

## A RAPID METHOD FOR THE CARRIER-FREE DETERMINATION OF INDIVIDUAL RARE EARTHS BY ION EXCHANGE AT ROOM TEMPERATURE

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### INTRODUCTION

Rare earth and yttrium fission product radionuclides of comparatively short half-lives, *e.g.*, 9-h  $^{150}\text{Sm}$ , 5.9-h  $^{145}\text{Pr}$ , 3.9-h  $^{141}\text{La}$ , are difficult to study because of the amount of time at present required for their chemical separation and recovery. A faster separation procedure is thus desirable. Also, a decrease in the time for separations permits more analyses in a given period of time.

In a previous report on a quantitative separation and recovery procedure<sup>1</sup> carrier-free yttrium and the rare-earth radionuclides were separated first from a gross fission product mixture by liquid-liquid extraction with di-(2-ethylhexyl) phosphoric acid (HDEHP) and then were absorbed on a Dowex 50W-X4 cation exchange resin. Yttrium and the individual rare earths were separated from each other at room temperature in 35 h by gradient elution with 1M  $\alpha$ -hydroxyisobutyric acid (AHIB) between pH 2.79 and 3.40 at a flow rate of 1 ml per 10 min. Ion exchange at room temperature<sup>2,3</sup> can be performed with simpler apparatus and more easily than by previous methods using high temperatures<sup>4,5</sup>. The absence of carriers<sup>2,6</sup> makes possible better separations because of less tailing.

Preliminary experiments indicated that a faster ion exchange separation may be accomplished by decreasing the ligand and hydrogen ion concentrations. This approach was investigated more thoroughly because of its simplicity and because of the high cost of the eluant  $\alpha$ -hydroxyisobutyric acid. Conditions were established which permit the quantitative separation and recovery of individual rare earth radionuclides by ion exchange at room temperature in 14 h. This work is described in the following.

### EXPERIMENTAL

The gradient elution technique<sup>6-8</sup> was used in the separation scheme developed in this study. A schematic diagram of the apparatus employed is shown in Fig. 1. Two vessels, operated under air pressure, served as the reservoirs for the eluant. The air pressure from the laboratory compressed air line was controlled through a pressure gauge. Each vessel was 7 in. long with an internal diameter of 1 in. The Tygon tubing leading from the low pH (3.83) reservoir to the resin column was 3/16 in. I.D.  $\times$  22 in. and contained 11 ml of the low pH eluant. A 3-in. piece of Tygon tubing of 3/16 in.

I.D. connected the low and high pH (8.34) reservoirs. A small magnetic stirrer was used during the elution in order to ensure a complete and continuous mixing of the solution in the low pH reservoir. Since both vessels had the same dimensions, the volume removed from the low pH reservoir was replaced with half as much volume from the higher pH reservoir which resulted in a gradual increase in the pH of the eluant.

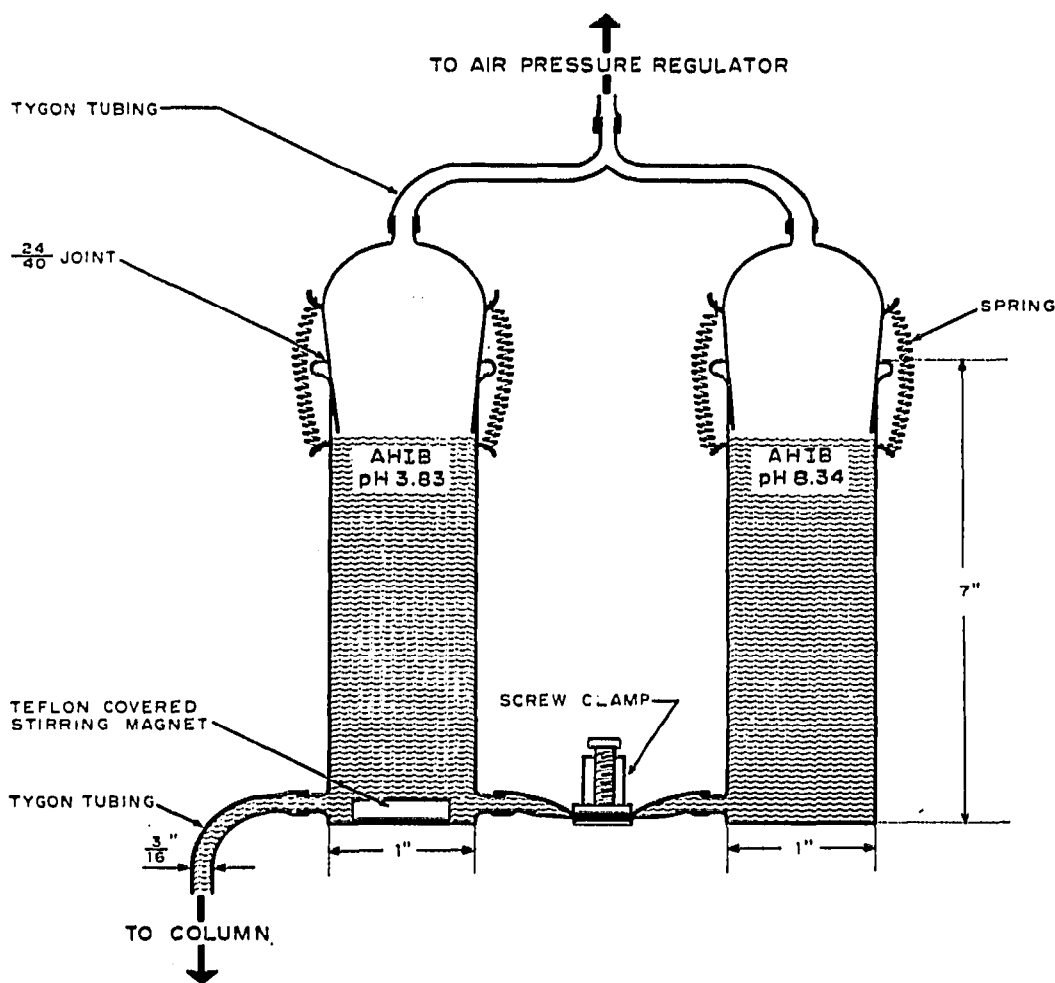


Fig. 1. Gradient elution equipment.

A 51-in. long column was made from 3-mm precision capillary glass tubing. The top of the column had a ground glass joint attachment, and the bottom of the column contained a sintered glass disc of medium porosity. The column was loaded with a slurry of the Dowex 50W-X4 resin in the ammonium form. The resin was equilibrated with the initial eluant before each run. The height of the resin was  $47.25 \pm 0.25$  in. after equilibration when the column was operated between 5 and 10 p.s.i.g. The volume of the eluant above the resin in the column was about 1 ml. The fractions were collected in 10-ml glass tubes placed in an automatic sample changer. These tubes were transferred directly to a gamma-ray well scintillation instrument for counting.

### *Reagents*

The AHIB was obtained from the Aldrich Chemical Company of Milwaukee, Wis. and used without further purification. Initial solutions were made 2 *M* in the reagent and were slightly turbid. They were filtered and diluted to 0.25 *M*. The pH of the 0.25 *M* AHIB stock solution was 2.4. The eluants were made from this stock solution by adjusting the pH with small amounts of concentrated ammonium hydroxide. The Dowex 50W-X<sub>4</sub> cation exchange resin (200 to 400 mesh) was purchased from the Bio-Rad Laboratories of Berkeley, Calif.

### *Radionuclides*

Yttrium-91, europium-155, praseodymium-143, cerium-144 and lanthanum-140 were carrier-free tracers obtained commercially or separated from fission products. Terbium-160, gadolinium-159, samarium-145, promethium-145, and neodymium-147 were of high specific activity and were made by neutron-irradiation of suitable stable isotopes. The purity of the isotopes was checked by comparing the gamma-ray spectra with previously published data. These longer-lived radionuclides were used for convenience in the experimental approach.

### *Procedure*

The resin column was equilibrated initially with 0.25 *M* AHIB at pH 3.83. During the equilibration the flow rate was adjusted to 1 ml per 10 min by regulating the air pressure. The volume of each fraction was determined by weighing the effluent. The eluant density had been determined previously by weighing a known volume.

A mixture of the yttrium and rare earth radionuclides in nitric acid solution was evaporated to dryness. The residue was taken up with 300  $\mu$ l of the pH 2.4 AHIB stock solution and transferred quantitatively to the top of the resin column using a small amount of the AHIB solution at pH 3.83 as a wash. The space above the resin in the column was filled with 0.25 *M* AHIB at pH 3.83. The reservoirs contained 50 ml of the pH 3.83 and 52 ml of 0.25 *M* AHIB eluant at pH 8.34. The additional 2 ml of pH 8.34 AHIB eluant in the high pH reservoir compensated for the space between the two vessels. A small Teflon-covered magnet was placed in the low pH vessel. The vessels were attached to the air pressure system and the delivery tube connected to the resin column. The magnetic stirrer under the low pH vessel was started. Air pressure was applied to give a flow rate of 1 ml per 10 min (1 drop every 53 to 57 sec). The first ml of effluent, which consisted mainly of the loading solution, was discarded. The automatic fraction collector, set with a time interval of 10 min, was then started. After the first 2 h the pressure was increased to give a flow rate of 1.25 ml per 10 min (1 drop every 42 to 45 sec). This increase in the pressure effected a decrease of 3 h in the total elution time without causing any measurable cross-contamination.

## RESULTS AND DISCUSSION

Fig. 2 shows the elution curves for yttrium and the rare earth tracers from a synthetic mixture. The first radionuclide out, yttrium, started to elute in about 1 h. The last, cerium, was recovered in 13.5 h. Lanthanum remains on the ion exchange column after the elution of cerium and can be eluted within 0.5 h by a sharp increase

TABLE I  
 ELUTION\* OF INDIVIDUAL RARE EARTHS FROM DOWEX 50W-X4 AT ROOM TEMPERATURE  
 Flow rate 1 ml per 10 min, increased to 1.25 ml per 10 min after the first 2 h.

Column	Y	Tb	Gd	Eu	Sm	Pm	Nd	Pr	Ce
<i>Run 1</i>									
1	6-10	11-14	18-22	23-29	32-36	41-49	52-58	60-68	70-79
2	6-10	11-14	—	24-30	32-38	43-50	52-60	61-68	71-80
3	6-10	11-15	—	23-28	32-37	40-48	51-59	60-68	69-78
<i>Run 2</i>									
1	6-11	11-15	—	23-28	32-37	41-48	50-59	60-68	69-80
2	7-11	11-14	—	23-30	31-37	41-48	51-58	61-68	70-78
3	6-11	11-15	—	23-29	31-38	41-49	52-59	—	70-79
Elution range	6-10	11-15	16-22	23-30	31-39	40-49	50-59	60-68	69-80
Volume (ml)	6-11	11-17.0	17.0-25.7	25.7-35.7	35.7-47.0	47.0-59.5	59.5-72.0	72.0-83.2	83.2-98.2
Time (min)	0-100	110-150	150-220	220-300	300-390	390-490	490-590	590-680	680-810 (13.5 h)

\* Characterized by index number of 10 min fractions in which element appeared.

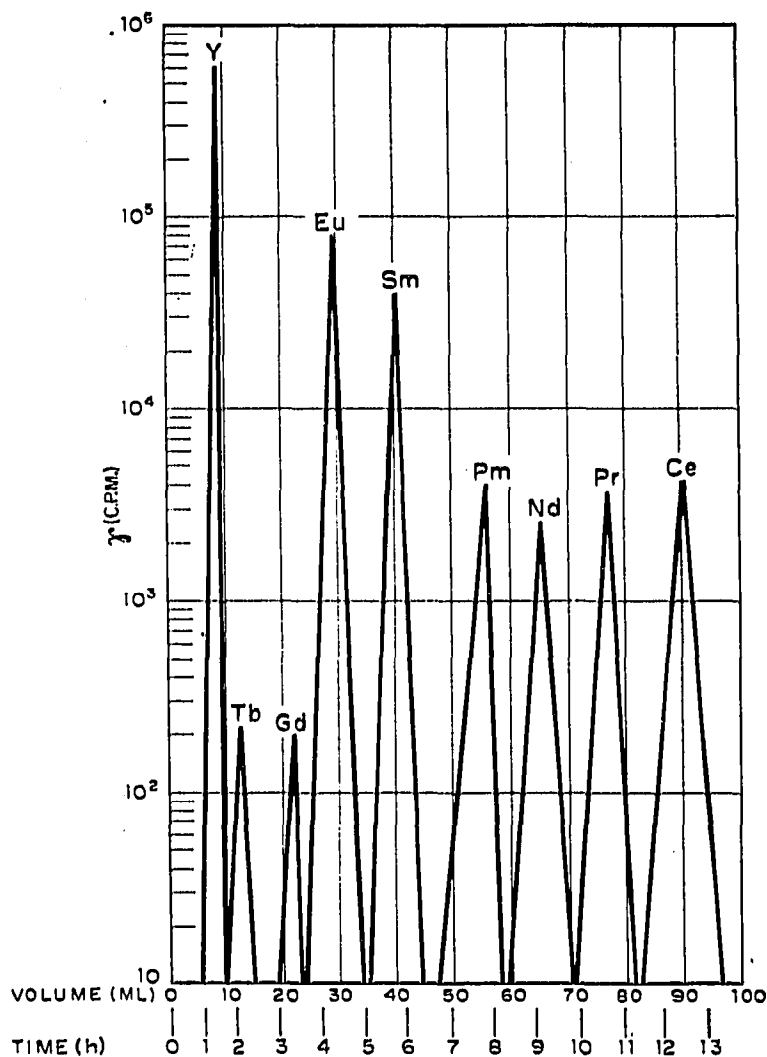


Fig. 2. Elution of yttrium and rare earth radionuclides from Dowex 50W-X4 cation exchange column at room temperature.

in the pH of the eluant. In the elution of both the gadolinium–europium and the neodymium–praseodymium pairs, the times between pair nuclide separations were small. Therefore extra care should be taken for these pairs. The gamma-ray spectra of the individual fractions showed no evidence of cross-contamination. The beta-ray emitting  $^{143}\text{Pr}$ , which gives a bremsstrahlung spectrum, showed no gamma-ray contamination. The reproducibility of elution was determined on each of three columns with essentially the same flow rate. The results are given in Table I, which lists the 10-min fraction range in which each element was eluted. In the first run on each of the three columns all of the elements were clearly separated from each other; for these experiments the ratio of the yttrium to the terbium gamma-ray activity (gamma c.p.m.) in the rare earth synthetic mixture was  $3.5 \times 10^2$ . In these three cases yttrium started to elute on the sixth fraction and was recovered by the tenth fraction. Terbium was found in the next five fractions, etc. In fission product samples the ratio of yttrium to terbium gamma-ray activity greatly exceeds  $10^3$ . Therefore, to test the yttrium–

terbium separation in such samples, the procedure was repeated on a rare earth synthetic mixture containing a yttrium-to-terbium gamma-ray activity ratio of  $1.5 \times 10^3$ . The ion exchange resin in each of the three columns was equilibrated back to pH 3.83 with AHIB before the second run. Yttrium was found in the eleventh fraction and contaminated the terbium fraction. All the other elements were separated cleanly. Gadolinium was available for only the first run column 1, and praseodymium for all except the second run, column 3. At the bottom of Table I are the range, volume, and times which best cover the elution of the nine tracers.

TABLE II

PERCENT RECOVERY OF YTTRIUM AND RARE EARTH TRACERS FROM A SYNTHETIC MIXTURE

Column	Y	Tb	Gd	Eu	Sm	Pm	Nd	Pr	Ce
<i>Run 1</i>									
1	100.5	100.8	100.3	99.6	100.8	99.6	99.6	98.2	98.2
2	99.5	101.0	—	100.4	101.4	99.8	99.6	100.4	100.2
<i>Run 2</i>									
1	99.9	118.0	—	98.8	101.2	99.4	99.4	101.7	102.3
2	99.9	117.4	—	99.4	99.6	100.0	99.0	98.5	100.2
Mean	99.9	—	—	99.6	100.6	99.7	99.4	99.7	100.6
S.D.	±0.4	—	—	±0.5	±0.8	±0.3	±0.3	±1.7	±0.4

For each of four runs (column 1, runs 1 and 2; column 2, runs 1 and 2) the fractions for each tracer were combined in accordance with the elution range results in Table I. The recovery of the nine tracers is given in Table II. The recovery of each radionuclide was obtained as the ratio of the eluted activity to the initial activity. The average recovery for each radionuclide with the exception of terbium in the second run, column 1 and 2, was 99 to 101 % with a standard deviation of 0.3 to 1.7 %. The terbium in the second run was contaminated with yttrium. This contamination resulted in apparent recoveries of 117.4 and 118 %. The yttrium contamination of the terbium can be eliminated by recycling the terbium fraction through another cation column.

The data in Tables I and II show that the carrier-free elution of rare earth

TABLE III

TIME FOR RECOVERY OF FISSION PRODUCT RARE EARTH RADIONUCLIDES BY THE PRESENT AND PREVIOUS METHOD

Radionuclide	Present time (h)	Previous time (h)
Y	2.5	4.3
Tb	3.5	7.7
Gd	4.6	11.0
Eu	6.0	14.0
Sm	7.5	19.6
Pm	9.2	24.3
Nd	10.8	27.7
Pr	12.3	31.0
Ce	14.5	36.0
La	15.0	36.5

elements was sufficiently reproducible to permit the collection of these elements in a predetermined time interval. Each column requires calibration and the flow rate must be kept within narrow limits, *e.g.*,  $1.0 \pm 0.05$  ml. per 10 min. Table III compares the time required for the quantitative separation and recovery of fission product rare earth radionuclides by our present and previous method of elution. One hour was required to separate the total rare earth group from the fission product mixture by solvent extraction in preparation for the ion exchange procedure. This time was added to the elution time for the separation and recovery of the individual rare earth radionuclides.

The half-lives of  $^{141}\text{La}$ ,  $^{145}\text{Pr}$  and  $^{156}\text{Sm}$  are such that 7, 22.7 and 56 % of the respective activities would remain after separation by the present method while only 0.15, 2.3 and 22.2 % remain by the longer elution method (Table III).

#### SUMMARY

The time for separations of rare earth radionuclides by ion exchange was reduced to 14 h by the use of one tenth of the concentration of the eluant ( $\alpha$ -hydroxyisobutyric acid) and a higher pH. This reduction in time of separations will make it possible to study shorter-lived rare earth radionuclides, *e.g.*,  $^{156}\text{Sm}$ ,  $^{145}\text{Pr}$ ,  $^{141}\text{La}$ . In addition, more analyses can now be performed in a given period of time.

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