ANION EXCHANGE BEHAVIOUR OF LIGHT RARE EARTHS IN AQUEOUS METHANOL SOLUTIONS CONTAINING NEUTRAL NITRATES

II. MACRO–MICRO SEPARATIONS

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It was shown in the first part of this work[1] that carrier-free rare earths of the cerium sub-group can easily be separated from each other on a column filled with strongly basic anion exchange resin using aqeuous methanol solutions of neutral nitrates as an eluent. In the field of the preparative nuclear chemistry of the rare earth elements, however, one frequently also meets the necessity of separating microamounts of rare earths from macroamounts of adjacent rare earths. This necessity generally arises in solving of the following problems:

(1) preparation of very pure rare earth targets,

(2) determination of rare earth impurities in rare earth samples,

(3) separation of carrier-free nuclear reaction products from macroamounts of non-isotopic target.

Commercial rare earth products, even the purest ones, always contain rare earth impurities. The quantity of these impurities, depending on the quality of the product, may amount to 10–100 μg contaminant element/g rare earth product. Their presence is, in some cases, of no great importance. These may give rise, however, to serious difficulties when carrying out many nuclear reactions, *e.g.* in the performance of spallation reactions for nuclear spectroscopic measurements. The presence of impurities in individual rare earths in quantities much greater than 10 μg makes it difficult to perform microchromatographic separations of the spallation rare earth products and to prepare sources by means of electrolysis.

The control of target purity requires a reliable and sensitive analytical method. The majority of the present analytical methods are based upon the preliminary separation of the rare earth impurities from the contaminated sample and from one another. The separation of microamounts from each other can easily be carried out. Thus, the highly sensitive method of activation analysis, in general, does not raise any difficult separation problems. Moreover, the analysis, in some cases, can be carried out without any preliminary separation, merely using electronic measuring devices. However, with the use of less sensitive analytical methods (*e.g.* spectrophotometric methods) the quantity of the sample from which one has to separate microamounts of impurities is often as much as 1–2 g. In the analytical chemistry of the rare earth elements, the process of concentration of the impurities gives rise to the greatest difficulties.

Similarly, processing of 2–3 g target quantities is also necessary in the preparation of neutron deficient rare earth isotopes for nuclear spectroscopic measurements.

It has already been shown in our previous paper[2] that anion exchange from methanolic solutions of neutral nitrates provides a useful method for the separation of carrier-free light rare earths from gadolinium targets irradiated with 680 MeV protons. Our work connected with processing of irradiated targets is in progress; results will be presented elsewhere. Therefore, in the present paper we deal only with the problems of the purification and analysis of the light rare earths.

EXPERIMENTAL

Materials

    The methanol and ammonium nitrate used in the course of this work were reagent grade and were used without further purification.

    The rare earth oxides used for the investigation of the elution conditions contained rare earth impurities on average in the quantity of 1–10 μg contaminant element/g product. In order to approach more nearly the actual conditions of practical macro–micro separations these oxides were not purified before use.

    The radioactive isotopes of the rare earths were isolated from a tantalum target irradiated with 680 MeV protons and were purified on a 2 mm × 80 mm Dowex 50 × 8 (-400 mesh, ammonium form) resin bed by eluting with ammonium α-hydroxyisobutyrate.
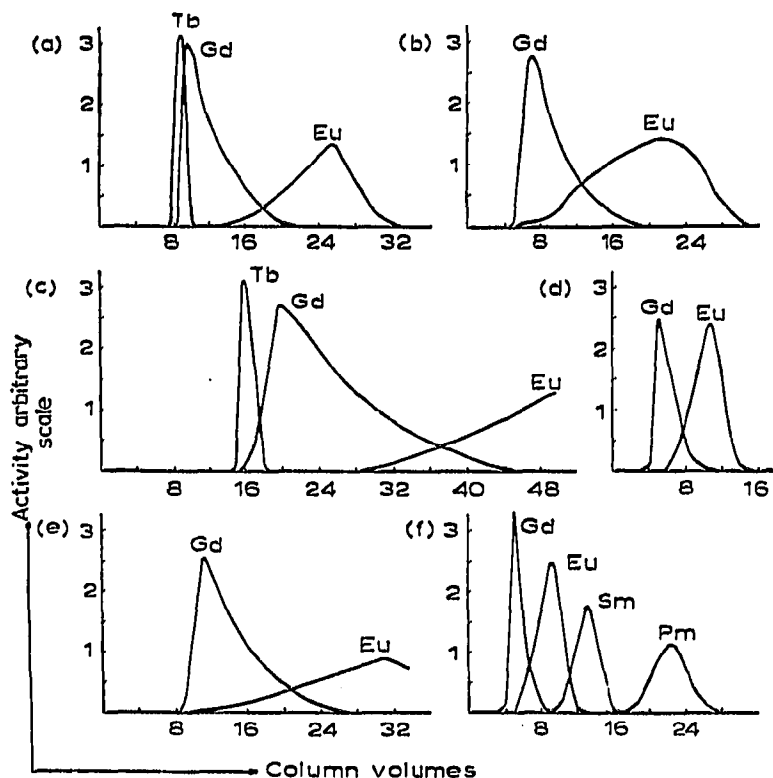

Fig. 1. Separation of light rare earth tracers from macroamounts of gadolinium. Column: 0.3 cm² × 22.5 cm Amberlite IRA-400 (200–400 mesh, nitrate form). (a) 60 mg Gd_2O_3; 80% CH_3OH–1.5 N NH_4NO_3; 1 ml/cm² min; 50°. (b) 120 mg Gd_2O_3; 80% CH_3OH–1.5 N NH_4NO_3; 1 ml/cm² min; 50°. (c) 60 mg Gd_2O_3; 85% CH_3OH–1.5 N NH_4NO_3; 1 ml/cm² min; 50°. (d) 60 mg Gd_2O_3; 70% CH_3OH–2.0 N NH_4NO_3; 1 ml/cm² min; 50°. (e) 60 mg Gd_2O_3; 80% CH_3OH–1.1 N HNO_3; 1 ml/cm² min; 20°. (f) 60 mg Gd_2O_3; 65% CH_3OH–2.5 N NH_4NO_3; 2 ml/cm² min; 50°.

In all anion exchange experiments the strongly basic anion exchange resin Amberlite IRA-400 (nitrate form) was used.

The alcoholic eluents in all cases were freshly made and were acidified with nitric acid up to 0.01 N.

Preliminary experiments

In order to obtain some information about the separability of microamounts of light rare earths from macroamount of an adjacent rare earth, experiments were carried out on a 0.3 cm^2 × 22.5 cm Amberlite IRA-400 (200–400 mesh, nitrate form) column using the experimental technique described earlier[2]. The separation conditions, i.e. the methanol content of the eluent, the concentration of ammonium nitrate and the temperature were selected on the basis of work presented earlier[1,2]. During these experiments the flow rate of the eluent and the working temperature were 1 ml/cm^2 min and 50°, respectively, except when otherwise stated. The results are presented in Figs. 1 and 2.
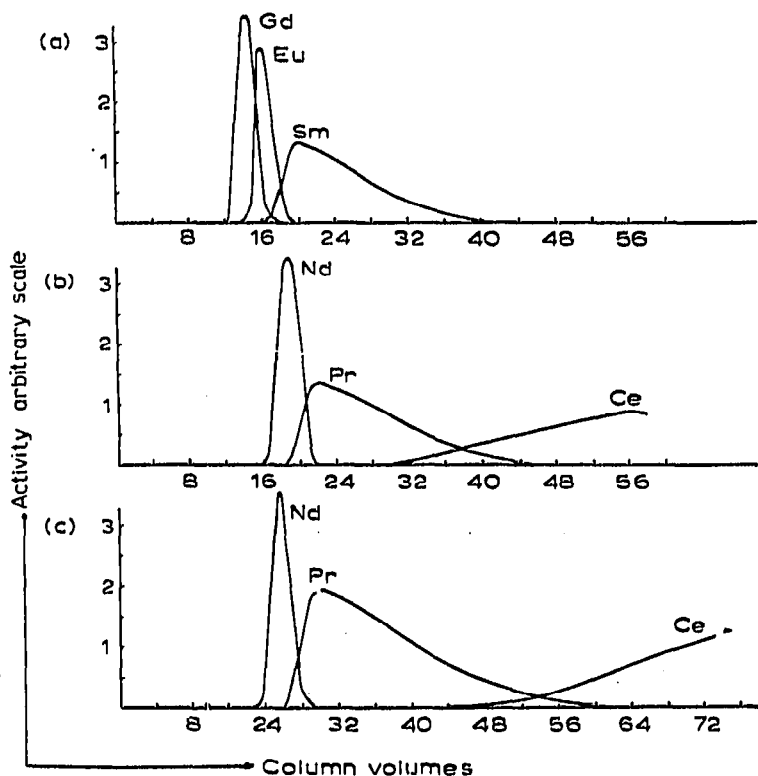

Fig. 2. Separation of light rare earth tracers from macroamounts of samarium and praseodymium. Column: 0.3 cm^2 × 22.5 cm Amberlite IRA-400 (200–400 mesh, nitrate form). (a) 60 mg Sm$_2$O$_3$; 80% CH$_3$OH–1.5 N NH$_4$NO$_3$; 1 ml/cm^2 min; 50° (Neodymium begins to elute after fraction 90). (b) 30 mg Pr$_6$O$_{11}$; 70% CH$_3$OH–1.5 N NH$_4$NO$_3$; 1 ml/cm^2 min; 50°. (c) 30 mg Pr$_6$O$_{11}$; 80% CH$_3$OH–0.5 N NH$_4$NO$_3$; 1 ml/cm^2 min; 50°.

Preparation of Gd$_2$O$_3$ target

For cyclotron irradiations we had to make a gadolinium oxide target of required purity. For this purpose a "large" column containing a 8.6 cm^2 × 25 cm Amberlite IRA-400 (200–300 mesh, nitrate form) bed was constructed. The free bed volume of

the column was about 90 ml. The purification of the gadolinium oxide was carried out using the experimental conditions shown in Fig. 1a.

Twenty grams of gadolinium oxide was dissolved in 5 N nitric acid. Excess acid was removed by two evaporations with water. After cooling the gadolinium nitrate was transferred into a 200 ml standard flask with minimum volume of distilled water. Then 24 g of ammonium nitrate and 160 ml of methanol were added and the flask was filled up to the mark with distilled water.

Twenty millilitres from this methanolic gadolinium nitrate solution was poured on to the column heated previously to 50° and washed with 3–4 bed volumes of eluent (80 % CH_3OH–1.5 N NH_4NO_3). After sorption gadolinium was eluted at a flow rate of 0.1 free bed volume/min. The effluent was collected in three fractions (see Fig. 3). The first 7 bed volumes did not contain gadolinium. Bed volumes 8–14 were put aside for gadolinium recovery. Bed volumes 15–21 contain impure gadolinium which was, after recovering, combined with the unprocessed product. The recovery of the gadolinium from the eluate was made by precipitation with oxalic acid.

After complete elution of the gadolinium the light rare earths remained on the column (from Eu to La) were removed by washing with two bed volumes of water.
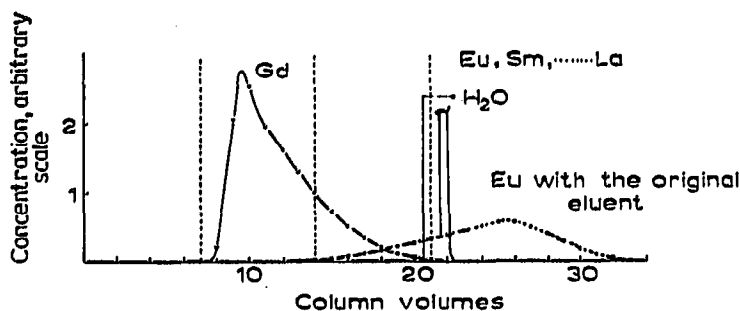

Fig. 3. Purification of gadolinium sample (2 g Gd_2O_3). Column: 8.6 cm^2 × 25 cm Amberlite IRA-400 (200–300 mesh, nitrate form); eluent: 80 % CH_3OH–1.5 N NH_4NO_3; flow rate: 1.1 ml/cm^2 min; temperature: 50°.

Determination of light rare earth impurities in gadolinium oxide and gadolinium metal

Two grams of gadolinium oxide (or equivalent amount of gadolinium metal) was dissolved in a slight excess of 5 N nitric acid. Excess nitric acid was removed by two evaporations with water. Before the second evaporation step, known amounts of [147]Eu + [148]Eu, [145]Sm, [147]Pm, [140]Nd and [139]Ce isotopes were added, partly to serve as indicators, partly for the determination of chemical yields.

The gadolinium nitrate was dissolved in 20 ml of 65 % CH_3OH–2.5 N NH_4NO_3 solution. (If gadolinium metal was processed, it was necessary to filter this solution to remove insoluble silica.) This solution was introduced into a column containing a 8.6 cm^2 × 25 cm Amberlite IRA-400 (200–300 mesh, nitrate form) resin bed which had previously been heated to 50° and washed with 3–4 bed volumes of the appropriate eluent.

The elution of the gadolinium was carried out under the conditions given in Fig. 1f. After 9.5 bed volumes the eluent was changed to distilled water and rare earth impurities retained on the column (from Eu to La) were eluted with 100 ml of water.

The aqueous solution of the impurities was evaporated to 20 ml. 1 mg of lute-

. tium carrier was added and the rare earths were precipitated with a slight excess of ammonia. The hydroxide precipitate was filtered on a S4 filter then redissolved in a few drops of 1.0 N hydrochloric acid. After diluting to 3 ml rare earths were adsorbed (in a centrifuge tube) on about 25 μl of Dowex 50 × 8 (-400 mesh, ammonium form) cation exchange resin. The resin was washed with 3 ml of 0.1 N ammonium chloride solution and 3 ml of distilled water and was transferred on to a 2 mm × 80 mm Dowex 50 × 8 (-400 mesh, ammonium form) column. The rare earths were eluted from this column with ammonium α-hydroxyisobutyrate using the gradient elution technique[3]. The concentration of the eluent was changed by an "exponential" mixing system containing two superimposed mixing chambers and a reservoir[4].

The eluate was collected drop by drop. The radioactivity of the drops was measured with the aid of an end-window GM counter, whereas their rare earth content was determined by spectrophotometric method using the colour reaction with Arsenazo III[5]. After correcting for chemical yields the total amounts of the individual rare earths were calculated.

RESULTS AND DISCUSSION

If a carrier-free rare earth is eluted from a strongly basic anion exchange resin bed with aqueous-methanol solution of nitrates we get a symmetrical elution peak. On increasing the amount of the rare earth this symmetry gradually disappears; the frontal, rising part of the curve becomes steeper, while its descending part is lengthened. Parallel with this, the rare earth begins to elute sooner (the elution curve shifts in the direction of the smaller effluent volumes).

The presence of macroamounts of a rare earth also influences the adsorption and elution of the adjacent rare earths present in microamounts. The elution curve of the adjacent microelement, having a smaller atomic number Z relative to that of the macroelement, is also distorted. Its leading edge becomes lengthened but its trailing edge more or less retains its original shape. The elution curve of this microelement, together with that of the macroelement, also shifts to the left. If the column loading is too large, as seen in Fig. 1b, the macro- and microelement begin to elute almost simultaneously. In such cases satisfactory conditions for the purification of the macroelement are already absent. A decrease in the working temperature likewise results in too early elution of the microelement, as well as in increased overlapping of the elution peaks.

A microelement having a larger Z relative to that of the adjacent macroelement, owing to the displacement effect of the macroelement, elutes in a very sharp and symmetrical elution band (Figs. 2a–c). This effect is very favourable for the purification of the macroelement.

Some data about the amounts of gadolinium, samarium and praseodymium recoverable from their purification process are summarised in Table I. These data were calculated from the appropriate elution curves and checked by concentration measurements.

For the preparation of pure gadolinium the experimental conditions shown in Fig. 1a and 1c are recommended. The essential features of the purification method used in our laboratory are illustrated by Fig. 3. The gadolinium oxide prepared by this method was not an exceptionally pure target. However, it must be mentioned

TABLE I

PRACTICAL RECOVERIES OF SOME RARE EARTH ELEMENTS PURIFIED TO A GIVEN DEGREE OF PURITY
USING THE EXPERIMENTAL CONDITIONS GIVEN IN FIGS. I AND 2

	Recoveries in %						
	1a	1b	1c	1e	2a	2b	2c
Recoverable amount of Gd containing less than 0.1 %							
of Tb,	70		90	65			
of Eu,	75	0	82	20			
both of Tb and Eu originally present	45	0	72	0			
Recoverable amount of Sm containing less than 0.1 %							
of Eu,					85		
of Nd,					100		
both of Eu and Nd originally present					85		
Recoverable amount of Pr containing less than 0.1 %							
of Nd,						76	88
of Ce,						80	85
both of Nd and Ce originally present						56	73

that there was no intention here to remove the heavier rare earths from gadolinium as these do not interfere with the post-irradiation chemical operations. Therefore, the gadolinium purified by us contains the original quantity of terbium as well as a part of the dysprosium originally present. If it is necessary to remove these two elements the experimental conditions corresponding to Fig. 1c should be employed.

In purifying samarium, only the europium must be taken into consideration because neodymium begins to elute long after the complete elution of samarium. As shown in Table I, 85 % of the samarium can be recovered from the purification process at a purity which satisfies all practical requirements.

For the separation of trace amounts of cerium from macroamounts of praseodymium, there are two possibilities (Figs. 2b and 2c). From these it is undoubtedly the latter which corresponds to the more favourable conditions. By this method 70–75 % of the original quantity of praseodymium can be recovered in a suitable degree of purity.

Separations such as those shown in Figs. 1 and 2 can be used not only for the purification of rare earths but for the concentration of rare earth impurities present in microamounts, hence also for analytical purposes. The light rare earth impurities of gadolinium oxide and gadolinium metal samples were concentrated by us using the conditions corresponding to Fig. 1f. If concentration is carried out in the presence of radioactive isotopes of the components we are able to avoid the difficulties connected with quantitative work. At the same time it is possible to arrange the conditions so that the concentrate of the impurities after separation would contain only an optimal small quantity of the product being investigated.

A cation exchange chromatogram of the concentrate from a gadolinium metal sample is shown in Fig. 4. In the figure the amounts of the individual components are also presented. It is noteworthy that the concentrate of the impurities separated from the gadolinium sample contains more than 30 % of the total europium but only 10^{-4} % of the total gadolinium. These data clearly show the high degree of purity of the anion exchange separation. A similar degree of purity could not be attained when work was carried out at room temperature.
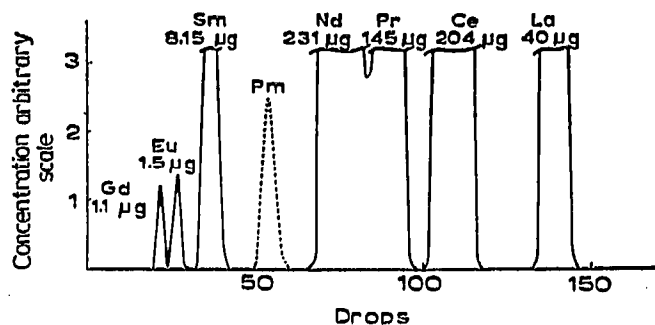

Fig. 4. Cation exchange chromatogram of light rare earth impurities separated from gadolinium metal sample. Column: 2 mm × 80 mm Dowex 50X8 (-400 mesh, ammonium form); flow rate: 1.5 ml/cm^2 min; temperature: 20°; eluent: ammonium α-hydroxyisobutyrate, pH 4.5, gradient elution. The starting concentrations in the lower mixing chamber, upper mixing chamber and reservoir are 0.22 M, 0.34 M and 2.19 M, respectively. The volumes of the lower mixing chamber and upper mixing chamber are 6.9 ml and 7.4 ml, respectively).

ACKNOWLEDGEMENT

SUMMARY

The separating power of methanolic solutions containing ammonium nitrate for the separation of trace amounts of light rare earths from macroamounts of adjacent rare earths was investigated. It was shown that anion exchange carried out from methanolic solutions of ammonium nitrate provides a useful means for the purification and analysis of the light rare earths. Methods for the purification of gadolinium and for the concentration of light rare earth impurities from gadolinium oxide and gadolinium metal samples are described in detail.

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