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THE ISOLATION OF PROMETHIUM BY DISPLACEMENT  
CHROMATOGRAPHY DUE TO COMPLEX FORMATION\*

K. V. CHMUTOV, P. P. NAZAROV, G. B. MASSLOVA AND V. N. SHEPTUNOV

*Institute of Physical Chemistry of the U.S.S.R. Academy of Sciences, Leninskii Prospekt 81, Moscow V-17 (U.S.S.R.)*

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## SUMMARY

The separation of a mixture of rare earth elements by means of solutions of ethylenediaminetetraacetic, diethylenetriaminepentaacetic and nitrilotriacetic acids is carried out. It is shown that nitrilotriacetic acid has the minimum value for the height equivalent to a theoretical plate. The high separation power of nitrilotriacetic acid is accounted for by the greater velocity of the diffusion processes as compared to the other complexones. The influence of kinetic factors on the height equivalent to a theoretical plate value in the elution of cerium and neodymium by diethylenetriaminepentaacetic acid solution is investigated as an example. The limiting stage for elution from a resin containing no more than 12% divinylbenzene, is shown to be the outer diffusion inhibition.

The method of displacement chromatography by complex formation can be used for separating the rare earth elements (r.e.e.). This method has been used successfully for preparing the stable isotopes of r.e.e., as well as for isolating radioactive r.e.e. in considerable amounts<sup>1,2</sup>.

The present communication is devoted to the use of this method for the isolation of promethium-147 from fission products.

A peculiarity concerning the isolation of the radioactive products is the necessity of completing an effective separation procedure over a minimum space of time in order to reduce radiation damage which could cause destruction of the resin and eluent and thus losses in the product being isolated.

In practice, considerable success has been achieved using the above-mentioned method, but theoretical studies relating to the conditions and the determination of the separation efficiency have only been reported recently<sup>3</sup>.

The efficiency of a chromatographic separation is determined by kinetic and thermodynamic parameters according to the theoretical conception proposed by POWELL AND SPEDDING<sup>1</sup> and is characterized by eqn. 1

$$\log \frac{c_A}{c_B} = \frac{\log \alpha_B^A}{h} \cdot l \quad (1)$$

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where

$c_A$  and  $c_B$  are the concentrations of the ions in solution,

$\alpha_B^A$  is separation factor for vicinal r.e.e.,

$h$  = height equivalent to a theoretical plate (HETP),

$l$  = distance along the axis of the column from the middle of the front.

If one compares the separation factors of promethium from its neighbours, samarium and neodymium, in the presence of those complexones most frequently used for separations, one would give some preference to diethylenetriaminepentaacetic acid (DTPA) and nitrilotriacetic acid (NTA), as opposed to ethylenediaminetetraacetic acid (EDTA) and hydroxyethylethylenediaminetriacetic acid (HEDTA) (Table I).

However, it was found experimentally<sup>2</sup> that NTA is notable for its considerably greater efficiency when carrying out the separation procedure as compared with the rest of the complexones.

This greater efficiency of NTA is in the opinion of WHEELWRIGHT<sup>2</sup> connected with the kinetics of the diffusion processes rather than with the thermodynamic parameters.

To compare the kinetic characteristics for these eluents we determined the HETP values on eluting a mixture of r.e.e. with solutions of NTA, DTPA and EDTA. The separation was carried out on several columns combined in sequence. The resin used was KU-2 with a granule size of 60-90 mesh. The results of the separations are given in Figs. 1, 2 and 3 and Table II.

TABLE I  
SEPARATION FACTORS FOR Pm/Sm AND Pm/Nd<sup>2</sup>

<i>R.e.e.</i>	<i>Eluent</i>			
	<i>EDTA</i>	<i>HEDTA</i>	<i>DTPA</i>	<i>NTA</i>
Pm-Nd	1.8	1.7	2.0	2.3
Pm-Sm	1.8	1.7	2.0	2.3

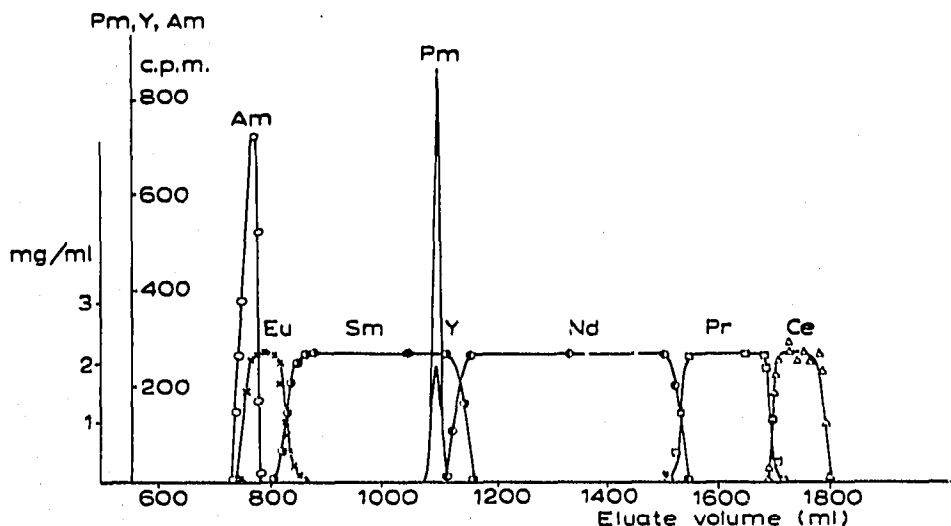


Fig. 1. Separation of the r.e.e. by EDTA solution.

As can be seen from the data in Table II, in order to gain the same degree of separation the least time is spent when NTA is used (the velocity of the band through the column amounts to 16 cm/h); the longest time is when EDTA is used (the velocity of the band is 4.8 cm/h). The band of promethium overlaps with neighbouring bands, since the promethium-147 used for the separation was only present in microquantities.

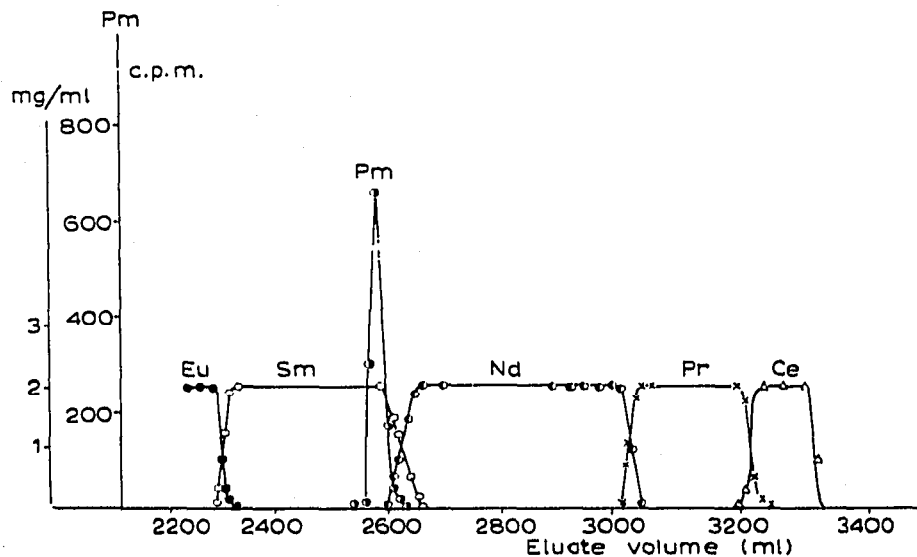


Fig. 2. Separation of the r.e.e. by DTPA solution.

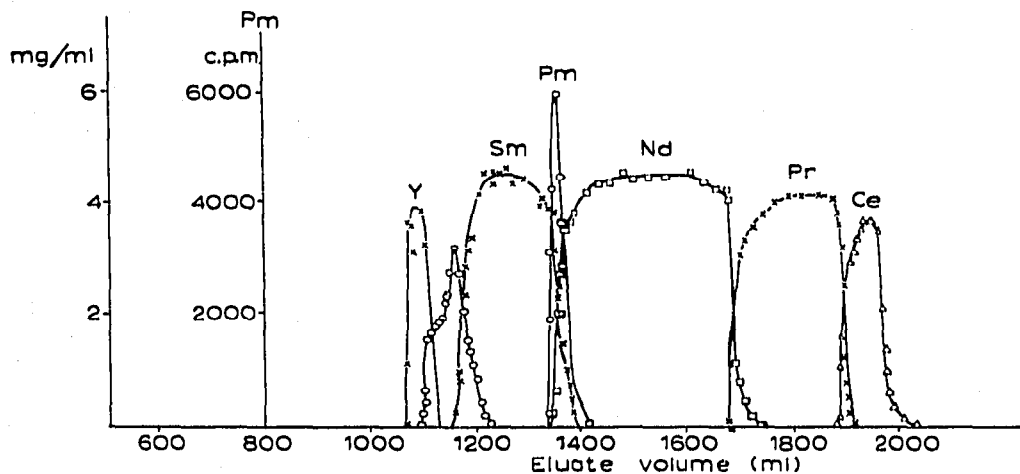


Fig. 3. Separation of the r.e.e. by NTA solution.

The poor elution by means of DTPA (the joint elution of yttrium and promethium) can be avoided by using a mixture of DTPA and EDTA solutions as eluent (Fig. 4).

The determination of the HETP was carried out by using eqn. 1 for the pair praseodymium-neodymium, since the partition factors, under conditions corresponding to those of the separation procedure, have been determined by us for these r.e.e. (Table III).

As would be expected from the data given in Table II, NTA has the least value of HETP when the velocity of the front is greatest. Thus it appears that the greater

TABLE II  
COMPARISON OF ELUENT EFFICIENCIES

Eluent	Columns	Experimental conditions	Velocity of solution filtration (ml/min/cm <sup>2</sup> )	Velocity of r.e.e. band shift (cm/h)	R.e.e. concentration in filtrate (g/l)	Quantity of displacement bands, $\nu$	Separation factor, $\alpha_{A/B}$
0.015 mole/l, pH 8.5, EDTA, $t = 70^\circ$ (Fig. 1)	Sorption column, $H = 86$ cm; $d = 0.86$ cm.	Resin KU-2 60-90 mesh	3.7	4.8	1.8	1.6	1.8
	Separation columns, $\Sigma H = 450$ cm; $d = 0.38$ cm.	Cu-form					
0.025 mole/l, pH = 6.0, DTPA, $t = 70^\circ$ (Fig. 2)	Sorption column, $H = 70$ cm; $d = 0.96$ cm.	Resin KU-2 60-90 mesh	3.5	10.00	2.2	1.35	2.2
	Separation columns, $\Sigma H = 286$ cm; $d = 0.38$ cm.	H-form					
0.1 mole/l, pH = 7.0, NTA, $t = 70^\circ$ (Fig. 3)	Sorption column, $H = 100$ cm; $d = 0.86$ cm.	Resin KU-2 60-90 mesh	4.0	16.0	4.5	1.6	2.2
	Separation columns, $H_1 = 93$ cm; $d_1 = 0.80$ cm; $H_2 = 97$ cm; $d_2 = 0.80$ cm; $H_3 = 93$ cm; $d_3 = 0.40$ cm.	Zn-form					

efficiency of NTA, compared to EDTA and DTPA, is perhaps connected with the greater velocity of the diffusion processes.

To find the optimum conditions for separating r.e.e. by means of different complexones, we then considered the influence of kinetic parameters on the HETP value. The data obtained allow one to ascertain the mechanism limiting the process in its stationary state in the case of a convex sorption isotherm and to find the most favourable conditions for separation.

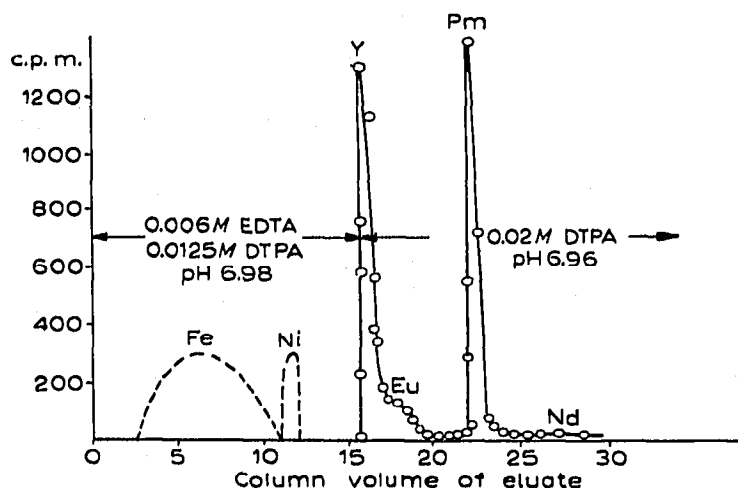


Fig. 4. Separation of the r.e.e. by a mixture of eluents. The elution is first performed with a mixture of 0.006 mole/l EDTA and 0.025 mole/l DTPA solutions at pH 6.98. It is then continued with 0.02 mole/l DTPA solution at pH 6.96. Temperature 70°; the sorption column was 60 cm long by 0.86 cm wide. Separation column:  $H = 95$  cm,  $d = 0.37$  cm. Flow rate: 3.5 ml/min/cm<sup>2</sup>. The number of substitution bands was 0.30. The rate of zone displacement was 5 cm/h.

TABLE III

PARTITION FACTORS OF Pr-Nd IN THE PRESENCE OF COMPLEXONES

Complexone	$t$ (°C)	$\alpha \frac{d}{B}$	HETP (cm)
EDTA	25	2.12	1.77
	70	1.80	
DTPA	25	3.08	2.30
	70	2.51	
NTA	25	1.78	1.17
	70	2.20	

The quantitative characteristics of eluting the r.e.e. bands were deduced from elution curves for the HETP values according to eqn. 1. With a view to determining the limiting diffusion mechanism a computation of the HETP according to GLUECKAUF's equations<sup>4</sup> (eqns. 2, 3, 4 and 5), reduced to a form convenient for such a calculation<sup>5</sup>, was performed.

In the case of film kinetics:

$$\Delta F = \frac{Vc_2 - Vc_1}{0.5q \left( \frac{\bar{X}}{C} + \beta \right) \left( \frac{\alpha_{13}^{\Lambda}}{\alpha_{13}^{\Lambda} - 1} \ln \frac{c_2}{c_1} - \frac{1}{\alpha_{13}^{\Lambda} - 1} \ln \frac{C - c_2}{C - c_1} \right)} \quad (2)$$

$$\Delta F = \frac{2\delta r \bar{F}}{(\bar{X} + \beta C)3D}, \quad (3)$$

where

$\Delta F$  is the HETP for outer diffusion,

$V_{c_1}$  and  $V_{c_2}$  are the elution volumes, at which the developing solution has concentrations  $c_1$  and  $c_2$ ,

$\bar{X}$  is volume capacity of exchanger,

$C$  = equivalent total ion concentration in solution,

$\delta$  = the film thickness,

$q$  = cross-section of the column,

$r$  = radius of the particles of the exchanger,

$\bar{F}$  = flow rate,

$D$  = factor of outer diffusion.

In the case of gel diffusion:

$$\Delta G = \frac{V_{c_2} - V_{c_1}}{0.5q \left( \frac{\bar{X}}{C} + \beta \right) \left( \frac{1}{\alpha_B^A - 1} \ln \frac{c_2}{c_1} - \frac{\alpha_B^A}{\alpha_B^A - 1} \ln \frac{C - c_2}{C - c_1} \right)} \quad (4)$$

$$\Delta G = \frac{r^2 \bar{F}}{(\bar{X}/C + \beta)14\bar{D}} \quad (5)$$

where

$\Delta G$  is the HETP for inner diffusion,

$\bar{D}$  = the factor of inner diffusion.

The experimental and calculated data for the elution of an equimolar mixture of neodymium and cerium by DTPA solution are given in Tables IV-VII.

It can be seen from the experimental data, concerning the influence of velocity and temperature on HETP, that the values of HETP decrease with increasing temperature and increase when the flow rate of the solution is increased.

The dependence of HETP upon the grain size of the resin is linear which is evidence in favour of a film type mechanism. The values of HETP do not change with an increase in the eluent concentration and in the crosslinking from 2% to 8% divinylbenzene, which also confirms the theory of a film type mechanism of diffusion (eqn. 3). The value of the HETP only increases up to a degree of cross-linking of 12%; this would seem to be connected with the passage of the system to a mixed mechanism of diffusion. Such conclusions are in accordance with the results published by HAGIWARA<sup>3</sup>.

The experimental results coincide with the conclusions which can be derived from the calculated data. The HETP values calculated from eqn. 1 are near to those calculated according to eqn. 2 for outer diffusion inhibition (columns 4 and 6 of Table VI). The exception is an experiment in which a resin was used which contained 12% divinylbenzene. The process in this case is determined by a mixed mechanism.

Thus on the grounds of calculated as well as experimental data one can conclude

TABLE IV

INFLUENCE OF TEMPERATURE AND FLOW RATE OF ELUENT ON HETP  
DTPA concentration 0.025 mole/l; pH 7.

Test No.	$t$ (°C)	Flow rate (ml/min/cm <sup>2</sup> )	HETP (cm)		
			$h$ (eqn. 1)	$\Delta G$	$\Delta F$
1	25	1.87	1.70	2.91	1.62
2	25	1.92	1.84	2.96	1.75
3	25	6.45	2.40	3.41	2.34
4	25	11.32	3.56	6.60	3.45
5	50	2.0	0.96	1.64	1.07
6	50	6.01	1.57	2.81	1.69
7	50	6.43	1.63	3.18	1.87
8	50	6.70	1.61	3.06	1.85
9	50	12.60	2.13	3.54	2.29
10	70	1.63	0.52	0.76	0.49
11	70	2.08	0.64	0.92	0.71
12	70	3.77	0.98	1.23	1.05
13	70	9.02	1.28	1.82	1.22
14	70	9.65	1.34	2.10	1.32
15	70	11.20	1.68	3.16	1.63
16	70	17.62	2.15	4.02	2.30
17	90	2.08	0.42	0.77	0.60
18	90	6.44	1.01	1.81	0.92
19	90	7.06	1.07	2.24	0.96
20	90	14.15	1.62	3.61	1.50

TABLE V

INFLUENCE OF THE GRAIN SIZE OF KU-2X8 ON HETP

DTPA concentration 0.025 mole/l, ionic strength 0.079; flow rate 3.8 ml/min/cm<sup>2</sup>; temperature 70°.

Test No.	$10^2 r$ (cm)	HETP (cm)			$10^3 \delta$ (cm)
		$h$ (eqn. 1)	$\Delta G$	$\Delta F$	
21	0.58 ± 0.06	0.78	1.12	0.74	1.26
22	0.72 ± 0.10	0.81	1.04	0.82	1.27
23	1.40 ± 0.29	1.52	2.58	1.46	1.28
24	2.18 ± 0.43	2.29	3.49	2.12	1.27

TABLE VI

INFLUENCE OF DEGREE OF CROSS-LINKING ON HETP

Resin Dowex-50, 100-200 mesh; DTPA concentration 0.025 mole/l, pH = 7, ionic strength 0.079; flow rate 3.8 ml/min/cm<sup>2</sup>; temperature 70°.

Test No.	$E = \bar{X} \frac{\text{mg} - \text{eq}^a}{\text{ml}}$	% DVB	HETP (cm)		
			$h$ (eqn. 1)	$\Delta G$	$\Delta F$
25	1.33	2	0.93	1.28	0.96
26	1.40	4	0.92	1.23	1.06
27	1.55	8	0.99	1.70	0.99
28	2.18	12	2.40	1.58	1.09

<sup>a</sup> Volume capacity of ionite.

that the outer diffusion inhibition under the conditions studied is the limiting factor for eluting the r.e.e. by a DTPA solution from a resin containing no more than 8 % divinylbenzene.

The results obtained allow one to predict, by use of eqn. 1, the zones of neighbouring elements overlapping promethium (observing the condition that HETP values for neighbouring r.e.e. differ very little from one another) and to choose the optimum conditions for separating this element.

TABLE VII

## INFLUENCE OF DTPA CONCENTRATION ON HETP

Resin KU-2, 60-90 mesh; ionic strength 0.079; flow rate 4.5 ml/min/cm<sup>2</sup>; temperature 70°.

Test No.	$C_{DTPA}$ (mole/l) $pH = 7$	HETP (cm)		
		$h$ (eqn. 1)	$\Delta G$	$\Delta F$
29	0.01	1.46	4.27	1.47
30	0.025	1.44	2.11	1.39
31	0.05	1.36	3.17	1.48
32	0.050	1.38	3.24	1.59

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