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

[CONTRIBUTION NO. 3 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

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 District, 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 *p*H 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 *p*H. 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 *p*H 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 $(NH_4)_2Ce(NO_3)_6$ which was dissolved in dilute nitric acid, reduced with sulfuric dioxide and precipitated as $Ce(OH)_3$. 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

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[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.

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spectroscopic analysis showed only traces of metal ions. The term "5% citric acid solution," used throughout this paper, refers to 50 g. of the citric acid monohydrate per liter of solution. The oxalic acid used as precipitating agent was commercial grade and contained no salts capable of introducing metallic ions into the precipitate.

Cerium and/or yttrium tracers were used in all the experiments; their use in analysis will be discussed later in this paper. The tracers were obtained by chemically separating the true rare earth group and yttrium from the other fission products in neutron irradiated uranium. The cerium was then oxidized to the quadrivalent state and separated, as the insoluble iodate, from the other active rare earths. After several months the activities, other than Y, had all decayed leaving radio-pure Y^{91} with its 57 day period and beta activity of 1.4 Mev. maximum energy. The Ce isotope was Ce^{144} with a 275 day half-life. The other cerium isotope, 28 day Ce^{141}, had decayed when the measurements were made; measurements were always made after the Ce^{144} had established equilibrium with its 17.5 min. Pr daughter. This pair of isotopes emits beta rays of 0.31 Mev. and 3.1 Mev., respectively. While the tracer solutions were not entirely carrier free the amount of inactive carrier was negligible. Individual stock solutions of these tracers were employed in the subsequent experiments.

2. **Calculation and Presentation of Data.**—Two methods have been employed in presenting the data, each one depending upon a measurement of the activity in a 1-ml. sample of eluate as the means of measuring the amount of material eluted.

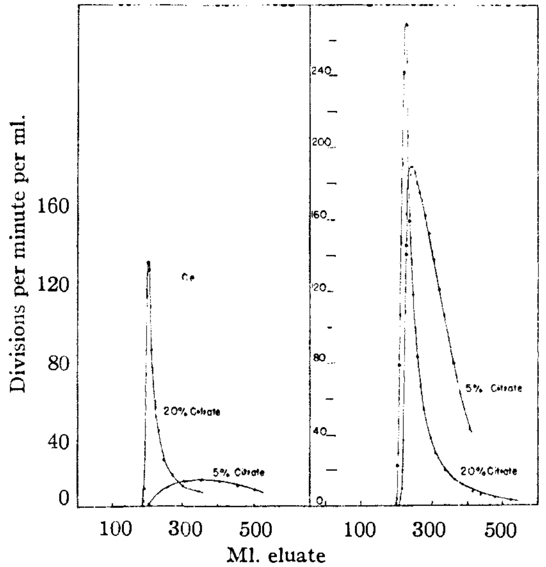

Fig. 1.—The elution of tracer amounts of Ce and Y using 5 and 20% citric acid: *p*H 2.75, flow rate 3 cm./min., column dimensions 1 cm. × 60 cm. The curves for Ce are on the left, Y on the right.

In the experiments designed to determine the nature of the elution curves for each ionic species, when only tracer amounts were employed (see Figs. 1 and 2), a very small aliquot of the original solution was evaporated on a watch glass and measured on the electroscope. This permitted a calculation of the total amount of activity used in the experiment. During the course of the elution 1-ml. samples of eluate were collected at various volume intervals and measured similarly. A graph showing activity/ml. as a function of volume was plotted. A simple integration under this curve permitted the calculation of the per cent. of the ionic species eluted at any desired point (see Fig. 3).

A somewhat similar method was employed in those experiments in which macro amounts of material were used. A known amount of inactive material was weighed out and dissolved. Tracer activity was added and the solution made up to known volume; a small aliquot was dried and measured on the electroscope. This gave the activity per unit weight of carrier or, conversely, the weight of carrier corresponding to unit activity. Samples were collected as above during the elution and their radioactivity measured. Using the conversion factor, the weight of material eluted was plotted as a function of volume of eluate. Integration under the curve to any point

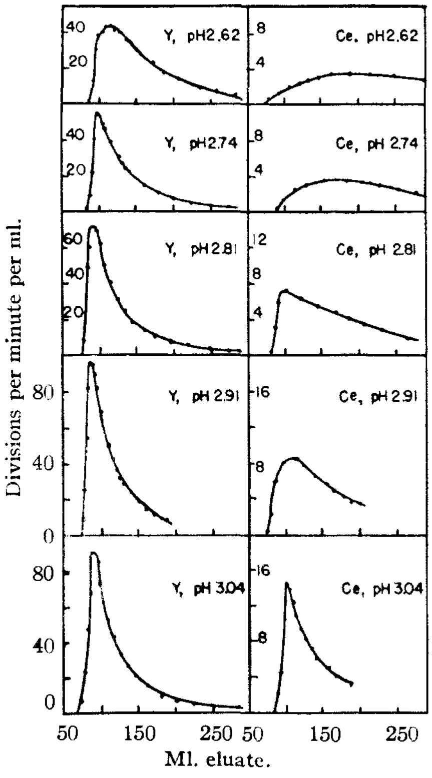

Fig. 2.—The elution of Ce and Y tracers in 5% citrate at various *p*H values: flow rate 3 cm./min.; column dimensions, 1 cm. × 60 cm.

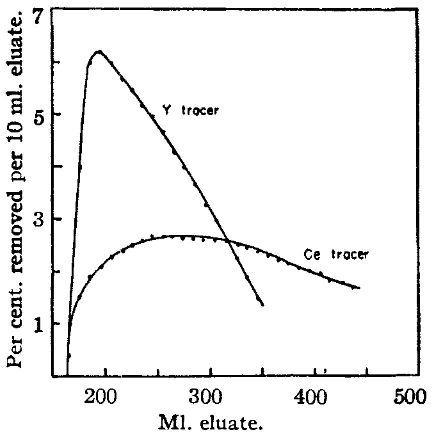

Fig. 3.—Individual elution curves for Ce and Y tracers: pH 2.74; flow rate, 3 cm./min.; column dimensions, 1 cm. × 160 cm.

along the abscissa gave the weight of material eluted to that point (see Fig. 4).

In general, in studies of mixtures of Ce and Y, only one species of tracer was added. This permitted a better determination of the intermediate region between the two peaks. The total elution curve was obtained by precipitating the mixture in any volume interval as oxalate, igniting to oxide and weighing. The weight per unit volume was plotted as a function of the volume of eluate. The difference between the total weight curve and the one obtained by using activity measurements is due to the species without the tracer.

Not only does this method give a means of assaying the samples which is faster and more accurate than simple weighing but it also allows the detection of small amounts of material at or near the point of break-through. The break-through represents the total volume of eluant at which the presence of the given element is first evident. At low concentrations of rare earths the oxalates may have sufficient solubility or tendency to supersaturate so that no precipitate is formed. Simple weighing of the ignited precipitate thus has a practical lower limit of detection of 5 mg. per liter. However, tracer measurements can be made much more sensitive by increasing the specific activity of the original sample.

3. **Description of Apparatus.**—The principal pieces of apparatus were long vertical glass tubes filled with the cation exchanger, Amberlite IR-1 resin. A cylindrical, silvered glass Geiger–Mueller tube of the type made by the Eck & Krebs Company was mounted in a copper housing having a small window opening. This unit was connected to a counting circuit and scaler by a long lead which made the G–M tube fairly portable. By moving the counter tube up and down the column, the position of the material could be determined at any time during those experiments in which radioactive tracers were used.

The samples of eluted Ce and Y were measured on a Lauritsen quartz fiber electroscope having a multiple stage mounting in which conversion factors had been worked out between the stages to facilitate the measurement of extremes of activity. The samples containing but little activity were read from a stage close to the ionization chamber and the highly active samples were read from a stage somewhat removed from the ionization chamber.

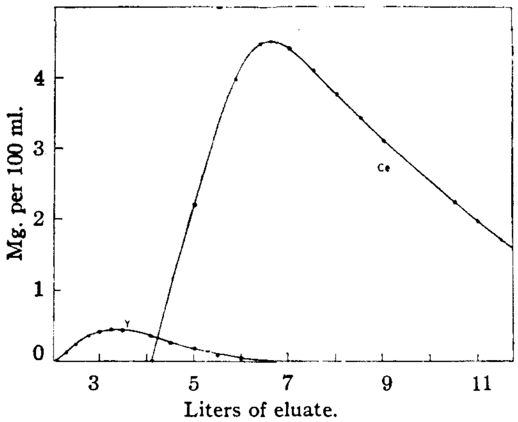

Fig. 4.—The elution of a small amount of Y in the presence of a large amount of Ce: pH 2.77; flow rate, 5 cm./min.; column dimensions, 1.6 × 190 cm.; composition of starting material, 10 mg. Y and 250 mg. Ce.

4. **Preparation of Columns.**—The columns were constructed by drawing out one end of the glass tube and sealing on a small outlet tube, finally resembling a buret. A plug of glass wool was inserted at the bottom of the column to prevent washing out of the resin; the tube was dented directly above the glass wool to prevent it from pushing up the resin bed during the process of backwashing.

The resin, Amberlite IR-1, was first screened to remove the large particles (>20 mesh) and then soaked in water. The resin slurry was added to the column and backwashed with water to remove fine resin particles which tended to plug the column and thus cut down the flow rate. The resin was conditioned as follows. A solution of 5% hydrochloric acid was passed through the column converting the resin to the acid cycle. The contact time was at least thirty minutes to insure complete conversion. This process was followed with a 2% sodium chloride solution to convert the resin to the sodium cycle. Treatment with acid and salt was repeated two or more times, the resin being finally left in the acid cycle.

III. Experimental

1. Elution of Ce and Y Singly

a. **Effect of Concentration of Citrate in Eluant.**—Preliminary experiments were undertaken to determine the effect of variation in original concentration of citric acid in the eluant. The concentrations of citric acid tested were 1, 5 and 20% adjusted to pH 2.74 by the addition of concentrated ammonium hydroxide; the elution was followed with both Ce and Y tracers. The 1% solution was ineffective at the pH employed. The change in citrate concentration had a large effect on the rate of elution of both Ce and Y tracers. At the higher concentration they, especially Ce, were eluted in a much smaller volume of eluant. The data for the higher concentrations of citrate are presented in Fig. 1. Since the 5% solution gave satisfactory results, it was chosen as standard for the subsequent experiments.

b. **Effect of pH Using Tracer Amounts.**—The resin bed was 60 cm. in height and 1 cm. in diameter. The 5% citrate solution was used as eluant at pH values of 3.04, 2.91, 2.81, 2.74 and 2.62. The flow rate was maintained at 3 ml. per minute per square cm. of cross-section area. This unit (ml./min./sq. cm.) is equivalent to cm. of column length per minute and is so designated in subsequent discussion. Samples for analysis consisted of 1 ml. of eluate on watch glasses. They were dried under infrared lamps and the activity read on the electroscope. The cerium samples were read through a 70 mg./sq. cm.

aluminum absorber to remove the soft beta rays; the yttrium samples were determined without an absorber.

The data obtained are shown in Fig. 2. The elution of both Ce and Y increased with increase in *p*H. Yttrium was satisfactorily eluted at all the *p*H values tested while the elution of Ce was relatively poor at *p*H values less than 2.81; the change in shape of the curve with varying *p*H is especially striking with this element. However, at lower *p*H values yttrium would undoubtedly have shown similar changes in shape of curve.

c. **Effect of Column Length Using Tracer Amounts.**—The preceding experiment showed that the Ce tracer moved down the column at a slower rate than did the Y tracer. These results indicated that a longer column should improve the separation. Experiments were performed by the same procedure as in the previous experiment except that the bed length was increased to 162 cm. and the *p*H was 2.75. The superimposed elution curves are shown in Fig. 3; it is evident that the Y is eluted much more rapidly, under these conditions, than is the Ce. The Y/Ce ratios, as a function of the per cent. of Y eluted are given in the second column of Table I.

d. **Elution of Macro Amounts of Ce and Y.**—Since the results with tracers, on a 162 cm. column, showed a separation of Y and Ce, the same procedure was applied to macro amounts of the materials. The Y/Ce ratios, as a function of the amounts of Y eluted, are given in the third column of Table I. It is evident that a much better separation was obtained with the macro amounts than with the tracer amounts.

2. Elution of Mixtures of Ce and Y in Macro Amounts

The previous discussion has dealt with elution in which the primary purpose was to determine the nature of the elution curve for each ionic species, under identical conditions, and in the absence of interfering ions. Data are now presented on the elution of macro amounts of mixtures of Ce and Y.

Table I

Y/Ce Ratio as a Function of the Per Cent. of Y Eluted

Y eluted, %	Y/Ce (tracer)	Y/Ce (macro)
10	5.0	..
20	4.0	42
30	3.7	30
40	2.9	13
50	2.6	8.3
60	2.3	5.2
70	1.9	3.7
80	...	2.7

a. **Effect of *p*H.**—A series of experiments was conducted with the *p*H values of the eluant varying in the range 2.50 to 2.87. The column beds were 190 cm. in length and the diameter 16 mm.; each sample adsorbed was equivalent to 250 mg. of Ce_2O_3 and 250 mg. of Y_2O_3. In one set of experiments Ce tracer and, in another set, Y tracer was added to the inert material. At *p*H values higher than 2.87 both Ce and Y were eluted so rapidly that there was little separation. The best *p*H value for separation is in the neighborhood of 2.60. The summary of the results of these experiments is given in Table II.

Table II

Effect of *p*H on Per Cent. Y Eluted before Ce Break-through

*p*H	Per cent. Y eluted before Ce break-through
2.87	70.0
2.77	82.0
2.66	96.0
2.61	98.5
2.50	91.0

b. **Effect of Original Y/Ce Ratio.**—In the previous experiment the Y/Ce ratio was unity. Since, in actual practice, the ratio may be far from unity, data were obtained for a mixture equivalent to 10 mg. of Y_2O_3 and 250 mg. of Ce_2O_3, a ratio of 1 to 25. The bed length of the resin was 190 cm., the diameter 16 mm. and the *p*H 2.77. The elution curves are shown in Fig. 4. When all of the Y had been eluted, about 60% of the Ce was still in the column and was subsequently eluted pure. Even when the Y was present in such a small relative amount, more than 60% of it was obtained in a pure form before the Ce break-through. It can be concluded that the procedure described can yield the products of spectroscopic purity.

c. **Effect of Length of Column.**—It has been shown that a separation of Ce and Y of greater than 96% can be effected, from a 1:1 mixture of these two components, on a column 190 cm. long and 16 mm. in diameter at a *p*H range of 2.55–2.65. It was also shown that when Ce and Y are eluted independently, they move at different rates, indicating that the band fronts might move farther apart as the length of the column is increased. It, therefore, seemed of interest to see whether the separation of the bands of the two elements continually increases or whether they move apart a certain distance and then proceed at much the same rate.

A column was prepared which was 610 cm. in bed length and 25 mm. in diameter. The mixture contained 250 mg. of each component employing tracers of Ce and Y. The *p*H of the eluant was 2.66 and the flow rate 5 cm. of column length per minute. The band fronts were determined by use of the portable counting apparatus. The data obtained are given in Table III.

Table III

Effect of Volume of Eluate on Separation of Band Fronts

Eluate, liters	Separation of band fronts, cm.
16	173 ± 15
20	193 ± 15
24	218 ± 15
28	236 ± 20
32	297 ± 20

Analysis of the eluates, after the break-through, showed that only 90–95% of the Y was obtained free from Ce even though the band fronts were moving further apart. This phenomenon is probably associated with channeling and possibly somewhat with back diffusion. This experiment indicates that there is a critical bed length of column beyond which no improvement in separation can be gained by increasing the length of the column.

IV. Summary

Conditions have been described for the separation of cerium and yttrium by adsorption on Amberlite IR-1 columns and elution with 5% citric acid–ammonium citrate solutions. The separations were studied both for tracer and macro amounts, using radioactive isotopes of the elements for the determination of the degree of separation. The factors studied included concentration of eluant, *p*H of eluant, the ratio of cerium and yttrium in the starting sample and length of columns. Conditions were established by which

the elements, of spectrographic purity, were separated in macro quantities. The principles established for the separation of cerium and yttrium are being applied to the development of methods for the large scale separation of adjacent rare earths; the details will be published in subsequent papers.

AMES, IOWA RECEIVED JULY 7, 1947

[CONTRIBUTION FROM THE CLINTON LABORATORIES, OAK RIDGE, TENN.]

The Chemical Identification of Radioisotopes of Neodymium and of Element 61[1]

BY J. A. MARINSKY,[2] L. E. GLENDENIN[2] AND C. D. CORYELL[2]

Introduction

In the comprehensive studies of the radioactive species produced in the fission of uranium[3] it has been found that over thirty are members of the rare earth family (isotopes of yttrium and the group lanthanum through europium). The chemical and physical identification of these was an important part of the research program of the Manhattan Project. Standard oxidative separations and fractional precipitations[4] and the use of radiochemical methods based on chain relations served to distinguish the activities of yttrium, lanthanum, cerium, and some of praseodymium, and those[5] of samarium and europium. The characterization of the sequence praseodymium, neodymium, and element 61 presented very difficult problems[6] that were solved only with the intensification of ion exchange methods originally developed by Boyd and co-workers[7] and applied to the rare earth field by Cohn and co-workers.[8] In this paper is reported the successful separation of these three elements, the first to have been achieved with radioisotopes of neodymium and of element 61.

Earlier work on the Manhattan Project had revealed the presence of two unidentified fission products in the rare earth region. A soft beta emitting activity of $\sim$4y half-life was discovered by Ballou[9] and independently by Goldschmidt and Morgan.[10] This activity was later studied by Seiler and Winsberg[6] who set the half-life at $\sim$3.7y. These investigators considered the activity to be an isotope of praseodymium, neodymium, or element 61 on the basis of detailed qualitative chemical separations between lanthanum and praseodymium. Another unidentified rare earth activity was later discovered by Davies[11] through its characteristic gamma radiations. This was confirmed by Hume and Martens[12] who determined its half-life as $\sim$11d and showed that the activity was not cerium. We have been able to identify these two activities as isotopes of element 61 and of neodymium, respectively, both of mass number 147. In addition the 47h 61^{149} has been identified among the fission products. All three of these activities, together with a previously unidentified 1.7h isotope of neodymium, are also produced as the result of the activation of neodymium with slow neutrons.

Chemical Identification

The 11d activity was first subjected to standard qualitative serpations[4,6] in order to limit the identification problem to a definite group of rare earth elements. Separations by carbonate digestion definitely eliminated yttrium and all rare earth elements of atomic number greater than 61. Oxidative fusion with sodium nitrate[4,6] demonstrated that the activity was not an isotope of lanthanum and must therefore be identified with praseodymium, neodymium or element 61. Finally, the activity was limited to an isotope of neodymium or element 61 by demonstration of separation from praseodymium with potassium hydroxide fusions.

Positive identification of the 3.7y and the 11d radioisotopes was then achieved by the recently developed ion-exchange method using a synthetic organic cation exchanger (Amberlite IR-1) of the sulfonated phenol-formaldehyde type. This new

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[1] This document is based on work performed at the Clinton Laboratories operated under contract No. W-35-058-eng-71 for the Manhattan Project, classified reports of which are referred to here as "Manh. Proj. Rep." The information covered herein will appear in the Plutonium Project Record (Plut. Proj. Rec., Vol. 9B, papers 7.54.3, 7.54.4, 7.54.5, 7.54.6, and 11.1), in Division IV of the Manhattan Project Technical Series.

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