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ANION EXCHANGE ADSORPTION  
OF GADOLINIUM AND EUROPIUM FROM  
AQUEOUS-METHANOL SOLUTIONS CONTAINING  
NEUTRAL NITRATES

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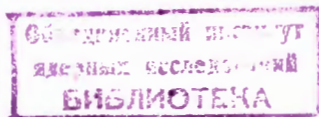
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ANION EXCHANGE ADSORPTION  
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Submitted to Radiochemistry



Rare earths are known to be adsorbed only to a slight extent on strongly basic anion exchangers of the quarternary amine type from pure nitric acid solutions<sup>1-3/</sup>. Their adsorbability increases with decreasing atomic number, but is insufficient to serve as a basis for their anion exchange separation even in the case of the lightest rare earths. Rare earths have shown, however, an increased adsorbability from lithium nitrate solutions, and using these solutions as an eluant, light rare earths could easily be separated from each other by anion exchange chromatographic<sup>4/</sup>.

Anion exchange adsorption of the rare earths from nitrate solutions can be promoted to a greater extent by replacing a part of the aqueous phase with suitable solvent such as methanol<sup>5,6/</sup>. Aqueous-methanol solutions containing nitric acid have been used for purification of some rare earths<sup>7/</sup> as well as for performing other chromatographic separations<sup>6,8/</sup>. Nevertheless, little attention has been paid to the employment of neutral nitrates. To our mind, solutions of these nitrates in certain cases are more convenient to work with than nitric acid ones. Therefore, we made an attempt to study the adsorption of rare earths from aqueous-methanol solutions of neutral nitrates. Our aim was to obtain data necessary for working out a method of separation of light rare earths in application to nuclear spectroscopy from gadolinium targets irradiated with 680 MeV protons. Isotopes with half-lives of  $1.8 \cdot 10^3 - 1.8 \cdot 10^4$  sec (0.5 - 5 hours) are of the greatest interest among the products of the nuclear reaction. For a more rapid chromatographic separation of the nuclear reaction products and the material irradiated, we have to deal with systems in which the distribution coefficients are small. These systems were the goals of our investigations.

## EXPERIMENT

All chemicals were reagent grade and were used without preliminary purification.

Radioisotopes of rare earths were produced from a tantalum target irradiated with 680 MeV protons at the Dubna synchrocyclotron and were purified by eluting them from a cation exchanger column with  $\alpha$ -hydroxy-isobutirate of appropriate concentration. All radio-isotopes were used in a carrier-free form, unless otherwise stated.

In the course of this study the strongly basic anion exchanger Amberlite IRA 400 (nitrate form) was used.

All eluants were acidified with nitric acid to pH 2. The distribution coef-

ficients were determined in dynamic conditions by the conventional elution technique using a 0,04 cm<sup>2</sup> x 7cm resin bed. The radioactive isotopes of the rare earths were introduced into the column in a drop (0,025 - 0,035 ml) of the proper eluant. The column was previously heated up to the desired temperature and washed with the eluant. The effluent was collected drop by drop on paper pieces of 3cm x3cm large. The radioactivity of these pieces was measured with an end-window GM counter. Then the elution curve was constructed in the usual manner. Distribution coefficients were calculated with the aid of the following relationship:

$$C = \frac{n_m - n_1}{n_1} ,$$

where

$n_m$  = the drop number corresponding to the peak maximum,

$n_1$  = the free volume of the column, expressed in drops.

As the drop volume depends upon the composition of the eluant,  $n_1$  was determined for each of the eluants.

The experimental values of the distribution coefficients were treated by the least squares method, and slopes and intercepts as well as separation factors were calculated. The number of theoretical plates was determined from the half-width of the elution peaks on the basis of the Glueckauf's elution theory<sup>9/</sup>.

Separation of carrier-free gadolinium and europium was carried out on a column with a 0,04 cm<sup>2</sup> x 10cm resin bed, the flow rate being 0,4 ml/cm<sup>2</sup> min. The mixture of rare earths dissolved in a drop of the eluant was added to the column which had been heated to the desired temperature and treated with the eluant. The effluent was collected and measured as mentioned above.

Separation of carrier-free europium (samarium, promethium) from macro amount of gadolinium. 60 mg of Gd<sub>2</sub>O<sub>3</sub> was dissolved in 0,3 ml of 5 N nitric acid containing radioactive gadolinium isotope. This solution was then mixed with 0,7 ml of 4 N lithium nitrate in methanol. The resulting mixture was poured onto a column of 0,3 cm<sup>2</sup> x 22,5 cm heated previously to 50°C and washed with the eluant. The solution flow rate in the sorption step was 1 ml/cm<sup>2</sup> min. Gadolinium was eluted at a flow rate of 2 ml/cm<sup>2</sup> min. The effluent was collected in fractions of 2,4ml with a fraction collector of LKB type. Aliquots from these fractions were evaporated on aluminium disks under an infra-red lamp and were counted with a bell-type GM counter.

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<sup>x</sup>LKB - Produkter AB

P.O.Box 12220, Stockholm, Sweden

In order to investigate the behaviour of carrier-free europium (samarium, promethium) being together with macro amount of gadolinium the above runs were repeated by using radioactive europium (samarium, promethium) instead of the gadolinium tracer.

## RESULTS AND DISCUSSION

As the extent of the ion exchange adsorption is greatly affected by the solvation of ions, it was expected that for solutions of identical composition but containing various cations, the values of the distributions coefficients should be also different. For this reason we have first studied the effect of cations. The results are summarized in Table 1. For the monovalent cations, as may be expected, distribution coefficient of gadolinium is the largest in the presence of the strongly hydrated cation of lithium. Among divalent cations calcium is notable. In its presence the distribution coefficient of gadolinium is unexpectedly small.

Table 1

Distribution Coefficients of Gadolinium in 65% Methanol-1N Nitrate Solutions at 20°C.

Cation	C <sub>Gd</sub>	Cation	C <sub>Gd</sub>
H <sup>+</sup>	2.44	Be <sup>++</sup>	3.17
Li <sup>+</sup>	4.16	Ca <sup>++</sup>	0.89
NH <sub>4</sub> <sup>+</sup>	1.70	Mg <sup>++</sup>	3.25
Na <sup>+</sup>	1.49		

Fig. 1 shows the effect of methanol concentration in solutions containing 1N and 2,2 N ammonium nitrate, respectively. For eluants containing 1N ammonium nitrate, the logarithm of the distribution coefficient is a linear function of the methanol concentration<sup>x/</sup>. Separation factors relating to systems containing 1 N ammonium nitrate are enlisted in Table II.

Figs. 2-4 show the variation of the distribution coefficients of gadolinium and europium with various concentrations of lithium, ammonium and calcium nitrates, respectively. It is worth noting that with eluants containing ammonium nitrate and

<sup>x/</sup> This linearity, however, cannot be observed with eluants containing 2,2N ammonium nitrate.

calcium nitrate, the function of log distribution coefficients vs log nitrate concentration gives a straight line, but with eluants containing lithium nitrate the distribution coefficients are increased more rapidly with nitrate concentration.

Table II

Separation Factors in Several Neutral Nitrate-Methanol Mixtures at 20°C (calculated by the Least-Squares Method )

1N  $\text{NH}_4\text{NO}_3$  -  $\text{CH}_3\text{OH}$

% $\text{CH}_3\text{OH}$	50	55	60	65	70	75	80	85
$\alpha$ Eu-Gd	1,08	1,14	1,21	1,29	1,37	1,45	1,54	1,64

65%  $\text{CH}_3\text{OH}$  -  $\text{LiNO}_3$

N $\text{LiNO}_3$	0,5	0,75	1,0	1,25	1,5	1,75
$\alpha$ Eu-Gd	1,31	1,34	1,37	1,42	1,49 <sup>x</sup>	1,55 <sup>x</sup>

55%  $\text{CH}_3\text{OH}$  -  $\text{NH}_4\text{NO}_3$

N $\text{NH}_4\text{NO}_3$	0,5	1,0	1,5	2,0	2,5	3,0	3,5	4,0
$\alpha$ Eu-Gd	1,22	1,41	1,44	1,46	1,47	1,47	1,48	1,48

65%  $\text{CH}_3\text{OH}$  -  $\text{Ca}'\text{NO}_3/2$

N $\text{Ca}'\text{NO}_3/2$	0,5	1,0	1,5	2,0	2,5	3,0	3,5	4,0	
$\alpha$ Eu-Gd		1,14	1,30	1,42	1,51	1,58	1,63	1,68	1,72

55%  $\text{CH}_3\text{OH}$  -  $\text{LiNO}_3$

N $\text{LiNO}_3$	0,5	0,75	1,0	1,25	1,5	1,75	2,0	2,5
$\alpha$ Eu-Gd	1,13	1,20	1,26	1,31	1,37	1,42	1,45	1,54 <sup>x</sup>

55%  $\text{CH}_3\text{OH}$  -  $\text{NH}_4\text{NO}_3$

N $\text{NH}_4\text{NO}_3$	2,5	3,0	3,5	4,0	4,5	5,0
$\alpha$ Eu-Gd	1,41	1,38	1,37	1,35	1,35	1,34

<sup>x</sup> Experimental values.

In all the systems studied the separation factors are increased with nitrate concentration in the eluent except the systems of 55%  $\text{CH}_3\text{OH}-\text{NH}_4\text{NO}_3$  where a definite decreasing trend appears (Table II). The lack of sufficient experimental data does not allow to give an unambiguous explanation of the variation of distribution coefficients and therefore of separation factors in various systems.

The effect of temperature of the distribution coefficients of gadolinium and europium is shown in Fig. 5, and the corresponding separation factors are presented in Table III.

Table III

Variation of Separation Factors with Temperature  
(Calculated by the Method of Least Squares)

65%  $\text{CH}_3\text{OH} - 2.5\text{N Ca}(\text{NO}_3)_2$

t(°C)	20	30	40	50	60
$\alpha$ Eu-Gd	1.57	1.57	1.57	1.57	1.57

65%  $\text{CH}_3\text{OH} - 2.5\text{N NH}_4\text{NO}_3$

t(°C)	20	30	40	50	60
$\alpha$ Eu-Gd	1.51	1.50	1.49	1.48	1.47

55%  $\text{CH}_3\text{OH} - 1.75\text{N LiNO}_3$

t(°C)	20	30	40	50	60
$\alpha$ EU - Gd	1.43	1.44	1.44	1.45	1.45

These data show that with solution of 65%  $\text{CH}_3\text{OH} - 2.5\text{N Ca}(\text{NO}_3)_2$  the distribution coefficients increase slightly with increasing temperature whereas with solution of 65%  $\text{CH}_3\text{OH} - 2.5\text{N NH}_4\text{NO}_3$  they decrease. On the basis of this opposing tendency it is reasonable to suppose that the variation of distribution coefficients with respect to cations present in the eluant depends mostly upon the solvation of these cations. The separation factor in the case of the former system is independent of temperature, while in the latter it gets a decreasing trend.

With eluant of 55%  $\text{CH}_3\text{OH} - 1.75\text{N LiNO}_3$  distribution coefficients decrease significantly with increasing temperature, the separation factor being constant. To be more strict, there is a slight increase, but it is so small that may be considered as an experimental error. The distribution coefficient of europium in the case of

55% CH<sub>3</sub> OH - 2.5 N LiNO<sub>3</sub> changes in parallel manner as for the eluant of  
55% CH<sub>3</sub> OH - 1.75 N LiNO<sub>3</sub>.

The variation of the number of theoretical plates (separation steps) with temperature is shown in Fig. 6. Although determinations cannot be carried out with appropriate accuracy because of the small number of experimental data, being at hand, the general trend appears to be clear from Fig.6.

Data on the distribution coefficients and separation factors show that it is possible to separate europium from gadolinium on an anion exchange column using aqueous methanol solutions of neutral nitrates as eluants. Separation factors given in our paper are smaller than those observed with solutions containing higher methanol concentration<sup>/3/</sup>. In our case this drawback is compensated by the fact that with small concentrations of alcohol the rate of the ion exchange is larger and the distribution coefficient is smaller. Therefore, separations can be carried out within a shorter time, which may be an important factor in the treatment of radioactive substances. Furthermore, by employing neutral nitrates, it is possible to work at elevated temperatures too, which has an importance in respect of separation purity. As an example it may be mentioned that with the eluant of 55% CH<sub>3</sub> OH - 2.5 N NH<sub>4</sub> NO<sub>3</sub> the separation of carrier-free gadolinium and europium is nearly complete at 60° (Fig. 7a), while at 20°, the ordinate of the minimum between the two elution peaks is more than 50% of the highest ordinate of the gadolinium peak. (Peak-to-valley ratio is smaller than 2). With separation presented in Fig. 7b peak-to-valley ratio is approximately 6 at 20°C.

Separability of carrier-free europium from macro amount of gadolinium depends also on the quantity of gadolinium present. Fig.8 shows elution curves where the loading to the column was 200 mg Gd<sub>2</sub>O<sub>3</sub>/cm<sup>2</sup>. With this loading under the given conditions, only about 40% of europium can be obtained which does not practically contain ponderable amounts of gadolinium. This is comparatively small, but a similar efficiency (taking into account separation time and eluant volume) cannot be achieved by other chromatographic methods. (If time is not a limiting factor, separation can be still improved using higher methanol and nitrate concentration and approaching more to the equilibrium conditions). Samarium and rare earths lighter than samarium can entirely be separated from gadolinium.

As for separation shown in Fig. 8, the elution of gadolinium takes place within about 45 minutes. Carrier-free rare earths remaining on the resin bed can be eluted with dilute nitric acid within some minutes. It is interesting to note that gadolinium and europium are eluted with a relatively high separation factor. The reason for this is that the distribution coefficient of macro amount of gadolinium is smaller than that of tracer, but the presence of mg amounts of gadolinium does not affect the adsorption of carrier-free europium very much.



## CONCLUSIONS

The anion exchange behaviour of gadolinium and europium was investigated in aqueous methanol solutions containing neutral nitrates. Eluants containing methanol nitrates were found to be suitable for the anion exchange separation of light rare earths. A method for the separation of light rare earths from gadolinium targets irradiated with 680 MeV protons is described.

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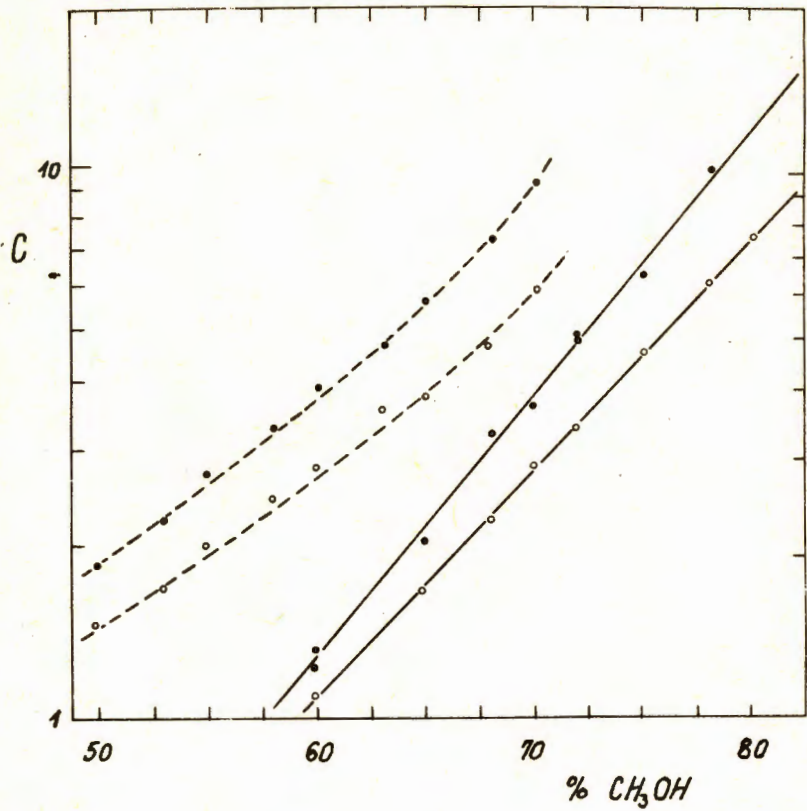


Fig. 1. Variation of the distribution coefficients with methanol content.

- - gadolinium
- - europium
- 1.0N  $\text{NH}_4\text{NO}_3$
- - - 2.2N  $\text{NH}_4\text{NO}_3$ .

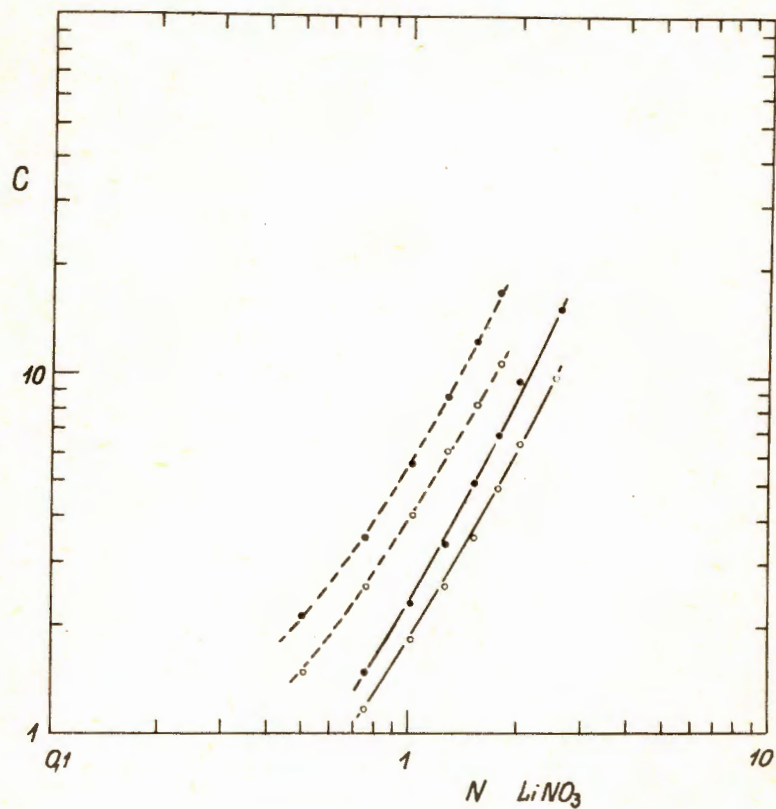


Fig. 2. Variation of the distribution coefficients with concentration of lithium nitrate.

- - gadolinium
- - europium
- 55%  $\text{CH}_3\text{OH}$
- - - 65%  $\text{CH}_3\text{OH}$ .

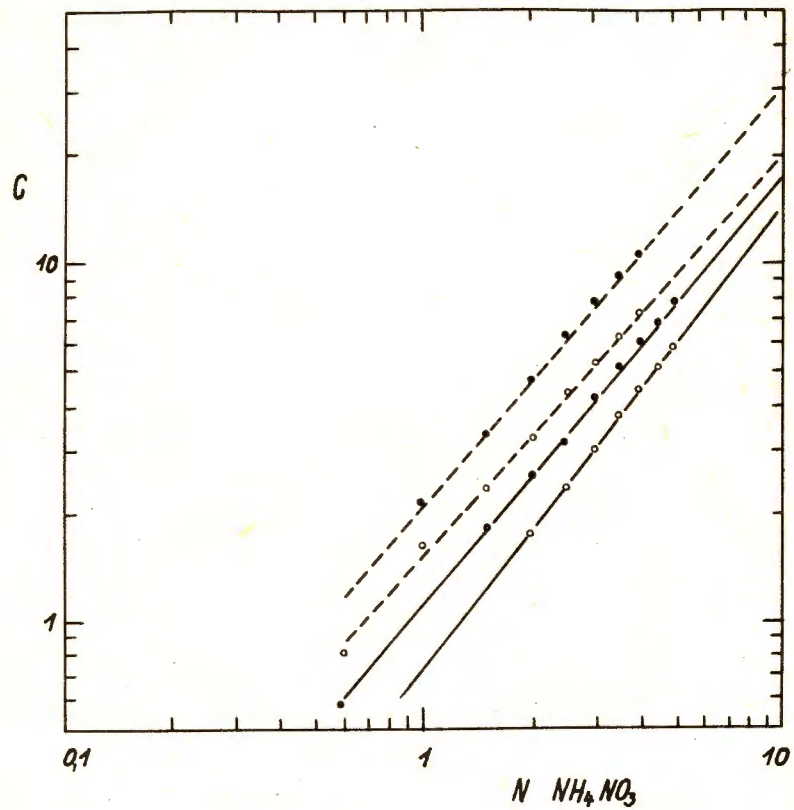


Fig.3. Variation of the distribution coefficients with concentration of ammonium nitrate.

- - gadolinium
- - europium
- 55%  $\text{CH}_3\text{OH}$
- - - 65%  $\text{CH}_3\text{OH}$ .

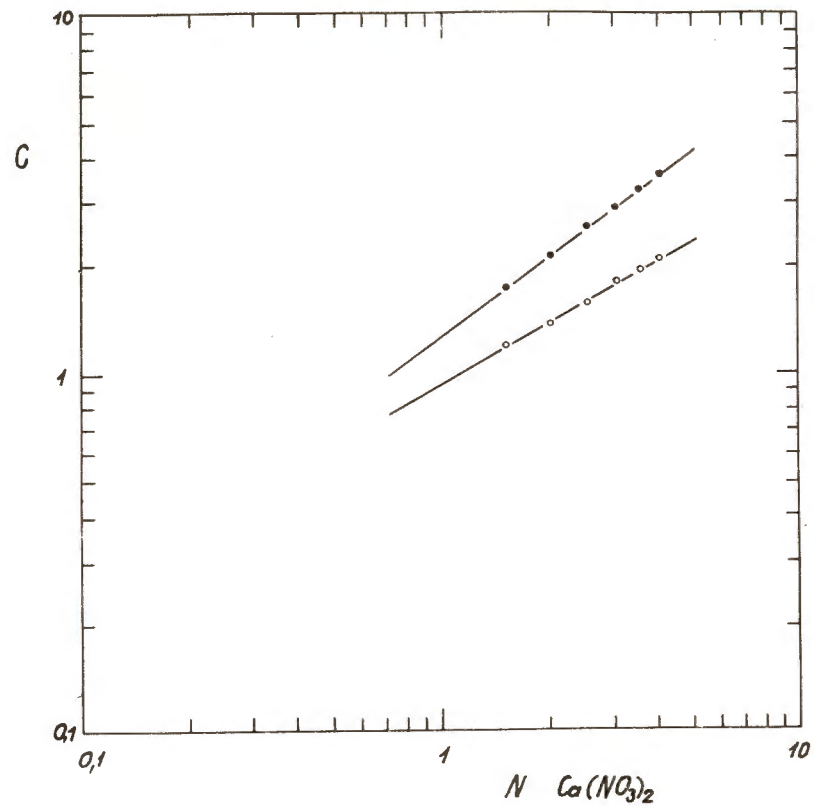


Fig.4. Variation of the distribution coefficients with concentration of calcium nitrate in 65% methanol solutions.

- - gadolinium
- - europium

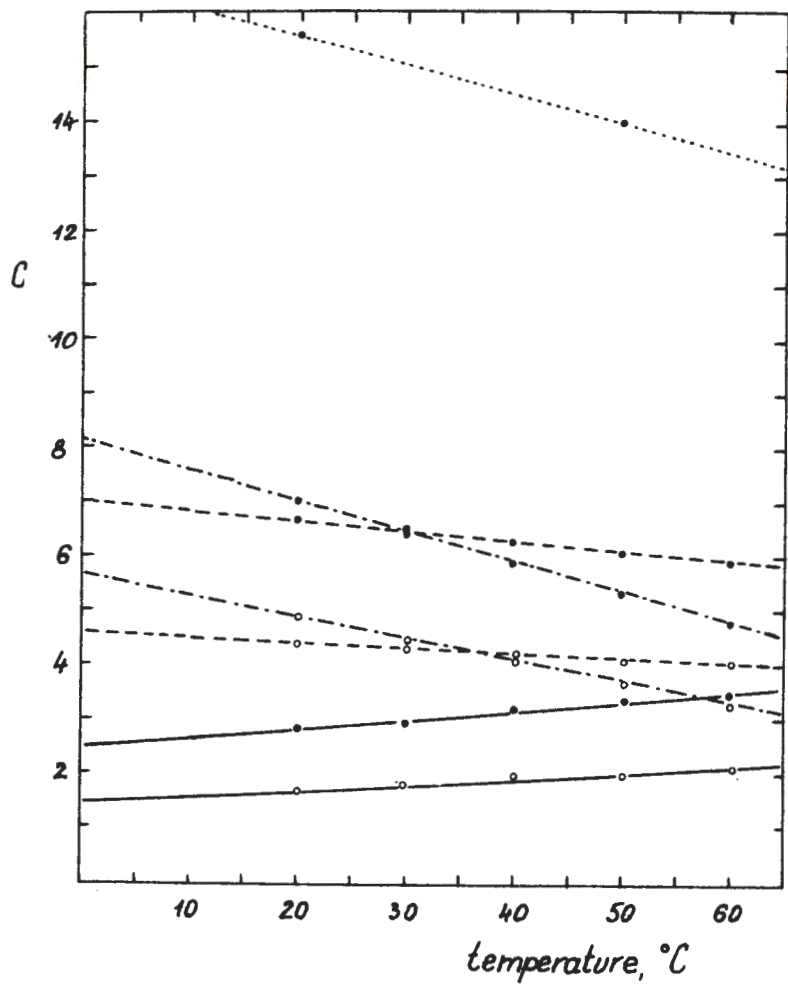


Fig. 5. Effect of temperature on the distribution coefficients.

- - gadolinium
- - europium
- 65%  $\text{CH}_3\text{OH}$  - 2.5N  $\text{Ca}(\text{NO}_3)_2$
- - - 65%  $\text{CH}_3\text{OH}$  - 2.5N  $\text{NH}_4\text{NO}_3$
- ..... 55%  $\text{CH}_3\text{OH}$  - 1.75N  $\text{LiNO}_3$
- · - · 55%  $\text{CH}_3\text{OH}$  - 2.5N  $\text{LiNO}_3$

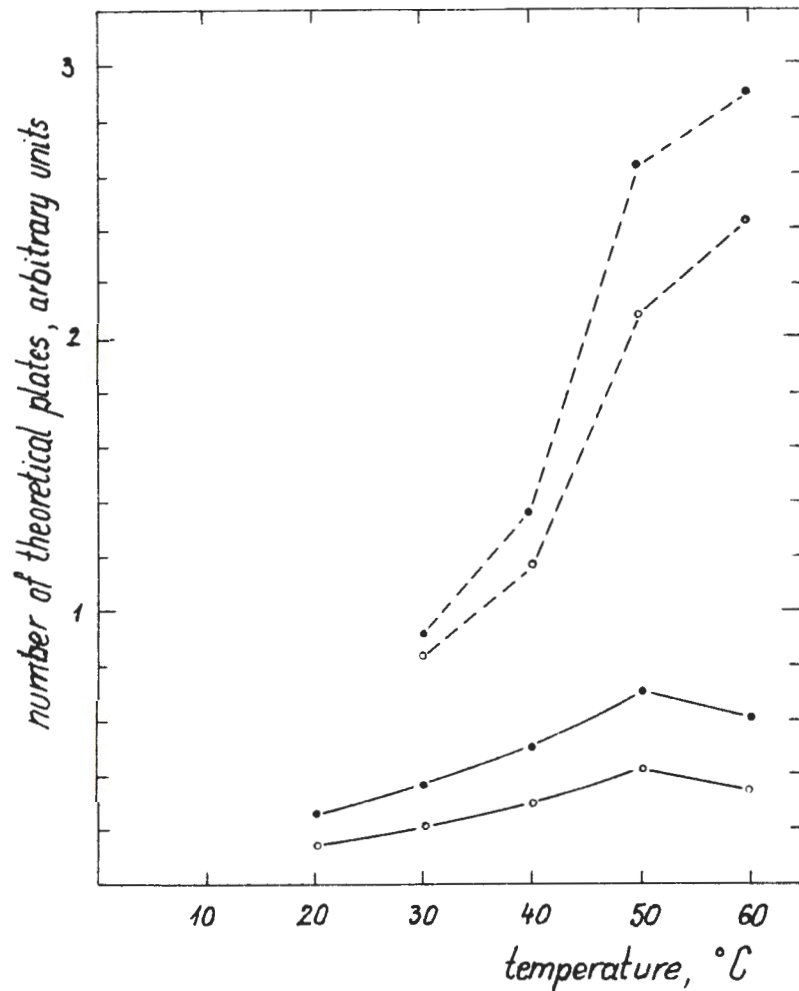


Fig. 6. Effect of temperature on number of theoretical plates of the column.

- - gadolinium
- - europium
- 65%  $\text{CH}_3\text{OH}$  - 2.5N  $\text{Ca}(\text{NO}_3)_2$
- - - 65%  $\text{CH}_3\text{OH}$  - 2.5N  $\text{NH}_4\text{NO}_3$

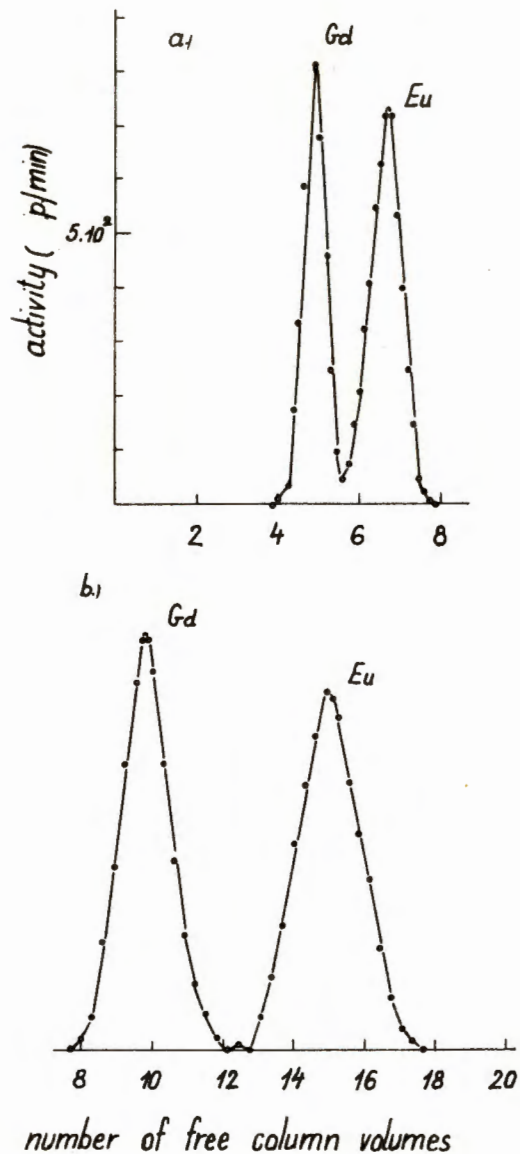


Fig.7.

Separation of carrier-free gadolinium and europium.  
 Resin bed:  $0,04 \text{ cm}^2 \times 10 \text{ cm}$  Amberlite IRA 400 (nitrate form) -  
 400 mesh, flow rate:  $0,4 \text{ ml/cm}^2 \text{ min}$ .  
 a. Eluant:  $65\% \text{ CH}_3\text{OH} - 2,5\text{N NH}_4\text{NO}_3$ , temperature:  $60^\circ\text{C}$ .  
 b. Eluant:  $55\% \text{ CH}_3\text{OH} - 2,5\text{N LiNO}_3$ , temperature:  $50^\circ\text{C}$ .

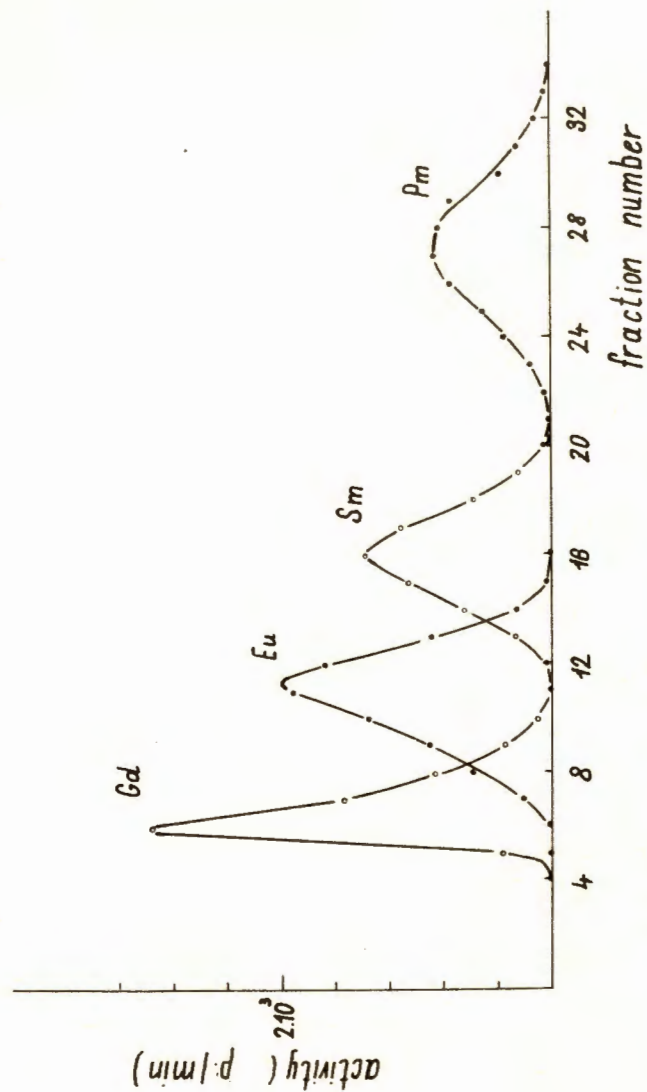


Fig.8.

Separation of carrier-free europium, samarium and promethium from  
 $60 \text{ mg}$  of  $\text{Gd}_2\text{O}_3$ . Resin bed:  $0,3 \text{ cm}^2 \times 22,5 \text{ cm}$  Amberlite IRA 400  
 (nitrate form) - 200-400 mesh. Eluant:  $65\% \text{ CH}_3\text{OH} - 2,5\text{N NH}_4\text{NO}_3$ ,  
 temperature:  $50^\circ\text{C}$ . Number of theoretical plates: 109 (calculated from  
 the half-width of the samarium peak on the basis of Glueckauf's  
 elution theory).