

crease continuously with increasing lattice parameter.

3. The structures of the systems hydrogen-tantalum, hydrogen-columbium, and for tantalum nitride, and columbium nitride have been investigated by means of X-ray diffraction.

4. Columbium nitride, CbN, was found to become a superconductor at 15.2°K. the highest

transition temperature reported to this time for any superconductor.

5. Tantalum nitride, TaN, was found not to be a superconductor above 1.88°K., the lowest temperature reached.

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[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

Ion-Exchange as a Separations Method. I. The Separation of Fission-Produced Radioisotopes, Including Individual Rare Earths, by Complexing Elution from Amberlite Resin¹

BY EDWARD R. TOMPKINS, JOSEPH X. KHYM AND WALDO E. COHN

Introduction

It was necessary for the Plutonium Project to isolate the major fission species in the forms, purities and amounts needed for the solution of the physical, chemical and biological problems raised by the quantity production of plutonium. The stimulus to the work reported here actually came from the need to assess the radiotoxicological^{1a} hazards of the fission products. The investigation of the toxicity of these elements required the biological testing of each one in the carrier-free² form in which it would be encountered in the plutonium process, while the large variations in biochemical behavior among the fission product elements themselves imposed exceedingly high purity specifications on each.

The major radioactive fission species (*i. e.*, those of high fission yield, of half-life greater than one week and having measurable radiations) which contain practically all of the radioactivity remaining after about thirty days of decay are listed in Table I. Together with the stable species isotopic with them, they make up 70% of the total mass of the fission products. (The residual 30% of the fission product mass is made up principally of stable Rb, Mo, Rh, Pd, La, Sm and Eu.) The separation of these fission products was required to be nearly quantitative,³ not only for the sake of economy but in order to prevent contamination

(1) This work was done at Clinton Laboratories, a part of the Plutonium Project, during the period October, 1943, to June, 1945, 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) The study of toxicology due to the radiation, not the chemical action, of chemical entities is termed "radiotoxicology."

(2) As used in this and subsequent papers, this term means that no stable isotope is knowingly added. Stable isotopes produced in fission are, of course, always present and the presence of isotopic impurities in the original uranium and in reagents is always assumed to be likely.

(3) The specifications actually set were: 0.1-1.0 curie amounts of each major fission product per cycle, free of added carrier; radiochemical purity of 95-98% (depending on the element in question); total solids below 1 mg. per 100 mc.; no visible precipitates at pH 4 and no sulfide-insoluble metals

TABLE I^a

RELATIVE AMOUNTS OF MAJOR RADIOACTIVE FISSION PRODUCTS COEXISTING IN URANIUM ABOUT ONE MONTH FROM THE END OF A SEVERAL MONTH EXPOSURE IN A CHAIN-REACTING PILE

Element	Total mass, mg. ^b	Radioisotopes		
		Mass no.	Half-life ^c	Curies
Sr	0.44	89	53 d	1.0
		90	25 y	0.035 ^d
Y	0.22	91	57 d	1.25
Zr	1.2	95	65 d	1.35
Cb	0.35	95	35 d	1.7
43	.3	99	1.5 × 10 ⁶ y	0.7 × 10 ⁻⁶
Ru	65	103	42 d	0.9
		106	1 y	.065 ^d
Te	.16	127	90 d	.0075
		129	32 d	.03
I	.075	131	8 d	.065
Cs	1.1	137	33 y	.032
Ba	0.47	140	12.5 d	.35 ^d
Ce	1.12	141	28 d	1.0
		144	275 d	0.85
Pr	0.4	143	13.8 d	0.4
Nd	1.34	147	11 d	0.12
61	0.17	147	3.7 y	0.14

^a Calculated by W. E. Cohn from data in THIS JOURNAL, 68, 2411 (1946). ^b Includes all isotopes arising from fission whether stable or radioactive. ^c d = days; y = years. ^d Radiations of short-lived daughter not included.

of each radioelement by the others. Finally, the multicurie activities made remote-control adaptability an essential feature of any method developed. The process described in this paper was developed specifically to separate 0.1-1 curie quantities of each of the major fission species in radiochemically and chemically pure form and without resort to carrier materials. The principle which was applied to the solution of this problem has led^{4a} to the discovery of a new and powerful

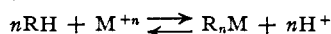
(4) One curie of a given species is defined as that amount of the species which exhibits 3.7 × 10¹⁰ disintegrations per second.

(4a) The history of the development of ion-exchange separations within the Manhattan Project is given by Johnston, Quill and Daniels. *Chem. Eng. News*, 25, 2494 (1947).

method of effecting ionic separations, most dramatically illustrated by its successful application to the old problem of separating the rare earth elements from their mixtures.

Principles and Preliminary Work.—Of the several known types of separation procedures (precipitation, extraction, distillation, ion-exchange, electrolysis), only two were considered to lend themselves to a fairly immediate solution of the problem: (1) precipitation of a given species with a non-isotopic carrier (*e. g.*, Ba⁺⁺ with PbSO₄) followed by separation of the carrier; (2) selective adsorption on, or selective elution from, an ion-exchange column.

The work of Adamson, Russell, Schubert and others associated with Boyd in the Plutonium Project had already demonstrated the unique applicability of the ion-exchange technique to the adsorption of fission product ions in trace amounts. The particular ion-exchanger used was Amberlite IR-1, a phenol-formaldehyde polymer containing free methylenesulfonic acid, carboxyl and phenolic groups, the anion being insoluble but holding ionizable (hence exchangeable) cations.⁵ When an aqueous solution containing cation M⁺ⁿ is brought into contact (*e. g.*, by shaking) with the resin, M⁺ⁿ ions in the solution exchange with those cations originally held on the resin by its free acid groups. This may be indicated as a reversible reaction (R⁻ being the resin anion and H⁺ its original cation)



The final equilibrium concentrations of M⁺ⁿ and H⁺ depend, as in any chemical reaction, principally upon the activities of the two cations and upon the respective affinities of each for the resin.⁶ In general, the cation-resin bond strength increases with the charge on the cation and decreases with the ionic (hydrated) radius. A typical series, from strong to weak, is: Th > La > Ce > Rare Earths > Y > Ba > Cs > Sr > K > NH₄ > Na > H.⁶

To free an adsorbed cation from its resin-bound state requires its physical replacement by another cation. If the relative affinity for the resin and/or the concentration of the ion introduced in the solution phase is sufficiently greater than that of the ion originally combined with the resin, replacement will be nearly complete. The effective concentration of an ion may be lowered by complex formation. Thus any cation may be effectively replaced from its resin compound by a relatively dilute solution of a second cation containing a compound which will complex the other cation. For example, when equivalent molar concentrations of zirconium and hydrogen ions compete, the resin is largely in the zirconium form. If oxalate is added to form the negatively-charged zir-

conium oxalate complex, the resin is converted nearly quantitatively to the hydrogen form.

Simple replacement of adsorbed fission species (*i. e.*, all of those in Table I excepting only I, 43, Te and Ru) by H⁺ was tried first but very little specificity was achieved. However, elution by complex-formation resulted in the discovery of a new separation technique. The first clue was given by Russell,⁷ who demonstrated the selective elution of Zr and Cb from IR-1-adsorbed fission mixture with dilute oxalic acid. Swartout, Hume, *et al.*,⁷ made detailed fission product analyses of an adsorption-elution cycle utilizing this procedure, demonstrating its specificity for Zr and Cb. This directed our attention to the possible use of other organic acids as specific complexing agents for individual fission species. Several such were tried, including citric acid (by analogy with the well-known calcium citrate complex), but the importance of pH, which influences the proportions of H₃Cit, H₂Cit⁻, HCit⁻² and Cit⁻³ as well as the behavior of the acid groups on the resin, was not at first realized. Once this pH-dependence was noted and utilized, the experiments indicated below were performed, leading at once to a solution of the problem.

Experimental

Apparatus.—The essential apparatus, as shown in Fig. 1, consists of a glass tube, closed at one end by a coarse sintered glass disc upon which the resin bed rests, and a means of introducing solutions into the top of the column and collecting the effluent from the bottom. The length of the columns varied according to the experiment. In most cases the open end of the effluent tube was above the top of the resin bed to prevent the liquid head from dropping below the top of the resin bed. In the curie-scale production runs, a flow-type ionization chamber⁸ was used to monitor the effluent solutions continually.

Resin.—Amberlite IR-1⁹ (or 100) was ground and dry-screened. That portion between 40 and 60 mesh was used in most of the work reported in this paper. The resin was slurried into the column which was half-filled with water. The resin settled as the water flowed from the effluent tube. The resin bed was then washed exhaustively with strong hydrochloric acid (*ca.* 3 *N*), in order to convert it to the hydrogen form, and finally with water to remove the excess hydrochloric acid.

Solutions.—The stock solutions of "5%" citric acid were made by diluting 50 g. of C. P. citric acid monohydrate crystals to 1 liter with distilled water. Portions of this were then converted to the desired pH with concentrated ammonia. Tartaric and oxalic acid solutions were made in the same way, using C. P. tartaric and oxalic acid crystals, respectively. The carrier-free fission products used in both experimental and production runs were maintained in dilute (about 0.1 *N*) hydrochloric acid.

Procedure.—The desired fission products were adsorbed on the resin by simply allowing a dilute (0.01–0.1 *N*) acid solution to flow through the resin bed at a predetermined rate. After washing out the solvent with water, the elution procedures consisted simply of passing the desired eluant through the column and collecting samples of the effluent for assay. In the production runs, a continuous automatic recording of the radioactivity in the effluent was made.

(7) J. A. Swartout, E. Russell, D. N. Hume, B. H. Kettelle, Project Work, May, 1944.

(8) E. R. Tompkins, to be published.

(9) Resinous Products Company, 226 W. Washington Square, Philadelphia, Pa.

(5) The IR-1 anion is thus analogous to the immobile (protein) ion involved in Donnan theory.

(6) C. E. Boyd, J. S. Schubert and A. W. Adamson, *THIS JOURNAL*, **69**, 2818 (1947).

In most of the tracer-scale investigations, a separate column was used for each of the ions whose elution characteristics were being investigated. This made it possible to analyze the effluent by simple counting technique instead of tedious radiochemical analyses. The results obtained by the use of parallel columns are strictly applicable to the situation where all elements are on one column as long as no appreciable saturation of the resin results.

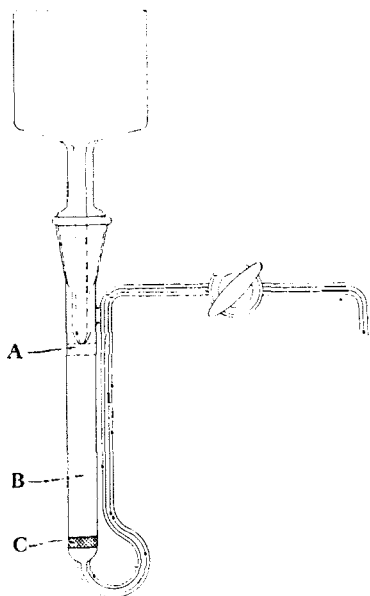


Fig. 1.—Experimental column: The funnel is removable to facilitate resin addition and removal. The resin bed, B, in this column is 1 sq. cm. \times 10 cm. and rests on the porous glass disc, C. A stopcock in the outlet tube allows regulation of the flow rate. The opening in the outlet tube is above the top of the resin bed, thus maintaining a liquid layer, A, above the resin at all times.

Calculations and Method of Presentation of Data.—The data are presented in figures, since the purpose of this paper is to describe a general procedure rather than to delineate optimum conditions for specific separations. The amounts of radioactive species present in various fractions or volumes are expressed in terms of their radioactivities, which were determined by the measurement of suitable aliquots on Geiger-Mueller counters and by continuous ion-chamber monitoring, with subsequent corrections for absorption, decay, etc.; these are plotted on the ordinates as either *per cent. of total activity* or as *amount of activity per unit volume* (*i. e.*, concentration). On the abscissas are plotted either *time* or *volume* of effluent; since rates were usually held constant, these are usually proportional to each other.

Results

Separation of Zr and Cb from Fission Mixture.—Both Zr and Cb form very stable oxalate complexes. It was this that led Russell to demonstrate the use of, and Swartout, Hume, *et al.*,⁷ to utilize oxalic acid as a specific agent to remove Zr and Cb from Amberlite columns. In

our experience also, 0.5% oxalic acid strips Zr and Cb quantitatively; none of the trivalent or divalent elements are removed by this treatment.

Separation of Tri- and Divalent Species.—In Fig. 2 are shown the results of the experiments using citrate solutions of varying pH to elute a mixture of resin-adsorbed fission products. At a pH of 3, 5% citrate removes the trivalent fission species (also Zr and Cb, if present); at a pH of 5, the remaining divalent and monovalent species are stripped from the resin. It will be noted from this figure that the concentration of the eluted species increases as the flow rate is decreased.

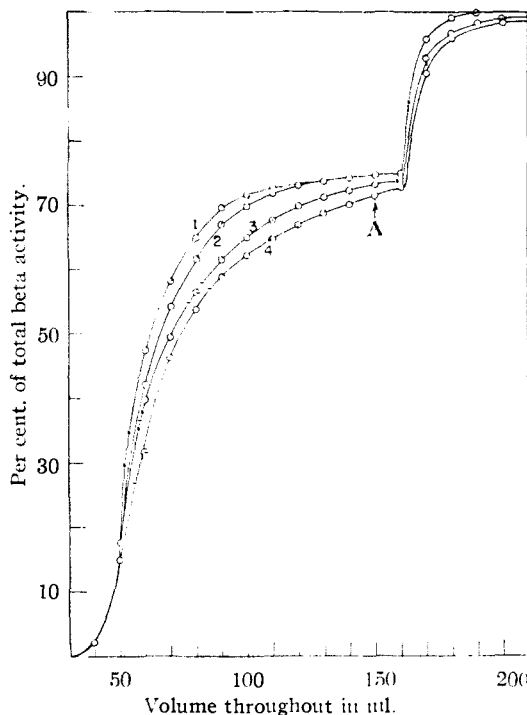


Fig. 2.—Separation of divalent and trivalent fission-produced radioisotopes by complex elution from Amberlite Resin, and the effect of rate: resin, Amberlite IR-1, 40-60-mesh, hydrogen form; bed, 0.75 sq. cm. \times 13 cm.; influent, 5% citric acid plus ammonia to pH of 3.00 (up to A), to pH of 6.00 (after A); 1, 2, 3 and 4, respectively. Source of tracers: mixed fission products obtained in carrier-free state by extraction of uranium from dissolved, pile-exposed uranium. Analyses indicate near-quantitative removal of Y, Ce, rare earths, Zr and Cb only up to (A), similar removal of Sr and Ba after (A).

Separation of Y and Ce.—Separation of the two major components of the trivalent group, Y and Ce, is accomplished by closer attention to the effect of pH on the rate of elution by citrate solution. The elution of Y and Ce at pH's 2.7 to 3.0 with citrate solutions is typified by the experiments shown in Fig. 3. Each curve was obtained from one of a series of parallel, identical columns

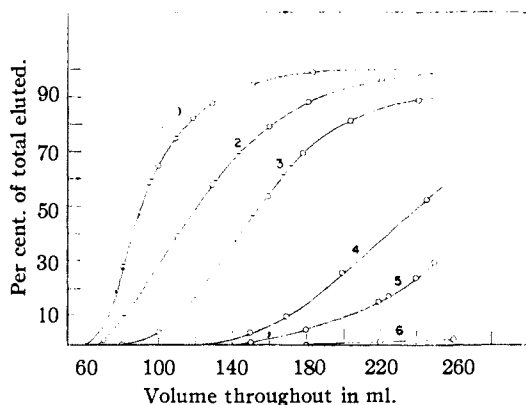


Fig. 3.—Elution of carrier-free Y^{91} and $Ce^{141,144}$ from Amberlite IR-1 resin columns by 5% citrate solutions and the effect of pH : resin, Amberlite IR-1, 40–60 mesh, acid form; bed, 1 sq. cm. \times 10 cm.; influent, 5% citric acid plus NH_4OH to pH shown; rate, 0.5 ml./min.; source of tracers, tracers prepared carrier-free from mixed fission products. Each curve obtained from a separate experimental column.

Curve	Element	pH
1	Y	2.85
2	Ce	3.00
3	Y	2.75
4	Y	2.70
5	Ce	2.90
6	Ce	2.80

Separation of Sr and Ba.—In the elution of Sr and Ba from Amberlite IR-1 (or 100), the relatively lower affinity of these divalent elements for the resin as compared to the trivalent species becomes apparent. The tendency of such divalent elements to form complexes with Cit^{-3} , which exist in appreciable amounts only at $pH > 4$, is well known. However, ammonium ion, which reaches a concentration of 0.5 M in 5% citrate at pH 5.0, also contributes effectively to the Sr and Ba removal. The relative importances of NH_4^+ and of citrate as eluting agents are shown by two comparisons in Fig. 4: (1) 0.25 M NH_4Cl-NH_4OH at pH 7.5 (curve 6) versus the same plus 1.7% citrate (curve 2); (2) 0.5 M NH_4Cl (curve 4) versus 5% citrate at pH 5 (curve 1) which has the same NH_4^+ content. Ba^{++} behaves similarly. However, since Ba is less strongly complexed than Sr and is also less easily replaced from the resin by monovalent cations, both mechanisms act in the same direction; thus the use of 5% citrate at pH 5 effects a very marked separation of the two elements. This separation is shown in Fig. 5, which is a reproduction of the continuously recorded ionization current produced in the flow-type ionization chamber⁸ in the effluent solution from a production (curie-scale) run (D-9).

Separation of Rare Earths.—The separation of Y and Ce has been discussed above. The rare earths demonstrate a continuous decrease in

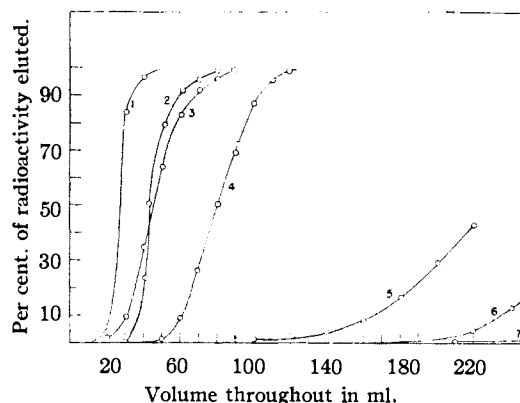


Fig. 4.—Elution of carrier-free $Sr^{89,90}$ from Amberlite resin with various reagents, illustrating complex effect, "conditioning" effect and relative value of H^+ and NH_4^+ in removing Sr^{++} : resin, Amberlite IR-1, 40–60 mesh; bed, 1 sq. cm. \times 10 cm.; influent, as noted below; rate, 0.5 ml./sq. cm./min.

Curve	Influent
1	5% (0.23 M) citrate, pH 5.0 (NH_4^+ 0.5 M)
2	0.25 M NH_4Cl-NH_4OH plus 0.087 M citrate (1.7%) at pH 7.5; resin in H^+ form.
3	Same as 2, resin pre-converted (conditioned) to NH_4^+ form with NH_4Cl-NH_4OH at pH 7.5
4	0.5 M NH_4Cl
5	0.5 M HCl
6	(a) 0.25 M NH_4Cl , pH 5; (b) 0.25 M NH_4Cl-NH_4OH , pH 7.5; resin in H^+ form or in NH_4^+ form
7	10% (0.5 M) citric acid (pH \sim 1.8).

ionic radius and basicity of hydroxide,¹⁰ both of concern in this discussion, in the order; La, Ce, Pr, Nd, (61),¹¹ Sm, Eu and Gd. (One can infer that this should also be the order of increasing stability of citrate complexes.) The properties of Y, although it is not a rare earth in the strict sense, would place it after Gd, which is the heaviest known fission product. Thus, Ce and Y bracket the rare-earth fission products. Since the elution curves of Y and Ce at pH 's around 2.8 are so well separated (*cf.* Fig. 3), those of the other rare earths might be expected to fall in between.

The first opportunity to demonstrate the separation of some of these intermediate rare earths came in the course of the first curie-scale production run (D-9, September, 1944). Two fractions were collected between the main Y and Ce fractions (Fig. 6). The decay curves of these fractions demonstrated that they contained short-lived activities which were not Y or Ce; analyses both of these fractions and of the neighboring Y and Ce fractions,¹² using differential absorption of

(10) T. Moeller and H. E. Kremers, *J. Phys. Chem.*, **48**, 395 (1944).

(11) Inferred position.

(12) Marinsky had been working independently on the problem of identification of a gamma-emitting rare earth fission product with an eleven-day half-life. His investigation of our D-9 rare-earth fractions furnished the data from which the curves in Fig. 6-b are

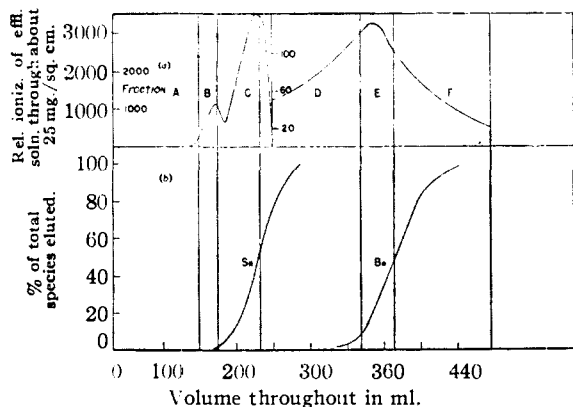


Fig. 5.—(a) Separation of fission-produced strontium (Sr^{90} , Sr^{90}) and barium (Ba^{140}) by complex elution (Run D 9): resin, Amberlite IR-1, 40–60 mesh, after stripping of Zr–Cb and Y, Ce and rare earths (Fig. 6), containing 500 mc. $Sr^{90,90}$ and 150 mc. Ba^{140} plus their daughters Y^{90} and La^{140} ; bed, 1 sq. cm. \times 100 cm.; influent, 5% citric acid, pH adjusted with NH_4OH to pH 5.0; rate, 1–2 ml./sq. cm./min.

COMPOSITION OF FRACTIONS

Fraction	Volume, ml.	Radioactivity, mc.	Analyses ^a
A	160	0	
B	23	12.5	Y^{90} , La^{140} , (>90%) ^b
C	45	257	>99% Sr
D	108	240	94% Sr, 6% Ba
E	36	56	>99% Ba
F	105	96	>99% Ba

(b) Elution curves of Sr and Ba, reconstructed from analyses.

^a Ignoring daughter elements (Y^{90} and La^{140}) except in fraction B.

^b Daughters of Sr^{90} and Ba^{140} which grew in during overnight shutdown of column.

the β and γ radiations as well as chemical separation of the Pr–Nd–61 fraction, permit the reconstruction of elution curves for Pr and for Nd or 61 (or both), which are consistent with our decay data. These curves are shown in Fig. 6(b).

Following this demonstration of the separation of rare earth species,^{12a} the experiments shown in Fig. 7 were performed. These experiments proved the feasibility of the separation of rare earths, both carrier-free and with milligram amounts of carrier present, by a citrate elution procedure. This was again demonstrated by the analysis of another rare earth sample from a similar production run (D-14, February, 1945). From this fraction, Marinsky¹² separated Y, Eu, Sm and Ce by chemical methods. He then adsorbed the remaining rare earths on an IR-1 column and eluted

constructed and led to the work by Marinsky and Khym described below and in Fig. 7. Marinsky and Glendenin subsequently isolated and furnished positive chemical identification of 61^{147} in another of our fractions as described below (Fig. 8). It was a fortunate coincidence that Marinsky and we were able thus to lend support to each other's investigations.

(12a) Presented before the Plutonium Project Council Meeting in Chicago, December, 1944.

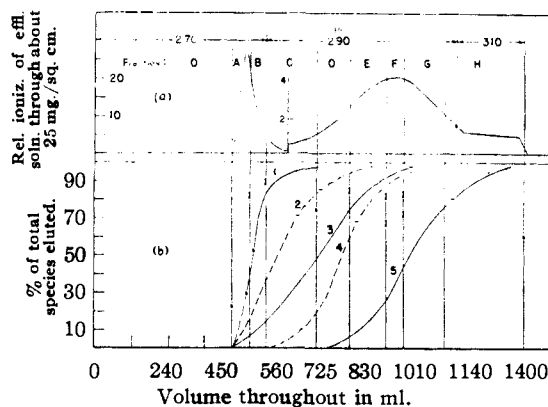


Fig. 6.—(a) Separation of fission-produced rare earths, yttrium and cerium, by complex elution (Run D-9): resin, Amberlite IR-1, 40–60 mesh, acid form. 400 mc. Zr + Cb eluted previously with 0.5% oxalic acid; 500 mc. Sr and 150 mc. Ba eluted subsequently (see Fig. 5); bed, 1 sq. cm. \times 100 cm.; influent, 5% tartaric acid, pH adjusted with NH_4OH ; rate, 2 ml./sq. cm./min.; composition of mixture eluted (gross activities at 10 mg./sq. cm. total absorption): Y, 41%; Nd + 61, 7.4%; Pr, 8.2%; Ce, 43%; Sr, 0%; gross activity, 1300 mc.

COMPOSITION OF FRACTIONS

Fraction	Volume, ml.	Radioactivity, mc.	Principal constituents	Radiochemical composition ^a
O	450	4	Y	...
A	60	225	Y	95% Y
B	50	230	Y	95% Y
C ^b	165	135	Y, (61), Nd, Pr	50% Y, 3% Ce
D ^b	105	75	Pr, Ce, Y	15% Y, 30% Ce
E	120	160	Ce, Pr	75% Ce
F	60	100	Ce	94% Ce
G	132	180	Ce	99% Ce
H	258	120	Ce, La	99% Ce
I	140	60	Ce, La	3% Sr

(La^{140} grows in from Ba^{140} on column)

(b) Elution curves of individual species in the above mixture, reconstructed from analyses of fractions.

Curve	Component
1	Y
2	Nd (+61), calculated from gamma content of 3
3	Observed Pr (Pr, Nd, 61) beta
4	Pr, calculated from 3 minus 2
5	Ce

^a Greater accuracy than that shown in making radiochemical analyses for Y and rare earths (except Ce) in such mixtures was not possible at the time these runs were made. ^b In these cuts, and in similar cuts from later runs, Marinsky and Glendenin¹³ found and isolated the $11d\ Nd^{147}$ and the $4y\ 61^{147}$.

them with citrates in the manner described above, obtaining data from which the curves shown in Fig. 8 were derived. The first separation and chemical identification of element 61 was thus accomplished.¹³

Interaction between Ion-Exchanger and Complexing Eluant: $NH_4^+ - H^+$ Exchange.—When

(13) Marinsky and Glendenin, *THIS JOURNAL*, **69**, 2781 (1947).

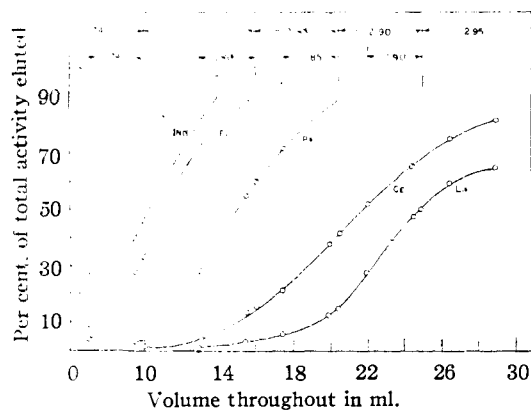


Fig. 7.—Elution of some radioactive rare earths from Amberlite IR-1 with 5% citrate solutions^a: resin, Amberlite IR-1, 40–60 mesh, in acid form; bed, 0.75 sq. cm. \times 12.5 cm.; influent, 5% citric acid, converted with NH_4OH to pH shown at top; rate, ~ 1 ml./sq. cm. min. Each rare-earth was adsorbed and eluted from a separate column. Source of tracers: Y, Ce and La obtained in carrier-free form from mixed fission products. Nd, Eu and Pr obtained by exposure of stable elements to neutrons in pile; as used, there was about 10 mg. of carrier in each. (The purity of the Nd is questionable from the shape of the observed decay curve.)

^a Data obtained in October, 1944, by Khyrn and Marinsky; curves first published June 1, 1945, cf. ref. (13).

an ammonium citrate buffer is put through an IR-1 resin bed which contains H^+ as its predominant cation, there is an exchange of NH_4^+ in the buffer for the resin H^+ which results in a fall in the pH of the elution solution. Thus the pH of the first effluent is essentially that of citric acid, rising to the influent pH as equilibrium with the resin is approached. Due to the release of H^+ into the eluting solution, the citrate-metal complex is decomposed, resulting in readsorption of the metal ion; this persists until the $\text{NH}_4\text{-H}^+$ exchange has diminished to the point where the complex ion is stable. For this reason, no metal-complex ions can precede in the effluent that pH which will permit their existence; the rate of movement of such a pH boundary limits the rate of movement of the eluted ions. The appearance of a given species in the effluent under these conditions coincides with the arrival of a certain pH , as is demonstrated by Fig. 9; Ba appears in the effluent only when the pH of the latter has risen above a certain critical value.

Variations in Citrate Concentration and pH .—The pH ranges indicated for "5%" citrate are related to the citrate concentration, which was arbitrarily chosen. Many variations of citrate concentration, pH and salt concentration have been tried, and ion-exchangers in both H^+ and NH_4^+ forms were used. None of the variations from the standard 5% citrate and H^+ form of resin have given any advantages from the prac-

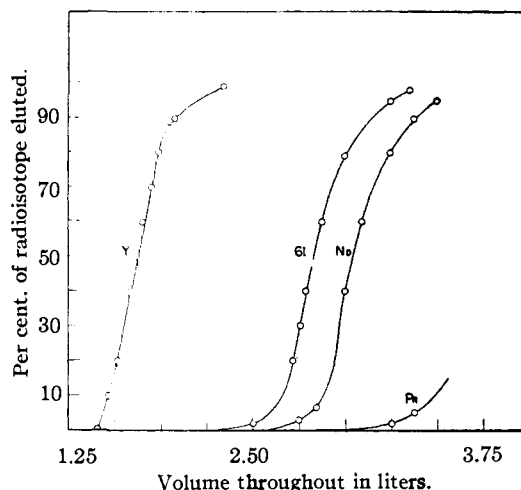


Fig. 8.—Separation of fission-produced rare earths by complex elution (from data of Marinsky¹³): resin, Amberlite IR-1, 100 mesh, acid form; bed, 1 sq. cm. \times 125 cm.; influent, 4.75% citric acid, converted to pH 2.75 with NH_4OH ; rate, 1–2 ml./min. Source of tracers: Fission activities obtained from D-14⁸ rare earth fraction; Y, Eu, Sm and Ce removed chemically, leaving Pr, Nd, Gd and Y (trace) with 20 mg. La carrier in relative amounts of 64%, 17.5%, 17.5% and 0.005% of gross beta activity. Analyses of fractions made by differential absorption and decay technique.

tical standpoint of separations. These variations do, however, shed light upon the mechanisms which are operative in the elution.

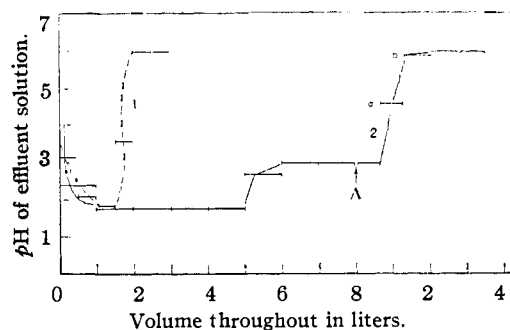


Fig. 9.—Change in pH of citrate buffers upon passage through Amberlite resin column in hydrogen form and the relation of Ba elution to effluent pH : resin, Amberlite IR-1, 40–60 mesh, hydrogen form; bed, 5 sq. cm. \times 100 cm.; influent, 5% citric acid converted to desired pH with NH_4OH ; rate, as shown; curve 1, pH 6.00 at 10 ml./min.; curve 2, pH 3.00 at 22 ml./min. to (A); pH 6.00 at same rate thereafter; 65% of Ba removed in cut a, 35% in cut b (each 360 ml.).

The elution of Y by 2% citrate at pH 's 3–8 is shown in Fig. 10. There seems to be a maximum efficiency at a $\text{pH} \sim 4.0$. The sharp initial rise at lower volumes noted at $\text{pH} > 4.0$ is probably due to the $\text{NH}_4^+\text{-H}^+$ exchange, which renders the first eluates more acid than the influent solution.

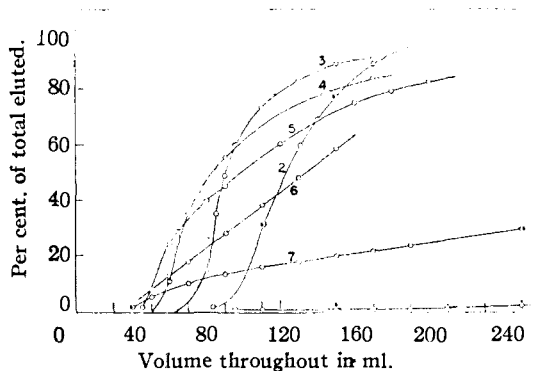


Fig. 10.—Elution of tracer Y^{91} from Amberlite IR-1 by 2% citrate solutions: resin, Amberlite IR-1, 40–60 mesh, acid form; bed, 1 sq. cm. \times 10 cm.; influent, 2% citric acid, converted to pH shown with NH_4OH ; rate, about 1 ml./sq. cm./min.

Curve	1	2	3	4	5	6	7
pH	3.0	3.5	4.0	5.0	6.0	7.5	8.0

Once equilibrium with regard to pH is attained, however, the slower rate is established. From the data alone it is not to be deduced whether the decrease in rate of elution is due to the shift in concentration of the various citrate anions, to an effect of pH on Y (for which there is other evidence; e. g., 1 M HCl elutes Y rapidly while 1 M NH_4Cl does not appear to elute it at all) or to an effect upon the resin. However, no such reversal of rate is found in the case of Sr (Fig. 11). This fact supports the possibility that the diminution of elution of Y at higher pH's is due to hydroxide formation.

Discussion

As has been mentioned above, the purpose of these experiments was to devise, in the shortest possible time, a method for the separation of carrier-free fission products in a form suitable for biological experimentation. This practical purpose did not allow a methodical search to find optimum conditions, nor a systematic exploration of the theoretical and practical implications of the results obtained in the period of the work reported (September, 1943–March, 1945). The application of these results and the basic principle involved to the problem of high level fission product separation and mass rare-earth separation will require further investigation of the effects of a number of variables on the separation efficiency. However, the results of this and related studies have established the general applicability of this method of separations and have defined the range of conditions under which a given separation can be made.

The nature of the method developed for the production runs, in which pure fission species in curie quantities were prepared, is obvious from the data presented. Elution of the Zr–Cb mixture is effected by 0.5 oxalic acid. Following this,

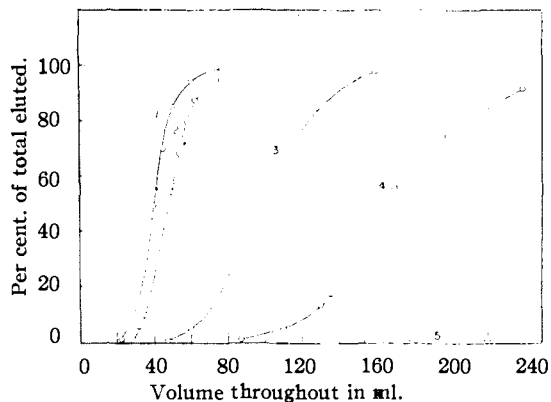


Fig. 11.—Elution of tracer $Sr^{89,90}$ by 2% citrate and the effect of pH: resin, Amberlite IR-1, 40–60 mesh, hydrogen form; bed, 1 sq. cm. \times 10 cm.; influent, 2% citric acid, converted to pH shown with ammonia; rate, 1 ml./min.;

Curve	1	2	3	4	5
pH	8.0	6.0	5.0	4.5	4.0

Y is eluted with 5% citrate (or tartrate) at pH 2.7, after which the pH is shifted either gradually or at once to about 3.0 and the rare earths collected serially until Ce appears. Sr and Ba are then removed successively by 5% citrate at pH 5. The degree of separation of individual rare earth species or of Sr and Ba depends upon the particular rates and pH's chosen.¹⁴ Ru and Te, the major anionic species, may be recovered from the effluent of the original adsorption step.

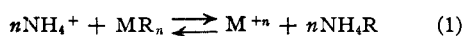
It will be noted (cf. Table I) that about 10 curies of fission product radioactivity are contained in about 5 mg. of elements. Thus, in the curie-level runs reported (D-9, Figs. 5 and 6) around a tenth of a milligram of each of the major fission products, including Ce, Pr, Nd and 61, was adsorbed and eluted. The experiments shown in Fig. 7, which demonstrate the separability of rare earths by this method, involved up to 10 mg. quantities of rare earths. In most of the tracer experiments which have been described, only a few microcuries of activity were used; this would amount to only about 10^{-3} μ g. The amount of resin in these experiments varied from about 3 g. (tracer and 10 mg. experiments) to about 30 g. (curie scale runs), or on the order of 10–100 milliequivalents of combining capacity; hence, it is obvious that no appreciable fraction of the resin was saturated by the cations used in any of the experiments reported. It may be concluded that the active species were always adsorbed at the very top of the column; this conclusion has been confirmed in many random tests. From this we conclude that larger masses of material may be separated in the manner demonstrated by simply increasing the mass of resin used in order to keep the same ratio of cation mass to resin mass. In-

(14) In practice, it is sometimes desirable to elute whole groups from the fission mixture, then to reabsorb these *in toto* and fractionate each into specific components

deed, since we may have been operating well below the critical value of this ratio (the value where the cation masses exert appreciable effects on the degree of separation), it may be possible to increase considerably our present maximum ratio of 10 mg./3 g. without loss of specificity.

The problem of separation then becomes one of moving one of the cations out of a narrow adsorption band at the top of the column at a more rapid rate than the others, so that most of it reaches the bottom of the column before much of the second component does. To attain optimum separations, one must choose an eluting agent which will preferentially remove one component with minimum movement of the others down the column. The separation of Zr-Cb mixture from the other fission products with 0.5% oxalic acid approaches the limiting condition of zero movement of the other elements from the adsorption band at the top of the column. However, the rare earths (including Y and Ce) constitute a group of elements whose almost identical properties do not readily lend themselves to such specificity. Here one must take advantage of relatively smaller differences in complex stability and, therefore, in rate of elution.

The reactions concerned in complex elution can be formulated simply as follows. Consider a cation M^{+n} adsorbed on a resin column which is primarily in the form NH_4R (R = resin equivalent). When an ammonium citrate solution, at a pH which will barely support the formation of a complex ion, is passed through the column, NH_4^+ in the solution exchanges with M^{+n} on the resin, in accordance with the reversible reaction



The cation then enters into the further equilibrium



where A is a citrate anion of charge $-m$. The fraction of total M found in the citrate complex is determined by the relative equilibrium constants of reactions (1) and (2).

When the resin is in the hydrogen form, a similar exchange is initiated, namely



The hydrogen ion liberated into solution competes with M^{+n} for the citrate anion



This forces (2) to the left, the net effect being a drop in pH and a readorption of M^{+n} on the resin by a reversal of (1).

Just as a packed distilling column may be considered to contain a certain number of theoretical plates, so may an ion-exchange column be regarded as containing a certain number of theoretical batches of resin. The exchange reactions (1) and (3) take place a certain number of times in each unit length of the resin column and the more often per unit length, the greater the effective length of the column and the greater the separa-

tions achieved. Thus, the closer the approach to equilibrium conditions, the greater the number of theoretical plates and so the greater the degree of separation per unit length of column. Improvement in separations involves the finding of conditions (*e. g.*, particle size and flow rate, which influence the diffusion of ions into the resin particles) which lend themselves to the most rapid attainment of equilibrium under the practical conditions of the experiment. The setting of optimum conditions is essentially a balancing of the desire for longer columns (*i. e.*, more theoretical plates), slower flow rates, finer resin particles and small cation-to-resin ratios against the desire for high yield and speed.

Another factor influencing separations is the preliminary adsorption step itself. If the adsorbed material is scattered throughout the length of the column before elution begins, one of the attributes of a good separation, a narrow elution band, will have been lost. A narrow band is favored by low mass of cation, slow flow rate and low ionic strength of the input solution.

The quantitative separation of macroscopic quantities of adjacent rare earths is thus a matter of process development involving the study of the above-mentioned variables (*i. e.*, pH and concentration of complexing agent and its total ionic strength, column length, mass of rare earths per unit area of column, resin mesh size and flow rate), which affect the equilibrium and rate constants of the reactions taking place in the column. The separation of pure, carrier-free rare earth fission products has already been discussed as a practical demonstration of this method on the milligram scale. It may be noted at this point that the fission products which are being distributed¹⁵ from Clinton Laboratories are separated by the procedures described above, using the same apparatus upon which these separations were first demonstrated.

It should also be noted that, as the degree of separation is improved, analytical and investigative applications of the method suggest themselves. The fact that it can be applied to millimicrogram (tracer) amounts of elements as efficiently as to larger samples indicates a potential usefulness in radiochemical investigations and in the determination of physico-chemical properties and constants of very dilute solutions. From this preliminary study, it appears that a complete system of analysis by ion-exchange may be devised to rival the classical precipitation procedures, with their many limitations imposed by occlusion, solubility products, etc.

Summary

By a process of elution from ion-exchange columns with complex-forming reagents, it is possible to separate cationic species when these are present in from trace amounts to macroscopic

(15) Manhattan Project. *Science*, **108**, 697 (1946).

amounts. Specific separations of the fission product radioisotopes, including the individual rare earth species, have been demonstrated. The application of the results to the problem of curie-level fission product separation is shown and the necessary development steps required for the

quantitative separation of large masses of rare-earth elements are outlined. The principles involved can be applied to the determination of physico-chemical constants and to the development of new types of analyses.

P. O. BOX W, OAK RIDGE, TENN. RECEIVED JULY 7, 1947

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The Separation of Rare Earths by Ion Exchange.^{1,2} I. Cerium and Yttrium

BY F. H. SPEDDING, A. F. VOIGT, E. M. GLADROW AND N. R. SLEIGHT

I. Introduction

For many years one of the most difficult processes in the field of chemistry has been the separation of the rare earths from each other into their pure states. Their chemical and physical properties are so similar that in general a single operation leads only to a partial separation or enrichment.

Ever since the beginning of the Manhattan Project there has been a constant demand for samples of rare earths of exceptional purity in gram amounts or greater. This demand arose for numerous reasons, but mainly because some of the rare earths are formed as fission fragments during fission of the heavy elements. It was highly desirable, therefore, to have a means of preparing pure rare earths so that their nuclear properties could be studied and also to allow a more thorough consideration of their chemical behavior. Their radioisotopes are less well understood than those of any other group of elements.

In general, the best means of separating these elements has been the well known but laborious method of fractional crystallization as used by James and further developed in many laboratories. Exceptions are cerium with its quadrivalent state, and samarium, europium and ytterbium with their di-valent states which do permit a means of separation from the normal trivalent rare earth ions.

A number of workers have reported studies on the application of chromatographic and ion exchange methods to the separation of the rare earths^{3,4,5,6} While they obtained considerable enrichment their results were not sufficiently promising to lead to further intensive investigation or to the quantity production of pure rare earths. The history within the Manhattan Dis-

trict, of the use of columns of Amberlite type resins for the separation of fission products, both with and without the use of citric acid-ammonium citrate eluants at controlled pH has been described elsewhere and will not be discussed here.⁷

The present paper is the first of a series, from this laboratory dealing with the successful separation of macro quantities of rare earths of spectrographic purity, by adsorption on Amberlite type resins and subsequent elution with complexing agents such as citric acid-ammonium citrate solutions at controlled pH. This paper establishes that cerium and yttrium can be separated relatively rapidly by these methods on any desired scale.

The marked success of the process described depends on the fact that the rare earths form complexes with the citrate ions. If the pH is suitably adjusted, competition is set up for the rare earth ions between the citrate complexes and the active centers of the resin. Therefore, as the citrate solution washes the rare earths down the column, each rare earth ion is adsorbed and desorbed many times. Since the equilibrium constants for the rare earth citrate complexes vary slightly among the different rare earths, their rates of travel down the column differ sufficiently to lead to their separation. The repeated cycles in the columns effectively replace the thousands of individual operations required by the older methods for separating the rare earths and lead to a highly effective process analogous to the use of distillation columns.

II. Materials, Apparatus and General Procedure

1. **Materials.**—The cerium stock solution was prepared from pure $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ which was dissolved in dilute nitric acid, reduced with sulfuric dioxide and precipitated as $\text{Ce}(\text{OH})_3$. The hydroxide was filtered off, dissolved in sulfuric acid and stored. The yttrium stock solution was commercial yttrium chloride having a purity greater than 80%.

The citric acid was of commercial grade but

(7) F. Daniels, W. C. Johnson and L. L. Quill. *Chem. Eng. News*, **25** 2494 (1947).

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

(2) This work was done during the period of January to March, 1945, and was presented before the Manhattan Project Council, Chicago, Illinois, on April 15, 1945, and before the Chicago Section of the American Chemical Society in November, 1945.

(3) E. Lange and K. Nagel, *Z. Elektrochem.*, **42**, 210 (1936).

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(5) U. Croatto, *Ricerca sci.*, **12**, 157 (1941).

(6) R. G. Russell and D. W. Pearce, *This Journal*, **65**, 595 (1943)