

# Production of highly radioactive sources of neutron-deficient isotopes of the rare-earth elements for use in nuclear spectroscopy

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Methods are discussed for separation of neutron-deficient isotopes of rare-earth elements from macro quantities of lanthanide targets irradiated with 660-MeV protons. The procedures used were: 1) extraction chromatography with di(2-ethylhexyl) orthophosphoric acid, 2) anion-exchange chromatography from aqueous methanol solutions of neutral nitrates, 3) cementation of micro quantities of lanthanides of the cerium subgroup with sodium amalgam, and 4) the Szilard-Chalmers effect in diethylenetriaminepentaacetate complexes of rare earths. A description is given of the chromatographic separation of the combined highly radioactive sample of nuclear reaction products into individual elements and the preparation of the separated elements for measurement of the conversion electron spectra and for mass separation.

## INTRODUCTION

The neutron-deficient isotopes of the rare-earth elements have been investigated by the Laboratory of Nuclear Problems at the Joint Institute for Nuclear Research and by many laboratories in the countries who are participants in the Joint Institute for Nuclear Research.<sup>1</sup> The extensive development of these studies has been possible as a result of the high intensity of the internal proton beam of the synchrocyclotron at the Laboratory of Nuclear Problems: 2.3  $\mu\text{A}$  at an energy 660-680 MeV.

The cross sections for deep spallation reactions in which isotopes of individual elements with a deficit of 5-10 neutrons can be obtained are small even for the optimal choice of the target material; they are not greater than 30-50 mb for some nuclei and substantially lower for most other nuclei.<sup>2</sup> However, in those cases in which it is necessary to obtain highly radioactive sources of some element by means of deep spallation reactions, the low production cross sections can be compensated by the large mass of the target, since the transparency of all materials for high-energy protons permits uniform irradiation of samples 30-40 g/cm<sup>2</sup> thick. Therefore, in bombardment of metallic targets inside the accelerator vacuum chamber by 660-680-MeV protons, accumulation of individual forms of nuclei will occur at a rate  $10^{10}$ - $10^{11}$  atoms/(gram-atom- $\mu\text{A}$ ). As a result, a target of mass 2-3 g after 1 hour of bombardment is equivalent in its  $\gamma$  radiation to  $\approx 3$  grams of radium, and the radioactivity of the individual isotopes with half-lives in the interval 1-10 hours reaches several tens of millicuries. These quantities are quite sufficient for study of the properties of isotopes with precision spectrometers, which ordinarily have a low aperture and consequently require radiation sources of high activity.<sup>1</sup>

Obviously, before the physical measurements are made it is necessary first to separate the nuclear reaction products from the target material by radiochemical methods, to separate pure samples of the elements, and to prepare the radiation sources from them. Nuclear spectroscopy presents a number of extremely severe requirements for studies of this type.

1. Work carried out at Dubna in nuclear spectroscopy has been directed mainly toward short-lived isotopes which are not available to laboratories which do not have accelerators. The time required for chemical preparation

of the samples for measurement in a given case is determined by the conditions of measurement and by the half-lives  $T_{1/2}$  of the isotopes studied. Magnetic spectrometers and spectrographs permit investigation of nuclei with  $T_{1/2} \geq 1$  hour. Shorter-lived isotopes are studied by means of crystal detectors with multichannel pulse-height analyzers. Here it is desirable that the chemistry occupy the shortest possible time: The quicker the method, the more isotopes become available for study.

2. The need of obtaining intense sources of individual radioisotopes leads to the processing of highly radioactive targets. Chemical processing at such a high level of ionizing radiation without injury to the worker can be carried out only by means of heavy biological shielding and duplicating manipulators or other remote control devices. Working in enclosures makes it considerably more difficult to monitor the separation process, and all parameters of a "hot" experiment are chosen on the basis of results of model tests at the tracer level of radioactivity.

Consequently, the chemical technique must be well carried out, must not require constant monitoring during the separation process, and must be suitable for remote control of all operations. In other words, the complication due to the high radioactivity must not have a negative effect on the chemical yields of the elements separated, which must be as high as possible. This is due to the fact that neutron-deficient isotopes are in the category of rare isotopes, obtainable only in limited quantities as a result both of the nuclear production mechanism and of the irradiation conditions and the half-life  $T_{1/2}$ . As a rule, in chemical preparation of radioactive sources for spectroscopic research it is not permissible to introduce isotopic carriers. This is also an important factor which complicates the choice of the method and the performance of the chemical processing. Finally, the sources obtained must have not only high total and specific activities, but also macro concentrations in solution, which will allow intense thin sources to be prepared with minimal loss on metallic bases of area 3-5 mm<sup>2</sup>.

3. The requirements on chemical purity hardly need to be spelled out in detail. For correct physical interpretation of the experimental results, the amount of radioactive contamination in the radiation source, as a rule, should not exceed 1%. In some cases the permissible

levels of contamination are even lower. This requires that in the choice or development of a chemical technique we devote more attention to questions of selectivity and purity than to the other factors enumerated.

It is quite evident that it is practically impossible to develop a chemical technique which completely satisfies all of the requirements of nuclear spectroscopy. The radiochemical methods which we will discuss below for obtaining rare-earth sources are the optimal methods emerging from the work of chemists and to some degree from the investigations of physicists.

In the first years of work with lanthanides, the main attention was given to the heavy rare earths from Lu to Tb. Investigation of the neutron-deficient isotopes of these elements with mass numbers from 150 to 173 provided extensive information on the structure of deformed nuclei of the lanthanides,<sup>1</sup> which were prepared by bombardment of Ta by 660–680-MeV protons.

Metallic tantalum is a very convenient material for preparation of synchrocyclotron targets: The high melting point permits bombardment by a proton beam of maximum intensity without danger of melting the target; the mechanical properties of the metal are a guarantee against contamination by radioactive aerosols of the accelerator room and laboratory in transportation of the target; the low cost of tantalum of rigorously high purity makes this material easily obtainable. In addition there is no great difficulty in separation of tantalum from the rare-earth products of deep spallation reactions: Ta rapidly dissolves in a mixture of hydrofluoric and nitric acids. Micro quantities of rare earths from this solution are adsorbed on lanthanum fluoride, which plays the role of an isomorphic collector. Unfortunately, however, Ta is not very suitable as a target material for preparation of isotopes of the light lanthanides from Gd to La with mass numbers  $130 \leq A \leq 150$ . The cross sections for the nuclear reactions for production of these isotopes from Ta are an order of magnitude lower than for the heavy rare earths<sup>4</sup> (Fig. 1). Therefore the activities of individual elements and isotopes obtained were insufficient for performance of certain accurate measurements of the conversion electron spectra of excited nuclei lying outside the deformation region.

Increasing the duration of the bombardment and the mass of the bombarded material does not solve the problem of obtaining intense sources of short-lived isotopes. The only possible means is replacement of the tantalum target by a lighter target prepared of some metal in the middle of the rare-earth group. For example, calculations based on Rudstam's empirical equation (Fig. 2) show that, other conditions being equal, in bombardment of a terbium target the activity of light lanthanide sources can be raised by a factor of 5–10. However, this replacement requires solution of a complicated chemical problem: the rapid performance of the separation of micro quantities ( $\sim 10^{-7}$  g) and macro quantities (2–3 g) of rare earths of very similar properties. This problem is naturally further complicated by all of the requirements on radiochemical techniques for obtaining sources for nuclear spectroscopy which were mentioned above.

At first glance it appears obvious that the most simple separation can be achieved by using specific prop-

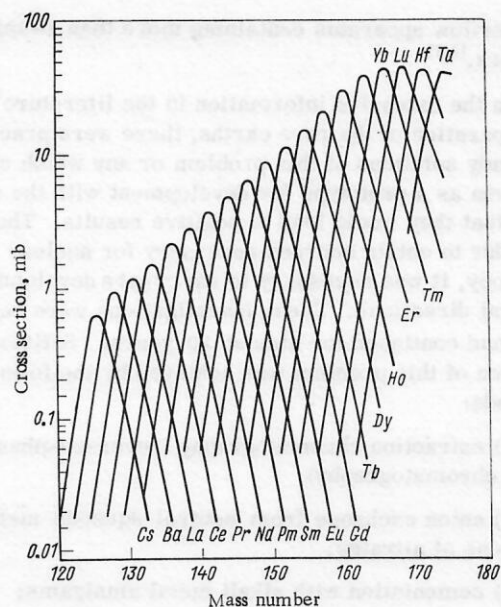


Fig. 1. Cross sections for production of rare-earth isotopes in bombardment of tantalum with protons of energy 660 MeV (ref. 4).

erties of individual lanthanides which are not characteristic of other rare-earth elements. Lavrukina and co-workers<sup>5–7</sup> took this course in proposing bombardment of Eu or Sm. These elements are rather easily removed from solution by reduction to the metals at a mercury cathode. However, complete purification from the target material is impossible. Up to 1% of Eu and Sm remains in the solutions. This practically excludes subsequent qualitative separation of the mixture into individual rare-earth elements in a microchromatographic column, since the impurities of macro quantities of lanthanides must not exceed 1 mg in this operation. For the same reasons it is also unsuitable to use the method based on the reduction  $\text{Eu(III)} \rightarrow \text{Eu(II)}$  in Jones' reducer with subsequent extraction of trivalent lanthanides.<sup>8</sup>

If we use for separation from gram quantities of a heavier element of tracers of lighter rare-earth elements such a powerful multistep method as elutive chromatography in sulfocationites with an increasing concentration gradient of the ion-complexing agent, then to achieve satisfactory separations it would be necessary to use large volumes of the eluants and large columns. After the separation process there remains the complicated problem of preparation of micro quantities of lanthanides for measurement, which, taking into account the large volumes of solutions containing complexing agents, also requires no little time. If we judge from the existing data,<sup>9,10</sup> the total time required to separate macro-micro quantities of rare earths in cation-exchange resins will be of the order of 10–20 hours, which is, as a rule, unsuitable for our problems.

Liquid counterflow extraction is used for separation and division of rare-earth elements no less often than ion exchange.<sup>11</sup> In industrial installations it is not difficult to carry out a multistage process leading to extreme purification of a fraction of elements, but under laboratory conditions this method encounters certain difficulties of an instrumental and design nature. For example, separation of the simplest mixtures requires



counterflow apparatus containing more than 10 mixer-settlers.<sup>12,13</sup>

In the extensive information in the literature<sup>9,14-18</sup> on separation of the rare earths, there were practically no ready solutions of this problem or any which could be taken as a prototype for development with the assurance that they would lead to positive results. Therefore, in order to obtain sources necessary for nuclear spectroscopy, it was necessary to carry out a development in several directions. These investigations were begun in 1961 and continued for almost 10 years. Satisfactory solution of this problem was achieved by the following methods:

- 1) extraction chromatography (reversed-phase partition chromatography);
- 2) anion exchange from neutral aqueous methane solutions of nitrates;
- 3) cementation with alkali metal amalgams;
- 4) the Szilard-Chalmers effect in bombardment of rare-earth chelates.

Each of these methods can separate from a lanthanide target, in a relatively short time, radioactive samples containing all of the rare earths. A diagram of the entire process for obtaining radiochemically pure and monoisotopic preparations of rare-earth elements is shown in Fig. 3. In all cases the chemical composition and the solution volumes of the combined samples permit rapid and simple preparation for separation into elements by means of cation-exchange chromatography in a column with a small quantity of resin: not more than 150 mg. Use of a microchromatographic column was dictated by the necessity of having small volumes of the individual lanthanide fractions for preparation of conversion electron sources and of rare-earth samples for separation in mass separators.

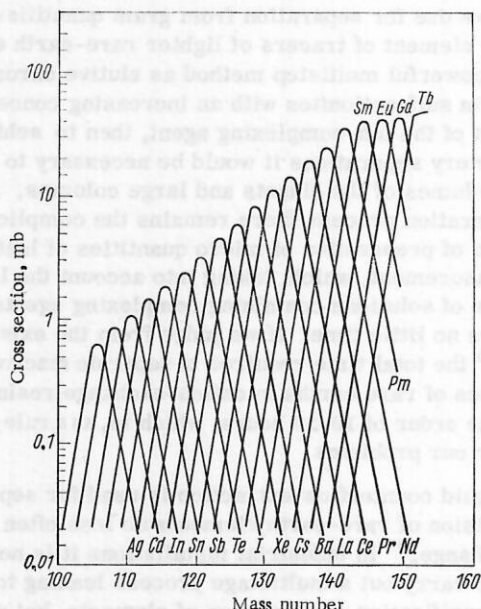


Fig. 2. Cross sections for production of isotopes of rare-earth elements on bombardment<sup>4</sup> of terbium by protons of energy 660 MeV.

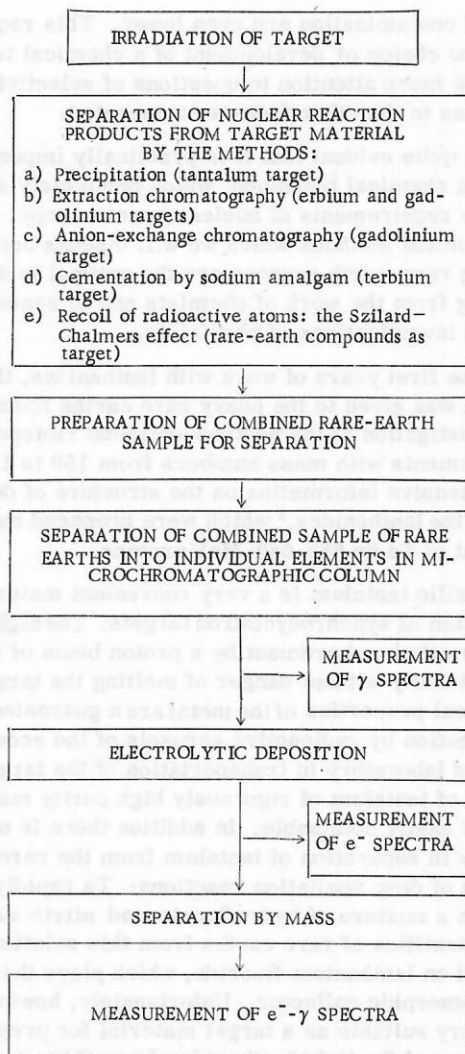


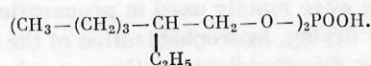
Fig. 3. Diagram for preparation of sources of neutron-deficient isotopes of rare-earth elements.

The present review is devoted to questions associated with the separation of submicrogram and gram quantities of lanthanides: to separation of the combined rare earths resulting from deep spallation reactions from the target material, and to description of the subsequent operations of preparing the rare-earth samples for measurement of  $e^-$  and  $\gamma$  spectra and mass separation.

#### 1. SEPARATION OF MACRO AND MICRO QUANTITIES OF RARE EARTHS WITH EXTRACTION CHROMATOGRAPHY (REVERSED-PHASE PARTITION CHROMATOGRAPHY)

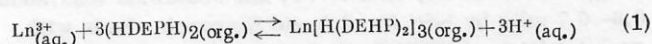
Extraction chromatography, like liquid extraction, is based on the partition of the compounds being separated between two immiscible liquid phases. The important difference is that in the latter case extraction equilibrium is established between an immobilized extractant fixed in a hydrophobic material and an aqueous solution flowing through this extractant. Here the effect is achieved of multistage extraction, permitting separation of compounds with nearly identical extraction properties. The method of separation of mixtures of inorganic ions is discussed, for example, in a detailed review<sup>19</sup> by Cerrai and Ghersini.

Extraction chromatography for separation of the combined rare-earth elements was first proposed by Siekierski.<sup>20,21</sup> Using as an immobilized extractant tributyl phosphate (TBP) deposited on kieselguhr made hydrophobic by dichlorodimethyl silane, he obtained satisfactory results even in separation of the "difficult" rare-earth pair Gd and Eu. The separation process was not time-consuming. The solution flowing out of the column contained only HNO<sub>3</sub> which was removed by evaporation. The deficiencies of this method include the necessity of using concentrated nitric acid and the relatively low separation factor for neighboring rare earths, of the order of 2. These deficiencies led to the search for a more convenient extractant for preparation of beds for extraction-chromatographic columns. This extractant turned out to be that proposed previously by Peppard and co-workers,<sup>22</sup> di(2-ethyl hexyl) orthophosphoric acid:

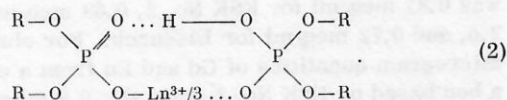


One of the generally accepted abbreviated descriptions of this compound is HDEHP; it belongs to a class of monobasic diethers of phosphoric acid with the general formula (RO)<sub>2</sub>POOH.

In nonpolar solvents and in pure form HDEHP and its other analogs are dimerized.<sup>23,24</sup> On extraction the ion of trivalent lanthanide reacts with three dimers of the acid:



It is suggested<sup>25</sup> that a compound of the chelate type is formed of the following structure:



If we neglect the activity coefficients and assume that other complexes are not formed, we can write down the following expression for the partition coefficient of the metal between the two phases:

$$E = \frac{[\text{Ln}[\text{H}(\text{DEHP})_2]_{3(\text{org.})}]}{[\text{Ln}^{3+}]_{(\text{aq.})}} = k \frac{[(\text{HDEHP})_2]_{(\text{org.})}^3}{[\text{H}^{+}]_{(\text{aq.})}^3}, \quad (3)$$

where k is the extraction constant or

$$\lg E = \lg k + 3 \lg [(\text{HDEHP})]_{\text{org.}} - 3 \lg [\text{H}^{+}]_{\text{aq.}} \quad (4)$$

The third-power dependence of E on the extractant and hydrogen-ion concentrations permits control of the extraction process and creation of optimal conditions.

In extraction processes at high concentrations of lanthanides, there often arises in the solutions a third, gelatinous phase.<sup>22</sup> This is due to formation of a polymer with a three-dimensional structure:

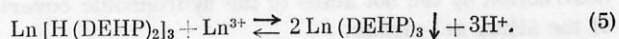


TABLE 1. Characteristics of Silica Gels Used for Preparation of Beds. All Samples Are Classified "For Chromatography"

| Type of silica gel | External surface, m <sup>2</sup> /g | Mean radius of pores, Å | Porosity, % | Apparent density, g/cm <sup>3</sup> | Moisture capacity in 200% humidity air, weight, % | Pore volume, m <sup>3</sup> /g |
|--------------------|-------------------------------------|-------------------------|-------------|-------------------------------------|---------------------------------------------------|--------------------------------|
| Eisenach (GDR)     | 295                                 | —                       | —           | —                                   | —                                                 | —                              |
| KCK № 2            | 338                                 | 70                      | 72.2        | 0.611                               | 119                                               | 1.19                           |
| KCK № 2.5          | 376                                 | 51.6                    | 67.4        | 0.706                               | 97.9                                              | 0.971                          |

The separating capability of an extraction system for two elements I and II can be expressed by the separation factor

$$\beta = E_I/E_{II}. \quad (6)$$

The average separation factor of two neighboring elements for the entire group of rare earths from La to Lu in extraction by HDEHP<sup>22</sup> in accordance with Eq. (6) is

$$\bar{\beta}_{(\text{Ln}_I/\text{Ln}_{II})} = \bar{\beta}_{(\text{Lu/La})} = \sqrt[14]{E_{\text{Lu}}/E_{\text{La}}} \approx 2.5. \quad (6a)$$

In the radiochemistry, analytical chemistry, and chemical technology of nuclear fuel and rare metals, HDEHP is widely used because of its lower values of E in comparison with other monobasic diethers of phosphoric acid. This property of HDEHP permits use of the extractant without dilution by a carrier diluent, extraction into small volumes of the organic phase of large quantities of metals, in particular, rare-earth metals, and reextraction of most of them with achievable concentrations of strong mineral acids in the aqueous phase. Therefore this extractant<sup>1</sup> was used in our investigations.<sup>26-31,74</sup>

Use of HDEHP for extraction-chromatographic separation of rare-earth mixtures permits best utilization of the positive qualities of this extractant. The HDEHP carriers can be any hydrophobic materials which firmly sorb the extractant, which are chemically inert to the reagents used for the separations, whose mechanical properties permit layers with low hydrodynamic resistance to be obtained in columns, which are not deformed in filtration through them of eluants at increased pressure (1-2 atm), and which do not change their properties over the range 20-100°C. The well-known HDEHP carriers used in separation of rare-earth elements are aluminum oxide,<sup>34</sup> polystyrenedivinylbenzene,<sup>35</sup> cellulose,<sup>36</sup> polyvinylpolyacetate (Corvic),<sup>37-39</sup> polychlorotrifluoroethylene (Kel-F, CTFE 2-300, Hostaflon C2),<sup>40-43</sup> polytetrafluoroethylene (fluoroplast-4)<sup>8,44,45</sup> kieselguhr hydrophobized by dimethyldichlorosilane (diatomite)<sup>46-53</sup>, and silica gel.<sup>26-31,54-59,74</sup>

The quality of extraction-chromatographic columns with different beds is usually evaluated by the height equivalent to a theoretical plate (HETP) — a concept transferred to chromatography from the mathematical description of the separation process in distillation and extraction columns.<sup>60</sup> The height equivalent to a theoretical plate corresponds to the height of a segment of the column in which the same separation effect is achieved



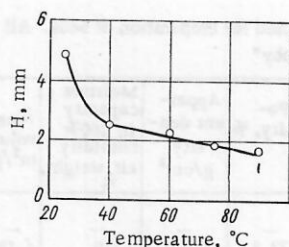


Fig. 4. Temperature dependence of the HETP in elution of submicrogram quantities of Er from a column 4.3 mm in diameter and 148 mm long. The bed is based on Eisenach silica gel of  $45 \pm 14 \mu$ ,  $Q = 0.6 \text{ ml/g}$ ; the eluant is 0.8 M HCl,  $1.3 \text{ ml/cm}^2 \cdot \text{min}$ .

as in an individual equilibrium experiment under static conditions. The smaller the HETP ( $H$ ), the greater number of theoretical plates  $N$  are placed along the column length  $l$ , the more effectively the separation process proceeds, and the better the quality of the column:

$$N = l/H. \quad (7)$$

The HETP is usually calculated from elution curves by means of Glueckauf's formula,<sup>61</sup> which is valid for columns with a number of plates greater than 25:

$$H = lW^2/8V_{\max}^2 \quad (8)$$

where  $V_{\max}$  is the volume of eluant corresponding to the maximum in the yield curve,  $W$  is the width of the yield curve at  $1/e$  of the height of the maximum,  $V_{\max}$  is related to  $E$  by the well-known equation

$$E = (V_{\max} - V_0)/V_E, \quad (9)$$

where  $V_0$  is the volume of the immobilized phase, and  $V_E$  is the volume of HDEHP in the column.

Of the enumerated HDEHP carrier materials used for preparation of column beds in separation of micro and macro quantities of rare-earth elements, the most frequently used is silica gel. Under optimal conditions of separation of rare earths for a column based on hydrophobic kieselguhr and silica gel,<sup>38,47,48,52,54</sup> a somewhat lower HETP is observed than in the case where polymeric materials are used. In addition, silica gel is a radiation-stable material and columns of it do not change their properties in the course of an extended period in which tens of separation cycles are carried out.<sup>26,27</sup> Last, but not least important, is the fact that silica gel is an easily available industrial material which exists in several varieties with strictly standardized properties, from which the necessary types can be chosen. After a series of preliminary experiments<sup>29,30</sup> it was found that high-porosity large-pore silica gels with small grains are most suitable as carriers in extraction-chromatographic columns intended for separation of macro and micro quantities of rare-earth elements. In this case a high capacity of the column is also assured, as well as good separative qualities (low HETP). We selected the large-pore high-capacity silica gels of Soviet manufacture, KSK No. 2 and KSK No. 2.5, and Eisenach silica gel from East Germany. The characteristics of the varieties of silica gel used are given in Table 1.

The technique of preparing the beds for extraction-chromatographic columns has been described in detail in

TABLE 2. Separation Factors for Neighboring Rare-Earth Elements in the HDEHP-HCl System at Various Temperatures

| Rare-earth pairs | 23° C | 40° C           | 65° C           |
|------------------|-------|-----------------|-----------------|
| Ce/La            | 2.6   | $2.92 \pm 0.05$ | $2.9 \pm 0.06$  |
| Pr/Ce            | —     | $1.36 \pm 0.02$ | $1.49 \pm 0.01$ |
| Nd/Pr            | —     | $1.33 \pm 0.01$ | $1.31 \pm 0.02$ |
| Pm/Nd            | —     | $2.20 \pm 0.03$ | 2.4             |
| Sm/Pm            | 2.7   | $2.63 \pm 0.06$ | $2.56 \pm 0.07$ |
| Eu/Sm            | 2.0   | $1.94 \pm 0.02$ | $1.93 \pm 0.03$ |
| Gd/Eu            | 1.5   | $1.53 \pm 0.01$ | $1.48 \pm 0.01$ |
| Tb/Gd            | 5.0   | $4.35 \pm 0.08$ | $4.02 \pm 0.07$ |
| Dy/Tb            | 2.6   | $2.51 \pm 0.03$ | $2.31 \pm 0.04$ |
| Ho/Dy            | —     | $1.89 \pm 0.02$ | $1.84 \pm 0.02$ |
| Er/Ho            | —     | $2.51 \pm 0.03$ | $2.31 \pm 0.04$ |
| Tm/Er            | —     | $3.13 \pm 0.03$ | $3.03 \pm 0.03$ |
| Yb/Tm            | 2.6   | $3.14 \pm 0.06$ | $2.73 \pm 0.08$ |
| Lu/Yb            | 1.8   | $1.74 \pm 0.02$ | $1.70 \pm 0.3$  |

refs. 26 and 30. Two fractions with grain sizes of  $15 \pm 4 \mu$  and  $63-80 \mu$  were mainly used in preparation of the beds. After careful drying, hydrophobization of the silica gel is carried out by dimethyldichlorosilane at  $0.2 \text{ ml/g}$  of silica gel. This quantity of hydrophobizer permits a firmly held HDEHP carrier to be obtained. From columns prepared in this way, micro quantities of rare-earth elements are eluted in sharp symmetric peaks.

Saturation of the carriers by HDEHP is accomplished by addition of undiluted acid to the silica gel with continuous mixing. The different types absorbed different maximum amounts of HDEHP while externally remaining dry and powdery. The greatest amount, of the order  $0.8 \text{ ml/g}$ , is absorbed by KSK No. 2, and somewhat less, about  $0.6-0.7 \text{ ml/g}$  by KSK No. 2.5 and Eisenach. Beds with such loadings of HDEHP ( $Q$ ) form in the columns uniform layers consisting of individual grains, with minimal HETP values for separation of rare-earth elements. The loadings given are considered optimal for these silica gels. The specific volume capacity of a column with of  $15 \pm 4 \mu$  bed was  $0.81 \text{ meq/ml}$  for KSK No. 2,  $0.63 \text{ meq/ml}$  for KSK No. 2.5, and  $0.72 \text{ meq/ml}$  for Eisenach. For elution of submicrogram quantities of Gd and Eu from a column with a bed based on KSK No. 2 ( $15 \mu$ ,  $Q = 0.8 \text{ ml/g}$ ,  $0.73 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ ,  $65^\circ\text{C}$ ) we obtained  $H = 0.09 \text{ mm}$ .

A fine-grained bed which provides good separation creates a high hydrodynamic resistance in the column. Therefore the grain size of the filling is chosen to be optimal depending on whether or not distinct separation must be obtained independently of the time of the process or whether it is possible to accept somewhat poorer quality in return for speed, as is sometimes the case in processing of samples containing short-lived isotopes.

In separation of rare-earth elements by the extraction-chromatographic method in the HDEHP-HCl system, an increase of the working temperature of the column has a positive effect. In this case the rates of the diffusion processes are increased and this substantially decreases the HETP (Fig. 4). The sharpest drop in HETP values occurs in the region  $20-40^\circ\text{C}$ . A temperature  $45 \pm 5^\circ\text{C}$  is optimal for operation of large separation columns intended for repeated use. At higher temperatures, for example, at  $65^\circ\text{C}$ , a process of slow "slipping" of the HDEHP from the carrier begins. This may be due to destruction by the hot acids of the hydrophobic covering of the silica gel grains.

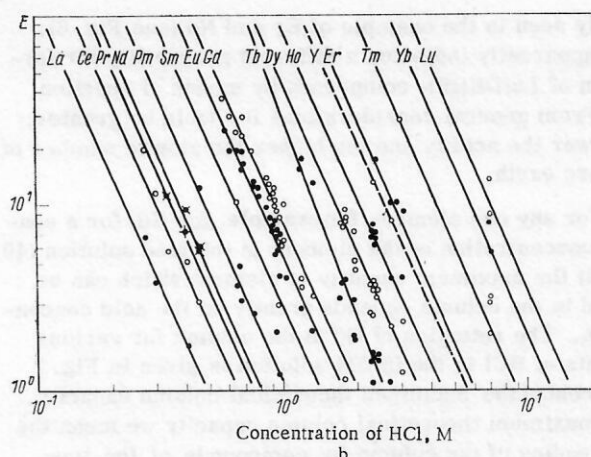
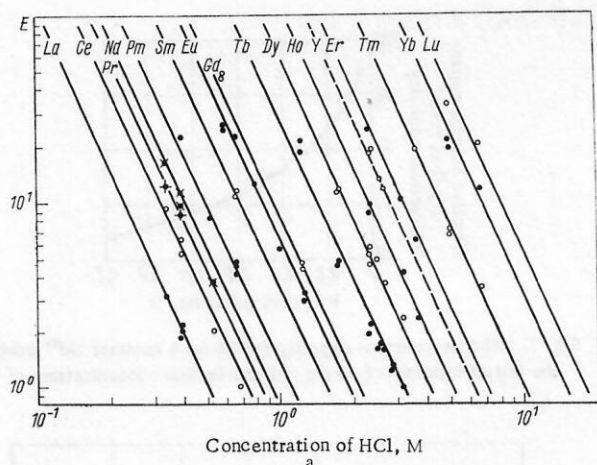


Fig. 5. Partition of rare-earth elements between undiluted HDEHP sorbed on silica gel and the HCl solution as a function of eluant acidity at 40°C (a) and 65°C (b).

The effect of temperature on separation of lanthanides is not limited to the decrease in the HETP values. The partition coefficients  $E$  of the individual elements (as can be seen in comparison of Figs. 5a and 5b) and consequently the separation factors of pairs of rare-earth elements ( $\beta$ ) also change appreciably with temperature (Table 2). The mean separation factor for the entire group of lanthanides at 40°C is  $\bar{\beta}(\text{Lu/La}) = 2.24$ ; it is lower for elements of the cerium subgroup:  $\bar{\beta}(\text{Gd/La}) = 1.91$  and higher for heavier elements:  $\bar{\beta}(\text{Lu/Gd}) = 2.64$ .

The distribution of micro quantities of rare-earth elements between HDEHP sorbed on silica gel and the aqueous phase as a function of the acidity of the eluant is in satisfactory agreement with that which we would expect on the basis of Eq. (4): in a log plot of  $E$  versus  $[\text{H}^+]$  the curves for all lanthanides have approximately a linear nature with a slope of about  $-3$  (see Fig. 5).

The experimental data presented on the influence of various factors in the separation of rare-earth elements in extraction-chromatographic columns with silica gel as the HDEHP carrier material were obtained with radioactive lanthanide isotope sources containing less than  $10^{-8}$  g of the element. These data enabled us to obtain clear representations of the optimal conditions for preparation of the bed and operation of the column. However, they do not provide an answer to the question of the use of these columns for rapid separations of macro-micro quantities of rare-earth elements.

Experiments on separation of micro quantities of lanthanides from macro quantities of a rare-earth element of heavier atomic weight were carried out with gadolinium and erbium. Use of these metals as target material is promising from the point of view of obtaining with high yields nuclei of the transition rare-earth elements (Tb, Gd) and elements of the beginning of the lanthanide group. Here it is taken into account also that the two metals are relatively cheap and easily obtainable.

Macro quantities of lanthanides are sorbed by the bed from dilute HCl solutions and form easily visible, distinct, colored bands. The Er band, for example, is rose colored, and the Dy, Y, and Gd bands are white. The bands increase the hydrodynamic resistance of the column, and

to maintain a constant rate of flow of the solutions it is necessary in the course of the loading, and at the beginning of the elution, to raise the pressure of air or nitrogen in the column and in the flasks containing the eluants.

As can be seen from Fig. 6, the size of the band is always somewhat greater than would follow for saturation of the bed only with compounds of the type  $\text{Ln}(\text{DEHP})_3$ . Other conditions being equal, the deposition band is longer, the lower the temperature and the larger the grain size of the filler. It is possible that the gel  $\text{Ln}(\text{DEHP})_3$  walls in the mouths of the pores of the silica gel in which the HDEHP is contained and in this way impedes the interaction of a certain part of the extractant with the lanthanide ions. For identical acidities of the initial solutions the relative length of the deposition band of a heavier lanthanide is shorter than for a lighter lanthanide, as can be

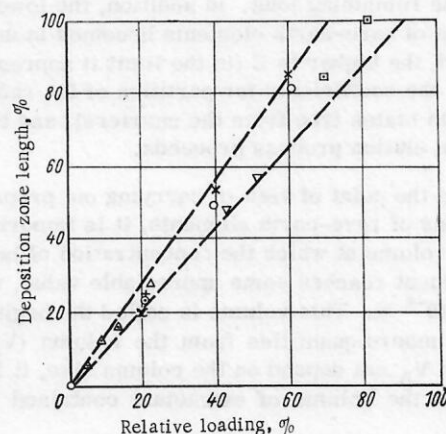


Fig. 6. Relative lengths of sorption bands for macro quantities of lanthanides in extraction-chromatographic columns with undiluted HDEHP, as a function of column loading. In calculation of the loading it was assumed that in the deposition band the lanthanide is in the form  $\text{Ln}(\text{DEHP})_3$ . The composition of the initial solutions is:  $[\text{Ln}^{3+}] = 0.2 \text{ M}$ ,  $[\text{HCl}] = 0.1 \text{ M}$ ;  $\times$ ) Nd, temperature 40°C, silica gel grain size 30-60  $\mu$ , flow rate 1.2  $\text{ml/cm}^2 \cdot \text{min}$ ;  $\odot$ ) Nd, temperature 75°C, silica gel grain size 30-60  $\mu$ , flow rate 1.3  $\text{ml/cm}^2 \cdot \text{min}$ ;  $\Delta$ ) Gd, temperature 65°C, grain size 15  $\mu$ , flow 1.3  $\text{ml/cm}^2 \cdot \text{min}$ ;  $\square$ ) Er, temperature 21°C, grain size 15  $\mu$ , flow rate 1.3  $\text{ml/cm}^2 \cdot \text{min}$ ;  $+$ ) Er, temperature 40°C, grain size 80-100  $\mu$ , flow rate 1.2  $\text{ml/cm}^2 \cdot \text{min}$ ;  $\times$ ) Er, temperature 40°C, grain size 50-70  $\mu$ , flow rate 1.2  $\text{ml/cm}^2 \cdot \text{min}$ ;  $\nabla$ ) Er, temperature 65°C, grain size 15  $\mu$ , flow rate 1.5  $\text{ml/cm}^2 \cdot \text{min}$ .



clearly seen in the example of Er and Nd (see Fig. 6). This apparently indicates a different probability for formation of  $\text{Ln}(\text{DEHP})_3$  compounds by means of reaction (5): From general considerations it should be greater, the lower the acidity and the higher the atomic number of the rare earth.

For any one element, for example, for Gd, for a constant concentration of the element in the feed solution (40 mg/ml) the maximum quantity of element which can be sorbed in the column depends greatly on the acid concentration. The retention of Gd in the column for various contents of HCl in the initial solution is given in Fig. 7 in percent of the maximum theoretical column capacity. By a maximum theoretical column capacity we mean the total loading of the column by compounds of the type  $\text{Ln}(\text{DEHP})_3$ . It is evident that complete saturation of the column by Gd is possible only for  $\text{pH} > 2$ .

The amount of loading determines the beginning of the elution of the lanthanide from the column and the shape of the elution curve (Fig. 8): The higher the loading and the earlier the elution begins, the sharper is the rise of the elution curve and the more drawn out is the descending portion. This shape of the curves can be explained by the fact that as the loading increases the content of free extractant in the organic phase decreases and therefore  $(\partial E / \partial [\text{Ln}^{3+}]) < 0$ . Consequently, the higher the loading, the more rapidly the lanthanide moves along the column. With statistical smearing of the rise of the elution band, the forward excursion of small quantities of the element has the result that these quantities fall in a region of higher E and the main portion of the lanthanide rapidly overtakes them. Thus, there is at all times a self-regulation of the sharpness of demarcation of the front of the band. The extended tail in elution of macro quantities from an extraction-chromatographic column can be explained in a similar way. The main mass of the element in no way affects the remaining ions. In addition, the lower the concentration of rare-earth elements becomes in unit volume of the bed, the higher is E (in the limit it approaches the values of the coefficients for partition of the radioactive isotopes in states free from the carriers), and the more slowly the elution process proceeds.

From the point of view of carrying out preparative separations of rare-earth elements, it is important to know the volume at which the concentration of lanthanide in the effluent reaches some appreciable value, which is taken as  $10^{-6}$  M. This volume is called the beginning of elution of macro quantities from the column ( $V_A$ ). In order that  $V_A$  not depend on the column size, it is normalized to the volume of extractant contained in the bed ( $V_E$ ):

$$A = (V_A - V_0) / V_E. \quad (10)$$

Figure 9 shows the normalized beginning of elution A as a function of the loading of the column by Er, Gd, and Y. It can easily be seen that parallel straight lines can be drawn in the semilog plots through the experimental points obtained for all elements in the loading range from 3 to 25% for various concentrations of acid in the eluants.

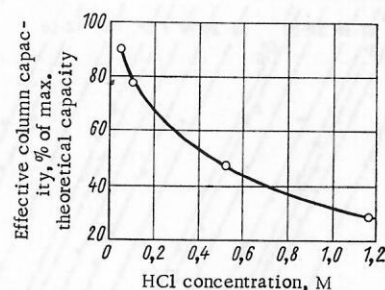


Fig. 7. Effective column capacity for Gd for a constant  $\text{Gd}^{3+}$  content in the initial solutions of 40 mg/ml and various concentrations of HCl.

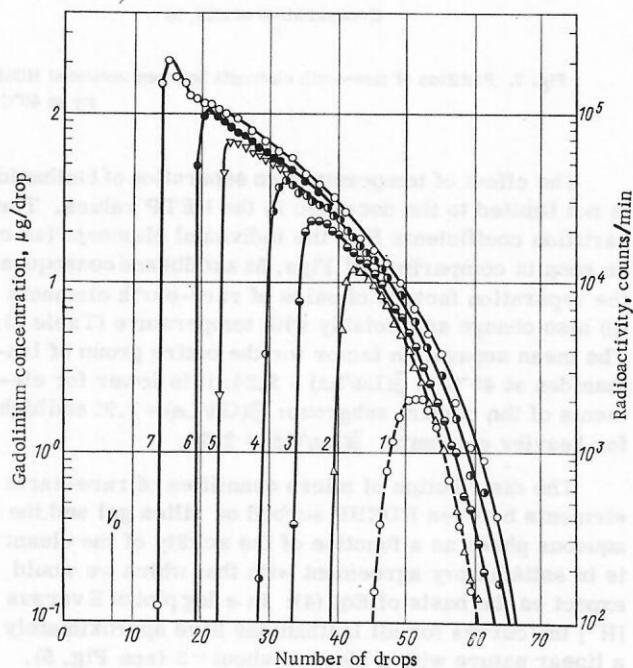


Fig. 8. Elution of gadolinium as a function of loading of the column by the element: 1)  $^{149,146}\text{Gd}$  without carrier; 2) 0.8% (0.1 mg); 3) 2.0% (0.25 mg); 4) 4.1% (0.6 mg); 5) 8.2% (1.0 mg); 6) 12.3% (1.5 mg); 7) 20.5% (2.5 mg); column is 2.2 mm in diameter and 68 mm long; eluant is 0.87 M HCl, 1.3 ml/cm<sup>2</sup> · min.

If we assume that for all lanthanides, independent of the concentration of acid in the eluant, first, there will be observed variations of A as a function of the loading<sup>2)</sup> B similar to those shown in Fig. 9 and, second, that the ratio  $E/A_0 = \text{const} = 1.4$ , where E is the partition coefficient for micro quantities of a given rare-earth element and  $A_0$  is the value of A obtained for B = 0 by linear extrapolation, we can then derive an empirical equation which permits calculation of A for macro quantities of any lanthanide for a given loading of the column and a known concentration of acid in the eluant:

$$\lg A = \lg E - 0.15 - 0.036B. \quad (11)$$

Calculation with this equation for a 20.5% loading of the column by dysprosium and its subsequent elution by 1.7 M HCl gives  $A = 1.70$ . The experimental determinations give a value  $A = 1.73$ .

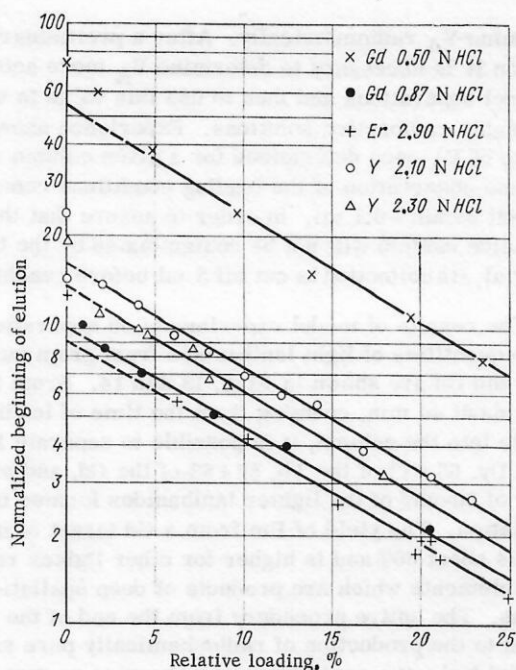


Fig. 9. Normalized beginning of elution of macro quantities of lanthanides (A) as a function of the loading of the column by the element. The points on the ordinate axis show the partition coefficients for micro quantities of the lanthanides considered for the corresponding concentrations of HCl in the eluants.

It is evident from Eq. (11) that for a constant loading of the column by rare earths  $A = E \text{ const.}$  Consequently the normalized value of the beginning of elution, like the partition coefficient, is inversely proportional to the cube of the concentration of hydrogen ions. In actual experiments with Gd the dependence of  $\log A$  on  $\log [H^+]$  is linear with a slope of approximately  $-3$  (Fig. 10).

In separation from macro quantities of lanthanides of traces of lighter rare-earth elements the column loading does not affect the partition coefficients of the micro elements being separated  $E_{\text{micro}}$  and the height equivalent to a theoretical plate  $H$  [Eq. (8)] as long as the elution bands of the macro and micro quantities do not overlap. In practice this means that for  $1 \leq E_{\text{micro}} \leq 2$ , good separation is possible if

$$A_{\text{macro}}/E_{\text{micro}} \geq 1.5. \quad (12)$$

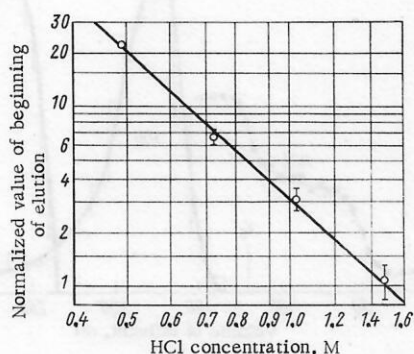


Fig. 10. Variation of the normalized value of the beginning of elution of gadolinium as a function of the HCl concentration in the eluant. The column loading is 12.4%.

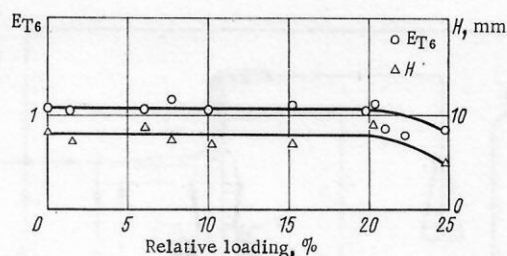


Fig. 11. Separation coefficient and HETP for micro quantities of terbium as a function of column loading by erbium.

As an example we can report results obtained in separation of Tb from Er (Fig. 11).

The greater the ratio (12) (the lower the loading), the more complete is the separation and the smaller the tail on the micro-element peak. With increased loading the tail increases, a noticeable overlap of the elution bands is observed, and in the limiting case the two elements are eluted together. There is only a certain enrichment in the micro element of the loading edge of the macro element peak.

The main cause of appearance of the tail is inclusion of the micro element in a gel structure of the type  $\text{Ln}(\text{DEHP})_3$  which is formed on sorption of the macro element from weakly acid initial solutions. The micro element transfers to the aqueous phase in the elution process only in proportion to the destruction of tri-dialkylphosphate.

Formation of compounds of the type  $\text{Ln}(\text{DEHP})_3$  can be suppressed to a certain degree if transport of the mixture being separated into the column is carried out with increased concentrations of  $H^+$  ions.<sup>58</sup> However, here there is a danger of passing through the macro component.

Fixation of micro elements by the gel  $\text{Ln}(\text{DEHP})_3$  leads to the result that fulfillment of the conditions given by Eq. (12) is a necessary but not sufficient factor for carrying out qualitative separations. Even in those cases where for the elements considered  $A_{\text{macro}}/E_{\text{micro}} \gg 1.5$ , for example, in separation of Nd and lighter rare-earth elements from Tm, only for column loadings  $B \leq 50\%$  is a high enrichment factor achieved for the combined sample of micro elements, since transfer of the tri-dialkylphosphates of the lanthanides to  $\text{Ln}[\text{H}(\text{DEHP})_2]_3$  is necessary for elution of these elements. However, for close pairs of elements the ratio (12) permits estimation of the maximum column loading for which satisfactory separation can be carried out. In particular, for separation of Tb from Er  $B_{\text{max}} = 21\%$ . This loading permits samples to be obtained which contain up to 80% of the Tb formed in nuclear reactions or present as an impurity. The content of erbium in the sample was no more than  $2 \cdot 10^{-4}\%$  of that loaded into the column.

The separation column for processing of highly radioactive targets had a diameter of about 26 mm and a bed height of 400-410 mm (Fig. 12). The glass tube 1 containing the bed is mounted with rubber gaskets into a glass heating jacket 2 containing water and the heating elements 3. Thermistor probes 5 monitor the heating temperature and maintain it at a given level. A system of glass and magnetic valves provides remote servicing of the column, which is placed behind a biological shield.



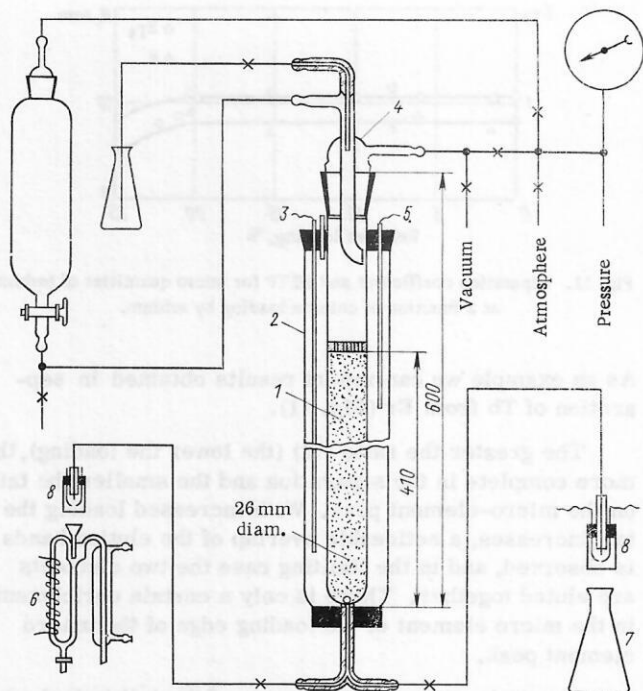


Fig. 12. Diagram of a column for separation of submicrogram quantities of rare-earth nuclear-reaction products and macro quantities of the lanthanide target material: 1) bed; 2) heating jacket; 3) heating elements; 4) head; 5) thermistor probes; 6) evaporator; 7) flask; 8) contact probes.

They permit a partial vacuum or excess pressure to be produced in the column, the active solution to be loaded to the head 4, the active solution to be forced down through the bed and collection of the effluent either in the fast acting evaporator 6 or in the flask 7. Contact probes 8 connected to electromechanical counters (type SB-1 M/100) permit the volume of solution which has passed through the column to be determined accurately from the number of drops ( $\pm 0.1$  ml). The latter is very important, since the complex chemical and isotopic composition of the sample obtained after bombardment of the rare-earth target by high-energy protons makes it impossible to

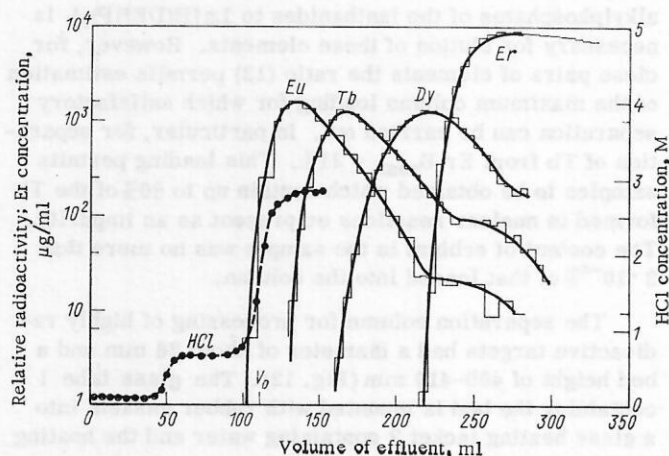


Fig. 13. Separation of micro quantities of Eu, Tb, and Dy from 2 g of erbium. The column is 26 mm in diameter and 410 mm long, the bed is based on Eisenach silica gel of  $70 \pm 10 \mu$ ,  $Q \approx 0.6$  ml/g, the eluant is 2.86 M HCl,  $1.3 \text{ ml/cm}^2 \cdot \text{min}$ ,  $40^\circ\text{C}$ .

determine  $V_A$  radiometrically. After a preliminary calculation it is necessary to determine  $V_A$  more accurately in model separations and then to use this value in working with highly radioactive solutions. Experience shows that a value of  $V_A$  once determined for a given column with accurate observation of the loading conditions remains constant within  $\pm 0.1$  ml. In order to assure that the light lanthanide sample will not be contaminated by the target material, its collection is cut off 3 ml before reaching  $V_A$ .

The results of model experiments on separation of micro quantities of light lanthanides from gram quantities of Er and Gd are shown in Figs. 13 and 14. From 2 g of Er in about 40 min, counting from the time of loading the sample into the column, it is possible to separate  $15 \pm 5\%$  of the Dy,  $68 \pm 8\%$  of the Tb,  $82 \pm 6\%$  of the Gd, and of the order of 90–95% of the lighter lanthanides formed in the irradiation. The yield of Pm from a Gd target of mass 1.9 g is about 60% and is higher for other lighter rare-earth elements which are products of deep spallation reactions. The entire procedure from the end of the irradiation to the production of radiochemically pure samples of individual rare-earth elements occupies no more than 3 hours. The method described is very reliable. The bed in the columns does not change its property in the course of two or three years while performing in it during this time several tens of working and model separations.

Erbium targets for obtaining highly radioactive sources of light rare-earth elements have been used for an extended cycle of investigations of excited levels of nuclei of the transition region formed in decay of Tb isotopes<sup>62,63</sup> and Gd, Eu, and Sm isotopes.<sup>64–69,74</sup> These nuclei are near the limit of the region of static deformation, and in some excited states they may have a quite appreciable deformation. For the correct theoretical interpretation of the properties of these nuclei it was also necessary to have accurate and comprehensive information on their nuclear spectroscopy.

Since we also obtained from erbium targets with a relatively high yield rare earths lighter than Sm, some measurements were made<sup>70–73</sup> with sources of Nd, Pr,

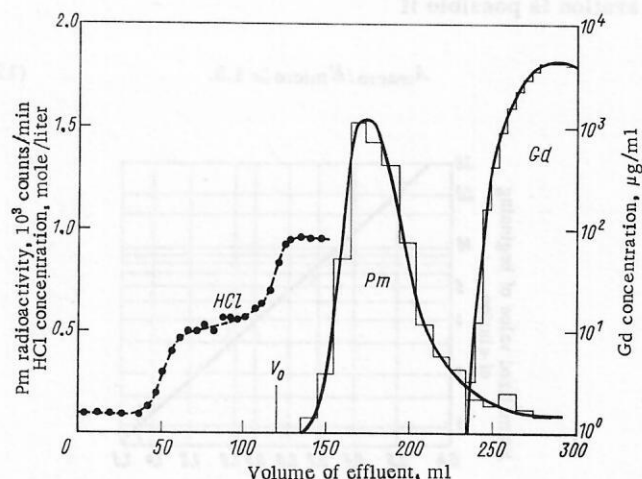


Fig. 14. Separation of Pm from 1.9 g of gadolinium. The column is 26 mm in diameter and 410 mm long, the bed is based on Eisenach silica gel of  $70 \pm 10 \mu$ ,  $Q \approx 0.6$  ml/g, the eluant is 0.95 M HCl,  $1.3 \text{ ml/cm}^2 \cdot \text{min}$ ,  $40^\circ\text{C}$ .

Ce, and La. However, a gadolinium target was generally used in preparation of these rare-earth isotopes.

In addition to their radiochemical use, silica gel columns with HDEHP are very useful in the analytical scheme.<sup>27</sup> Together with our colleagues of the State Rare-Metals Research Institute (GIREDMET), we have developed on the basis of extraction chromatography a technique for increasing the sensitivity of analysis of Y of high purity for content of rare-earth impurities.<sup>28</sup> An enrichment of  $10^5$  times substantially increases the sensitivity of the analysis of Y in quantitative determination of the content of impurity elements by the methods of emission spectroscopy and neutron-activation analysis.

## 2. SEPARATION OF MACRO AND MICRO QUANTITIES OF RARE-EARTH ELEMENTS BY MEANS OF ANION-EXCHANGE RESINS

The anion-exchange method of processing targets of rare-earth metals was developed in parallel with extraction chromatography. It was evident beforehand that, in contrast to the universal technique of reversed-phase partition chromatography, the field of application of anion-exchange resins (anionites) was limited mainly to the cerium subgroup of the lanthanides. However, for solution of particular problems, for example, in processing of a gadolinium target, the anion-exchange process is more convenient than extraction by HDEHP — a liquid cationite.

Use of anionites for separation of rare-earth elements has been discussed in great detail in several reviews.<sup>16,76,77</sup> It is known that rare-earth elements are not sorbed from mineral acid solutions by ionites of the quarternary ammonium base types.<sup>9,78,79</sup> The only exceptions are the very lightest rare earths: La, Ce, and Pr; in study of the sorption of these elements in Dowex-1 in 4–8 M  $\text{HNO}_3$ , partition coefficients  $2 < D < 10$  have been observed.<sup>80,81</sup> The low separation factors of the light rare-earth elements permit use of anion exchange in nitric-acid solutions only for group enrichment.

Significantly better sorption of lanthanides occurs in strongly basic anionites from concentrated nitrate solu-

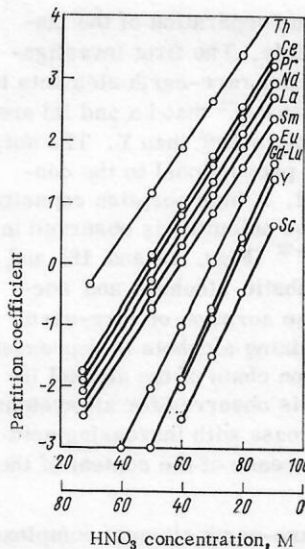


Fig. 16. Effect of methanol concentration on the coefficients for partition of rare-earth elements between nitric-acid (0.5 M  $\text{HNO}_3$ ) aqueous-methanol solutions and anionites of Dowex 1X8, 100-200 mesh.<sup>85</sup>

tions. Thus, Danon<sup>82</sup> showed that the partition coefficients of praseodymium are directly proportional to the concentration of nitrates and increase in the following sequence as the nature of the cation is changed in the solutions:  $\text{H} < \text{NH}_4 < \text{Li} < \text{Ca} < \text{Cu} < \text{Fe} < \text{Al}$ . When 4.4 M  $\text{LiNO}_3$  is used as eluant in a column of the anionite Dowex 1  $\times$  6, La and Ac are satisfactorily separated.<sup>82</sup>

The use of  $\text{LiNO}_3$  for separation of lanthanides has been studied in more detail by Marcus and co-workers.<sup>83,84</sup> The authors reached the conclusion that only this salt is suitable for chromatographic fractionation of the combined light lanthanides. The partition coefficients and separation factors of the rare earths increase with increasing concentration of  $\text{LiNO}_3$ . These quantities are negatively affected by reduction of the pH below 2. For  $[\text{LiNO}_3] > 4$  M and  $\text{pH} \approx 3$  the values of  $D$  and  $\beta$  obtained indicate the possibility of carrying out anion-exchange separation of the light lanthanides. Actually, by using gradient elution by a  $\text{LiNO}_3$  solution whose concentration falls from 6 to 3 M at a rate 0.16 mole/free volume, it is possible to carry out a successful fractionation of a mixture of light rare earths at 78°C.<sup>83</sup>

By analogy with the extraction of rare earths by high-molecular-weight quarternary amines, it is suggested<sup>84</sup> that a nitrate complex of the form  $[\text{Ln}(\text{NO}_3)_5]^{2-}$  is sorbed as the anionite. Experiments on electromigration confirm the existence of negatively charged compounds of rare-earth elements in concentrated nitrate solutions.

Anion exchange in solutions of  $\text{LiNO}_3$  (and possibly<sup>80</sup>  $\text{NH}_4\text{NO}_3$ ), while it permits separation of neighboring lanthanides to be carried out at elevated temperatures and with the gradient-elution technique, is not very suitable for application to highly radioactive samples, mainly because of the subsequent processing of the effluents. A certain difficulty is also contributed by the need for obtaining large quantities of lithium nitrate of high purity.

A more promising direction of the search for realization of anion-exchange methods for separation of lanthanides is the use of aqueous-organic systems, which have been successfully used<sup>85</sup> in analysis of complex mixtures of elements. It has been shown<sup>86</sup> that in hydrochloric acid aqueous organic solutions all lanthanides behave identically.

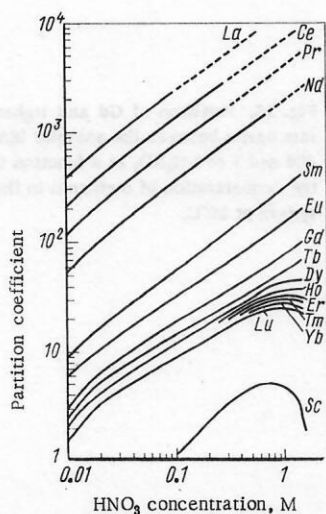


Fig. 15. Variation of rare-earth partition coefficient as a function of nitric-acid concentration. The anionite is Dowex 1X4, 200-400 mesh, 10% aqueous solution of  $\text{HNO}_3$ —90%  $\text{CH}_3\text{OH}$  (ref. 76).



However, in nitric acid systems separation of the lanthanides turned out to be possible. The first investigations of the behavior of individual rare-earth elements in ethanol-nitric acid solution showed<sup>81</sup> that La and Nd are sorbed by anionites significantly better than Y. The sorption in Dowex 1 × 8 is directly proportional to the concentration of HNO<sub>3</sub> and alcohol. A high sorption capacity of lanthanides by strongly basic anionites is observed in aqueous methanol solutions<sup>87-92</sup> (Figs. 15 and 16) and in solutions containing other aliphatic alcohols and acetone.<sup>88,93-96</sup> In the general case sorption of rare-earth elements from solutions containing alcohols is depressed as the length of the hydrocarbon chain of the alcohol is increased. A similar pattern is observed for all systems; The partition coefficients increase with increasing acid concentration and fall with decrease of the content of the nonaqueous component.

The composition of the rare-earth element complexes sorbed from nitric-acid aqueous alcohol solutions has apparently not been determined experimentally. In acetone solutions it was found that all lanthanides form nitrate complexes of the same composition: [Ln(NO<sub>3</sub>)<sub>5</sub>]<sup>2-</sup> (ref. 97). Sorption of rare-earth elements from alcohol and acetone solutions is qualitatively quite identical.<sup>95</sup> On the basis of this we can suggest that in both cases similar compounds are sorbed. It is most likely that, as in sorption of concentrated LiNO<sub>3</sub> solutions,<sup>84</sup> these are pentanitrates of lanthanides. Mixed aqueous alcohol solutions are used successfully for group separations of lanthanides of heavier atomic weight from the lighter lanthanides.<sup>88,90,92,93</sup> For example,<sup>90</sup> in an anion-exchange column of diameter 1.4 cm and length 9 cm a model mixture was separated which consisted of Y (8 mg), Er, Dy, Gd, Eu, Sm, (0.8 mg each), Nd, Pr, Ce, and La (1 mg each). The combined heavy elements (Sm-Er) and yttrium were eluted with 65% CH<sub>2</sub>OH-35% 3.5-N HNO<sub>3</sub>, 0.75 ml/min, and the combined light elements (La-Nd) by water (Fig. 17). In this experiments the column loading was about 1% if we proceed from the assumption that the resin sorbs an anion complex which connects the two functional groups of the anionite: R<sub>2</sub><sup>+</sup>[(NO<sub>3</sub>)<sub>5</sub>La]<sup>2-</sup> (ref. 84). A time of 4-5 hours was required for the separation shown in Fig. 17.

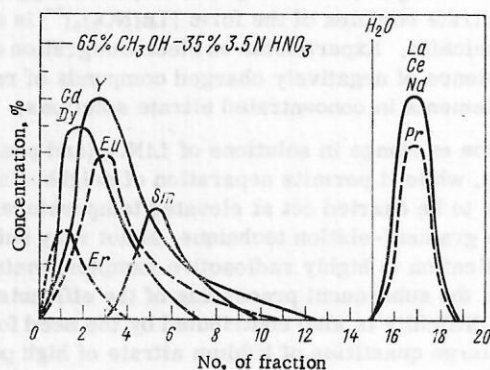


Fig. 17. Curves for elution of rare-earth elements from a column filled with anionite De Acidite FFX7-9, 100-200 mesh, diameter 14 mm by length 90 mm; elution by HNO<sub>3</sub>-CH<sub>3</sub>OH solution 0.75 ml/min, by water 1 ml/min. The initial sample was 8 mg Y, 0.8 mg each of Er, Dy, Gd, Eu, and Sm, and 1 mg each of Ce, Nd, Pr, and La in 5 mg of eluting solution. The volume of the fraction was 14 ml (ref. 90).

TABLE 3. Coefficients for Partition of Gadolinium between IRA 400 and 65% Methanol-1N Nitrate Solution at 20°C

| Cation                       | D   | Cation           | D   |
|------------------------------|-----|------------------|-----|
| H <sup>+</sup>               | 3,6 | Ba <sup>2+</sup> | 4,8 |
| Li <sup>+</sup>              | 6,4 | Ca <sup>2+</sup> | 1,2 |
| Na <sup>+</sup>              | 2,2 | Mg <sup>2+</sup> | 4,9 |
| NH <sub>4</sub> <sup>+</sup> | 3,2 |                  |     |

TABLE 4. Values of Parameters  $\alpha$  and Separation Factors  $\beta$  of Light Lanthanides in the Systems 65% CH<sub>3</sub>OH-NH<sub>4</sub>NO<sub>3</sub>-IRA 400 at 20°C,  $\beta = 1.50$

| Element  | Gd   | Eu   | Sm   | Pm   | Nd   | Pr   | Ce   | La   |
|----------|------|------|------|------|------|------|------|------|
| $\alpha$ | 3.2  | 4.5  | 6.5  | 11.1 | 17.3 | 27.1 | 40.4 | 53.0 |
| $\beta$  | 1.40 | 1.44 | 1.71 | 1.56 | 1.56 | 1.49 | 1.31 |      |

In some original and review papers on anion-exchange chromatography of rare-earth elements in nitric-acid aqueous alcohol solutions the suitability of the method for separation of neighboring elements is indicated. However, nowhere are specific experimental data presented. Furthermore, in the review by Stewart et al.<sup>77</sup> it is remarked that in aqueous alcohol and particularly in aqueous methanol mixtures it is hardly possible to carry out chromatographic separation of rare-earth elements in anionites, because of the partial overlapping of the elution bands of the neighboring lanthanides. The only relatively successful separation has been accomplished with replacement of alcohol by acetone.<sup>95</sup> An important deficiency of the method is, first, its duration and, second, the instability of the eluant used [for example, a mixture of 40% HNO<sub>3</sub> (d = 1.42 g/ml)-60% acetone spontaneously exploded after 24 hours].

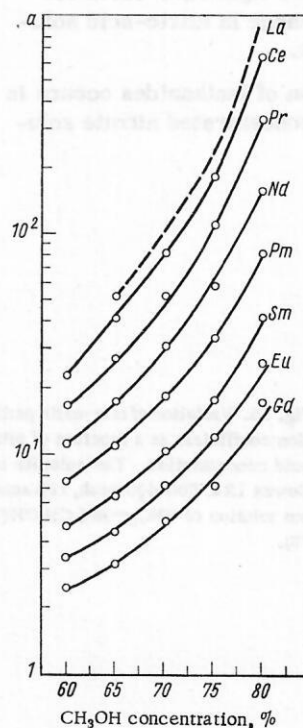


Fig. 18. Partition of Gd and lighter rare earths between the anionite IRA 400 and 1 M NH<sub>4</sub>NO<sub>3</sub> as a function of the concentration of methanol in the system at 20°C.

It appeared evident that anion-exchange separation of rare earths from aqueous organic solutions can be carried out more cleanly at elevated temperatures of the chromatographic column. Then as the result of improvement in the kinetic factors the separation time is shortened and more sharply defined bands for elution of individual elements are obtained. However, for systems containing relatively large amounts of  $\text{HNO}_3$ , an increase in the temperature will be accompanied by acceleration of oxidation reactions between alcohol and the anionite.

It appeared to us that a solution of the problem would be to use as eluants diluted aqueous organic solutions of nitrates, which are stable at elevated temperatures. Such systems had not been used previously for chromatographic anion-exchange separation of rare earths. Therefore we made a check of the possibility of using them for this purpose.<sup>98</sup>

Methanol was chosen as the nonaqueous component mainly because the sorption of lanthanides in anionites has been studied in greatest detail in nitric-acid aqueous methanol systems, in which good reproducibility of the results is observed. These results were very useful both for comparison and for orientation in the first stages of the work with neutral nitrate systems. A large part of the experiments were carried out with a highly basic anionite of the quarternary ammonium type IRA 400 (400 mesh) in nitrate form. On replacement of this anionite by Dowex 1  $\times$  8, practically identical results are obtained.

The principal objects of our investigations were systems with relatively low  $D$  values ( $D < 10^2$ ), since the final purpose of the studies was to choose the optimal conditions for rapid removal of the target materials and for obtaining concentrates of radioactive isotopes of the light lanthanides with a macro-component content no greater than  $10^{-4}$  g. The partition coefficients were calculated from the results of experiments with radioactive rare-earth isotopes, carried out either under statistical conditions on the basis of the specific radioactivities of the resin and solutions after equilibrium is reached or under dynamic conditions from the volume  $V_{\text{max}}$  corresponding to the maximum radioactivity of the effluent [Eq.(19)]:

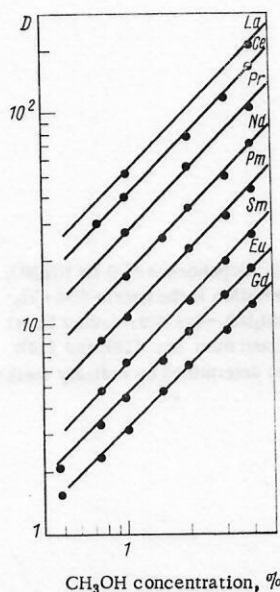


Fig. 19. Partition coefficients for Gd and the lighter rare earths as a function of  $\text{NH}_4\text{NO}_3$  concentration in a system of 65%  $\text{CH}_3\text{OH}$ - $\text{NH}_4\text{NO}_3$ -IRA 400 at 20°C.

$$D = (V_{\text{max}} - V_0)/g, \quad (13)$$

where  $V_0$  is the free volume of the column and  $g$  is the mass of absolutely dry resin loaded into the column in grams.

The first determinations, which were carried out with micro quantities of Gd, confirmed the suggestion that rare-earth elements can be sorbed by anionites from aqueous methanol solutions of nitrates. As was expected, on the basis of our ideas on the effect of solvation of lanthanide ions on their anion-exchange sorption, in solutions of identical composition but containing different cations the distribution coefficients  $D$  were different (Table 3). For systems with monovalent cations the highest  $D$  values were observed in the presence of  $\text{Li}^+$  - the most strongly hydrated cation. We particularly note the low  $D$  in  $\text{Ca}(\text{NO}_3)_2$  solutions. Under these conditions evidently  $\text{Ca}$  is sorbed by the anionite and thus reduces the probability of sorption of Gd. The dependence of the absorption by the IRA 400 resin of Gd and the lighter lanthanides on the content of methanol in the mixture (Fig. 18) and the concentration of ammonium nitrate (Fig. 19) is qualitatively the same as in sorption of rare-earth elements in Dowex 1  $\times$  8 from nitric-acid aqueous methanol solutions (see Figs. 15 and 16). In the region of  $\text{NH}_4\text{NO}_3$  concentration studied,  $\log D$  for all light lanthanides is a linear function of  $\log [\text{NH}_4\text{NO}_3]$  with a slope close to unity. This means that the dependence of  $D$  on the  $\text{NH}_4\text{NO}_3$  concentration in aqueous methanol mixtures is described by equations of straight lines passing through the origin. Consequently in this case to a good approximation we can write

$$D = a [\text{NH}_4\text{NO}_3], \quad (14)$$

where  $a$  is a constant characteristic of each lanthanide for given methanol content, temperature, and the form of the anion-exchange resin. Equation (14) is valid for methanol contents  $55\% \leq C \leq 85\%$ . The ratio of the parameters  $a$  of two lanthanides corresponds to their separation factor  $\beta$  under the specific experimental conditions. The values of  $a$  and  $\beta$  for the system 65%  $\text{CH}_3\text{OH}$ - $\text{NH}_4\text{NO}_3$ -IRA 400 at a temperature of 20°C are given in Table 4.

With increase of the temperature to 60°C the coefficient  $D$  decreased, but the separation factors remained

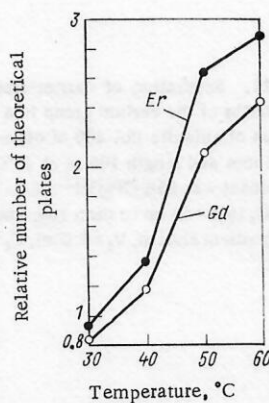


Fig. 20. Effect of temperature on relative number of equivalent theoretical plates of a column filled with the anionite IRA 400. The eluant was 65%  $\text{CH}_3\text{OH}$ -2.5 M  $\text{NH}_4\text{NO}_3$ .



practically constant.<sup>98</sup> As we should expect, with increasing temperature the quality of the chromatographic separations of the light rare earths in highly basic anionites improved sharply as the result of the rise in the number of equivalent theoretical plates in the columns (see Fig. 20).

At increased temperatures, by utilizing elution of lanthanides by an aqueous methanol solution with decreasing concentration of ammonium nitrates, we succeeded for the first time in achieving in an anion-exchange column the chromatographic separation of the combined group of all elements of the cerium subgroup of the rare earths<sup>99</sup> (Fig. 21). A continuous variation of the eluant composition is achieved by means of a simple system consisting of a closed mixing chamber and a reservoir. The variation of the nitrate concentration in the mixing chamber can be described by the equation<sup>100</sup>

$$C(v) = C_0 + (C_1 - C_0) \exp(-v/V_1), \quad (15)$$

where  $C_0$  and  $C_1$  are the initial concentrations of nitrate in their reservoir and in the mixing chamber, and  $V_1$  is the mixing chamber volume. Since in our experiments  $C_0 = 0$ , Eq. (15) takes the form

$$C(v) = C_1 \exp(-v/V_1). \quad (16)$$

The linear nature of the dependence of the light-lanthanide partition coefficients on the concentration of the salt in the system  $\text{CH}_3\text{OH}-\text{NH}_4\text{NO}_3$ -IRA 400 as shown by Eq. (14) permitted us to derive an equation which, for elution of an element from an anion-exchange column by a solution with decreasing  $\text{NH}_4\text{NO}_3$  concentration, relates the volume  $V_Z$  corresponding to the maximum in the rare-earth elution curve to the atomic number  $Z$  and the constant parameter  $a$  for this lanthanide:<sup>99</sup>

$$V_Z = V_0 + V_1 \ln \left( \frac{aC_1g}{V_1} + 1 \right). \quad (17)$$

It is particularly valuable to be able to calculate with Eq. (17) the value of the parameter  $a$  over a wide range of experimental conditions:

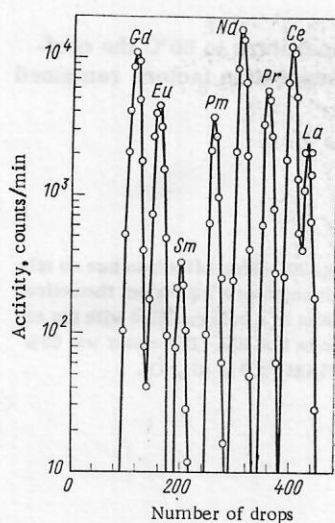


Fig. 21. Separation of carrier-free rare earths of the cerium group in a column of anionite IRA 400 of diameter 2 mm and length 105 m at 50°C. The eluant was 65%  $\text{CH}_3\text{OH}$ -2.5 M  $\text{NH}_4\text{NO}_3$  (pH = 2) up to drop 100, and then gradient elution,  $V_1 = 2.0$  ml,  $C_1 = 2.5$  M.

TABLE 5. Values of  $a$  and Separation Factors for Light Rare-Earth Elements in the System 80%  $\text{CH}_3\text{OH}-\text{NH}_4\text{NO}_3$ -IRA 400 at 20°C

| Element | Gd   | Eu   | Sm   | Pm   | Nd   | Pr   | Ce   | La   |
|---------|------|------|------|------|------|------|------|------|
| $a$     | 16.2 | 26.1 | 42.0 | 81.4 | 156  | 330  | 631  | 1065 |
| $\beta$ | 1.52 | 1.61 | 1.94 | 1.92 | 2.12 | 1.91 | 1.69 |      |

$$a = V_1 [\exp(V_Z - V_0)/V_1 - 1]/C_1g. \quad (18)$$

By carrying out a separation of the combined light lanthanides by the gradient elution method for any chosen methanol contents and temperatures, it is possible to obtain the dependence of  $a$  and consequently  $D$  on these factors for the entire group of elements simultaneously under the conditions of interest. This method requires much less time than other methods of determining  $D$ .

The values of  $a$  determined by the gradient-elution method are given in Table 5.

In Fig. 22 we have shown the calculated values of  $D$  and those determined by the ordinary methods. It is evident that the results are in good agreement.

The studies of anion-exchange sorption of microquantities of rare-earth elements from aqueous methanol solutions of nitrates served as a basis for design of the experiments which were carried out for the purpose of collecting information on separation of the combined microquantities of light rare earths and macro quantities of a neighboring lanthanide. The elution of macro quantities of Gd, Sm, Nd, and Pr from columns filled with highly basic anionites was studied<sup>101-103</sup> with a 10% loading of the resin (Figs. 23-25). The shapes of the peaks for (see Fig. 23c, Figs. 24a and b, and Figs. 25a and b).

The conclusion of all the experiments performed is clearly that anion exchange from aqueous methanol solutions of neutral nitrates presents new possibilities for efficient separation of rare-earth products of deep-spall-

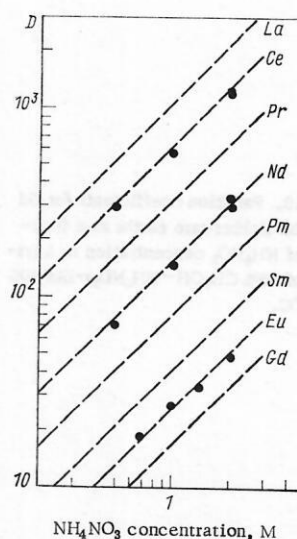


Fig. 22. Dependence of  $D$  on  $\text{NH}_4\text{NO}_3$  concentration in the system 80%  $\text{CH}_3\text{OH}-\text{NH}_4\text{NO}_3$ -IRA 400: dashed lines) calculated from Eqs. (18) and (14); circles) determined by ordinary methods.

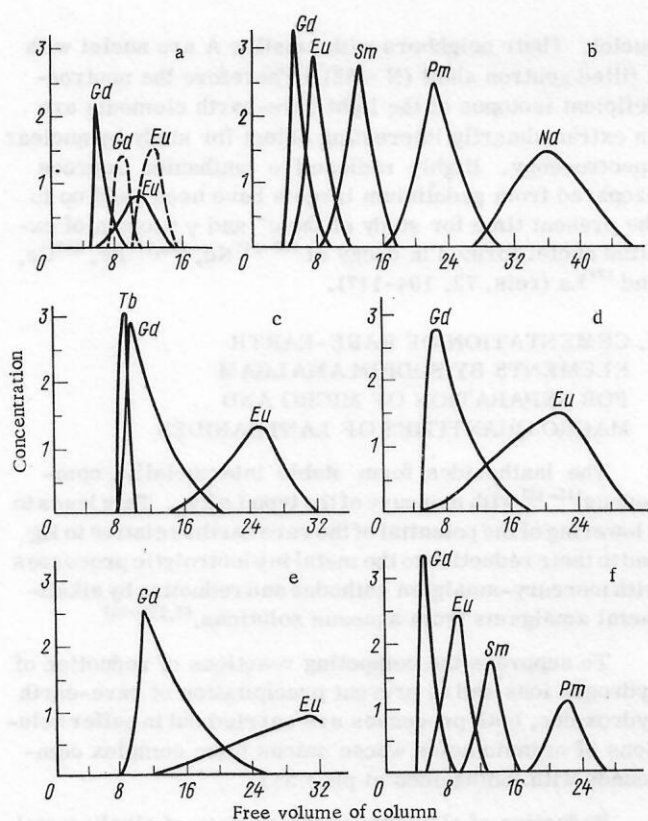


Fig. 23. Anion-exchange chromatographic separation of traces of light rare-earth elements and macro quantities of Gd in a column anionite IRA 400, 200-400 mesh, 0.3 cm<sup>2</sup> by 22.5 cm long; 60 mg Gd<sub>2</sub>O<sub>3</sub> for elution by: a) 70% CH<sub>3</sub>OH-2 M NH<sub>4</sub>NO<sub>3</sub>, 2 ml/cm<sup>2</sup>·min; at 50°C; dashed curves) separation of submicrogram quantities of Eu and Gd under similar conditions; b) 80% CH<sub>3</sub>OH-0.3 M NH<sub>4</sub>NO<sub>3</sub>, 2 ml/cm<sup>2</sup>·min, at 50°C; anionite Dowex 1 × 8; c) 80% CH<sub>3</sub>OH-1.5 M NH<sub>4</sub>NO<sub>3</sub>, 1 ml/cm<sup>2</sup>·min; at 50°C; d) 80% CH<sub>3</sub>OH-1.5 M NH<sub>4</sub>NO<sub>3</sub>, 1 ml/cm<sup>2</sup>·min, at 50°C; 120 mg Gd<sub>2</sub>O<sub>3</sub>; e) 80% CH<sub>3</sub>OH-1.1 M NH<sub>4</sub>NO<sub>3</sub>, 1 ml/cm<sup>2</sup>·min, at 20°C; f) 65% CH<sub>3</sub>OH-2.5 M NH<sub>4</sub>NO<sub>3</sub>, 2 ml/cm<sup>2</sup>·min, at 50°C.

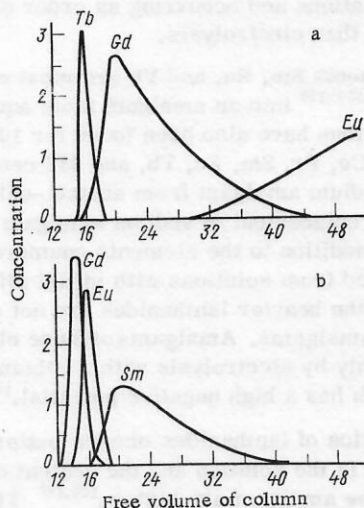


Fig. 24. Anion-exchange chromatographic separation of traces of rare-earth elements and 60 mg of Gd<sub>2</sub>O<sub>3</sub> or Sm<sub>2</sub>O<sub>3</sub>. Anionite IRA 400, 200-400 mesh; the column is 0.3 cm<sup>2</sup> in area and 22.5 cm long; temperature is 50°C; 1 ml/cm<sup>2</sup>·min of: a) 85% CH<sub>3</sub>OH-1.5 M NH<sub>4</sub>NO<sub>3</sub>; b) 80% CH<sub>3</sub>OH-1.5 M NH<sub>4</sub>NO<sub>3</sub>. Under these conditions neodymium is washed out after the 90th free volume of the column.

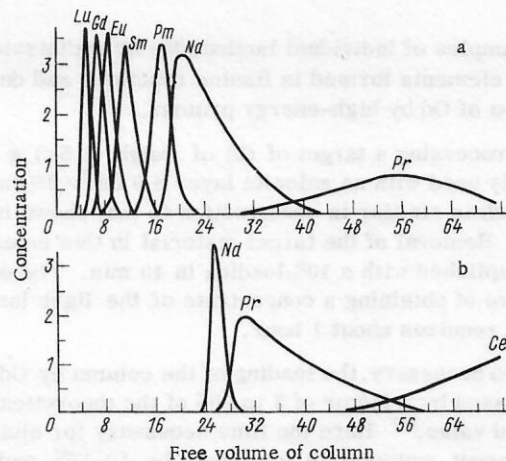


Fig. 25. Separation of macro quantities of Nd or Pr and traces of rare-earth elements. The column is 0.3 cm<sup>2</sup> by 22.5 cm; 50°C: a) 60 mg Nd<sub>2</sub>O<sub>3</sub>, 80% CH<sub>3</sub>OH-0.5 M NH<sub>4</sub>NO<sub>3</sub>, Dowex 1 × 8; 2 ml/cm<sup>2</sup>·min; b) 30 mg Pr<sub>6</sub>O<sub>11</sub>, 80% CH<sub>3</sub>OH-1.5 M NH<sub>4</sub>NO<sub>3</sub>, IRA 400; 1 ml/cm<sup>2</sup>·min.

lation reactions in lanthanide targets. The conditions of separation are easy to vary, depending on the physical problem at hand. For example, from bombarded Gd it is not expedient, as a rule, to separate Eu, since it can be obtained with a high yield from Er. In this case the purpose of the primary processing of the target is rapid removal of Gd with subsequent elution of a radioactive concentrate containing Sm and lighter elements. For carrying out this operation it is most convenient to elute Gd by 65% CH<sub>3</sub>OH-2.5 M NH<sub>4</sub>NO<sub>3</sub> (see Fig. 23f) or 80% CH<sub>3</sub>OH-0.3 M NH<sub>4</sub>NO<sub>3</sub> (see Fig. 23b) with subsequent elution of Sm and other light lanthanides by 0.02 M HNO<sub>3</sub>.

As the dimensions of the anion-exchange column are increased in proportion to the quantity of lanthanide sorbed on the resin, provided that the loading remains of the order of 10% of the theoretically suggested loading, satisfactorily reproducible yields of the micro elements and purification of their concentrates from the target material are always obtained. The stability of the results of the separation permits successful processing of highly radioactive samples on the basis merely of model-experiment data and without monitoring the composition of the effluents, which is relatively complicated to do in a hot experiment.

In Fig. 26 we have shown as a qualitative illustration a radiochromatogram obtained<sup>162</sup> on elution from an anion-exchange column of Gd and the nuclear-reaction products formed on its bombardment by 660-MeV protons. The radioactivity of the primary fractions (1-5 column free volumes) is due to elution of Rb, Cs, Ca, Sr, Ba, Sc, Y, Ti, V, Cr, Mn, Zr, Co, Cu, Ag, Zn, Cd, Ga, In, and probably certain other elements whose behavior has not been investigated. Then Tb and Gd were eluted. The maximum radioactivity in 10-12 column free volumes corresponds to elution of Gd and Eu. The effluent is practically free from the target material after 13 column free volumes. The combined light lanthanides are therefore then eluted with 0.02 M HNO<sub>3</sub>. The concentrate obtained contains of the order of 10<sup>-5</sup>% of Gd, 10% of Eu, 85% of Sm, and 100% of lighter lanthanides. Separation of this group in a cationite in the course of elution of it by ammonium  $\alpha$ -hydroxyisobutyrate did not reveal any contamination



of the samples of individual lanthanides by radioisotopes of other elements formed in fission reactions and deep spallation of Gd by high-energy protons.

In processing a target of Gd of weight 1.5-3 g a column is used with an anionite layer  $8.5 \text{ cm}^2 \times 25 \text{ cm}$  long which is similar in construction to that shown in Fig. 12. Removal of the target material in this column is accomplished with a 10% loading in 40 min. The entire procedure of obtaining a concentrate of the light lanthanides requires about 1 hour.

When necessary, the loading of the column by Gd can be increased by a factor of 2 to 20% of the theoretically predicted value.<sup>102</sup> Here the time necessary for elution of the target material is increased by 10-15% and the extraction of Eu and Sm in the concentrate of radioisotopes is somewhat reduced (to 5% and 75%, respectively). In addition to Gd targets, targets of Nd have also been processed<sup>102</sup> by anion-exchange chromatography.

Examples of anion-exchange separations of macro and micro quantities of rare-earth elements illustrate the instability of the technique as applied to problems of preparative radiochemistry of the elements of the cerium subgroup of the lanthanides.

Anion-exchange chromatography in aqueous methanol solutions of neutral nitrates at elevated temperatures has become the principal method of separating macro and micro quantities of rare earths in processing of Gd targets. In this particular case, in our opinion, the method is somewhat more convenient to use than extraction chromatography with HDEHP as an immobilized phase. In the first place, the preparation of the separation columns, which are filled with commercial resins, is simpler and, in the second place, the combined light lanthanides are eluted from the column with water or very dilute acid, which permits faster and simpler preparation of the concentrates for separation into individual elements by means of a cation-exchange microchromatographic column.

The main purpose in using Gd targets is to obtain lanthanide isotopes with  $135 < A < 145$ , which lie between the new deformation region and the region of spherical

nuclei. Their neighbors with smaller  $A$  are nuclei with a filled neutron shell ( $N = 82$ ). Therefore the neutron-deficient isotopes of the light rare-earth elements are an extraordinarily interesting object for study by nuclear spectroscopy. Highly radioactive lanthanide sources prepared from gadolinium targets have been used up to the present time for study of the  $e^-$  and  $\gamma$  spectra of excited nuclei formed in decay of  $^{136-141}\text{Nd}$ ,  $^{138,140}\text{Pr}$ ,  $^{132}\text{Ce}$ , and  $^{134}\text{La}$  (refs. 72, 104-117).

### 3. CEMENTATION OF RARE-EARTH ELEMENTS BY SODIUM AMALGAM FOR SEPARATION OF MICRO AND MACRO QUANTITIES OF LANTHANIDES

The lanthanides form stable intermetallic compounds<sup>118-121</sup> with mercury of the type  $\text{LnHg}_n$ . This leads to a lowering of the potential of the rare earths relative to Hg and to their reduction to the metal in electrolytic processes with mercury-amalgam cathodes and reduction by alkali-metal amalgams from aqueous solutions.<sup>67,121-157</sup>

To suppress the competing reactions of reduction of hydrogen ions and to prevent precipitation of rare-earth hydroxides, both processes are carried out in buffer solutions of organic acids whose anions form complex compounds with lanthanides at  $\text{pH} = 3-7$ .

Reduction of elements at the surface of alkali-metal amalgams is called cementation, like similar electrochemical processes in which the metal being separated acquires the electrons of the displacing metal, which goes into solution. The general concepts of the cementation of metals by amalgams have been well described in Kozlovskii's monograph.<sup>158</sup>

For separation of macro and micro quantities of lanthanide target material and the nuclear-reaction products it has turned out to be possible to use both electrolysis and cementation. However, preference has been given to the cementation process as more convenient for remote separations and occurring an order of magnitude more rapidly than electrolysis.

The elements Sm, Eu, and Yb are most easily extracted<sup>122-125,139-150</sup> into an amalgam from aqueous solutions. Conditions have also been found for 100% cementation of La, Ce, Pr, Sm, Eu, Yb, and 93% cementation of Nd by 0.2% sodium amalgam from acetate-chloride solutions.<sup>126</sup> On replacement of sodium amalgam by 0.06% Li amalgam, in addition to the elements enumerated 30-35% Gd is extracted from solutions with initial  $\text{pH} = 3.09-4.19$ . Terbium and the heavier lanthanides are not cemented by alkali-metal amalgams. Amalgams of these elements can be obtained only by electrolysis with a lithium-amalgam cathode, which has a high negative potential.<sup>151,155-157</sup>

Cementation of lanthanides occurs better if their concentration in the solution and the content of the alkali metal Na in the amalgam are higher.<sup>126,128</sup> The efficiency of cementation is reduced in the transition from Li or Na amalgams to amalgams of K (ref. 128), Rb, and Cs (ref. 131).

Cementation of Sm, Eu, and Yb is less sensitive to the nature of the cementing metal.<sup>128</sup> It is suggested<sup>128,129,131</sup> that this is due to reduction of these rare-earth elements

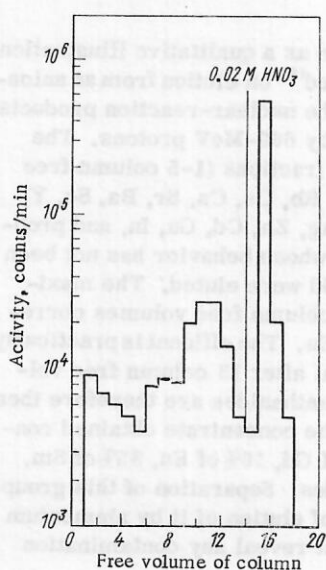
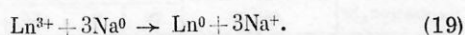


Fig. 26. Radiochromatogram of anion-exchange separation of Gd bombarded by 660-MeV protons, and the nuclear-reaction products. 260 mg of Gd, column with Dowex  $1 \times 8$ , 200-400 mesh,  $1.5 \text{ cm}^2 \times 25 \text{ cm}$ ; 80%  $\text{CH}_3\text{OH}$ -0.6 M  $\text{NH}_4\text{NO}_3$ , 2.6 ml/cm<sup>2</sup>·min.

to metals through divalent states where discharge of the triply charged ions occurs at the surface of the amalgam for the remaining lanthanides:



Although the extraction of lanthanides from aqueous solutions by cementation (and by electrolysis from a mercury-amalgam cathode) is unquestionably an electrochemical process, explanation of why some elements are quantitatively extracted by amalgams and others under these conditions remain completely in solution is not possible on the basis of only the normal oxidation potentials of the rare-earth elements<sup>159</sup> or the emf of the amalgam cells.<sup>128</sup> Therefore the observed general effect must be interpreted as the sum of electrochemical and hydrolytic reactions.<sup>128</sup> The sizes of the hydrated cations of the rare-earth elements increase from La to Lu and, consequently, the heavier the element, the more probable is the formation of mononuclear and polynuclear hydrolyzed cations in solutions even with relatively low pH values. The general tendency for a reduction in the capacity to be cemented with increasing atomic number of the rare-earth elements is explained by the formation of nonreducible polynuclear hydroxy and aqua complexes of the lanthanides. For elements which form stable divalent weakly hydrolyzed ions, this tendency is destroyed.

There is also another point of view regarding the causes of the different amalgamation of the lanthanides (and actinides).<sup>146</sup> These authors proceeded from the idea of stability of the eventual divalent state of the rare-earth elements. The idea of an "amalgamation period" was proposed to describe the transition of the elements to the amalgam. The less stable the intermediate divalent state, the longer the amalgamation period and the poorer the extraction of the elements into the amalgam. Cementation by sodium amalgam of Cf, Es, Fm, and Md is considered from the same point of view by Maly and co-workers.<sup>132-134</sup>

Separation of rare earths by cementation has not been greatly used in preparative radiochemistry. We know of only two articles, on the separation by means of Na amalgam of short-lived isotopes of Eu with mass numbers 142, 143, and 144 from Sm bombarded by protons,<sup>135</sup> and on the cementation by lithium amalgam of <sup>155</sup>Eu from a solution containing a mixture of fission products.<sup>136</sup> In both cases an isotopic carrier was used. Information on the cementation of lanthanides in states free of carriers is practically nonexistent except for certain data in refs. 132-134.

The cementation of micro quantities of rare-earth elements ( $10^{-10}$ – $10^{-12}$  g) has been investigated by us for the case of lanthanide extraction by sodium amalgam from acetate-chloride solutions.<sup>160</sup> Study of the cementation of micro quantities of Sm, Eu, and Yb, which have a stable divalent state, showed that, other conditions being equal, the quantity of an element which transfers to the amalgam depends on the concentration of the sodium acetate buffer (Table 6).

This effect is due, first of all, not to complex formation but is the result of the different degrees of oxidation by  $\text{Na}^0(\text{Hg})\text{H}^+$  acetic-acid ions. For example, from 0.65

TABLE 6. Cementation of Yb, Eu, and Sm by 2 ml of 0.53% Na Amalgam from 10 ml of Acetate Buffer Solutions of Various Concentrations with Initial pH = 2.8. Mixing Was by Bubbling  $\text{N}_2$  for 2 min at a Temperature  $20 \pm 2^\circ\text{C}$

| [Na <sup>+</sup> + H <sup>+</sup> ] Acet | pH after cementation | Cementation, % |    |    | [Na <sup>+</sup> + H <sup>+</sup> ] Acet | pH after cementation | Cementation, % |     |     |
|------------------------------------------|----------------------|----------------|----|----|------------------------------------------|----------------------|----------------|-----|-----|
|                                          |                      | Yb             | Eu | Sm |                                          |                      | Yb             | Eu  | Sm  |
| 0.4                                      | 6.4–6.5              | 97             | 98 | 98 | 0.75                                     | 5.20–5.28            | 33             | 48  | 88  |
| 0.5                                      | 6.1–6.3              | 98             | 97 | 96 | 0.80                                     | 5.10–5.16            | 2.6            | 9.0 | 52  |
| 0.6                                      | 5.6–5.8              | 96             | 98 | 97 | 0.85                                     | 5.0–5.13             | 0.23           | 2.2 | 6.0 |
| 0.65                                     | 5.65–5.75            | 97             | 96 | 98 | 0.90                                     | 4.85–4.93            | —              | 1.2 | 2.4 |
| 0.70                                     | 5.58–5.62            | 74             | 84 | 98 | 0.95                                     | 4.8                  | —              | —   | 1.3 |

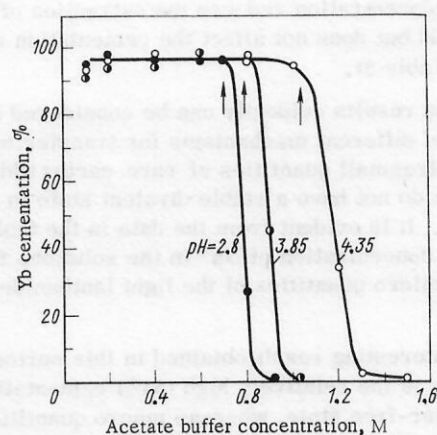


Fig. 27. Cementation of carrier-free ytterbium by 0.56% sodium amalgam from sodium-acetate buffer solutions of various concentrations. The arrows mark points corresponding to equivalent quantities of  $\text{Na}^0$  and  $\text{HAcet}$  in the system before cementation.

M buffer solution in 2 min, 96% of Eu is cemented. Because of neutralization the pH rises to 5.75, which corresponds to  $[\text{CH}_3\text{COO}^-] = 0.59$  M. If we use a 0.8 M buffer, then 9% of Eu is cemented, although under these conditions the neutralization proceeds only to pH = 5.16 and, consequently, the acetate-ion concentration is smaller:  $[\text{CH}_3\text{COO}^-] = 0.57$  M. A high degree of cementation ( $\geq 95\%$ ) is only achieved when the initial quantity of  $\text{Na}^0(\text{Hg})$  is equivalent to (or greater than) the content of  $\text{CH}_3\text{COOH}$  in the buffer solution (Fig. 27). If this condition is not

TABLE 7. Cementation of Ce, Pr, Nd, and Eu by 2 ml of 0.53% Na Amalgam from 10 ml of Acetate Buffer Solutions of Various Concentrations with Initial pH = 3.85. Mixing by Mechanical Agitator for 2 min at  $20 \pm 2^\circ\text{C}$

| $\Sigma [\text{Acet}], \text{M}$ | pH after cementation | Cementation, % |    |    |    |
|----------------------------------|----------------------|----------------|----|----|----|
|                                  |                      | Ce             | Pr | Nd | Eu |
| 0.2                              | 6.8–7.15             | 86             | 88 | 89 | 88 |
| 0.3                              | 6.85–6.91            | 88             | 90 | 89 | —  |
| 0.4                              | 6.58–6.71            | 88             | 90 | 88 | 94 |
| 0.5                              | 6.25–6.42            | 89             | 87 | 85 | —  |
| 0.6                              | 5.87–6.03            | —              | 81 | 68 | 94 |
| 0.7                              | 5.77–5.84            | 85             | 71 | —  | —  |
| 0.8                              | 5.63–5.71            | 69             | 54 | 40 | 81 |
| 1.0                              | 5.18–5.24            | 44             | 30 | 17 | 5  |
| 1.2                              | 4.89–4.93            | 22             | 17 | 10 | 1  |



satisfied, then, after the Na, oxidation of micro quantities of the cemented lanthanides by  $H^+$  ions begins (see Fig. 27).

For elements which do not have a stable divalent state, other conditions being equal, cementation also decreases with increasing acetate-buffer concentration but not so rapidly as for Sm, Eu, and Yb (Table 7).

This is apparently due to the higher stability of amalgams of Ce, Pr, and Nd. In particular, it has been shown<sup>124</sup> that Nd amalgam is more stable than Sm amalgam.

Since the Na amalgam potential decreases with increasing concentration of  $Na^+$  in the buffer solution, it was possible to predict that for this reason the cementation of the lanthanides will also be reduced. Actually an increase in NaCl concentration reduces the extraction of Ce, Pr, Nd, and Gd but does not affect the cementation of Sm, Eu, and Yb (Table 8).

These results evidently can be considered as an indication of different mechanisms for transfer to Na amalgam of ultrasmall quantities of rare earths which have and which do not have a stable divalent state in aqueous solutions. It is evident from the data in the table that the tolerable concentration of  $Na^+$  in the solutions for cementation of micro quantities of the light lanthanides is less than 1 M.

An interesting result obtained in this series of experiments is the relatively high (54%) cementation of Gd in a carrier-free state, whereas macro quantities of Gd are practically not extracted by Na amalgam. In working with the lanthanides from Lu to Tb, which are not cemented by Na amalgam in macro quantities, it was found that their radioactive isotopes in carrier-free states also are not cemented: The extraction of Lu, Tm, and Er was less than 10<sup>-3</sup>%.

The first experiments on separation of micro and macro quantities of rare earths by cementation were carried out with Ce, Nd, Eu, and Tb. It was learned that the cementation is sharply reduced at a Tb concentration as low as 0.1 mg/ml (Fig. 28). This is probably due to sorption of micro quantities of the hydroxide of Tb, which is formed directly at the surface of the amalgam where neutralization of  $H^+$  ions results in a zone<sup>161,162</sup> with pH = 11-12. Therefore it appeared quite possible that in cementation of micro quantities in a background of noncementing macro quantities the extraction increases with intensive mixing of the amalgam and the solution as the result of a decrease in the thickness of the hydroxide layer and an increase and partial renewal of the amalgam surface. This hypothesis was checked in the case of micro quantities of Ce and Eu which were cemented by a 0.52% amalgam of Na from 0.4 M buffer-acetate solutions with pH = 3.75 containing various quantities of heavy lanthanides.<sup>163</sup> In one series of experiments only the solution above the amalgam was stirred, and in another, the solution and the amalgam simultaneously. In order to be able to compare the effect of macro quantities of heavy lanthanides on the cementation process for different mixing conditions, the solution and amalgam were stirred 3 min, and the solution only, for 10 min; in both cases about 85% of the Ce was extracted from solutions not containing macro quantities of rare earths.

TABLE 8. Effect of NaCl Concentration on Cementation of Lanthanides by 2 ml of 0.33% Na Amalgam from 10 ml of 0.25 M Acetate-Buffer Solutions with Initial pH = 3.85. The Mixing Is by Mechanical Stirring for 4 min at 20 ± 2°C

| NaCl concentration, M | pH after cementation | Cementation, % |    |     |    |    |     |    |  |
|-----------------------|----------------------|----------------|----|-----|----|----|-----|----|--|
|                       |                      | Ce             | Pr | Nd  | Sm | Eu | Gd  | Yb |  |
| 0.1                   | 6.11-6.28            | 94             | 93 | 95  | 95 | 95 | 54  | 96 |  |
| 0.3                   | 5.45-5.60            | 90             | 93 | —   | —  | —  | —   | —  |  |
| 0.5                   | 5.55-5.87            | 88             | 92 | 86  | 95 | 95 | 11  | 97 |  |
| 1.0                   | 5.49-5.63            | 81             | 90 | 77  | 97 | 98 | 6.5 | 96 |  |
| 1.5                   | 5.23-5.43            | 71             | 80 | 51  | 95 | 95 | 1.8 | 97 |  |
| 2.0                   | 5.35-5.56            | 65             | 75 | 43  | 97 | 97 | 0.8 | 96 |  |
| 2.5                   | 5.34-5.4             | 56             | 52 | 26  | 97 | 98 | —   | 97 |  |
| 3.0                   | 5.12-5.3             | 48             | 45 | 14  | 98 | 99 | —   | 97 |  |
| 3.5                   | 5.10-5.18            | 41             | 25 | 11  | 96 | 96 | —   | 97 |  |
| 4.0                   | 5.05-5.20            | 34             | 16 | 7.5 | 97 | 97 | —   | 97 |  |

TABLE 9. Dependence of the Degree of Cementation of Micro Quantities of Ce and Eu on the Concentration of Noncementing Rare-Earth Elements; 5 ml 0.52% Na(Hg), 25 ml 0.4 M Acetate-Buffer Solution with Initial pH = 3.75, at 20 ± 2°C; Propeller Mixer with d = 25 mm, 500 rpm.

| Noncementing element | Concentration of noncementing element, M | Mixing of solution             |                                | Mixing of amalgam and of solution |                                |
|----------------------|------------------------------------------|--------------------------------|--------------------------------|-----------------------------------|--------------------------------|
|                      |                                          | degree of cementation of Ce, % | degree of cementation of Eu, % | degree of cementation of Ce, %    | degree of cementation of Eu, % |
| Tb                   | 10 <sup>-5</sup>                         | 84±2                           | 83±4                           | —                                 | —                              |
|                      | 10 <sup>-4</sup>                         | 55±2                           | 57±5                           | 90±9                              | 95±4                           |
|                      | 10 <sup>-3</sup>                         | 29±5                           | 42±7                           | 78±4                              | 92±3                           |
|                      | 10 <sup>-2</sup>                         | —                              | —                              | 65±4                              | 84±3                           |
| Er                   | 10 <sup>-5</sup>                         | 83±6                           | 83±3                           | —                                 | —                              |
|                      | 10 <sup>-4</sup>                         | 45±4                           | 61±3                           | 90±8                              | 96±2                           |
|                      | 10 <sup>-3</sup>                         | 23±7                           | 48±4                           | 79±6                              | 89±2                           |
|                      | 10 <sup>-2</sup>                         | —                              | —                              | 60±8                              | 61±12                          |
| Lu                   | 10 <sup>-5</sup>                         | 80±6                           | 87±3                           | —                                 | —                              |
|                      | 10 <sup>-4</sup>                         | 38±8                           | 60±2                           | 84±8                              | 96±2                           |
|                      | 10 <sup>-3</sup>                         | 4±1                            | 42±10                          | 74±4                              | 92±2                           |
|                      | 10 <sup>-2</sup>                         | —                              | —                              | 58±4                              | 69±2                           |

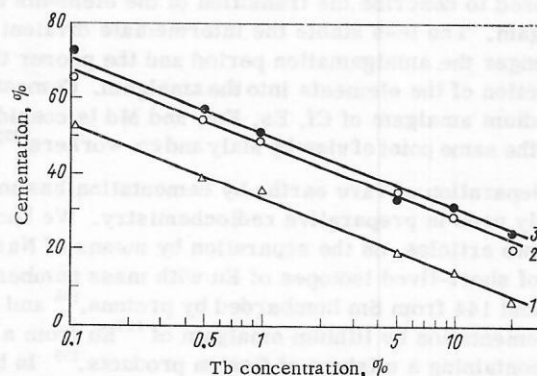


Fig. 28. Dependence of cementation of submicrogram quantities of Nd (1), Ce (2), and Eu (3) on the concentration of noncementing Tb: pH = 3.85, 2 ml 0.53% Na(Hg), 10 ml, 0.4 M sodium-acetate buffer; mixing by bubbling nitrogen for two minutes.

The most important result of the experiments on cementation of Ce and Eu in the presence of weighable quantities of heavy elements (Table 9) is the decrease of the negative effect of noncementing rare earths on extraction of light lanthanides with simultaneous stirring of the amalgam and the solution. If only the solution is stirred, the cementation is practically suppressed even at centimolar concentrations of Tb, Er, and Lu. Under these conditions for millimolar concentrations of Tb and Lu the dependence of the cementation on the nature of the noncementing ion is very clearly observed.

TABLE 10. Dependence of the Degree of Cementation of Micro Quantities of Light Rare-Earth Elements on the Concentration of Chloride of Tb in the Solution, with Mixing of the Amalgam and Solution by a Propeller Stirrer with 25 mm Diameter and 500 rpm; 5 ml 0.52% Na(Hg), 25 ml 0.4 M Acetate-Buffer Solution with Initial pH = 3.75, at  $20 \pm 2^\circ\text{C}$

| Terbium chloride concentration, M | Degree of cementation, % |                   |                   |                   |                   |                                    |                                    |                   |
|-----------------------------------|--------------------------|-------------------|-------------------|-------------------|-------------------|------------------------------------|------------------------------------|-------------------|
|                                   | <sup>140</sup> La        | <sup>144</sup> Ce | <sup>143</sup> Pr | <sup>146</sup> Nd | <sup>143</sup> Pm | <sup>152</sup> , <sup>153</sup> Eu | <sup>151</sup> , <sup>159</sup> Gd | <sup>169</sup> Yb |
| $10^{-4}$                         | 88±6                     | 90±9              | 88±3              | 90±5              | 91±3              | 95±2                               | 60±5                               | 93±4              |
| $10^{-3}$                         | 80±7                     | 68±4              | 81±6              | 83±4              | 80±6              | 92±3                               | 54±5                               | 88±4              |
| $10^{-2}$                         | 66±2                     | 65±4              | 70±4              | 62±4              | 67±4              | 84±3                               | 41±4                               | 83±4              |
| $10^{-1}$                         | 55±3                     | 54±4              | 50±6              | 52±5              | 53±3              | 75±4                               | 39±4                               | 76±5              |

These data are in good agreement with existing ideas<sup>128</sup> according to which cementation of rare earths by amalgams of alkali metals is a combination of two processes: hydrolysis of rare-earth ions at the surface of the amalgam where neutralization of  $\text{H}^+$  ions produces a solution layer with a high pH, and electrochemical reduction of rare-earth ions at the cathode portions of the amalgam.

It is quite likely that in buffer solutions, as occurs in our case, the pH rises monotonically as the Hg surface is approached. If this assumption is correct, the layer of hydroxide of Lu, other conditions being equal, will be larger than the layer of Tb, since the solubility product<sup>164</sup> of  $\text{Lu}(\text{OH})_3$  is smaller than that of  $\text{Tb}(\text{OH})_3$ :  $1 \cdot 10^{-27}$  and  $4.9 \cdot 10^{-27}$ , respectively. However, the larger the hydroxide layer, the more probable is the capture by the hydroxide of micro quantities being cemented, and therefore Ce is cemented more poorly from solutions containing Lu than from terbium solutions.

Europium, which has a stable divalent state, is less sensitive to the presence of weighable quantities of Tb, Er, and Lu. This can be explained by the fact that the first stage of the reduction  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  cannot be suppressed as the result of hydrolysis of  $\text{Eu}^{3+}$  ions, since the standard potential of this pair relative to a mercury cathode is about  $-0.6$  V relative to a saturated calomel electrode, and the  $\text{Eu}^{2+}$  formed is not captured by the hydroxides of noncementing additives.

The results of cementation of most light rare earths and Yb, obtained with simultaneous mixing of the amalgam and solutions containing from  $10^{-4}$  M to  $10^{-1}$  M of Tb, are shown in Table 10. They demonstrate that even for a decimolar concentration of Tb about half of all light rare earths is separated from the solution by a single cementation. Consequently the products of deep-spallation reactions in Tb can be relatively simply and rapidly separated from the target material by cementation with Na amalgam.

On the basis of the results obtained we developed and successfully checked by experiment a method of separating Gd and lighter rare earths from Tb bombarded by 660-MeV protons in the internal beam of the JINR synchrocyclotron.<sup>163</sup> The main advantage of the cementation method was rapid elimination (no more than 10 min) of the target material with a relatively high chemical yield of radioactive sources of rare earths of the cerium subgroup: at least 40% of Gd and more than 60% of other elements after double extraction of lanthanides by 20 ml of Na amalgam from 100 ml of solution. Unfortunately, the necessity of using large quantities of highly toxic mercury with

remote operation is a substantial drawback of the method, and for this reason cementation, given the existence in our laboratory of other methods,<sup>28,33,38,101</sup> has not found wide application for separation of macro and micro quantities of lanthanides.

However, separation of rare earths on the basis of the cementation method, which is rapid and selective with respect to individual rare earths, in some cases turns out to be the most convenient and sometimes even the only possible solution of the problems of source preparation which arise in nuclear spectroscopy. In particular, cementation by Na amalgam is used by us<sup>165</sup> for separation of daughter elements from <sup>167</sup>Lu, <sup>164</sup>Yb, <sup>142</sup>Sm, and <sup>149</sup>Tb.

Rapid cementation purification with Na amalgam yields sources of <sup>167</sup>Yb ( $T_{1/2} = 17.3$  min) which contain  $10^{-4}\%$  of radioactive impurities at the beginning of the measurements. As a result of the exceptionally high purity it is possible to observe<sup>166</sup> positron decay in this isotope and new weak transitions to the excited nucleus <sup>167</sup>Tm.

A high degree of purification has been achieved also in production of monoisotopic sources of <sup>145</sup>Eu ( $T_{1/2} = 5.6$  days) by the amalgam method from the Tb fraction, where it has accumulated as the result of  $\alpha$  decay of <sup>149</sup>Tb. The contamination of the separated Eu source by radioactive isotopes of Tb and Gd did not exceed<sup>167</sup>  $10^{-3}\%$ .

Sources of the short-lived isotopes <sup>164</sup>Tm ( $T_{1/2} = 2.0 \pm 0.1$  min) and <sup>142</sup>Pm ( $T_{1/2} = 41.3 \pm 0.4$  sec) were obtained by extraction into amalgam of the parent nuclei <sup>164</sup>Yb ( $T_{1/2} = 75$  min) and <sup>142</sup>Sm (73 min).

With suppression of the cementation of Pm, samarium is extracted from solutions 6 M in  $\text{NaClO}_4$ . At the beginning of the measurements the level of impurity of daughter isotopes was 3-5% of the total radioactivity. Although the purification was substantially poorer than in extraction of the element studied into amalgam, it was nevertheless sufficient to improve the half-lives of the isotopes and to study the  $\gamma$ -ray spectrum.<sup>168</sup>

#### 4. USE OF THE SZILARD-CHALMERS EFFECT TO OBTAIN SOURCES OF SHORT-LIVED NEUTRON-DEFICIENT ISOTOPES OF LANTHANIDES

Interest in the properties of neutron-deficient isotopes remote from the  $\beta$ -stability line and therefore having short half-lives has stimulated the search for fast methods of preparing radioactive sources for measurements with semiconductor detectors. In this case sources are required whose radioactivity is two or three orders of magnitude lower than in measurement of internal-conversion electron spectra by magnetic spectrometers.

Such sources are satisfactorily obtained on bombardment of targets by the external proton beam of the synchrocyclotron at the Laboratory of Nuclear Problems, Joint Institute for Nuclear Research, which at the present time has an intensity of  $6 \cdot 10^{11}$  protons/cm<sup>2</sup> · sec. The targets, on bombardment by the external beam, are heated only to 40-50°C, which permits bombardment of materials which are not thermally stable, suspensions, and solutions, as well as the use for separation of the recoil effect and chemical effects in nuclear transformations.



In particular, for preparation of short-lived isotopes of heavy rare earths, good results were obtained in bombardment of a suspension (0.5 g/ml) of 0.5–2 micron  $\text{Ta}_2\text{O}_5$  which had been heated<sup>169</sup> at 800°C. In 0.1 M HCl the partition coefficient of rare-earth products of nuclear reactions between the target material and solution was  $D \leq 0.1$  ml/mg. After the bombardment, of the order of 40% of the lanthanides are in the solution and are separated from the  $\text{Ta}_2\text{O}_5$  by filtration. The recoil effect permitted the time required for preparation of radioactive sources of neutron-deficient isotopes of heavy lanthanides to be shortened, which has led to discovery of new short-lived nuclei and to more careful study of those known previously,<sup>170</sup> for example,  $^{166}\text{Lu}$  ( $T_{1/2} = 3.2$  min) and  $^{168}\text{Lu}$  ( $T_{1/2} = 7$  min). Sources of lanthanides of the cerium subgroup of rare earths are obtained from a suspension of rare-earth phosphates;<sup>171</sup> however, phosphites are practically never used.

For separation of lanthanides on the basis of the nuclear recoil effect, rare-earth phthalocyanines specially synthesized for this purpose<sup>193</sup> are very promising. About 80% of the radioactivity was extracted from solutions of rare-earth phthalocyanines in quinoline diluted (5%) by  $\text{H}_2\text{SO}_4$  and bombarded by neutrons. With small radiation doses to the target material, the enrichment factors were of the order of  $10^4$ :

$$F = S_I/S_{II}, \quad (20)$$

where  $S_I$  is the specific radioactivity of the source of nuclear-reaction products in separated form and  $S_{II}$  is the specific radioactivity of the bombarded target. However, under intense fluxes of ionizing radiation the phthalocyanine compounds undergo relatively great radiation damage and the enrichment factors are greatly reduced.<sup>172,173</sup>

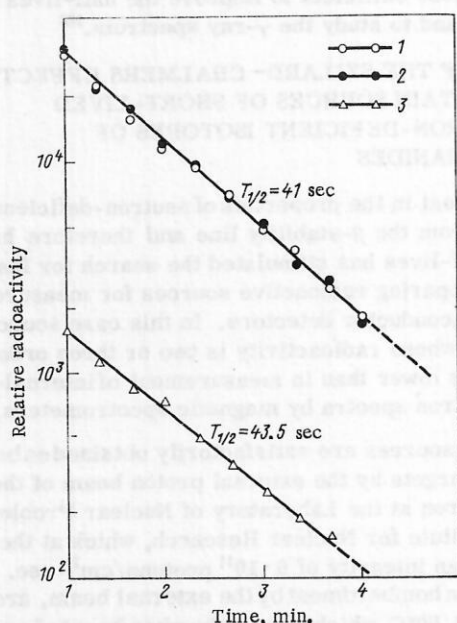


Fig. 29. Decay curves of  $^{142}\text{Pm}$  sources separated from samarium phthalocyanine by extraction (1), by extraction chromatography (2), and by elution from a finely dispersed precipitate of the compound (3).

Use of phthalocyanine compounds permitted for the first time the separation of nuclear isomers of neutron-deficient isotopes of lanthanides: Sources of the isotopes  $^{158}\text{Ho}$ ,  $^{160}\text{Ho}$ , and  $^{162}\text{Ho}$  were obtained in the ground state.<sup>174</sup> For separation of short-lived daughter isotopes from parent nuclei having a longer half-life, a continuous separation process was proposed in which a column filled with the finely dispersed phthalocyanine of the parent element was used.<sup>172</sup> With this method it was possible to separate  $^{161}\text{Ho}$  ( $T_{1/2} = 6.8$  sec) from  $^{161}\text{Er}$  ( $T_{1/2} = 3.8$  hours). Because of the high retention in the solid phase, the yield of the daughter products was small. The continuous-separation technique<sup>172</sup> was substantially improved by use of reversed-phase partition chromatography.<sup>175</sup> In this case hydrophobized silica gel is saturated with solutions of phthalocyanines in quinoline. This separation technique permitted the yield of daughter isotopes to be increased by 20–30 times in comparison with the method of Stenström and Jung<sup>172</sup> (Fig. 29).

In the case of dysprosium phthalocyanine<sup>176</sup> the possibility has been studied of using these compounds as the target material for bombardment by the external proton beam. It was established that the low radiation stability of the phthalocyanines and the relatively low content of the metal in the compounds make them rather unsuitable for this purpose.

It was desirable to find for replacement of the phthalocyanines compounds with a central lanthanide atom sufficiently strongly bound to assure a slow exchange-reaction rate and which had high radiation stability and solubility in water. These requirements were met by the very stable chelate complexes of rare earths with ethylenediaminetetraacetic acid ( $\text{H}_4\text{EDTA}$ ) and diethylenetriaminepentaacetic acid ( $\text{H}_5\text{DTPA}$ ). The possibility of using these compounds for separation of genetically related isobaric and isomeric pairs of lanthanides has been pointed out many times.<sup>177–179</sup> However, there were no publications on use of polyaminocarboxylic acids for rapid separation of sources by means of the Szilard–Chalmers effect. There were a few studies of the chemical effects of the decay of lanthanides bound with complexonates, and they were carried out entirely with  $\beta$ -active nuclei:  $^{177}\text{Yb}$  (ref. 177),  $^{143}\text{Ce}$  and  $^{144}\text{Ce}$  (refs. 178, 180–182).

The results of these studies lead to the following conclusions.

The multidentate nature of complexes in which radioactive decay of the central atom occurs prevents destruction of the initial molecules. The appearance of daughter atoms in ionic form is mainly due not to the effect of the recoil in  $\beta$  decay but to the appearance of ions of daughter elements whose charge is greater than +4. The high charge of the ion of the daughter element apparently is the main cause of the destruction of the initial molecule as the result of the appearance of repulsive Coulomb forces. Multiply charged ions are formed as the result of  $\gamma$ -ray internal conversion and "shaking" of the electron shells on the instantaneous change of the nuclear charge as the result of  $\beta$  decay.

The principal decay mode of neutron-deficient rare-earth isotopes is K capture and positron emission. As a rule the decay occurs to the excited levels of the daughter

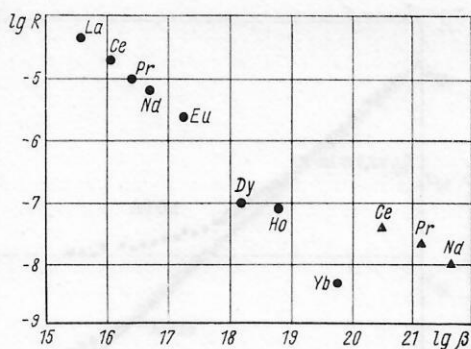


Fig. 30. Isotopic-exchange reaction rate  $R$  as a function of the stability constants  $\beta$  of the complexes  $\text{Ln}(\text{EDTA})^-$  (circles) and  $\text{Ln}(\text{DTPA})^{2-}$  (triangles). The rates in M/min were calculated from the data of refs. 178, 179, 182, 184-186 for  $\text{pH} = 6$ ,  $[\text{Ln}^{3+}] = [\text{Ln Y}] = 10^{-4}$  M at  $25^\circ\text{C}$ .

nuclei. The processes of K capture and  $\gamma$ -ray internal conversion are accompanied by emission of Auger electrons, which leads to accumulation of positive charges at the periphery of the atom. For example, the average charge of Xe ions formed as the result of the Auger effect is  $^{183} + 8.5$ .

Thus, it is evident that neutron-deficient nuclei of the lanthanides, after K capture or a converted  $\gamma$  transition, should destroy the initial molecule and be stabilized in ionic form. The above remarks refer entirely to nuclei formed in reactions induced by high-energy protons.

The enrichment factors and the extent of retention in the form of the initial molecules should only depend on the exchange-reaction rate and the radiation stability of the compounds. Careful studies<sup>178,179,184-187</sup> have been made of the rates of isotopic-exchange reactions of lanthanides in water solution containing ions and polyamino-polyacetate complexes of these elements. The principal factor affecting the exchange-reaction rate is the instability of the carboxyl groups of chelates with respect to interaction with  $\text{H}^+$  ions.<sup>184,186</sup> Therefore the isotopic-exchange reaction rates are directly proportional to the hydrogen-ion concentration. They also increase with increasing total concentration of lanthanides in the system and with increasing temperature. Other conditions being equal, the isotopic-exchange reaction rates are inversely proportional to the atomic number of the rare earth. This order corresponds in the first approximation to the thermodynamic stability of chelates in the lanthanide group.<sup>188</sup> As a result of the high stability of rare-earth complexes with  $\text{H}_5\text{DTPA}$ , which has eight coordination groups, reactions with isotopic exchange of  $^*\text{Ln}^{3+}/(\text{LnDTPA})^{2-}$  occur with a rate almost three orders of magnitude lower than in systems with  $\text{H}_4\text{EDTA}$  (Fig. 30).

The exchange of lanthanide-group elements of similar properties when one of them is in ionic form and the other in complex form occurs according to the same mechanism as in an isotopic-exchange reaction.<sup>184</sup> If macro and micro quantities of rare earths are taking part in the exchange, the exchange rate in the system  $^*\text{Ln}^{3+}_{\text{micro}}/(\text{LnEDTA})^-_{\text{macro}}$  is directly proportional to the concentration of  $(\text{LnEDTA})^-_{\text{macro}}$  and inversely proportional to  $[\text{Ln}^{3+}_{\text{macro}}]$  and to the ratio of the stability constants of the complexes<sup>184,186</sup>  $\beta_{\text{macro}}/\beta_{\text{micro}}$ . No studies

have been made of rare-earth exchange reactions in  $^*\text{Ln}^{3+}_{\text{micro}}/(\text{LnDTPA})^{2-}_{\text{macro}}$  systems. However, it is quite likely that the exchange rates will depend on the same factors as in systems with  $(\text{LnEDTA})^-$  and, other conditions being equal, they will be smaller.

From analysis of the data in the literature it follows that diethylenetriaminepentaacetate complexes of lanthanides are most promising for the purposes of source preparation in separation of isobaric and isomeric pairs of rare earths and for separation of rare-earth nuclear-reaction products from the target material. These compounds were the principal ones studied in our investigations aimed at development of methods of obtaining sources of short-lived neutron-deficient isotopes of elements of the rare-earth group.<sup>176,189-191</sup>

The separation of genetically related nuclear isobars was developed in the pairs  $^{134}\text{Ce}$  ( $T_{1/2} = 72$  hours)– $^{134}\text{La}$  ( $T_{1/2} = 6.5$  min) and  $^{140}\text{Na}$  ( $T_{1/2} = 3.3$  days)– $^{140}\text{Pr}$  ( $T_{1/2} = 3.5$  min); as an isomeric pair we selected  $^{160\text{m}}\text{Ho}$  ( $T_{1/2} = 5.3$  hours)– $^{160\text{g}}\text{Ho}$  ( $T_{1/2} = 28$  min). The optimum conditions for separation were selected in the case of the pair  $^{144}\text{Ce}$  ( $T_{1/2} = 284$  days)– $^{144}\text{Pr}$  ( $T_{1/2} = 17.3$  min). The purity and yields were estimated on the basis of data obtained in analysis of the decay curves of the daughter materials. By extrapolation of the curves to the end of the accumulation period  $t_0$ , we determined the total radioactivity  $J_{2,1}$  of the daughter isotopes and the contamination during this time.

Decomposition of the decay curves permitted determination of the quantity  $J_1$ : the radioactivity due to contamination of the daughter material with the parent isotopes, and the radioactivity of the daughter isotopes. The relative contaminations of the daughter materials by the parent isotopes are calculated according to the following equation:

$$V = (J_1/J_{2,1}) \cdot 100\%. \quad (21)$$

The relative yields of the daughter isotopes are determined from the equation

$$A = \frac{\lambda_2 - \lambda_1}{\lambda_2} \cdot \frac{J_{2,1} - J_1}{J_2} [\exp(-\lambda_1 \Delta t) - \exp(-\lambda_2 \Delta t)]^{-1} \cdot 100\%, \quad (22)$$

where  $\lambda_1$  and  $\lambda_2$  are the radioactive decay constants of the parent and daughter isotopes;  $J_2$  is the radioactivity of the daughter isotope in the material, which is taken for separation when radioactive equilibrium is reached; and  $\Delta t$  is the period of accumulation. The value of  $J_2$  was determined experimentally for each isobaric pair by means of standard sources of the parent isotopes. For the isomeric pair  $^{160\text{m}}\text{Ho}/^{160\text{g}}\text{Ho}$  the relative value  $J = 60 \pm 10\%$  was calculated on the basis of the known decay schemes and the positron energies of the ground and isomeric states.<sup>192</sup>

Genetically related isobaric and isomeric pairs of lanthanides were separated according to the following scheme.

To the initial preparation of carrier-free radioactive lanthanide we added a complexing agent and neutralized



the solution to pH = 8. Then we added to this solution a lanthanide carrier in amounts superequivalent with respect to the complexing agent, and a sulfocationite in  $\text{NH}_4^+$  form. The suspension obtained was violently mixed during the entire accumulation. After this the resin was filtered out and washed and the source was transferred to measurement. The filtrate was used for repeated separations of the daughter elements. For this purpose a lanthanide carrier and a new portion of ionite were added to it.

The optimal concentration of rare-earth chelate complexes in solutions prepared for separation of daughter isotopes is  $2 \cdot 10^{-4}$  M. It can be increased or decreased by an order of magnitude without loss of quality of the separations. However, the concentration of lanthanides in ionic form in these solutions did not exceed  $10^{-4}$  M. Under these conditions good separation can be obtained for any volume of solution. In working with  $(^{144}\text{CeEDTA})^-$  in the interval pH = 7.3–8.2 the contamination of  $^{144}\text{Pr}$  by the parent radioactivity reaches 4%. Significantly better results from the source point of view were obtained with  $(^{144}\text{CeDTPA})^{2-}$ . For this complex the contamination of about 0.3% remains constant over the range pH = 6.6–9.0. The source purity is practically unaffected by change of temperature over the range 0 to 25°C.

The data on the optimum pH values obtained in experiments with  $^{144}\text{Ce}/^{144}\text{Pr}$  were used in performing the separation of other pairs of nuclei:  $^{134}\text{Ce}/^{134}\text{La}$ ,  $^{140}\text{Nd}/^{140}\text{Pr}$  (Figs. 31 and 32), and  $^{160}\text{mHo}/^{160}\text{gHo}$  (Fig. 33). The yields of the daughter nuclei in separation of neutron-deficient isobaric and isomeric pairs were about 70% and did not depend on which complexing agent was used: EDTA or DTPA. The contamination by the parent radioactivity in the work with DTPA was from 0.05 to 0.5%, and in the work with EDTA it was respectively an order of magnitude higher.

The method of single separation of isobaric and isomeric pairs of lanthanides permits separation of daughter isotopes with half-lives of 3 min or longer from relatively long-lived parent isotopes ( $T_{1/2} \geq 1$  hour). Shorter-

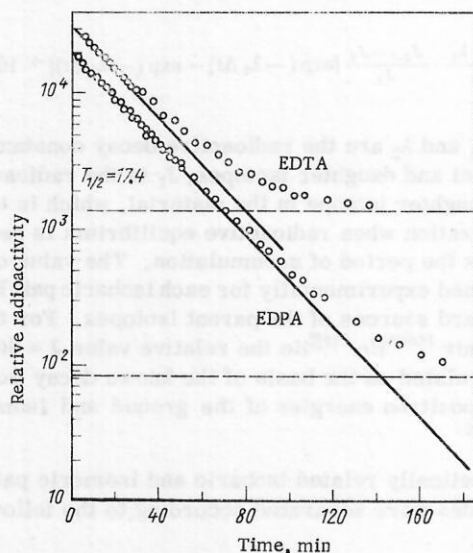


Fig. 31. Decay of  $^{144}\text{Pr}$  sources separated from  $^{144}\text{Ce}$  by EDTA and from  $^{144}\text{Ce}$  by DTPA on the basis of the Szilard–Chalmers effect.

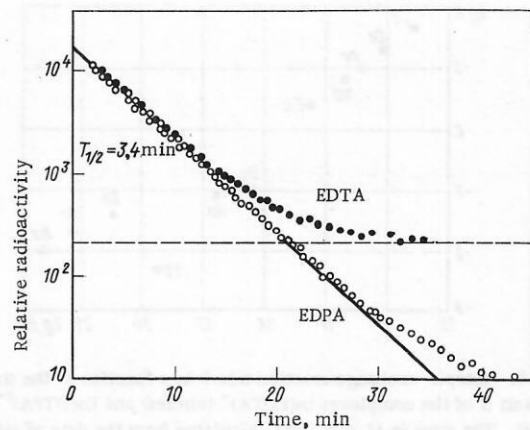


Fig. 32. Decay of  $^{140}\text{Pr}$  sources separated from  $^{140}\text{Nd}$  by EDTA and from  $^{140}\text{Nd}$  by DTPA on the basis of the Szilard–Chalmers effect.

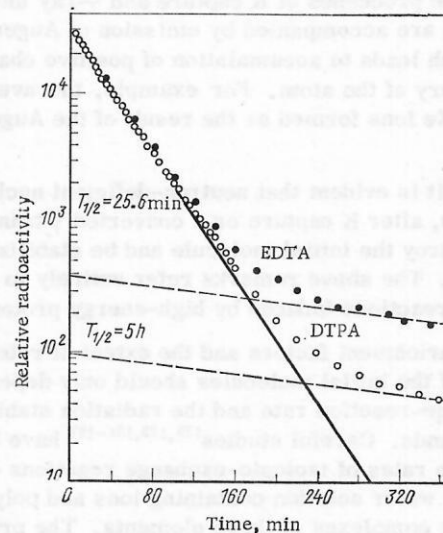


Fig. 33. Decay of  $^{160}\text{gHo}$  sources separated from  $^{160}\text{mHo}$  by EDTA and from  $^{160}\text{mHo}$  by DTPA on the basis of the Szilard–Chalmers effect.

lived daughter isotopes can be separated continuously by means of a small anion-exchange column in which the ionite is in the form of a complex anion of the parent element,  $(\text{LnDTPA})^{2-}$ . In separation of the pair  $^{140}\text{Nd}/^{140}\text{Pr}$  by this method with elution by a neutral  $10^{-6}$  M solution of  $\text{Pr}^{3+}$ , the daughter isotope in the flux of effluent is transferred to the  $\gamma$ -ray detector after  $15 \pm 3$  sec. The effluent contains  $30 \pm 15\%$  of the daughter nuclei, and the contamination by the parent radioactivity is 0.2–0.3%. Continuous separation permits in principle the measurement of  $\gamma$  spectra of daughter elements with  $T_{1/2} \geq 5$  sec. Here the measurement time is limited only by the half-life of the parent isotope and its loss with the effluent, which is mainly due to exchange reactions.

Thus, methods based on the chemical effects accompanying the decay of the parent nucleus in the complex anion  $^{189,190}(\text{LnDTPA})^{2-}$  satisfy rather well the requirements presented for separation of genetically related isobaric and isomeric pairs of rare earths from the point of view of purity, speed, chemical yield of the daughter isotopes, simplicity, and reproducibility. We should also note the relatively high radiolytic stability of solutions of

DTPA complexes of lanthanides. For example, from a sample of about 5 millicuries of  $^{134}\text{Ce}$  the daughter  $^{134}\text{La}$  was separated without appreciable contamination by the parent isotope assignable to radiolytic destruction of the initial compounds.

Dry compounds of the type  $(\text{LnDTPA})(\text{NH}_4)_2$  also reveal satisfactory radiation stability in a high-energy proton beam, which permitted their use as target materials in production of short-lived rare-earth isotopes.<sup>176,191,194</sup>

The radiolysis and retention were determined for complexes of Er, Dy, and Gd whose composition corresponded to the formula  $(\text{NH}_4)_2\text{LnC}_{14}\text{H}_{18}\text{N}_3\text{O}_{16} \cdot \text{H}_2\text{O}$ . The content of metal in the compounds was  $27.5 \pm 0.5\%$ . Synthesized compounds contain some accurately known excess of the target element within the limits of 0 to 1.8 mole%, which in solution of the complex goes into the solution in the ionic form

$$u \approx [\text{Ln}^{3+}]/[\text{Ln DTPA}^{2-}] \cdot 100\%. \quad (23)$$

It seems apparent that the data obtained will be valid also for compounds of other lanthanides. The bombardment of rare-earth complexes is carried out at room temperature. Under the action of the protons the target, according to our determinations, is heated to  $40^\circ\text{C}$ . The dose received by the target in the course of 1 hour was measured by means of a plastic dosimeter<sup>195</sup> and amounts to  $1.8 \cdot 10^7$  rad for an integrated flux of  $2 \cdot 10^{15}$  protons. The radiolytic destruction of  $(\text{NH}_4)_2\text{LnDTPA}$  is shown in Fig. 34 as a function of the integrated proton flux. Since the main purpose in the bombardments in the external proton beam was to obtain isotopes with  $T_{1/2} < 30$  min, exposures of more than 30 min are not desired. Radiolysis of the irradiated compounds led to formation during this time of 100  $\mu\text{g}$  of lanthanides in ionic form per gram of complex.

The relative total retention  $R_\Sigma$  of nuclear-reaction products was the result of two processes: retention as the result of stabilization of the radioactive atom in the solid phase  $R_s$  and the transition of ions to the complex as a result of exchange reactions  $R_i$  in solution of the irradiated complex,

$$R_\Sigma = R_s + R_i. \quad (24)$$

As a result of the exchange process the value of  $R$  is larger, the smaller the excess  $u$  (Fig. 35). For an  $\text{Ln}^{3+}$

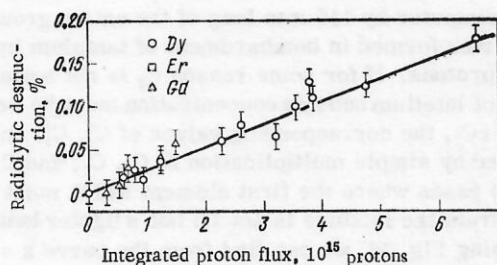


Fig. 34. Radiolytic destruction of dry complexes of compounds of Dy, Er, and Gd with DTPA on bombardment by 660-MeV protons, as a function of the integrated proton flux.

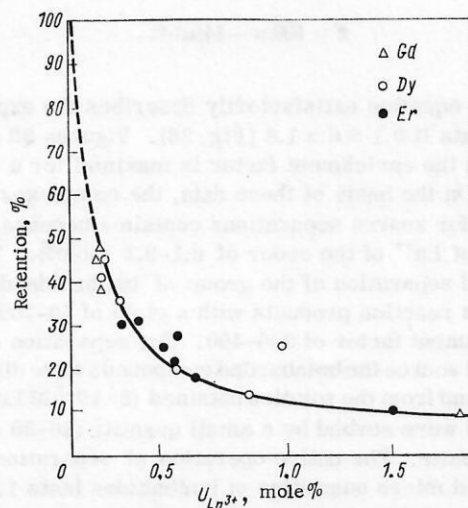


Fig. 35. Combined retention of radioactive rare-earth isotopes in complex form after bombardment of  $(\text{NH}_4)_2\text{Ln DTPA}$  by 660-MeV protons as a function of the stoichiometric excess of  $\text{Ln}^{3+}$  in the target compound  $u$ .

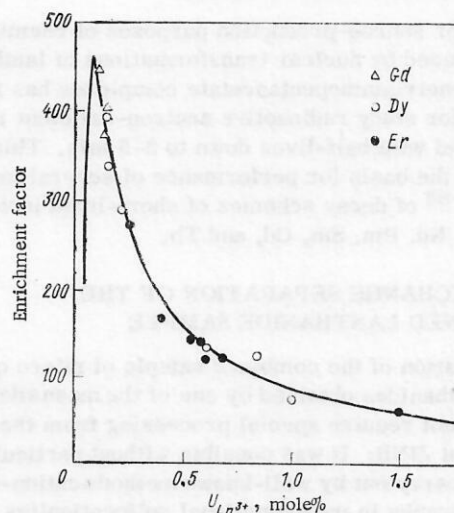


Fig. 36. Enrichment of a sample of radioactive rare earths in ionic form obtained in bombardment of  $(\text{NH}_4)_2\text{Ln DTPA}$  by 660-MeV protons, as a function of the stoichiometric excess of  $\text{Ln}^{3+}$  in the target compound  $u$ .

concentration in the range from 0.1 to 1.8 mole% the combined retention is satisfactorily described by the empirical equation

$$R_\Sigma = 14/u^{0.6}, \%. \quad (25)$$

The combined retention of radioactive rare earths in complex form depends very weakly on the concentration of the element in ionic form added during solution and is uniquely determined by the value of  $u$  in the target. The enrichment factor under the conditions of our experiments is not a constant, but changes as a function of the retention and the quantity of the target element present in ionic form:

$$F = (100 - R_\Sigma)/u. \quad (26)$$

If we replace  $R_\Sigma$  in Eq. (26) by Eq. (25), we obtain the expression:



$$F = 100/u - 14/u^{1.6}. \quad (27)$$

This equation satisfactorily describes the experimental data if  $0.1 \leq u \leq 1.8$  (Fig. 36). Figures 35 and 36 show that the enrichment factor is maximal for  $u = 0.1$  mole%. On the basis of these data, the complexes synthesized for source separations contain a necessary admixture of  $\text{Ln}^{3+}$  of the order of 0.1–0.2 mole%. This permitted separation of the group of lanthanide deep-spallation reaction products with a yield of 50–70% and an enrichment factor of 300–450. For separation of the combined source the bombarded compounds were dissolved in water and from the solution obtained ( $8 \cdot 10^{-2} \text{ M LnDTPA}^{2-}$ )  $\text{Ln}^{3+}$  ions were sorbed by a small quantity (20–30 mg) of sulfocationite. The entire operation of separation of macro and micro quantities of lanthanides lasts 1.5–2 min. The combined rare earths sorbed in the resin are then chromatographically separated into individual elements. Measurement of the separated lanthanide sources or their preparation for mass separation begins 10–15 min after the end of the irradiation.

Use for source-production purposes of chemical effects produced by nuclear transformations of lanthanides in diethylenetriaminepentaacetate complexes has made available for study radioactive neutron-deficient rare-earth nuclei with half-lives down to 3–5 min. This has served as the basis for performance of several investigations<sup>196–202</sup> of decay schemes of short-lived isotopes of Ce, Pr, Nd, Pm, Sm, Gd, and Tb.

##### 5. ION-EXCHANGE SEPARATION OF THE COMBINED LANTHANIDE SAMPLE

Separation of the combined sample of micro quantities of lanthanides obtained by one of the means described above did not require special processing from the radiochemists at JINR: It was possible without particular difficulty to carry out by well-known methods cation-exchange chromatography in monofunctional sulfocationites of a strongly acid type. As eluants in such cases it is most common to use solutions of salts of lactic acid (Lact) and  $\alpha$ -oxyisobutyric acid ( $\alpha$ -But) (refs. 203–218), with which rare earths give stable complex compounds<sup>219</sup> (Fig. 37). It is preferable to work with  $\alpha$ -But, which permits successful separation at room temperature.<sup>209, 213, 215, 216</sup>

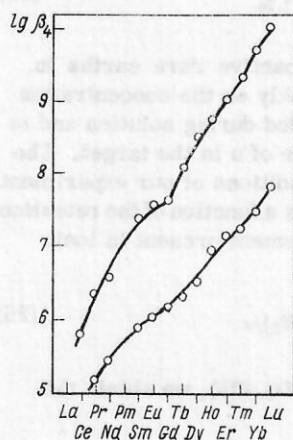


Fig. 37. Stability constants of lactate (lower curve) and  $\alpha$ -oxyisobutyrate (upper curve) complexes of lanthanides.<sup>219</sup>

In those cases in which the number of lanthanides to be separated in the mixture is greater than four, use is recommended of an eluant with a positive concentration gradient of ligand in the solution. Use of gradient elution greatly reduces the time necessary for separation without appreciable reduction in the quality. The monotonic increase in the eluting ability of the eluant is achieved by two means: a rise in the pH of the solution for a constant concentration of the complexer<sup>204</sup> and a rise in the concentration<sup>207</sup> for constant pH. The latter means is more convenient for practical realization and gives the best results: Separation of the entire group of rare earths from Lu to La with ammonium lactate occupied 3–4 hours, whereas with a pH gradient about 8 hours is required.

A positive concentration gradient of the eluting solution is achieved in eluant feed systems consisting of a vessel with a concentrated solution and one,<sup>204, 207</sup> two,<sup>216</sup> or three<sup>218</sup> mixing chambers. The conditions suggested in ref. 216 have been used for many years for separation of combined samples of micro quantities of lanthanides at JINR. With correct and carefully carried out preparation the separations always occur without any complications and the individual rare-earth fractions are obtained with high radiochemical purity.

The larger the mixing chambers in the eluant feed system, the easier it is in principle to select the complexing agent concentration gradient in the eluant most favorable for a given separation. The concentration of complexing agent in the solution flowing from a system which has  $k$  closed mixers of equal volume  $V$  can be calculated as follows:<sup>218</sup>

$$C_k(v) = C_0 + \sum_{p=1}^k (C_p - C_0) (v/V)^{k-p} \exp(-v/V) / (k-p)!, \quad (28)$$

where  $C_0$  is the concentration of complexing agent in the concentrated solution;  $C_1, C_2, \dots, C_k$  are the concentrations in the first, second, and  $k$ -th mixers for  $v = 0$ .

Molnar<sup>218</sup> discusses in detail the question of the choice of optimal mixer volumes and complexing agent concentrations for a three-chamber eluant feed system which permits uniform successive elution of the individual rare-earth fractions from the chromatographic column.

Figure 38 shows the concentrations of  $\alpha$ -But calculated from Eq. (28) at the exists from the first, second, and third mixing chambers (curves 1, 2, and 3) for  $V = 2$  ml,  $C_0 = 1.65 \text{ M}$ ,  $C_1 = 0.3 \text{ M}$ ,  $C_2 = 0.15 \text{ M}$ ,  $C_3 = 0.1 \text{ M}$ . The eluant solutions had pH = 4.7–4.8. The conditions were chosen for separation in a column with a resin layer 2 mm in diameter by 110 mm long of the entire group of rare earths formed in bombardment of tantalum by high-energy protons. If for some reason  $C_3$  is not suitable for elution of lutetium and this concentration must be replaced by  $C_3' = \epsilon C_3$ , the corresponding values of  $C_0'$ ,  $C_1'$ , and  $C_2'$  are found by simple multiplication of  $C_0$ ,  $C_1$ , and  $C_2$  by  $\epsilon$ . In those cases where the first element which must be separated from the mixture is not Lu but a lighter lanthanide, then, using Fig. 38, we can find from the curve  $k = 3$  the corresponding values of  $C_3$  and then  $C_2$  and  $C_1$ . Naturally  $C_0$  remains unchanged. The choice of mixing system parameters suggested by Molnar,<sup>218</sup> in spite of a certain incorrectness, permits a satisfactory orientation in choice

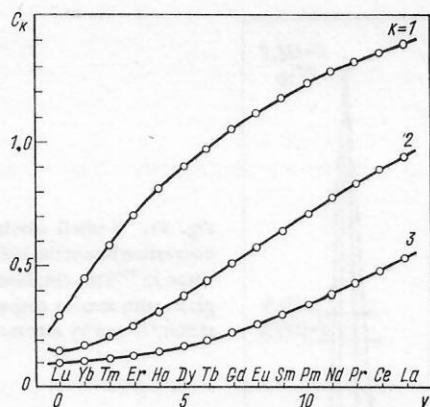


Fig. 38. Change in concentration of complexing agent at the exits of the first, second, and third mixing chambers in a closed three-chamber eluant feed system, as a function of the volume of solution flowing through the system.

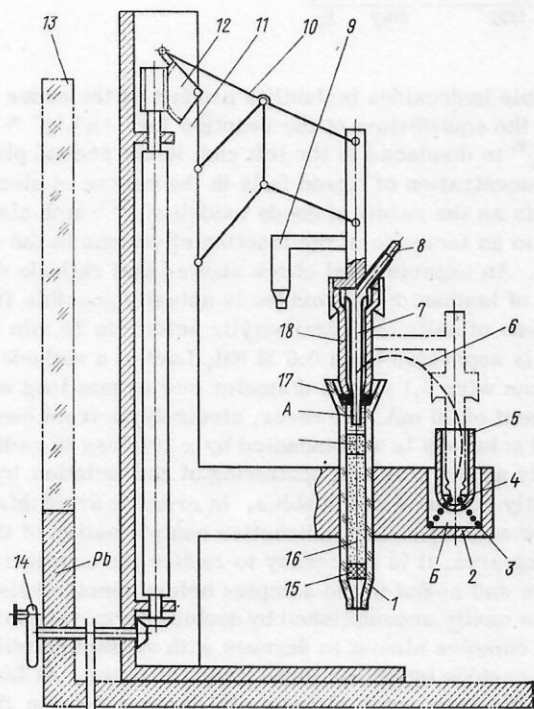


Fig. 39. Diagram of remotely controlled microchromatographic column for separation of highly radioactive rare-earth sources: 1) chromatographic column; 2) holder; 3) shock-absorbing spring; 4) suspension of resin; 5) centrifuge tube; 6) path of tip of pipette; 7) glass pipette; 8) hose; 9) plug; 10) lever system; 11) stand; 12) worm drive; 13) lead glass; 14) hand wheel; 15) filter; 16) resin column; 17) rubber gasket; 18) metallic housing.

of the conditions for chromatographic separations of various mixtures of submicrogram quantities of rare earths with elution by  $\alpha$ -But, and for this reason it is very useful for experimenters.

The main difficulties arising in separation of the combined sample of lanthanide deep-spallation products were associated with the high radioactivity of the sample. While the removal of the target material, preparation of the solution of the concentrate, and sorption from this solution of micro quantities of lanthanides in a finely dispersed sulfocationite are easily carried out by means of

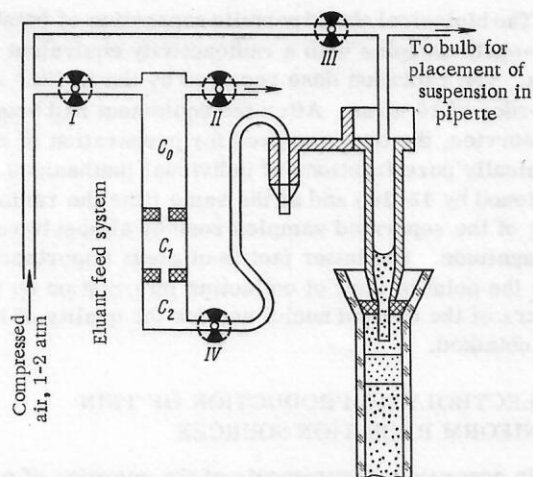


Fig. 40. Diagram of magnetic valves which control the flow of air and eluant to the remotely operated microchromatographic column.

duplicating manipulators, on the other hand, the transfer to the microchromatographic column of the active resin suspension, washing the walls of the upper part of the column free of the portion of the ionite which adheres to them, and other operations require work by the operator in the immediate vicinity of an intense source of ionizing radiation. This strongly limits the radioactivity of the separated samples to the norms of radiation safety procedure. It has been possible to overcome this bottleneck by means of an electromechanical remote-control system for operation of the microchromatographic column.<sup>220</sup>

A diagram of the remote-control system is shown in Fig. 39. A microchromatographic column 1 with a resin layer 2 mm in diameter by 100 mm long is mounted in a fixed location on a holder 2 fastened to a special support 11 on which all of the remaining parts are mounted. Next to the column and also in a fixed location there is a recess with a shock-absorbing spring 3 in which is placed a centrifuge tube 5 with the resin suspension 4. A glass pipette 7 placed in a metallic housing 18 can be moved along the path AB by means of the lever system 10 which is placed in motion by the handwheel 14 located beyond the biological shield. In position A the capillary end of the pipette is in the column and hermetically seals it by means of the rubber gasket 17. In position B the tip of the pipette touches the bottom of the test tube and the opening 9 through which the eluant is introduced is plugged to seal the column. The column is connected by a hose 8 to a small (1-2 ml) rubber bulb (or syringe) placed outside the biological shield. By this means the suspension is transferred from the test tube to the pipette. The system of magnetic valves (I-IV) used to control the supply of compressed air and the eluant is shown in the diagram in Fig. 40 and does not require special comment. The rate of flow of eluant through the column was of the order of 1 ml/cm<sup>2</sup> · sec.

The remotely controlled microchromatographic column is placed behind a biological shield with a device for semiautomatic collection of the effluent in individual drops, measurement of their radioactivity, and transport of the drops to a collector from which they can be distributed for the measurements.<sup>221</sup>



The biological shield permits separation of combined rare-earth samples with a radioactivity equivalent to 3 g of Ra. The radiation dose received by the worker is of the order of 10 mrad. After the equipment had been put into service, the time required for preparation of radiochemically pure fractions of individual lanthanides was shortened by 15–20% and at the same time the radioactivity of the separated samples rose by almost two orders of magnitude. The latter fact is of great importance both from the point of view of collecting information on the  $e^-$  spectra of the excited nuclei and for the quality of the data obtained.

## 6. ELECTROLYTIC PRODUCTION OF THIN UNIFORM RADIATION SOURCES

In accurate measurements of the energies of conversion electrons in magnetic spectrometers and spectrographs whose resolution in the low and medium energy range is of the order of 0.1%, very thin radiation sources of area 10–15 mm<sup>2</sup> are required. Problems of source quality are extraordinarily important for nuclear spectroscopy and have been repeatedly discussed in review articles.<sup>222–224</sup>

The most simple method, evaporation of a radioactive solution, even in those cases where there are no volatile compounds in the solution, gives sources with a nonuniform layer<sup>225</sup> and correction of this deficiency is practically impossible.<sup>222,226</sup> The quality of the sources is improved substantially if use is made of cathodic deposition of microquantities of the not highly soluble hydroxides of the lanthanides (and actinides) from solutions of organic and mineral acids and their salts with pH > 1.5 (refs. 161, 162, 238, 230–234). This method of preparing sources for measurements is simpler and more convenient than the other well-known methods.<sup>227–229</sup>

Deposition of hydroxides on a cathode is possible as the result of the alkaline layer arising in the region near the cathode. The thickness of this layer is determined by diffusion processes and by the current density.<sup>235,238</sup>

Other conditions being equal, the rate of deposition is determined by the following relation:<sup>162</sup>

$$n_t = n_\infty [1 - \exp(-kAt/V)], \quad (29)$$

where  $n_t$  is the fraction of deposition during an electrolysis time  $t$ , in %;  $n_\infty$  is the fraction of deposition on reaching saturation, in %;  $A$  is the cathode area, and  $V$  is the volume of electrolyte.

It follows from Eq. (29) that for a small cathode size such as occurs in our case a small volume of electrolyte is required to shorten the electrolysis time. For these reasons a microelectrolytic cell design was developed which differs substantially from the systems previously used in that the cathode is placed above the anodes of a bath containing 0.3 ml of electrolyte.<sup>236</sup> In spite of the fact that the rare-earth elements eluted from a microchromatographic column by solutions of Lact and  $\alpha$ -But are mainly in the form of neutral or negative complexes, it is possible to carry out cathode deposition of rare-earth hydroxides directly from the effluent. In the first place, as the result of formation on the cathode of rather

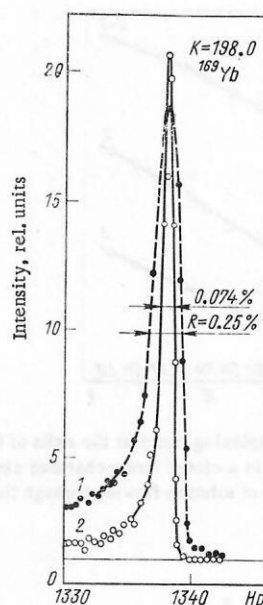


Fig. 41. K-shell electron internal-conversion line of the 198-keV  $\gamma$  transition in  $^{169}\text{Tm}$ , obtained in a spectrograph with sources prepared by evaporation (1) and by electrolysis (2).

insoluble hydroxides (solubility product of the order of  $10^{-20}$ ) the equilibrium of the reaction  $\text{Ln}^{3+} + n \text{Lig}^- \rightleftharpoons \text{Ln}(\text{Lig})_n^{3-n}$  is displaced to the left and, in the second place, the concentration of ligand falls in the course of electrolysis as the result of anode oxidation,<sup>237</sup> which also leads to an increase of the fraction of cations in the solution. An experimental check showed that cathode deposition of lanthanide hydroxides is actually possible from solutions of salts of oxycarboxylic acids: In 20 min 75% of Eu is separated from 0.5 M  $\text{NH}_4$  Lact at a cathode of platinum wire 0.1 mm in diameter and 10 mm long with a current of 30 mA. However, electrolysis from concentrated solutions is accompanied by a 20% loss in radioactivity as the result of spattering of the solution by violently released gas bubbles. In order to avoid this loss and the accompanying radioactive contamination of the working area, it is necessary to reduce the concentration of Lact and  $\alpha$ -But in the samples before electrolysis. This is easily accomplished by double or triple evaporation of the samples almost to dryness with subsequent dilution of the residue by two or three drops of water. At least 90% of the rare-earth elements is separated from the solutions obtained under optimal conditions ( $t = 20$  min,  $J = 10$  mA). The cathode material has essentially no influence on the completeness of the electrolytic deposition of the hydroxides and the quality of the radiation sources obtained. A certain care is required only in deposition of lanthanides on aluminum foil, cathodes of which begin to be destroyed for current densities above 150 mA/cm<sup>2</sup>.

The electrolytic method of preparing radiation sources of small area has been investigated in detail for solutions containing  $\text{NH}_4$  Lact. The conditions found by Novgorodov et al.<sup>236</sup> are completely suitable also for  $\alpha$ -oxyisobutyrate effluents. Furthermore, since  $\text{NH}_4\alpha$ -But, in contrast to  $\text{NH}_4$ Lact, even on evaporation to dryness does not give gummy products which interfere with electrolysis, deposition of microquantities of rare earths on metallic substrates is accomplished more rapidly and with better reproducibility in the latter case.

The quality of radiation sources obtained by electrodeposition was checked by measurement of conversion-

electron spectra. Figure 41 shows the  $^{169}\text{Yb}$  line K-150 obtained in a spectrograph with sources prepared by evaporation and by electrolysis. The electrolytic source allowed the theoretical resolution of the apparatus to be achieved.

The high quality of electrolytic radiation sources obtained by the method described in ref. 236 permits, in some cases, observation of new energy levels in excited nuclei, more accurate identification of previously observed transitions, and construction on this basis of more complete and reliable decay schemes of the radioactive isotopes of the lanthanides.

Electrolytic deposition of micro quantities of lanthanides is exceptionally useful in preparation of fractions of the individual rare earths for isotope separation in an electromagnetic mass separator with an ion source of the surface-ionization type.<sup>239-241</sup> Previously<sup>242,243</sup> in preparation of the fraction of a radioactive element ( $\approx 10^{-10}$  g) for separation it was mixed with several milligrams of oxide of an appropriate rare-earth carrier and chlorided, usually by  $\text{CCl}_4$ , in the plasma ion source of the mass separator. The process was extended: In the first hour of operation it was possible to collect on the collector no more than 40% of the isotopes with a maximal yield of 10%. In working with rare-earth sources without carriers it has been possible to greatly reduce the separation time and simultaneously to increase the efficiency of the isotope separation process. Absence of macro quantities of carrier material is a favorable factor which facilitates creation of a fast and simple ion source based on ionization of rare-earth atoms in collision with a heated W or Re surface.<sup>240,241</sup> The element being separated is introduced into this source in the form of sub-microgram quantities of oxide electrolytically separated onto a strip of tungsten foil of area about  $5\text{ mm}^2$ .

In model tests with  $^{140}\text{Nd}$ , within 3 min after turning on the ion source the separation efficiency reaches 78%. This value is different for different lanthanides and is determined by the surface-ionization coefficient which, in turn, depends on the first ionization potential of the rare-earth atoms (Fig. 42). Other conditions being equal, the quality of preparation of the source for separation greatly affects the results of the separation process. Satisfactorily reproducible results are obtained only with the electrochemical technique.

In application to the problems of electromagnetic separation of short-lived neutron-deficient isotopes of rare earths, the cathode deposition of hydroxides is shortened to  $5 \pm 1$  min. In combination with accelerated methods of separation of deep-spallation products from the target material,<sup>169,176,191,194</sup> this permits preparation of monoisotopic sources of lanthanides in 20-30 min after the end of the bombardment. In this way isotopes with half-lives of 5-10 min have become available for careful studies with semiconductor detectors.

## CONCLUSION

The radiochemical methods discussed have permitted solution of the main problem confronting the chemists of the Laboratory of Nuclear Problems, Joint Institute for

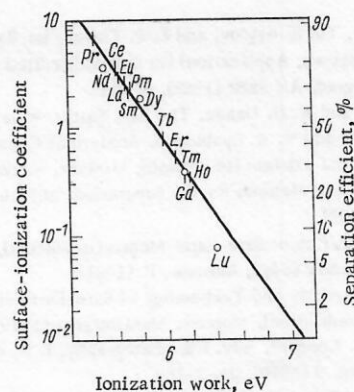


Fig. 42. Efficiency of separation of isotopes of various lanthanides with a surface-ionization source of tungsten with a rhenium ionizer. The hollow circles represent the experimental values. The temperature is  $3000^\circ\text{K}$ . The separation time is 5 min.

Nuclear Research: to provide high-quality radiation sources, including monoisotopic sources, for study of the properties of excited nuclei of the neutron-deficient isotopes of the lanthanides.

At the present time, for measurement of conversion-electron spectra in precision magnetic apparatus, it is possible to prepare radiochemically pure high-quality sources of all rare earths from La to Lu which permit study of isotopes with  $T_{1/2} \geq 30$  min. For measurements in semiconductor spectrometers, which present more severe requirements on the source intensity than magnetic spectrometers, sources are available of isotopes with  $T_{1/2} \geq 5$  min with separation directly from the bombarded target, and with  $T_{1/2} \geq 10$  sec if this is a daughter isotope formed in decay of a long-lived parent nucleus. Significantly shorter-lived lanthanide nuclei apparently cannot be prepared for measurements by radiochemical methods and will become available for investigation with use of equipment such as ISOLDA and YaSNAPP-2, which are electromagnetic separators operating on-line with high-energy proton accelerators.

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