different conditions, but the general pattern was not altered in any case. A levorotatory sample with an initial rotation of −4.4°S. was observed to be racemized completely in 1 minute 35 seconds at 90° under the same conditions as those described for the dextrorotatory sample reported in the figure.

No mathematical analysis was made of the curves because of the fact that the carbon becomes a less effective "catalyst" as time progresses. The carbon finally becomes essentially ineffective for bringing about further racemization, even at elevated temperatures. Further studies are planned with other complexes and other possible "catalysts."

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Ion Exchange as a Separations Method. VII. Near Optimum Conditions for the Separation of Fission Product Rare Earths with Lactic Acid Eluant at 87°

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Mayer and Freiling[1] have found lactic acid solutions to be considerably more selective than citric acid solutions for separating Eu, Sm and Tb by cation exchange chromatography. Using their results as a basis, near optimum conditions have been determined for separating the rare-earth activities known to be formed in uranium fission (*i.e.*, Y, La, Ce, Pr, Nd, Pm, Sm and Eu), together with Gd and Tb. This note presents the method used to achieve virtually complete separation of these activities from one another in 49 hr. using lactic acid eluants of various strengths at a *p*H of 3 and a temperature of 87°. The method is shown to be applicable to the precise radiochemical determinations of rare earth activities.

Experimental

Materials.—To obtain desired rare earth isotopes, uranyl nitrate was converted to U_3O_8 by ignition and bombarded with neutrons in the Oak Ridge Pile.

Eluant solutions were made up as described by Mayer and Freiling.[1] The strengths of the 1 *M* lactic acid solutions were based upon titrations with standard 0.1 *N* NaOH to the phenolphthalein end-point; no attempt was made to ensure dissociation of associated lactic acid. Solutions of strengths less than 1 *M* were made up by diluting the 1 *M* stock solutions.

Dowex-50 cation exchange resin 250 to 500 mesh was simultaneously cleaned and converted to the ammonium form by washing with *p*H 6 ammonium citrate solution and then graded to obtain that fraction which settled through 6 in. of water in 5 to 9 min. Subsequent microscopic examination revealed that the resin particle diameters were normally distributed with 98% of them falling between 29 and 62 μ.

Apparatus.—The apparatus used was essentially that of Mayer and Freiling[1] except that the inside diameter of the capillary was increased from 2 to 3 mm. and sintered glass in place of glass wool was used to support the resin bed. This substitution allowed faster and steadier flow rates to be maintained

Procedure.—The column was prepared by boiling 3.4 ml. of wet resin to remove air, slurrying the resin into a heated column, and allowing it to settle without flow of water.

The bombarded U_3O_8 was dissolved to 6 *N* HNO_3 to which had been added 20 mg. each of Ce, Pr, Nd and Sm carriers. The rare earth group was then isolated by the following series of fairly standard steps.[2] Fluoride precipitations in the presence of bromate ion and Zr holdback carrier removed U, Np, and most of the fission product contamination; hydroxide precipitations in the presence of Ba holdback carrier freed the samples from Ba and Sr activities; any remaining Zr activity was removed by precipitating zirconium iodate from nitric acid solutions using H_2O_2 to keep Ce in the trivalent state. At this point all contaminating activities had been removed and Ce could be separated from the other rare earths as ceric iodate by simply oxidizing the cerous ion with bromate ion. This oxidation was followed by a ceric iodate scavenging, after which the remaining rare earths were precipitated as the hydroxides.

The final precipitate of rare earth hydroxides was dissolved in a minimum amount of concentrated $HClO_4$, diluted to twice its volume, brought to a boil, and allowed to pass through the column. When the liquid level had dropped to within a centimeter of the top of the resin bed, the remainder of the column was filled with boiled, distilled water. After a milliliter of this had passed into the resin, the water was withdrawn, thus washing away unadsorbed activity. Activity adhering to the glass walls of the column, however, was sufficient to produce the small degree of tailing of the Y peak shown in Fig. 1. This activity can be removed, and the tail eliminated, by rinsing the column again with eluant.

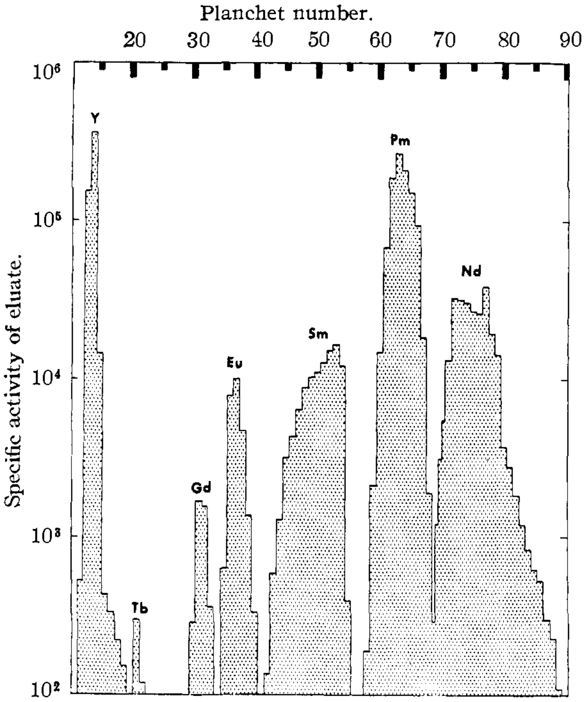

Fig. 1.—Elution history curve.

Depending upon the flow rate, fractions of 1 to 1.5 ml. were collected every half-hour in weighed polyethylene planchets. (It was sometimes found advantageous to reduce the collection time to 15 min. between peaks of difficultly separable rare earths.) The full planchets were reweighed and the volume of liquid reduced by evaporation with a heat lamp. The β-γ activity of each planchet was measured with a flow type proportional counter. An elution history curve was then prepared (Fig. 1) by plotting counts/min./g. of eluant *vs.* planchet number. This curve was used to de-

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(1) S. W. Mayer and E. C. Freiling, THIS JOURNAL, **75**, 5647 (1953).

(2) Coryell and Sugarman, "Radiochemical Studies: The Fission Products," National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1951.

termine which planchets were to be combined to form the various rare earth fractions. No sample of eluate escaped combination. The identity of the activities obtained, together with the radiochemical purity, was determined by standard decay and absorption measurements.

Results and Discussion

Mayer and Freiling[1] have shown that the use of 1 *M* lactic acid at *p*H 3 was sufficient to give complete separation of Eu and Sm in a reasonable time. The separation of Gd from Eu, and particularly the detection of minute amounts of Tb^{161} activity in the presence of large amounts of Y^{91} activity, require even better separations. To achieve these separations and still hold the time required for a run down to a reasonable value, use was made of discontinuous gradation in eluant strength. The best result of a number of trials is illustrated by the elution history curve in Fig. 1. These separations were obtained by eluting with 10 ml. of 0.85 *M* lactic acid, 10 ml. of 0.90 *M*, 10 ml. of 0.95 *M*, and using 1 *M* lactic acid for the remainder of the run. The extent of decontamination of each rare earth from its nearest neighbors is presented in Table I.

TABLE I

DECONTAMINATION OF RARE EARTHS FROM THEIR NEAREST NEIGHBORS IN THE ELUTION PROCESS

Planchets combined	Rare earth activity	Percentage of preceding activity in sample	Percentage of following activity in sample
11-18	Y^{91}	..	n.d.[a]
19-27	Tb^{161}	0.15	n.d.
28-34	Gd^{159}	n.d.	n.d.
35-41	Eu^{156}	n.d.	n.d.
42-56	Sm^{153}	0.3	n.d.
57-68	Pm^{149}	n.d.	0.01
69-98	Nd^{147}	n.d.	n.d.
..[b]	Pr^{143}	n.d.	..

[a] n.d. stands for none detected. [b] Eluate containing Pr was received in a beaker.

It is evident from the shape of the Nd peak, and especially the Sm peak, that the column was overloaded under these conditions. The use of wider columns and proportionately higher flow rates would be expected, therefore, to give still better separations in the Pm–Nd region without increasing the expenditure of time.

Treatment of duplicate samples has yielded the results shown in Table II. These data are comparable in precision to any radiochemical analytical results and illustrate the possibility of using this method to obtain much more accurate values of rare earth fission yields than those appearing in the current literature.[2]

TABLE II

COMPARISON OF RESULTS FROM DUPLICATE SAMPLES

Rare earth activity	Counts per minute per total sample × 10^{-5}	
	1	2
Eu^{156}	0.323	0.330
Sm^{153}	2.28	2.30
Pm^{149}	10.00	10.03
Nd^{147}	14.2	14.4

The source of the Tb and Gd activity found in these runs is unknown. Neither Tb nor Gd activity has been discovered among the fission products. The relative amounts of activity are such that they could reasonably have been formed either by fission or by neutron activation of microgram amounts of Gd impurity. We are presently engaged in the process of attempting to determine their source.

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The Densities and Thermal Expansion Coefficients for Cobaltous Chloride Hexahydrate and Ethyl Iodide[1]

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Some years back Sampson and Bleakney[2] reported the existence of a stable cobalt isotope, Co^{57}, to the extent of one part in 600 of Co^{59}. The later work of Mitchell, Brown and Fowler[3] showed that if Co^{57} exists, it could occur to an extent no greater than one part in 30,000 of Co^{59}. In the years 1940–1946, the writer was concerned with the experimental determination of precise absolute[4] and relative[5] densities of certain crystals, the relative densities being used to determine the efficiencies of electrolytic separations of isotopes. The dual purpose, to detect the existence of Co^{57} and, if found, to determine the extent of its electrolytic separation from Co^{59}, formed the basis for the present experimental work. Although the original purposes were found untenable because sufficient precision in the relative density of $CoCl_2 \cdot 6H_2O$ could not be attained without a tremendous expenditure of time, a large amount of the present work was already completed before such conclusions could be made.

Inasmuch as the experimental results obtained may be of help to some workers in connection with other problems, it was felt worthwhile to present the experimentally determined densities and expansion coefficients for $CoCl_2 \cdot 6H_2O$ and C_2H_5I.

The experimental technique of the determination of the densities of certain solid compounds has been described previously.[4] The method consists of suspending crystals of the substance, the density of which is to be determined, in a liquid of proper density. After a density–temperature determination of the suspension liquid, the temperature at which the solid crystal is suspended in the liquid forms the basis for obtaining the density of the solid.

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[1] This paper is a technical report of work done in the Chemistry Department and the State Engineering Experiment Station of the Georgia Institute of Technology, Atlanta, Georgia.

[2] M. B. Sampson and W. Bleakney, *Phys. Rev.*, **50**, 732 (1936).

[3] J. J. Mitchell, H. S. Brown and R. D. Fowler, *ibid.*, **60**, 359 (1941).

[4] H. L. Johnston and D. A. Hutchison, *ibid.*, **62**, 32 (1942). D. A. Hutchison, **66**, 144 (1944).

[5] D. A. Hutchison, *J. Chem. Phys.*, **14**, 401 (1946); D. A. Hutchison, *ibid.*, **13**, 536 (1945); H. L. Johnston and D. A. Hutchison, *ibid.*, **10**, 469 (1942).