Summary

1. A demonstration of the separation of all the rare earths by chromatographic techniques based on the use of synthetic organic ion-exchange adsorbents was made. With a 97 cm. by 0.26 sq. cm. bed of 270/325 mesh Dowex-50 adsorbent maintained at 100°, the optimum pH of the 4.75% citric acid eluant was 3.2 for the separation of the yttrium earths and 3.4 for the cerium earths.

2. The employment of a temperature of 100° permitted the use of elutriant flow rates of as high as 2 ml./sq. cm./min., thereby greatly reducing the time required for a separation. In a typical experiment, milligram quantities of lutecium, ytterbium, thulium, erbium, holmium, and yttrium were separated in thirty hours.

3. The fractionation of the heavy rare earths could be made sufficiently complete that the method was established as a promising procedure for the quantitative analysis of rare earths for cationic impurities. A previously exhaustively purified sample of erbium oxide, in which all other rare earths were reported as absent by spectrographic analysis, was shown to contain 10 p.p.m. of Tm by irradiation of the Er_2O_3 with neutrons and subsequent chromatographic separation.

4. The adsorbability of yttrium was shown to lie intermediate between holmium and dysprosium in quantitative agreement with the expectations based on considerations of the ionic radii. As a result, the separation of these elements was even more difficult to accomplish than the separation of the heavier rare earths.

5. The adsorbability of ytterbium and lutecium were shown to be more nearly the same than any other pair of rare earths in conformity with the trend in ionic radii. Predictions based upon crystal radii suggested that samarium, europium and gadolinium would be the most difficult of the cerium earths to fractionate.

The Separation of Rare Earths by Ion Exchange.[1] III. Pilot Plant Scale Separations

BY F. H. SPEDDING, E. I. FULMER, T. A. BUTLER, E. M. GLADROW, M. GOBUSH, P. E. PORTER, J. E. POWELL AND J. M. WRIGHT

Introduction

The previous papers[2,3] of this series dealt with the development of procedures for separating macro-amounts of the rare earths by adsorption on Amberlite IR-1 and subsequent elution with 5% citric acid–ammonium citrate[4] solutions at regulated pH. The use of this concentration of citrate proved costly in large scale operations. Therefore, experiments were undertaken to find the minimum concentration of the citrate consistent with efficient separations using Amberlite IR-100. Data also are presented on the development of the working conditions for pilot plant separation of the rare earths. For convenience of discussion, the data will be presented under the two headings: I. The Light Rare Earths (Cerium group), and II. The Heavy Rare Earths (Yttrium group.)

The separation of the rare earths was stepped up to pilot plant scale using the general procedures established for the smaller scale operations.[2,3]

There was urgent need not only to furnish pure rare earths to other members of the Manhattan Project, but also to obtain pure fractions to determine optimum conditions for their separation.

It follows that the conditions used in these studies were not optimum. There is no doubt that, under better conditions, less solution will be required, separation per passage will be more effective and the time of operation will be materially reduced. It is also likely that automatic features can be installed which will greatly decrease the hours of labor required. All of these factors are being studied and will be presented in subsequent papers.

I. The Light Rare Earths (Cerium Group)

1. **Effect of Concentration of Citrate.**—Three 1.00-g. samples of crude Nd_2O_3 were dissolved in a slight excess of hydrochloric acid. The pH was adjusted to 1.8 and each solution adsorbed on Amberlite IR-100 beds 28 inches in height and 16 mm. in diameter. The samples were eluted with 5.0, 0.5 and 0.05% citrate solutions at a pH of 5.0. The 5% solution eluted the sample rapidly but the breakthrough with the 0.05% eluant was much too slow for practical purposes; the 0.5% citrate solution eluted the sample at a somewhat slower rate than did the 5% solution but the results were sufficiently promising to warrant detailed studies of the effect of pH. The break-through represents the total volume of eluant at which the presence of the given element is first evidenced by precipitation as the oxalate.

2. **Effect of pH.**—Samples consisting of 35% Sm_2O_3 and 65% Nd_2O_3, weighing 0.9 g., were treated with hydro-

(1) This work was supported, in part, by a grant from The Manhattan District, U. S. Corps of Engineers.

(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) The term % refers to the grams of citric acid monohydrate per 100 ml. of original solution. The pH is adjusted by the addition of concentrated ammonia; the pH values are accurate to 0.02 pH unit.

chloric acid and adsorbed on the columns under conditions described above. The samples were eluted at a linear flow rate of 3 cm. per min. using 0.5% citrate solution at pH values of 5.00, 4.50 and 4.00. At pH 5.00 the sample was eluted in a volume of 3 liters with very little separation. At pH 4.50 a volume of 8 liters was required for elution and some separation was obtained. The separation at pH 4.00 was excellent considering the short bed height of the column. Typical elution data are given in Table I.

TABLE I

TYPICAL ELUTION DATA FOR A 0.9-G. SAMPLE R_2O_3 OF A MIXTURE OF 35% Sm_2O_3 AND 65% Nd_2O_3

Amberlite bed 28″ long and 16 mm. in diameter.

pH	Eluate, liters	R_2O_3, g.	R_2O_3 per liter, g.	Sm_2O_3, %	Nd_2O_3, %
4.5	0.0–1.5	0	0	0	0
	1.5–2.0	0.1376	0.2752	63.6	36.4
	2.0–2.5	.2717	.5434	40.7	59.3
	2.5–3.0	.1995	.3990	25.6	74.4
	3.0–3.5	.0946	.1892	..	...
	3.5–4.0	.0503	.1006	20.0	80.0
	4.0–4.5	.0312	.0624	..	...
	4.5–5.5	.0338	.0338	18.4	81.6
	5.5–6.5	.0186	.0186	..	...
	6.5–7.5	.0112	.0112	18.1	81.9
4.0	2.5–3.0	0.0081	0.0162	..	...
	3.0–3.5	.0204	.0408	97.9	2.1
	3.5–4.0	.0370	.0740	..	...
	4.0–4.5	.0500	.1000	91.3	8.7
	4.5–5.0	0601	.1202	..	...
	5.0–5.5	.0692	.1384	70.9	29.1
	5.5–6.0	.0766	.1532	..	...
	6.0–6.5	.0770	.1540	43.5	56.5
	6.5–7.0	.0787	.1574	..	...
	7.0–7.5	.0726	.1452	23.4	76.6
	7.5–8.0	.0613	.1226	..	...
	8.0–8.5	.0507	.1014	14.5	85.5
	8.5–9.0	.0390	.0780	..	...
	9.0–9.5	.0305	.0610	6.4	93.6
	9.5–10.0	.0226	.0452	..	...
	10.0–10.5	.0173	.0346	2.5	97.5
	10.5–11.0	.0137	.0274	..	...
	11.0–11.5	.0115	.0230	..	100

TABLE II

TYPICAL ELUTION DATA FOR A 1.0-G. R_2O_3 SAMPLE OF A MIXTURE CONTAINING 73.0% Nd_2O_3 AND 27.0% Pr_6O_{11}

Amberlite bed 72″ long and 16 mm. in diameter.

pH	Eluate, liters	R_2O_3, g.	R_2O_3 per liter, g.	Nd_2O_3, %	Pr_6O_{11}, %
4.1	0.0– 9.5	0	0	0	0
	9.5–10.5	0.0033	0.0033	...	..
	10.5–11.5	.0117	.0117	...	..
	11.5–12.5	.0285	.0285	...	..
	12.5–13.5	.0516	.0516	...	..
	13.5–14.5	.0750	.0750	100	0.0
	14.5–15.5	.0886	.0886	...	..
	15.5–16.5	.0997	.0997	95.2	4.8
	16.5–17.5	.1005	.1005	...	..
	17.5–18.5	.0884	.0884	82.3	17.7
	18.5–19.5	.0700	.0700	...	..
	19.5–20.5	.0518	.0518	58.0	42.0

pH	Eluate, liters	R_2O_3, g.	R_2O_3 per liter, g.	Sm_2O_3, %	Nd_2O_3, %
	20.5–21.5	.0399	.0399	...	..
	21.5–22.5	.0309	.0309	42.3	57.7
	22.5–23.5	.0229	.0229	...	...
	23.5–24.5	.0189	.0189	30.5	69.5
	24.5–25.5	.0130	.0130	...	..
4.0	0.0–16.0	0	0	0	0
	16.0–17.0	0.0101	0.0101	...	..
	17.0–18.0	.0230	.0230	...	..
	19.0–20.0	.0594	.0594	...	..
	20.0–21.1	.0723	.0723	97.8	2.2
	21.0–22.0	.0802	.0802	...	..
	22.0–23.0	.0775	.0775	94.3	5.7
	23.0–24.0	.0703	.0703	...	..
	24.0–25.0	.0593	.0593	87.2	12.8
	25.0–26.0	.0493	.0493	...	..
	26.0–27.0	.0416	.0416	77.0	23.0
	27.0–28.0	.0340	.0340	...	..
	28.0–29.0	.0279	.0279	61.1	38.9
	29.0–30.0	.0239	.0239	...	..
	30.0–31.0	.0111	0111	52.9	47.1
	31.0–32.0	.0096	.0096	...	..
	32.0–33.0	.0135	.0135	...	..
3.9	0.0–24.5	0	0	0	0
	24.5–25.5	0.0078	0.0078	...	..
	25.5–26.5	.0192	.0192	...	..
	26.5–27.5	.0346	.0346	...	..
	27.5–28.5	.0480	.0480	...	..
	28.5–29.5	.0554	.0554	100	0
	29.5–30.5	.0551	.0551	...	..
	30.5–31.5	.0546	.0546	100	0
	31.5–32.5	.0515	.0515	...	..
	32.5–33.5	.0466	.0466	97.3	2.7
	33.5–34.5	.0382	.0382	...	..
	34.5–35.5	.0347	.0347	92.4	7.6
	35.5–36.5	.0316	.0316	...	..
	36.5–37.5	.0264	.0264	86.0	14.0
	37.5–38.5	.0238	.0238	...	..
	38.5–39.5	.0204	.0204	...	..
	39.5–40.0	.0093	.0186	...	..
	40.0–41.0	.0183	.0183	...	..
	41.0–42.0	.0162	.0162	...	..
	42.0–43.0	.0154	.0154	...	..

TABLE III

BREAK-THROUGH (IN LITERS) AND TOTAL ELUTION VOLUME AS A FUNCTION OF pH

pH	Break-through	Total elution volume
4.10	10.5	25.5
4.00	17.0	33.0
3.90	25.5	43.0

Samples consisting of 27% Pr_6O_{11} and 73% Nd_2O_3, weighing 1.0 g. were dissolved in hydrochloric acid and adsorbed on columns of the Amberlite 6 ft. in height and 16 mm. in diameter; these columns were the same diameter as those employed in the previous experiment but were about 2.6 times as long. The samples were eluted with 0.5% citrate solutions at pH values of 4.10, 4.00 and 3.90; the best separation was obtained at pH 3.90; typical elution data are given in Table II. The separation of Nd and Pr at this pH is comparable to that obtained with 5% citrate solution at pH 2.55; the elution curve for pH 3.90 is shown in Fig. 1. Data are given in Table III showing the break-through and total elution volume as a function of pH.
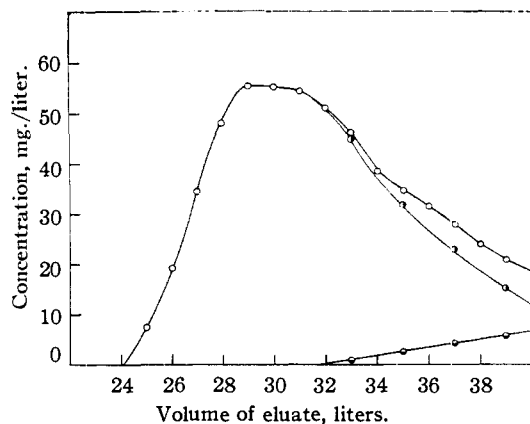
Fig. 1.—Elution curves for a mixture of Nd_2O_3 and Pr_6O_{11} at pH 3.9 (data from Table II): O, total R_2O_3; ◑, Nd_2O_3; ◐, Pr_6O_{11}.

3. Pilot Plant Separations.

—Conditions for pilot plant scale separation of rare earths, based on the above experiments, using Amberlite IR-100 and 0.5% citrate solution as eluant are

Height of bed	8 ft.
Diameter of column	4 in.
Size of sample	50–100 g. R_2O_3
pH	3.9
Flow rate	0.5 cm./min.

A total of 24 columns were erected in a vertical position on 4″ × 4″ wood supports arranged in a manner convenient for the collection of 45-liter volumes of eluate. The columns were Pyrex pipes 10 ft. long with 4 inches inside diameter. The tops of the columns were closed with standard flanges and stainless steel plates $1/2″$ in thickness. Neoprene gasket material was used between the glass and stainless steel plates to make an air and water tight seal. The bottoms were closed in a similar manner, except that a 40-mesh Monel screen was sealed between the two gaskets to retain the resin. The top and bottom plates were fitted with $1/4″$ stainless steel pipes to serve as inlet and outlet. The eluting solutions were allowed to flow, by gravity, from a constant head tank supplied from a main storage tank by means of a centrifugal pump.

Neodymium Carbonate, obtained from the Lindsay Light and Chemical Company, was the source material for the light rare earths (cerium group). The composition of this material calculated on the basis of a total R_2O_3 content of 73.5% was: Nd_2O_3, 80.1; Sm_2O_3, 10.4; Pr_6O_{11}, 8.4; and Gd_2O_3, 1%.

The columns, loaded with resin, were conditioned with the solution listed below, to receive the rare earths. After conditioning, the rare earth chlorides were prepared and adsorbed as previously described. The volumes of 5% solutions employed for conditioning each column were: rock salt 135 l.; citrate, $pH = 5$, 135 l.; NaCl, U.S.P. 90 l.; HCl, 90 l.; citrate, $pH = 5$, 90 l.; HCl, 90 l.; H_2O distilled, 20 l.

The optimum weight of R_2O_3, to be adsorbed per column, was determined by a set of experiments in which the conditions for elution were kept constant and the weights of R_2O_3 were 50, 75, 100 and 125 g. It was found that the separation of the component rare earths was practically the same for sample weights through 100 g. but was markedly poor for the 125-g. sample. In subsequent experiments the load was standardized at 100 g. of R_2O_3 per column.

A typical elution curve is shown in Fig. 2 from data in Table IV; the area between the total weight (R_2O_3) curve and the Sm_2O_3 curve is a measure of the amount of heavy rare earths present,

TABLE IV
TYPICAL ELUTION DATA FOR A 50-G. SAMPLE OF NEODYMIUM CARBONATE

Amberlite bed 8 ft. long and 4 inches in diameter, pH 3.9.

Eluate, liters	R_2O_3, g.	R_2O_3 per liter, g.	Sm_2O_3, %	Nd_2O_3, %	Pr_6O_{11}, %
411–457	0.382	0.008	45.5	0	0
458–495	2.807	.074	64.8	0	0
496–532	1.685	.046	78.5	0	0
533–563	0.332	.011	76.0	0	0
564–595	.113	.0035	71.6	28	0
596–620	.094	.004	29.5	70	0
621–662	.622	.015	1.1	98.5	0
663–685	.577	.025	Trace	99.5	0
686–729	1.565	.036	0	100	0
730–753	1.164	.049	0	100	0
754–798	3.176	.071	0	100	0
799–831	2.856	.087	0	100	0
832–868	3.829	.109	0	100	0
869–890	2.616	.119	0	100	0
891–935	6.371	.142	0	100	0
936–963	4.321	.1543	0	97.2	2.1
964–1003	3.777	.095	0	60.2	39.6
1004–1029	1.609	.062	0	13.4	89.0
1030–1071	2.0169	.048	0	2	96.5
1072–1093	0.667	.030	0	0	95
1094–1138	0.7790	.018	0	0	94.5

especially gadolinium. The approximate analysis of several combined fractions is given in Table V; values less than 1% were determined spectrographically since the spectrophotometric method will not detect these small quantities. At the present time 800 g. of Nd_2O_3 has been obtained with a purity of 99.9% Nd_2O_3, < 0.05% Sm_2O_3 and 0.1% Pr_6O_{11}.

TABLE V
APPROXIMATE ANALYSIS OF A TYPICAL LARGE COLUMN RUN

Fraction	Approximate composition
1	50% Sm_2O_3, 30% Gd_2O_3
2	50% Sm_2O_3, 50% Nd_2O_3
3	2% Sm_2O_3, 98% Nd_2O_3
4	99.5% Nd_2O_3, 0.5% Sm_2O_3
5	99.9% Nd_2O_3, <0.05% Sm_2O_3, <0.1% Pr_6O_{11}
6	98% Nd_2O_3, 2% Pr_6O_{11}
7	90% Nd_2O_3, 10% Pr_6O_{11}
8	50% Nd_2O_3, 50% Pr_6O_{11}
9	90% Pr_6O_{11}, 10% Nd_2O_3
10	99% Pr_6O_{11}, 1% Nd_2O_3
11 (strip)	90% Pr_6O_{11}, 10% impurities, oxides of Ce, La, Ca, etc.

The Sm–Gd fractions were further purified with sodium amalgam by the method of Marsh.[5] A 0.5% sodium amalgam was added to a near neutral solution of the Sm–Gd chlorides; the mercury and water phases were separated and the Sm leached from the mercury with dilute hydrochloric acid. By this procedure the Sm is obtained free from the other rare earths with the

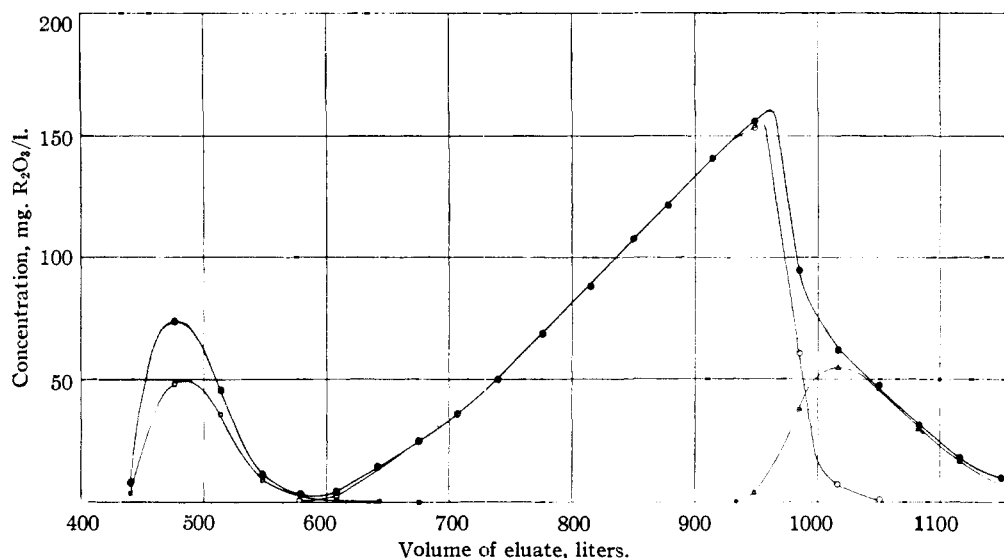(5) J. K. Marsh, J. Chem. Soc., 398, 523 (1942); 531 (1943).

Fig. 2.—Elution curves for Lindsay "neodymium carbonate" at pH 3.9 (data from Table V): ●, total R_2O_3; □, Sm_2O_3: O, Nd_2O_3; △, Pr_6O_{11}.

exception of Eu and Yb. A 160-g. sample of Sm_2O_3 is now on hand with a purity of > 99.9%; the impurities are < 0.01% Eu_2O_3 and 0.05% CaO.

II. The Heavy Rare Earths (Yttrium Group)

The techniques described in Section I, for the separation of the light rare earths (cerium group), have been applied to the heavy rare earths (yttrium group). By these methods there have been prepared multigram quantities of highly pure gadolinium and yttrium salts. In addition, considerable quantities of erbium and dysprosium fractions have been obtained.

1. Sources of Heavy Rare Earths and Preliminary Processing.—The sources of the heavy rare earths employed in these studies were: (1) concentrates obtained from the more soluble fractions left after the separation of the cerium group from Monazite sands and (2) ores containing high percentages of yttrium. While both sources have been employed in the present program, concentrates have been used for most of the work.

a. Concentrates from Monazite Sands.— Concentrates from Monazite sands were obtained from the Lindsay Light and Chemical Company. The concentrates were of two types designated by them as "crude yttrium oxalate" and "samar-

TABLE VI

TYPICAL ANALYSIS OF THE LINDSAY "CRUDE YTTRIUM OXALATE"

Constituent	%	Constituent	%
Loss on ignition (800°)	40	Y_2O_3	15
CeO_2	10	Dy_2O_3	3
Nd_2O_3	7	Er_2O_3	0.2-0.5
Sm_2O_3	5	Ho_2O_3	0.2-0.5
Gd_2O_3	6	SiO_2	10

ium oxalate." A typical analysis of the "crude yttrium oxalate" is given in Table VI.

It was found that the oxide, formed by the ignition of the crude yttrium oxalate, is not readily soluble in concentrated or dilute acids. However, dilute mineral acids do extract about 40% of the oxide on prolonged refluxing. This behavior proved to be advantageous since the heavier rare earths are preferentially extracted; all of the residue consists of silica and oxides of the cerium group together with a small amount of yttrium oxide. Accordingly, the following procedure was adopted for processing the crude yttrium oxalate.

Ignite the crude yttrium oxalate, at 800°, for eight hours under good oxidizing conditions. Place suitable portions of the oxide in reflux vessels and add double the volume of 6 N hydrochloric acid. Bring to a boil and reflux for two hours; a definite change in color of the residue, from dark brown to light tan, is observed during the refluxing process. Add a large excess of water and decant the supernatant liquid into a vessel for precipitation. Dilute the solution until the acid content is at or below 0.5 N and add 100% excess of the theoretical amount of oxalic acid. Filter off the oxalate and ignite to the oxide.

The "samarium oxalate" is an excellent source for gadolinium but is relatively poor in the other rare earths. It is available only in very limited quantities at a cost of ten to twenty dollars a pound. No special procedure is necessary for

TABLE VII

TYPICAL ANALYSIS OF LINDSAY "SAMARIUM OXALATE"

Constituent	%	Constituent	%
Loss on ignition (800°)	50	Nd_2O_3	1
Sm_2O_3	15	Dy_2O_3	1
Gd_2O_3	24	Y_2O_3 (by diff.)	9

TABLE VIII

TYPICAL ELUTION DATA FOR A 100-G. SAMPLE OF ACID SOLUBLE RARE EARTHS FROM CRUDE LINDSAY YTTRIUM OXALATE

Amberlite bed 8 feet long and 4 inches in diameter; pH 3.9

Eluate. liters	R_2O_3. g.	R_2O_3 per liter. g.	Er_2O_3 %	Ho_2O_3 %	Dy_2O_3 %	Gd_2O_3 %	Sm_2O_3 %	Nd_2O_3 %	Pr_2O_3 %	Y_2O_3. [a] %
0–388	1.82	...	..	..	..	..	..	..	..	..
388–443	5.23	0.095	20	10.5	31.5	..	..	..	..	38
443–482	5.58	.143	0	3	20	..	..	..	..	77
482–520	6.90	.182	..	..	10	15	7.7	..	..	67.3
520–575	12.85	.234	..	..	2	43.5	25	..	..	29.5
575–620	12.95	.288	..	..	..	45.2	38	7.5	..	9.3
620–675	14.30	.260	..	..	..	17.3	15.5	65.3	..	1.9
675–725	5.82	.116	..	..	..	3	2	70	25	..
725–768	1.60	.037	..	..	..	..	..	81	19	..
Strip[b]	27.00	...	..	..	..	..	..	..	..	..
Loss	5.95									

[a] Y_2O_3 determined by difference.   [b] Material remaining on column after elution of yttrium group completed.

effecting its solution. A typical analysis is given in Table VII.

b. **Ores.**—Satisfactory ore samples are difficult to obtain in sufficient quantities for separation of the rare earths in quantity. The composition of ore samples varies not only with the location of the deposit but also among different batches taken from the same deposit. Of the ores we have been able to obtain in quantity, those which have proved to be the best sources of the heavy rare earths are risörite, blomstrandine and gadolinite. Risörite is being used as a source of Er and Dy, blomstrandine for Ho and Dy, and gadolinite for Y. The methods employed in processing the ores are those found in the literature.

Fig. 3.—Elution curves for acid soluble fraction from Lindsay "crude yttrium oxalate" at pH 3.9 (data from Table VIII): —, total R_2O_3; ✕, Er_2O_3; ⊖, Ho_2O_3; ▢, Dy_2O_3; ○, Y_2O_3; ◐. Gd_2O_3; △, Sm_2O_3; ●, Nd_2O_3; -O-, Pr_6O_{11}.

2. Column Operations.—The procedures for processing the oxides, adsorption on the resin and elution were those described in Section I of this paper. Typical elution curves are shown in Figs. 4 and 5 which show the degree of separation

of the several rare earth constituents; the elution data are given in Tables VIII and IX. In practice, the various fractions are collected and reprocessed to obtain fractions of increased purity. The separations of the heavy rare earths are excellent with the exception of the Gd–Sm pair. These two elements elute together with practically no separation. However, they can be separated readily by the sodium amalgam procedure as described in Section I of this report.

III. Methods of Analysis

Analysis of the rare earth fractions, obtained by the various separation and processing procedures, has been accomplished chiefly by standard spectrographic and spectrophotometric methods. Solutions of the rare earth ions, with the exception of Y, La, Ce, Tb, and Lu, possess sharp strong absorption bands in the visible and ultraviolet regions which are suitable for analysis. Of the listed exceptions, Ce and La are easily separated from the other rare earths and determined gravimetrically or volumetrically. A spectrographic method has been developed in these laboratories for the determination of yttrium and the details will be described in a later communication.

The spectrophotometric analyses were made with a Beckmann Model DU quartz spectrophotometer equipped with quartz cells with a 1 cm. light path. The lack of sufficiently pure salts, in many cases, has not permitted the determination of accurate extinction coefficients. In view of the difficulties 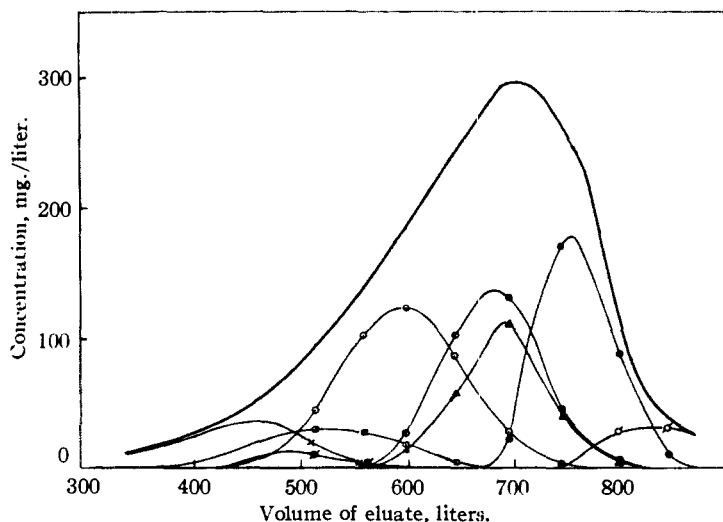in obtaining even provisional values, the data used at present for analysis are summarized in Table X. The values given an A rating were obtained with pure salts and are highly reliable. Those rated B were approximated from data obtained from measurements of an Er fraction of

60% purity or better, from which the impurities could be estimated with a fair degree of accuracy. The values given a C rating were taken from the data of Rodden[6]; they were obtained with a Coleman Spectrophotometer and are not strictly comparable with those which would be obtained with a Beckmann Spectrophotometer. As soon as sufficiently pure rare earth salts are prepared, accurate determinations of extinction coefficients will be determined with the Beckmann Spectrophotometer.

IV. Control of Growth of Molds in the Citrate Solutions

Growth of molds in the citrate solutions used as eluting agents has been a troublesome factor in massive production of rare earths, leading to frequent shut downs and causing erratic results. The mold problem was especially evident in rooms which had been previously used for microbiological studies. Exposure of agar plates for twenty minutes in one of these rooms developed about twenty mold colonies representing many types.

Fig. 4.—Elution curves for Lindsay "samarium oxalate" at pH 3.9 (data from Table IX): $\square$, Er_2O_3 and Ho_2O_3; $\triangle$, Dy_2O_3; O, Gd_2O_3; $\bullet$, Sm_2O_3; $\mathbb{O}$, Nd_2O_3.

TABLE IX[a]

TYPICAL ELUTION DATA FOR A 100-G. SAMPLE OF LINDSAY SAMARIUM OXALATE

Amberlite bed 8 feet long and 4 inches in diameter; pH 3.9.

Eluate, liters	R_2O_3, g.	R_2O_3, per liter, g.	Gd_2O_3, %	Sm_2O_3, %	Nd_2O_3, %
0–525[b]	0.50	...	..	..	..
525–575[c]	2.00	0.040	..	..	..
575–613	2.29	.060	39	30	..
613–650	3.70	.100	67	33	..
650–695	9.11	.200	77.8	22.2	..
695–735	12.78	.320	75	25	..
735–780	17.55	.391	73.5	26.5	..
780–828	19.18	.400	70	30	..
828–875	15.04	.320	71.3	28.7	..
875–915	7.86	.196	71.5	22.5	6
915–953	3.04	.080	22	10	68
953–1000	3.76	.080	2	3	95
Strip	1.50	...	..	..	..
Loss	1.69	...	..	..	..

[a] Since the extinction coefficients of Er, Ho and Dy are not known with any degree of accuracy, the values in the table are only approximations. Since the Y_2O_3 was not determined, it is impossible to estimate the true percentage of each rare earth. The percentages in the table are calculated from the ratio of the concentration of the individual rare earth to the total concentration of the rare earths which could be measured. Therefore, the Y_2O_3 fraction is not indicated but would be concentrated with the Dy_2O_3 and the early Gd_2O_3 fractions. [b] Contained Er_2O_3 30%, Ho_2O_3 10%, Dy_2O_3 60%. [c] Contained Er_2O_3 6%, Ho_2O_3 5%, Dy_2O_3 20%.

Fulmer and Werkman[7] list the following acids as produced by the action of molds on citric acid: acetonedicarboxylic acid (β-oxoglutaric acid), gly-

(6) C. J. Rodden. J. Research Natl. Bur. Standards. **28**, 265 (1942).

(7) "An Index of the Chemical Action of Microörganisms on the Non-Nitrogenous Organic Compounds." Charles C. Thomas. Springfield, Ohio, 1930.
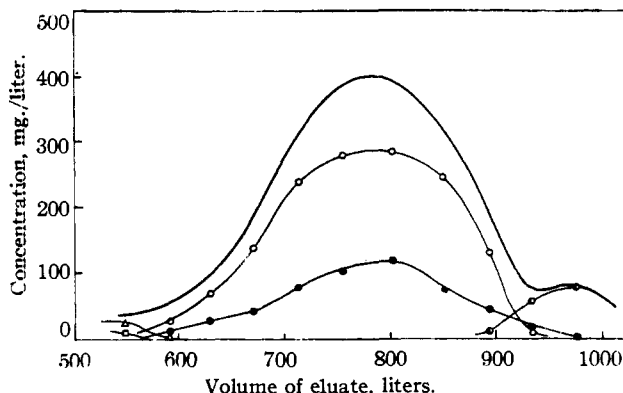
colic acid, glyoxylic acid, malonic acid and oxalic acid. Oxalic acid is the one most commonly formed and would seriously interfere due to the formation of the insoluble rare earth oxalate; while the other acids are formed in minor amounts, their presence would be highly undesirable. The molds also reduce the pH of the medium and might block the pores and surfaces of the resin.

TABLE X

DATA EMPLOYED IN THE SPECTROPHOTOMETRIC ANALYSIS OF THE RARE EARTHS

Element	Absorption band. $m\mu$.	Band width used. Å.	Extinction coefficient.[b] in Å.	Rating[a]	Interfering ions
Pr	444	10	7.30	A	...
Nd	740	10	6.27	A	...
	795	10	7.78	A	Dy
Sm	401	5	3.09	A	...
Eu	390	5	2.65	A	Sm
Gd	272.9	10	1.81	A	...
Dy	810	10	1.80	C	Nd
	912	10	2.73	C	...
Ho	541	10	2.75	C	...
	643	10	2.5	C	Er
Er	521	5	6.7	B	...
	653	5	4.0	B	Ho
	975	10	3.1	B	Yb
Tm	684	10	2.24	C	...
Yb	975	10	2.34	C	Er

[a] A = known with certainty, B = known approximately, C = poor approximation. [b] Units: liters × gram ms.$^{-1}$ × cm.$^{-1}$.

In the first efforts to solve this problem, toluene was used to prevent the growth of the molds. However, this reagent possessed several disadvantages including the presence of a second phase and difficulties in use and handling by the labor employed. The most desirable control chemical should be effective in low concentrations, be economical for large scale use, be easy to handle under controlled conditions and not interfere with

the elution curves on continued use. Phenol seemed to meet these requirements and was tested quantitatively.

Spore cultures of *Aspergillus 'oryzae* and of *Aspergillus niger* were used for massive spore inoculation of 0.5% citric acid solution adjusted to pH 4.0 with ammonium hydroxide. The following concentrations (g. per 100 ml.) of phenol were added to the citrate solution; 0, 0.01, 0.02, 0.03, 0.05, 0.07, 0.10, 0.20, 0.30, 0.50, 0.70 and 1.0. Growth was evident in the first three in twenty-four hours. After six days, there was some growth in 0.03 and a slight trace in 0.05 but no growth in the higher concentrations; the same situation was maintained after a period of about three weeks. It was decided to use 0.1% of phenol in the eluting agent giving a safety factor of about 2.

The effect of 1% phenol on column operation, a concentration ten-fold that employed as a disinfectant, was tested. The control and test columns (16 mm. in diameter and 33 cm. bed length) were charged with Amberlite IR-100 under identical conditions and the complete operation applied in processing 0.5 g. of didymium oxide. The elution curves were identical showing that a concentration of phenol as high as 1% did not interfere with the operations.

The use of 0.1% phenol in the citrate eluting agent was put into practice in the large-scale production columns. During a period of over five

months there has been no growth of mold and all columns have been in continuous operation with entirely satisfactory results.

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

V. Summary

Detailed procedures have been given for the large scale separation of the rare earths using Amberlite IR-100 and 0.5% citric acid ammonium citrate solutions as the eluant. The process employed 24 columns 4 inches in diameter and with 8 feet of resin bed length. The pH of the citrate eluant was 3.9; the growth of mold was eliminated by the use of 0.1% phenol. Large samples of rare earths, of high purity were obtained by these procedures, portions of which have been furnished to other members of the Manhattan Project. Examples of the quantity and quality of several fractions on hand include: (1) *Neodymium*, 800 g. 99.9% Nd_2O_3, < 0.1% Pr_6O_{11}; 770 g. 98% Nd_2O_3, 2% Pr_6O_{11}; (2) *Praseodymium*, 35 g. 99% Pr_6O_{11}, 1% Nd_2O_3; 160 g. 90% Pr_6O_{11} (impurities Ce, La, and Ca); (3) *Samarium*, 160 g. > 99.9% Sm_2O_3; 600 g. 99% Sm_2O_3, 0.5% Eu_2O_3, 0.5% Ca. In addition, considerable quantities of slightly impure heavy rare earth salts and yttrium salts have been prepared.

The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. I. Ion-exchange Equilibria[1]

BY G. E. BOYD,[2] J. SCHUBERT[3] AND A. W. ADAMSON[4]

Introduction

The observation that extremely small quantities of dissolved radioactive species could be extensively removed by base-exchanging substances from aqueous solutions of appreciable ionic strength was the starting point for much additional research and development work on the part of many individuals associated with the Plutonium Project. As a consequence, numerous adsorption techniques have been developed for the extraction, concentration and fractionation of a wide variety of radio-isotopes. Attempts to elucidate the principles governing these systems

led to the undertaking of quantitative studies of the equilibrium and rate processes governing ion-exchange adsorption. Further, these efforts led to the development of exact methods for describing adsorption processes in dynamic systems as, for example, when traces of solute are extracted from a solution flowing through a deep bed of adsorbent. The more important results from this program of basic research will be presented in a series of papers, of which the current article is the first. Here, the problem of the accurate formulation of the relations governing the equilibrium behavior of exchange adsorption systems, the experimental testing of these equations, and the generalizations concerning the adsorbability of cations arrived at will be treated.

Incidentally, the researches to be described will illustrate many of the advantages in the employment of radio-isotope techniques in dealing with physical chemical problems. By virtue of the convenience, sensitivity and accuracy with which *changes* in the amounts of radioactive substances can be estimated, the phenomenon of the exchange