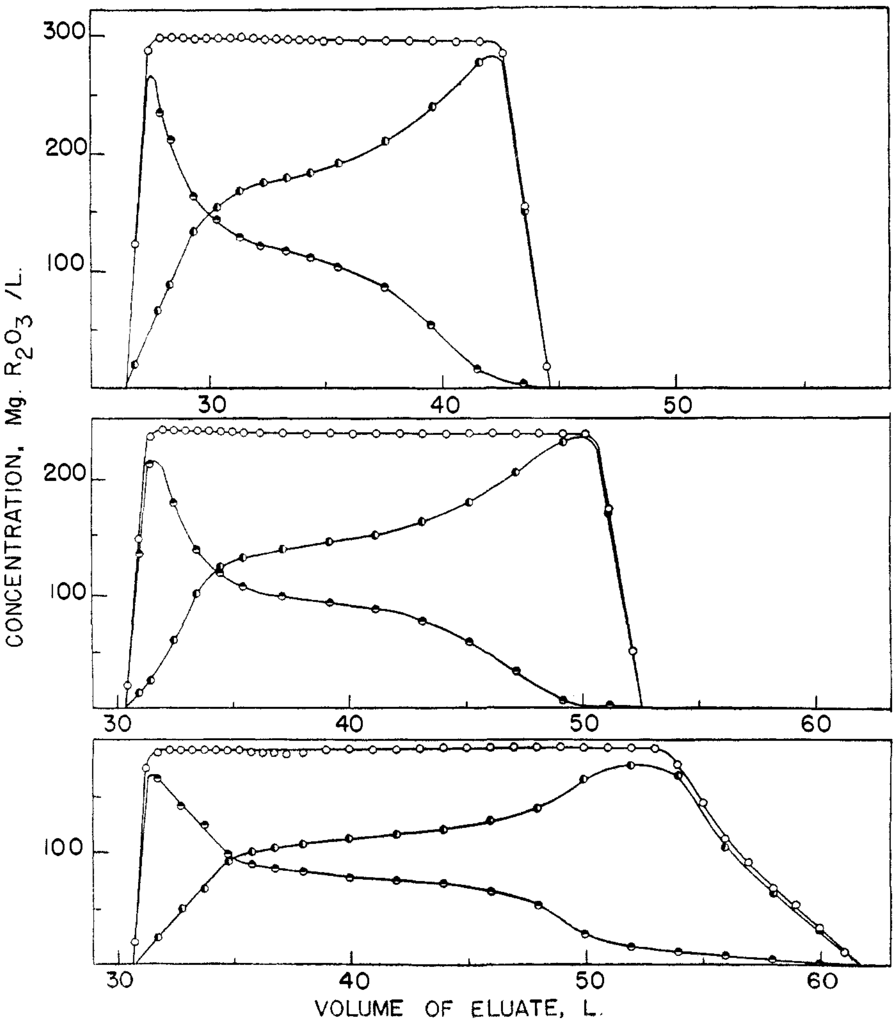

Fig. 7.—The elution of 5-g. samples of 34.7% Eu_2O_3 and 65.3% Sm_2O_3 from −40 + 50 Nalcite HCR resin beds, 22 mm. in diameter and 60 cm. long, with 0.1% citrate at *p*H values of 6.2, 6.0 and 5.8 and a flow rate of 0.5 cm./min.: ⊖, Eu_2O_3; ◐, Sm_2O_3; ○, total mixed R_2O_3.

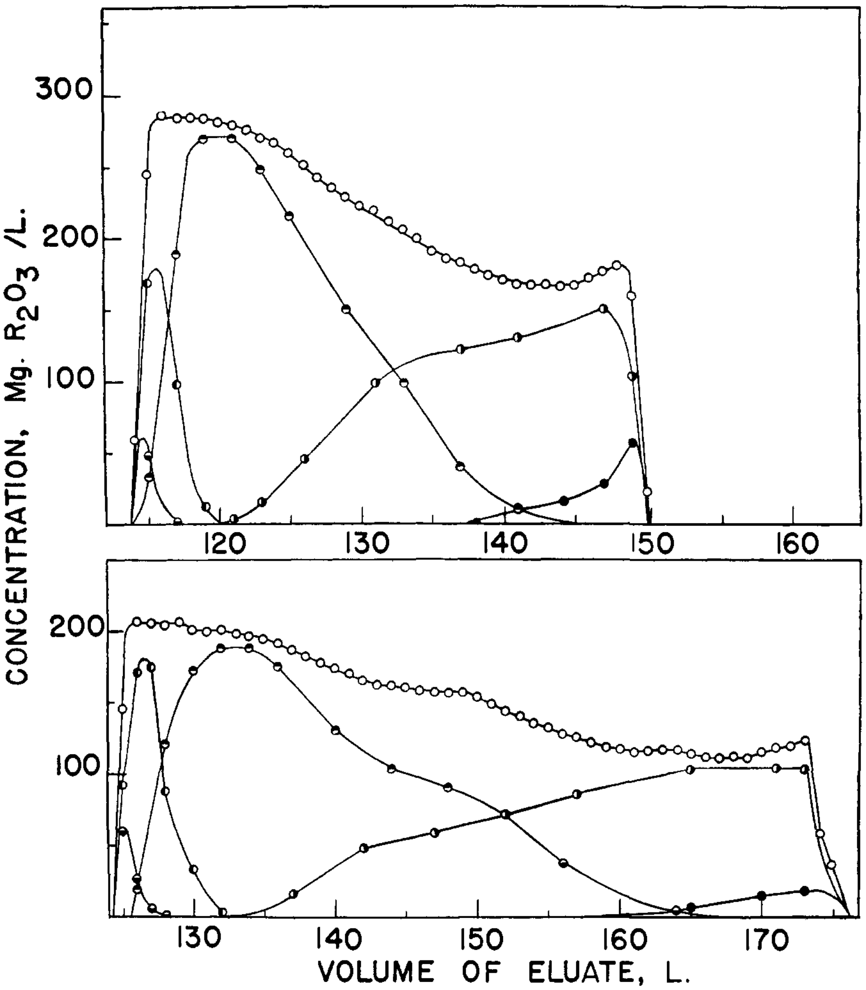

Fig. 8.—The elution of 8-g. samples of 49% Dy_2O_3, 41% Y_2O_3, 7% Ho_2O_3, 2% Tb_2O_3 and 1% Er_2O_3 from −40 + 50 Nalcite HCR beds, 40 mm. in diameter and 60 cm. long, with 0.1% citrate solution at *p*H values of 6.0 and 5.7 and a flow rate of 0.5 cm./min.: ⊖, Er_2O_3; ◐, Ho_2O_3; ◓, Dy_2O_3; ◑, Y_2O_3; ●, Tb_2O_3; ○ total mixed R_2O_3.

noted under any conditions studied. This difficulty has been illustrated in previous papers concerned with the use of Amberlite IR-100 resin with 0.5[3] and 0.1%[7] citrate solutions, and it is further demonstrated by the elution curves in Fig. 7. It should be noted that conditions used in these studies gave good separations when applied to other rare earth mixtures, and that the elements Gd, Eu and Sm can be separated readily, as a group, from other rare earths. These individual elements can be obtained in a pure state by using ion exchange as a concentrating step and then applying the methods of Marsh[14] and McCoy.[15]

8. **Separation of Ho, Dy and Y.**—Ketelle and Boyd[13] reported that this triad would also be a difficultly separable group, and that, when using 5% ammonium citrate on Dowex resin at 90°, the order of elution was Ho–Y–Dy. However, data obtained in this Laboratory using Amberlite IR-100 at room temperature, indicate that, while Dy and Y are difficult to separate, the order of elution is Ho–Dy–Y. Figure 6 shows that the Y was eluted after the Dy, and that a good separation of Ho from Dy was obtained. The position of Y in the elution of Ho, Dy, Y and Tb from Nalcite HCR at room temperature is shown in Fig. 8. Although no spectrophotometrically pure Ho_2O_3 was obtained, the Ho separated from the bulk of the Dy quite sharply. While a small amount of spectrophotometrically pure Dy was obtained, there is a great deal of overlap between the Dy and Y. Long before the Dy was completely eluted, Tb began to elute. Thus it appears that, when 0.1% citrate solution is employed at room temperature, Dy–Y–Tb is a difficultly separable triad and that Dy and Ho are fairly easy to separate from one another.[16]

AMES, IOWA

RECEIVED JANUARY 12, 1951

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[14] J. K. Marsh, *J. Chem. Soc.*, 523 (1942); 531 (1943).

[15] H. N. McCoy, THIS JOURNAL, **58**, 2279 (1936); **63**, 3432 (1941).

[16] NOTE ADDED IN PROOF: Recent work [F. H. Spedding and J. L. Dye, *ibid.*, **72**, 5350 (1950)] has shown that the order of elution using 5% ammonium citrate at *p*H values of 2.8–3.0 is Dy-Tb-Y at room temperature.