rich fractions, leading to larger yields of pure product by two or three passages.

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

AMES, IOWA RECEIVED JULY 7, 1947

[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

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

BY DARWIN H. HARRIS AND EDWARD R. TOMPKINS

Introduction

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

results in almost no fractionation at *p*H's above 3.2, and to get good separation the *p*H must not exceed 2.75.[1a] Elution from the Dowex resin at *p*H 3.2 gave a separation comparable to *p*H 2.75 with IR-1. The use of Dowex 50 with citrate at *p*H 2.75 gives a separation of Y and Ce many times greater than the width of the elution band of either. Thus it was reasonable to assume that the rare earths with properties intermediate between Y and Ce might be separated very efficiently by use of the new resin. Comparison between the two resins as to the effect of macroscopic quantities of Y and Ce was made by eluting these elements in concentrations up to 200 mg. of each per sq. cm. of column area. The elution curves and the separation of these elements at these concentrations were equivalent to those obtained with trace concentrations, when Dowex 50 was used in the column. In earlier experiments by Khym and Tompkins using IR-1, it had been shown that, with a column of this size, the use of as little as 0.1 mg. of either of these elements reduced their separation as compared to that obtained at the trace level. When 200 mg. of each element was eluted from the 1 sq. cm. × 10 cm. column of IR-1, no separation of the two could be detected. Thus it seemed that the chances of separating large masses of adjacent rare earths in one adsorption–elution cycle would be greatly increased by the use of the new resin.

The greatest disadvantage of Dowex 50 is that equilibrium is approached much more slowly than with IR-1. A previous study of IR-1 columns[5] had established the relationship between efficiency and flow rate. Comparative rate studies between the two resins made by L. S. Myers at these laboratories indicated that it requires about three times as long for equilibrium to be established with Dowex 50 as with IR-1. Thus for comparable operation the flow rate of the Dowex resin columns must be reduced to about one-third of that which had been used for IR-1.

Experimental

Selection of Rare Earths.—In order to determine the efficiency of the Dowex, it was desirable to study two adjacent rare earth elements. Analysis by differential counting to determine the extent of the fractionation is a desirable technique when radioisotopes are available but to use this method it is necessary to choose isotopes whose half lives are sufficiently long to ensure accurate activity determinations throughout the experiment and whose radiation characteristics are sufficiently different to make possible the determination of each in the presence of the other. The difficulty of obtaining pure rare earths for starting materials further limited this choice.[10]

It had been shown by Pool and Kurbatov[11] that Pr^{143} could be prepared by bombarding natural cerium with neutrons.[12] In addition, a small fraction of each of the other naturally occurring Ce isotopes are activated by the pile exposure.[13] The half lives of Ce^{141} and Ce^{143} are 28 days and 33 hours, respectively, while the periods of the other Ce isotopes are very short. Since the Pr^{143} has a half life of 13.8 days, the contributions of Pr^{143} and Ce^{141} to the total radiation of natural Ce, after an exposure of about forty-eight hours and a subsequent decay period of a week to ten days, are about equal. The radiation characteristics of these two isotopes[3] are sufficiently different to permit their analysis by differential counting. Furthermore, cerium can be easily separated by classical chemical methods from the other rare earths, and thus the chance of contaminating radiations from this source is small.

The concentration of Pr^{143} in the neutron bombarded cerium was exceedingly low ($\sim 10^{-3}$ μg per gram of Ce). Thus it was possible to test both the separation of these elements in concentrations differing by a factor of 10^9 and, by addition of inactive praseodymium, in roughly equivalent concentrations. The former case was of interest in regard to the radioisotope production program,[14] the latter in actual rare earth separations in macro quantities. Due to the lanthanum contamination of the praseodymium used as carrier (30% La), the separation of cerium and lanthanum by this column method was also demonstrated.

In the final column run of this series, a mixture of neodymium, praseodymium and cerium was separated into its constituent elements. The praseodymium and cerium used in this run were reclaimed from previous runs. The neodymium was obtained from Ames and was reported as 99.8% pure.[6] To produce a neodymium tracer, Nd_2O_3 was bombarded with neutrons in the pile. Of a number of radioactive isotopes of neodymium produced in this manner, only the 11 day Nd^{147} has a half life of sufficient length for use in these experiments.

Apparatus and Procedure.—The apparatus consisted simply of a glass column (Fig. 1) filled with the resin. Plastic tubes connected one end of this column to a bottle of feed solution and led from the other end to a vessel for collecting fractions of the effluent. The Ce–Pr mixture was adsorbed onto the column from a dilute solution of the chlorides. The portion of the column occupied depended upon the total mass of the mixed rare earths and the total ionic strength of the solution from which they were adsorbed. The length of this adsorption band, as determined by a probe type Geiger counter, was about 2 cm. per 100 mg. of rare earth per sq. cm. of bed area when the ionic strength was below 0.1.

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(10) Since the activation cross-sections of a few rare earth isotopes by pile neutrons are thousands of times as high as those of the others, as little as 0.1% impurity of one of these would produce a radioactivity larger than that due to the major constituent.

(11) M. L. Pool and J. D. Kurbatov, *Phys. Rev.*, **63**, 463 (1943).

(12) Pr^{143} results from an induced chain: $Ce^{142}(n,\gamma)Ce^{143} \xrightarrow[33\text{ h}]{\beta} Pr^{143} \xrightarrow[13.8\text{ d}]{\beta} Nd^{143}$.

(13) $Ce^{136}(n,\gamma)Ce^{137}$; $Ce^{138}(n,\gamma)Ce^{139}$; $Ce^{140}(n,\gamma)Ce^{141}$.

(14) Manhattan Project Announcement, *Science*, **103**, 697 (1946).

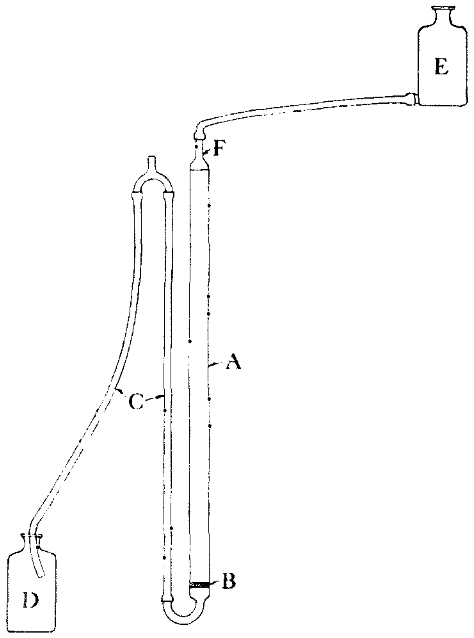

Fig. 1.—Typical column apparatus: the resin bed, A, rests on a porous disc, B, in the glass column F. The flow rate is adjusted by varying the height of the bottle, E, which contains the influent solution. The effluent is collected in a bottle, D. The vent in tube, C, ensures a continuous liquid layer over the resin bed.

The rare earths were eluted by passing a solution of 5% citrate at a carefully adjusted *p*H[15] through the column at rates generally between 0.2 and 0.4 ml./sq. cm./min. The effluent was collected in fractions, the level of radioactivity in the stream being evaluated periodically to indicate the progress of the elution and thus aid in determining the size of the fractions which should be collected. A larger number of fractions were taken in the earlier runs than in those made after the conditions for separation had been more definitely established.

Analysis of Fractions.—Aliquots of the eluate fractions were counted to evaluate the activity distribution, and counted differentially to establish their purity, when required. Also, in those experiments in which the mass of each rare earth was more than 20 mg., the recovery was checked independently by oxalate precipitation, and ignition to the oxide for weight determinations. Aliquots of the oxides were analyzed spectroscopically by the copper spark method developed at the Metallurgical Laboratory by M. S. Fred and his associates.

Counting Technique.—Aliquots of the eluate fractions were pipetted into cylindrical porcelain capsules 35 mm. in diameter and 12 mm. high. To each of these capsules was added a sufficient volume of 5% citrate to bring the total volume to 5 ml. Standards were prepared in a similar manner using a very small aliquot of the starting mixture. Upon evaporation, the citrate formed a uniform layer over the bottom of the dish and thus gave a constant amount of self-absorption for all samples.

The radioactivity of these samples was determined on a conventional Geiger-Mueller counter having a bell-type counter tube with a thin mica window. The samples of the various fractions were compared with the standards counted in a similar manner. From these data the percentage (activity basis) of rare earth present in each fraction was calculated (this method was based on the assumption that isotopic separation was negligible).

The absorption curves of the pure radioisotopes were obtained by counting the standards through aluminum absorbers of various thicknesses. The absorption curves for Pr^{143} and Ce^{141}, as determined in this manner, are shown in Figs. 2 and 3, respectively. As may be seen from these curves, the radiations of the two isotopes differ as to the range of their beta rays; also, the Ce isotope emits gamma radiation while the Pr isotope does not: Thus, if a

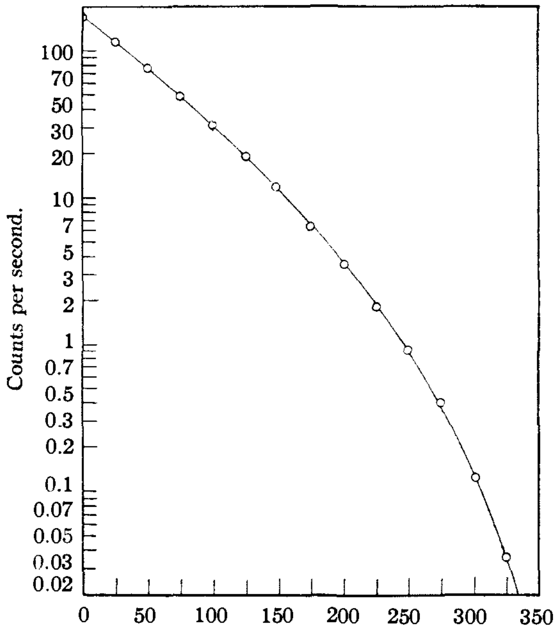

Fig. 2.—Aluminum absorption curve of Pr^{143}.

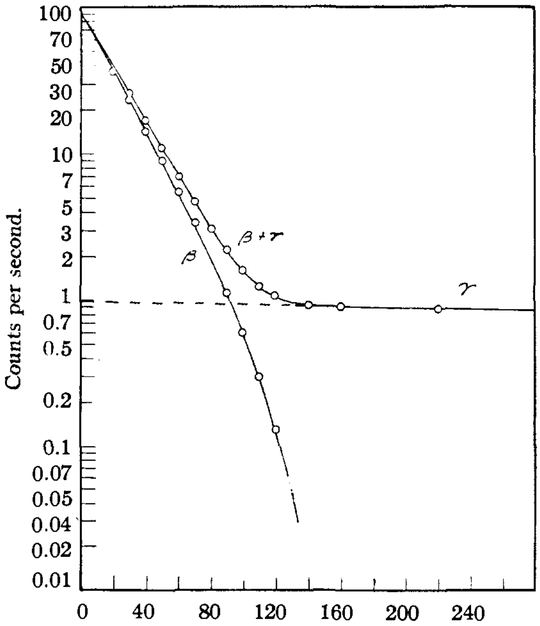

Fig. 3.—Aluminum absorption curve of Ce^{141}.

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(15) The *p*H was determined by comparing the citrate solutions to standard buffers by means of a Beckman *p*H meter using a glass electrode.

gamma count is found on a supposedly pure sample of Pr, when it is counted through 350 mg./sq. cm. (more than the range of the Pr beta) the presence of Ce is indicated. Pr contamination in Ce may be shown by counting the sample through 350 mg./sq. cm. and again through 140 mg./sq. cm. of aluminum (the latter at just beyond the range of the Ce beta but within the Pr beta range). If the two counts differ by more than 10 to 11%, Pr is probably present.

The counts through 350 and 140 mg./sq. cm. are useful as a qualitative test for purity, but to get a more quantitative estimation of the percentage of each constituent it is necessary to make two counts within the Ce beta range. (Zero and 40 mg./sq. cm. added absorber were chosen in these determinations.) The four counts thus obtained (*i. e.*, through zero, 40, 140 and 350 mg./sq. cm. of aluminum) were plotted on 4 cycle, semi-log paper, as shown in Fig. 4. The gamma curve of the Ce was then drawn from the 350 mg./sq. cm. point to the Y-axis, with a slope as determined from Fig. 3. Next, the gamma count at 140 mg./sq. cm., as read from this curve, was subtracted from the total counts found through this absorber, the resultant value plotted, and the Pr beta curve drawn through this point to the Y-axis with the proper slope as determined from the curve of Fig. 2 ($T^1/_2$ = 39 mg./sq. cm.). Finally, the Pr beta and the Ce gamma counts at 40 and 0 mg. added absorber (as read from the respective curves) were subtracted from the total counts through these absorbers to determine the counts due to Ce beta. The slope of the line drawn through these two points should then equal that of the Ce beta as seen in Fig. 3 ($T^1/_2$ = 13 mg./sq. cm.). A quantitative estimate of the percentages of each constituent was made by comparing the beta counts of Pr and Ce at zero added absorber. This method is illustrated in Fig. 4 with a mixture having about 89% Ce and 11% Pr.

The results of several analyses on synthetic mixtures of Pr^{143} and Ce^{141} in varying proportions are shown in Table I. Although the method gives only approximate results, it is possible to obtain a good estimate of the amount of cross-contamination. The accuracy of this method is greatest when the minor constituent is 5 to 25% of the total radioactivity. Qualitatively, as little as 1% impurity of Pr in Ce or Ce in Pr can be detected.

TABLE I

Sample	Percentage composition Pr	Percentage composition Ce	Analyses (by differential counting) Pr	Analyses (by differential counting) Ce
1[a]	10.8	89.2	10.9	89.1
2	19.4	80.6	25.6	74.4
3	52.0	48.0	42.7	57.3
4	71.1	28.9	70.7	29.3
5	75.5	24.5	73.6	26.4
6	93.9	6.1	94.4	5.6

[a] Analysis by differential counting shown in Fig. 4.

Results.—The results of these separation runs are shown in Figs. 5 to 9 and Tables II to VI, inclusive. For convenience of presentation, these runs are divided into (1) those in which tracer Pr in macro quantities of Ce was employed; (2) those in which the quantity of Pr and Ce was macroscopic and nearly equivalent; (3) one run in which Nd, Pr, and Ce were present in nearly equivalent macroscopic amounts.

(1) Tables II and III and Fig. 5 show the results of the two attempts (Pr-Ce-1 and Pr-Ce-6) to separate Pr^{143} in trace amount from a bulk quantity of Ce. As may be noted from the tables, the chief differences between the two runs is that in the first the resin was unused and in the acid form, the pH was 3.1, the flow rate was about 0.2 ml./sq. cm./min. and the direction of flow was downward, while in the second run the resin had been used in a previous run and was in the ammonium form, the pH was 3.0, the rate was about 0.4 ml./sq. cm./min. and the direction of the flow was upward. In another series of experiments using Y and Ce tracers, which was carried on

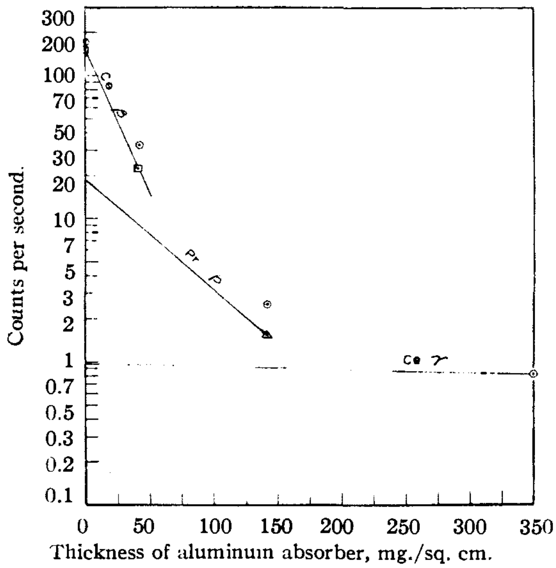

Fig. 4.—Analysis of a mixture of Ce^{141} and Pr^{143} by differential counting; counts were made through 0, 40, 140 and 350 mg. of added absorber: ⊙, total counts; ⊡, Ce beta counts; △, Pr beta counts.

TABLE II

(Pr-Ce-1): FRACTIONATION OF Pr IN TRACE QUANTITY FROM MACROSCOPIC Ce

Rare earth: ~15 mg. Ce^{+3} + ~10^{-8} mg. Pr^{143}. Column: area 1.24 sq. cm.; resin height 108 cm. Resin: Dowex 50, 40–60 mesh, previously unused, acid form. Flow: downward; average rate 0.190 ml./sq. cm./min. Elutrient: 5% citrate; pH 3.10 to fraction 18, then 3.5 to end.

Fraction number	Volume, ml.	Analyses[a] Pr	Analyses[a] Ce	% of Total Pr	% of Total Ce
1–3	1870	0	. . .	. . . .	. . . .
4	80	65	35	2.57	0.259
5	25	46	54	16.9	3.81
6	25	38	62	14.0	4.24
7	12.5	34	66	8.34	3.07
8	12.5	41	59	10.1	2.73
9	25	34	66	15.4	5.63
10	25	20	80	12.4	9.78
11	25	18	82	10.3	8.86
12	25	12	88	5.15	6.92
13	25	6.5	93.5	2.13	5.81
14	25	3.0	97.0	1.18	5.77
15	25	2.1	97.9	0.615	5.45
16	25	1.0	99.0	.298	5.52
17	40	0.93	99.1	.350	7.08
18	260	0.2	99.8	22	21.0
19	530		100.0		4.03

[a] Based on differential counting

TABLE III

(Pr-Ce-6): SEPARATION OF Pr^{143} FROM NEUTRON BOMBARDED Ce

Rare Earth: ~150 mg. Ce^{+3} + ~10^{-7} mg. of Pr^{143}. Column: area 0.5 sq. cm.; resin height 120 cm. Resin: Dowex 50, 50–60 mesh, previously used, ammonium form. Flow: upward, average rate 0.368 ml./sq. cm./min. Elutrient: 5% citrate, *p*H 3.00 through fraction 10; *p*H 3.6 during fraction 11. Yield of pure Pr^{143}: 93.8%. Yield of pure Ce: 89.9% (activity basis).

Fraction number[a]	Volume, ml.	Analyses[b]		% of total	
		Pr	Ce	Pr	Ce
1–4	3090	...	...	...	....
5 (A)	380	100	...	0.88	....
6 (B)	310	100	...	22.1	....
7 (C)	210	100	...	46.1	....
8 (D)	120	100	...	24.7	....
9 (E)	82	64	36	4.61	0.175
10 (F)	215	1.2	98.8	1.65	9.89
11 (G)	430	...	100.0	...	89.9

[a] The letters refer to the fraction designations in Fig. 5.
[b] Based on differential counting.

simultaneously with the first of these two runs,[10] the effect of a "conditioning" run in enhancing separation was demonstrated. Likewise, in the same series it was shown that the separation of a tracer from a bulk ion was increased by upflow, if the trace ion was eluted ahead of the bulk ion. Also, Pr-Ce-2 to Pr-Ce-5 had shown that *p*H 3.1 is too high for this separation. Thus, in the second Pr^{143} tracer run (Pr-Ce-6), the conditions were altered and 94% of the Pr^{143} was obtained free from Ce, even though the mass of the Ce in this run was about ten times that in Pr-Ce-1. The higher flow rate in the second run probably decreased the amount of separation to some extent.

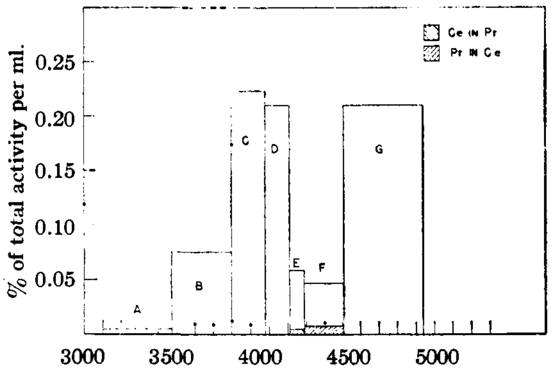

Fig. 5.—Separation of Pr^{143} in trace concentrations from neutron bombarded Ce. The radioisotopes counted were Pr^{143} and Ce^{141}; run Pr-Ce-6: rare earths, ~150 mg. Ce containing ~10^{-7} mg. of Pr^{143}; column area = 0.5 sq. cm.; resin height is 120 cm.; resin, Dowex 50, 50–60 mesh, previously used, ammonium form; flow, upward, average rate 0.368 ml./sq. cm./min.; elutrient, 5% citrate, *p*H 3.00 through fraction F; *p*H 3.6 during G; yield of pure Pr^{143}, 93.8% (activity basis); yield of pure Ce, 89.9% (activity basis). The letters on the graph represent the fractions collected.

In separations involving radioelements of relatively short half lives, however, the over-all yield is sometimes greater at a flow rate and *p*H higher than the optimum values, since the loss by decay is reduced.

(2) Figures 6 to 8, inclusive, and Tables IV and V show the results when approximately equivalent quantities of Pr and Ce are used. The Pr carrier used in runs Pr-Ce-2 and 4 was contaminated with about 30% La and about 1% of other earths, principally Nd. In Pr-Ce-5, the purified rare earths from previous runs were used. The variations of conditions in these runs are shown in the tables and in the legends to the figures.

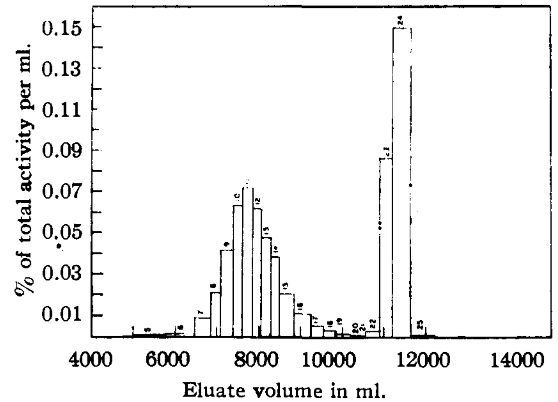

Fig. 6.—Separation of Pr and Ce, run Pr-Ce-2: rare earths, ~ 15 mg. Ce^{+3} and 20 mg. "Pr" (Pr^{+3} contained 30% La^{+3} impurity); column area 1.24 sq. cm.; resin height 108 cm.; resin, Dowex 50, 40–60 mesh, previously used, acid form; average flow rate, 0.186 ml./sq. cm./min.; elutrient, 5% citrate, *p*H 3.00; yields, Pr (pure), 99.76%, Ce (Pure), 99.24% (activity basis, by subtraction of activity in fractions 20, 21 and 22 from total activity). The numbers on the graph represent the fractions collected.

In Pr-Ce-2 about 15 mg. of the activated Ce and 20 mg. of praseodymium and were used. The experimental results obtained in this run are shown in Fig. 6 and Table IV. The large number of fractions collected permitted a good determination of the overlap between the elution curves of the two elements. As may be seen in Table IV, cross-contamination occurred only in fractions 20 and 22.[16] It will be noted that only 0.25% of the Pr and 0.76% of the Ce were contained in these fractions. Thus the separation, for all practical purposes, was complete.

In runs Pr-Ce-4 (Fig. 7) and Pr-Ce-5 (Fig. 8 and Table V), the quantity of rare earth is about ten times greater than that used in Pr-Ce-2. The starting *p*H of the first of these two runs was recorded as 2.9 but subsequent results indicated that it must have been higher. The results of this column run (Fig. 7) are included chiefly as a

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[16] There is some doubt as to the actual presence of Pr in fraction 22, since none could be detected in fraction number 21.

TABLE IV

(Pr-Ce-2): SEPARATION OF Pr AND Ce IN MACROSCOPIC AMOUNTS

Rare earth: ~15 mg. Ce^{+3} + 20 mg. "Pr" (with 30% La impurity). Column: area 1.24 sq. cm.; resin height 108 cm. Resin: Dowex 50, 40–60 mesh, previously used, acid form. Average flow rate: 0.186 ml./sq. cm./min. Elutrient: 5% citrate, *p*H 3.00 through fraction 23; *p*H 3.5 during fractions 24–25, inclusive. Yields: pure Ce, 99.24%; pure Pr, 99.76% (activity basis).

Fraction number	Volume, ml.	Analyses[a] Pr	Analyses[a] Ce	% of Total Pr	% of Total Ce
1–4	4990	100	...	.....	...
5	760	100	...	0.26	...
6	705	100	...	0.55	...
7	390	100	...	3.35	...
8	230	100	...	4.85	...
9	305	100	...	12.6	...
10	220	100	...	13.8	...
11	260	100	...	18.7	...
12	180	100	...	11.0	...
13	250	100	...	11.9	...
14	210	100	...	8.19	...
15	365	100	...	7.60	..
16	375	100	...	4.05	...
17	290	100	...	1.58	...
18	300	100	...	0.93	...
19	340	100	...	.43	...
20	270	23	77	.12	0.03
21	112	...	100	.....	0.01
22	300	1.4 (?)	98.6	.12(?)	0.72
23	320	...	100	.....	27.6
24	480	...	100	.....	71.5
25	500	...	100	.....	0.10

[a] Based on differential counting.

TABLE V

(Pr-Ce-5): SEPARATION OF Pr AND Ce IN MACROSCOPIC AMOUNTS

Rare earth: ~210 mg. Ce^{+3} + ~150 mg. Pr^{+3}. Column: area 0.9 sq. cm., resin height 120 cm. Resin: Dowex 50, 40–50 mesh, previously used, ammonium form. Average flow rate: 0.268 ml./sq. cm./min. Elutrient: 5% citrate; *p*H changed stepwise from 2.80, 2.85, 2.90 to 3.10 during fractions 1–5, inclusive; *p*H 3.10 maintained through fraction 10; *p*H 3.6 during fraction 11. Yields: pure Pr, 99.5–99.9%; pure Ce, 98.6–99.0% (activity basis).

Fraction number[a]	Volume, ml.	% of Total Pr^{143}	% of Total Ce^{141}	Weight, mg.[b] Pr	Weight, mg.[b] Ce
1–5	5111	..	..	....	...
6 (A)	965	80.5	..	123	...
7 (B)	575	18.1	..	24.7	...
8 (C)[c]	565	1.4	1.6	0.03	2.97
9 (D)	290	..	22.5	....	44.2
10 (E)	395	..	35.1	....	73.3
11 (F)	740	..	40.8	....	92.9

[a] The letters refer to the fractions shown in Fig. 8. [b] Based on direct weight of the oxides and their spectrographic analyses. [c] Qualitatively, all samples shown to be pure by differential counting were also spectroscopically pure. By spectroscopic analysis, fraction 8 was 1% Pr. The total and differential count showed that 1.4% of the Pr^{143} and 1.6% of the Ce^{141} were contained in this fraction. On this basis, fraction 8 was nearly 40% Pr. The anomaly may be due to a tendency for the heavier Pr^{143} isotope to concentrate in the last Pr fractions.

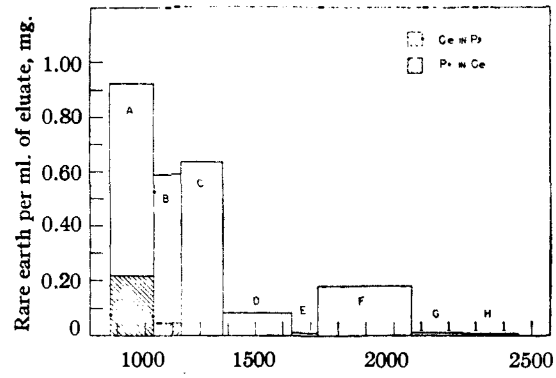

Fig. 7.—Separation of Pr and Ce, run Pr-Ce-4: rare earths, ~ 200 mg. Pr^{+3} (containing 30% La^{+3} impurity) and 200 · ıg. Ce^{+3}; column area 0.90 sq. cm., resin height 110 cm.; resin, Dowex 50, 40–50 mesh, previously used, acid form; average flow rate, 0.211 ml./sq. cm./min.; elutrient, 5% citrate, *p*H 2.9 (recorded); yields, no pure Pr, Ce (pure) 77% (activity and weight basis), La (pure) 99.3%. The letters on the graph represent the fractions collected.

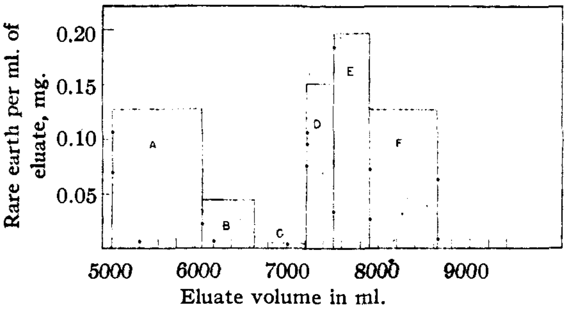

Fig. 8.—Separation of Pr and Ce, run Pr-Ce-5: rare earths, ~ 210 mg. Ce^{+3} and ~ 150 mg. Pr^{+3}; column area 0.9 sq. cm.; resin height 120 cm.; resin, Dowex 50, 40–50 mesh, previously used, ammonium form; average flow rate, 0.268 ml./sq. cm./min.; elutrient, 5% citrate, *p*H changed stepwise from 2.85, 2.95, 3.05 and 3.10 during Pr elution, *p*H 3.6 used to elute the Ce; yields, Pr (pure) 99.5–99.9% Ce (pure) 98.6–99.0% (activity basis). The letters on the graph represent the fractions collected.

demonstration of the separation of Ce from La. Fraction D was pure Ce while F was pure La. The quantity of rare earth in the intermediate fraction E was too small for spectroscopic analysis.

The separation of Pr and Ce in Pr-Ce-5 (Fig. 8) is nearly as complete as that shown in Pr-Ce-2 (Fig. 6). The fractions in Pr-Ce-5 are much larger than those collected in Pr-Ce-2 and thus the region of crossover from Pr to Ce is more poorly defined. From Table V it may be seen that only fraction C is a mixture and that it contained only about 1.5% of the total starting mass of each element. Thus, over 98% of each of the two rare earths were recovered in a high purity in this run. A slightly lower *p*H probably would have increased the separation. It is almost certain that the mass used in these runs (about 400 mg. per sq. cm. of column area) is not too high for good separations. In fact, experiments now in progress indicate that much larger amounts may be used without seriously affecting the separation.

(3) The results of the single column separation of Nd, Pr and Ce (Nd-Pr-Ce-1) are shown in Fig. 9 and Table VI. It may be seen that Nd and Pr were as readily separated by this method as were Pr and Ce in the earlier runs. The starting pH of this run was too low (pH 2.8) and so it was increased by 0.1 pH unit after several days when a radioactive survey showed that the Nd was not moving down the column at the rate observed for Pr in the previous separations of Pr and Ce. It is probable that the pH for optimum separation of Nd and Pr in the least time is in the range of 2.85 to 2.90. Pr and Ce should probably be separated at a pH of 3.00. Their separation at pH 2.96, noted in Nd-Pr-Ce-1, is greater than necessary. This increases the time required for the run and decreases the rare earth concentration, thus reducing the recovery by oxalate precipitation. (Ce and La may be separated at any pH from 3.2 to 4.0.)

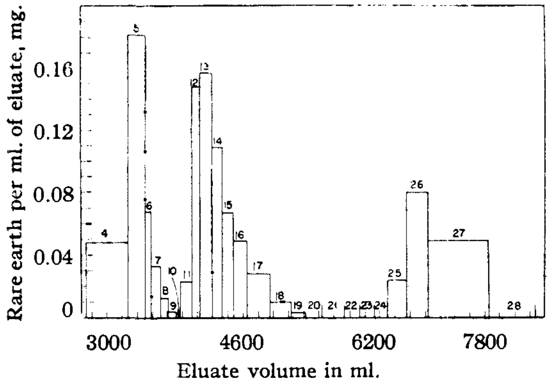

Fig. 9.—Separation of Nd, Pr and Ce in macroscopic amounts: rareearths, ~ 93 mg. Nd^{+3} + 100 mg. Pr^{+3} + ~ 80 mg. Ce^{+3}; column area 0.50 sq. cm., resin height 122 cm.; resin, Dowex 50, 60–80 mesh, previously used, ammonium form; flow rate, varied between 0.2 and 0.5 ml./sq. cm./min., average 0.418 ml. /sq.cm./min.; elutrient, 5% citrate, pH 2.80 during fraction 1, pH 2.90 during fractions 2–17 incl., pH 2.96 during fractions 18–26 incl., pH 3.60 during fractions 27–28 incl.; recoveries, ~ 85% Nd, 91% Pr, and ~ 88% Ce. The numbers on the graph represent the fractions collected.

It is interesting to note that in the crossover regions both from Nd to Pr and from Pr to Ce the concentrations of the rare earths in several intermediate fractions of this run were too low to be precipitated in one molar oxalic acid. The counting data showed, however, that the concentrations of rare earths in the eluate never dropped to zero in these regions (Table VI). Comparison between the results obtained by counting aliquots of the fractions and those obtained by direct weighing of the rare earth oxides obtained from the fractions may also be seen in Table VI. The small differences between the two may be due to inaccuracies in the method or may indicate a partial separation of radioactive from non-radioactive isotopes. All fractions were spectroscopically analysed. No cross-contamination could be de-

TABLE VI

(Nd-Pr-Ce-1): SEPARATION OF Nd, Pr AND Ce IN MACROSCOPIC AMOUNTS

Rare earths: ~93 mg. Nd^{+3} + 100 mg. Pr^{+3} + ~80 mg. Ce^{+3}. Column: area 0.50 sq. cm.; resin height 122 cm. Resin: Dowex, 50, 60–80 mesh, previously used, ammonium form. Flow rate: varied between 0.2 and 0.5 ml./sq. cm./min.; average = 0.418 ml./sq. cm./min. Elutrient: 5% citrate; pH 2.80 during fraction 1; pH 2.90 during fractions 2–17, inclusive; pH 2.96 during fractions 18–26, inclusive; pH 3.60 during fractions 27–28, incl. Recoveries: ~85% Nd, 91% Pr, ~88% Ce (mass basis[a]).

Fraction number	Volume, ml.	% of Total[d]	Weight, mg.[b]	Concentration, %/ml. (activity basis)	Concentration, %/ml. (weight basis[c])
			Neodymium		
1	990	...	...	....	....
2	825	...	...	....	....
3	715	...	...	....	....
4	555	35.0	26.9	0.0625	0.0605
5	228	50.4	41.8	.219	.229
6	75	6.91	5.1	.092	.084
7	124	4.84	3.9	.043	.041
8	94	1.89	1.3	.019	.017
9	103	0.82	0.4	.008	.001
10	76	0.23	...	.003	....
			Praseodymium		
11	142	4.11	3.2	.029	.024
12	115	21.2	17.8	.184	.169
13	155	27.7	25.1	.179	.178
14	130	17.0	14.1	.130	.119
15	155	11.7	10.7	.075	.076
16	175	5.92	8.8	.034	.055
17	300	5.07	8.4	.017	.031
18	280	3.75	2.7	.013	.010
19	190	1.34	0.4	.007	.002
20	225	0.86	...	.004	....
21	275	.59	...	.002	....
22	195	.42	...	.002	....
23	205	.22	...	.001	....
24	175	.13	...	.001	....
			Cerium		
25	245	10.2	6.2	.041	.036
26	290	35.0	23.4	.121	.115
27	820	54.7	40.5	.066	.070
28	630	0.12	...	.0002	....

[a] The relatively poor percentage mass recovery is due to the solubility of the rare earth oxalates in the citrate solutions. In separating larger total masses the percentage loss would be lessened. It may also be lessened by recovering the rare earth on the column.[3] [b] All recovered rare earths were spectroscopically pure, within limits of detection. [c] Mass percentages calculated on total mass recovered. [d] Activity basis.

tected by this method which had a limit of sensitivity of 0.1% Ce or Pr in Nd, 0.5% Pr and Nd in Ce and 0.5% Nd and Ce in Pr. Judging from the shapes of the elution curves of these rare earths, it is probable that their purities were greater than 99.9%.

The purities of all the "pure" rare earths whose separation is described here are known only to the limits of present analytical methods. Before these values can be determined more exactly, it will be necessary to devise better analytical methods for the determination of very minute amounts of one or more rare earths in the presence of others in practically pure form. Activation by neutron bombardment in the pile may prove to be an exceedingly sensitive analytical method for at least some of the rare earths.

Discussion

In a previous paper[1a] the probable over-all reactions involved in column separations of the type described here have been discussed. The reactions which were postulated for the elution of the rare earths with ammonium acid citrate are:

$$n\mathrm{NH_4}^+ + MR_n \rightleftarrows M^{+n} + n\mathrm{NH_4R}\ \text{(ion exchange)} \qquad (1)$$

$$M^{+n} + y\mathrm{H}_x\mathrm{Cit}^{x-3} \rightleftarrows \mathrm{M(H}_x\mathrm{Cit)}_y{}^{+z}\ \text{(complexing)} \qquad (2)$$

M^{+n} being the rare earth ion, $\mathrm{H}_x\mathrm{Cit}^{x-3}$ some citrate ion, R^- the resin ion, and z expressing the charge on the complex $[n + y(x - 3)]$.

Russell and Pearce[17] had shown that only a slight fractionation of the rare earths occurs in one cycle using an ion exchange mechanism alone. A similar observation was made by one of the authors[1a] in earlier work on this separation method, using Amberlite IR-1. On the other hand, it is obvious that reaction (2) will not produce the separation without the aid of a competing reaction. It is the competition between the resin and complexing agent, represented in the two equations (1) and (2), which results in the separation.[1a]

On the basis of the present available data, it has not been possible to determine the structure of the rare earth-citrate complexes. However, the distribution coefficients of the various rare earths between the citrate solution and the resin may be determined under varying conditions by equilibrating known amounts of resin with solutions of the different rare earth citrates. For such a study it was necessary to obtain pure rare earths if the tracer technique was to be used since impurities of other rare earths, even in very minute quantities, may result in a serious error.[10] Thus, it was necessary that the column separations precede the equilibrium studies in order that rare earths of sufficient purity could be obtained. A study of equilibrium distribution coefficients, using the pure rare earths described above, is now in progress. The results obtained to date indicate that the distribution coefficients for adjacent rare earths of the cerium group vary by about a factor of two under conditions similar to those used in these separations.

While it is very important that the strengths of the rare earth citrate complexes differ appreciably if separations of the type described above are to be successful, this factor alone does not determine the efficiency of the separation. It is also important that the distribution of the rare earth between the resin and the solution be within the correct range so that the difference in the rates of movement of the rare earths down the column will be maximized. Thus, if the tendency of the rare earths to complex is very large as compared to their tendency to adsorb on the resin, the separation will not be complete for in this case the rare earths will be eluted quite rapidly and therefore very close together. Removal of a rare earth mixture from IR-1 with 5% citrate at a *p*H of 3.5 to 4.0 is an example of such an elution.[1a] On the other hand, the concentration of rare earth in the eluate must be large enough so that the time required for elution is not unreasonably long.

Before this series of experiments with the Dowex resin was undertaken it seemed that by making the correct adjustments in conditions a reasonably good separation could be obtained, no matter what resin were used. Thus, by operating at lower *p*H's with more dilute citrate it is reasonable to expect the IR-1 column to be similar in its behavior to a Dowex 50 column at a higher citrate concentration and *p*H. Whether or not this will prove to be the case remains to be tested; even if good separations with IR-1 columns are proven possible, however, the use of a higher capacity resin is still advantageous when elements in bulk quantities are being separated. The largest rare earth mass to column volume ratio in this series of experiments occurred in runs Pr-Ce-5 and Nd-Pr-Ce-1. In subsequent runs it has been possible to increase this ratio by a factor of five without materially affecting the separation. If one now calculates the yield of pure rare earth obtained per liter of resin bed volume, the efficiency of these Dowex columns for separating Nd from Pr is found to be many times higher than that reported by Spedding[6] for the Amberlite resins.

In the fractionation of a pair of rare earths, if 20 to 25% of each component can be obtained pure and larger quantities somewhat enhanced, in one adsorption–elution cycle, quantitative separation of the two by recycling may be practical. However, if the mixture to be separated contains more than two rare earths, the elution curves of the adjacent pairs cannot overlap by as much as 50% if any of the intermediate elements are to be separated in pure form. For this reason, it is of importance to reduce the overlap of these elution curves to a minimum when mixtures

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[17] R. G. Russell and D. W. Pearce, THIS JOURNAL, **65**, 595 (1943).

of more than two rare earths are to be separated. To achieve this, it may be practical to operate at flow rates much lower than those reported previously.[1,6]

It is difficult to choose optimum conditions when a study of this type is being made. The length of time involved in making a run is so great that it is not practical to study many variables. For this reason, the conditions employed in these runs are not claimed as optimum. To establish such a set of conditions will require a much better knowledge of the equilibrium distribution coefficients of the rare earths between the resin and solution under various conditions and some information concerning the rates at which these reactions approach equilibrium.

Summary

By utilizing a column separations method in which a complexing agent is used to remove the cations from an ion-exchanger and a recently developed exchange resin of high combining capacity, it was possible to get essentially complete separations between several rare earths of the Ce group in a single adsorption–elution cycle. Pr was separated both in trace and bulk amounts from Ce. Ce was separated from La. In one run a mixture of nearly equivalent quantities of Nd, Pr and Ce was separated into its constituent elements. Each of these three rare earths in this run was obtained in a high yield. The impurities were below a detectable level (probably less than 0.1%).

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[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. IV. The Separation of the Yttrium Group Rare Earths[1]

BY B. H. KETELLE AND G. E. BOYD[2]

Introduction

The current state of development of the quantitative understanding of the physics and chemistry of the rare earth elements has been summarized in an excellent recent monograph by Yost, Russell and Garner.[3] In this work the extraordinary difficulty thus far met with in the separation of the rare earths has been remarked upon. Further, the possible general utility of radio-isotopic tracer techniques was recognized as a means in the overcoming of this classical chemical problem. Since investigation of this unique group of elements evidently has been impeded by the scarcity of pure compounds, it was considered important that any promising method of separation and purification be utilized to its full potentialities. Researches on ion-exchange adsorption techniques during the recent war years[4] had indicated that an efficient method of chromatographic separation was possible, and therefore deserved examination at a later time. In fact, the separation of the following fission product element groups had been achieved[5]: Zr + Cb; La + Ce + Pr + Sr + Ba; and Te + I.

The researches described below had as their objective the production, identification and/or characterization of the radio-isotopes of the yttrium group rare earths. Since separation procedures based on ion-exchange adsorption appeared to offer almost unique possibilities for employment as an analytical tool in this problem, the initial studies were directed toward their development. Prior to the initiation of the present program, a series of empirical studies on the separation and recovery of the uranium fission products had led to the development of a "citrate elution" technique by means of which the possibility of the rapid separation of the alkaline and rare earth ions from each other on a milligram scale was demonstrated.[6] Later this procedure was adapted to the separation of cerium and yttrium,[7] and to the production of gram amounts of pure neodymium from didymium earth mixtures.[8] Shortly thereafter, the method was applied to the separation and chemical identification of two radio-isotopes of element 61 formed by the fission of U-235.[9] Quite recently, decidedly superior fractionations of mixtures of approximately equivalent amounts of Ce, Pr and Nd have been achieved by using the new synthetic organic exchanger, Dowex-50.[10]

In spite of the gratifying success met with by the groups lead by Cohn and Tompkins, and by Spedding, there was good reason, on the basis of

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[1] This work was performed under the auspices of the Manhattan District at Clinton Laboratories, Monsanto Chemical Co., Oak Ridge, Tennessee, during the period May, 1945, to May, 1947.

[2] On leave from the Department of Chemistry, University of Chicago. Present address: Clinton Laboratories, Monsanto Chemical Co., Oak Ridge, Tennessee.

[3] D. M. Yost, H. Russell and C. S. Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, New York, N. Y., 1947.

[4] H. D. Smyth, "Atomic Energy for Military Purposes," Princeton University Press, Princeton, N. J., 1945, p. 137.

[5] J. A. Swartout, B. R. Russell, D. N. Hume and B. H. Ketelle, July, 1944, to be published.

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

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

[8] 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).

[9] J. A. Marinsky, L. E. Glendenin and C. D. Coryell, *ibid.*, **69**, 2781 (1947).

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