SEPARATION OF SOME FISSION PRODUCTS FROM URANIUM(VI) BY REVERSED-PHASE PARTITION CHROMATOGRAPHY

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Reversed-phase partition (extraction) chromatography with various extractants as stationary phase is a powerful method for the separation of ions of similar properties *e.g.* rare earths. In most of the previous work the ions to be separated were in tracer or microamounts, although successful attempts have been made to separate a microamount of one substance from a macroamount of another[1,2]. This type of separation is especially important in the recovery of radioisotopes from irradiated targets. A complex problem of this type is also found in the separation of some fission products from irradiated uranium. Because of the high selectivity of HDEHP as extractant it would seem possible to perform a group separation of some fission products while U is retained on a column which contains HDEHP as the stationary phase. The presumed retention of U on the column follows from the fact that U(VI) is extracted by HDEHP even from highly acidic solutions[3]. This paper presents an attempt to separate several important and representative fission products from U by reversed-phase partition chromatography. At this stage of the work, however, only experiments with synthetic samples and unirradiated U were performed.

EXPERIMENTAL

Column material and column preparation

Column material and column preparation were the same as described elsewhere[2]. HDEHP was adsorbed on the solid support by an evaporation technique. The ratio of HDEHP to kieselguhr was 1:10. The length of the bed was 10 cm and the diameter of the columns 3 mm. The HETP of the columns used was about 0.20 mm.

Reagents and radiotracers

HDEHP, supplied by Light and Co., was used without further purification. The solution of reagent grade uranyl nitrate containing 5 or 50 mg U/ml was standardized by titration with $K_2Cr_2O_7$ after reduction to U(III)[4]. Most of the radioisotopes used were prepared by irradiation of appropriate targets in the Polish reactor "EWA". Some radioisotopes were obtained from the Radiochemical Centre, Amersham, Great Britain.

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Elution

Elutions were carried out at 25° and 77° using nitric or hydrochloric acids of appropriate concentration, pre-equilibrated with HDEHP. The flow rate was 1.1 ml·cm^{-2}·min^{-1} or 0.2 ml·cm^{-2}·min^{-1}. Drops of eluate were collected automatically by the use of a fraction collector. The activity of the eluate was measured using a G.M. counter, or a scintillation counter. The purity of the fractions was controlled using a 100-channel analyzer. The content of U in the eluate was determined using dibenzoylmethane dissolved in a mixture of acetone and pyridine.

RESULTS AND DISCUSSION

Behaviour of U(VI) on the column

The behaviour of U(VI) on the HDEHP-treated columns was studied by the use of break-through curves. The solution of uranyl nitrate containing 5 mg U/ml was passed through the column at a flow rate of 0.2 or 1.1 ml·cm^{-2}·min^{-1}. The break-through curves were sharp and well defined. The amount of U retained on the column has been calculated by subtracting the free volume of the column from the volume when the U begins to appear in the eluate. The same ratio of HDEHP to U was obtained independently of the flow rate and of the concentration of nitric acid up to 2.4 N. This ratio varied from 2.15 to 2.5 with different columns. This result shows that the predominant complex existing in the organic phase contains two molecules of HDEHP for each atom of U.

The U is slowly eluted from the column with 5 M HNO$_3$. The volume at which the U begins to appear in the eluate is a function of the percentage saturation of the column with U. This dependency is illustrated in Fig. 1. Complete stripping of U from the column was achieved using concentrated HCl.

Separation of Tb from U

It has been observed in previous work from this Department[2] that when a mixture of a microamount of Tb and of a macroamount of Er is eluted from a column containing HDEHP as the stationary phase two well separated peaks were obtained, the first containing mainly Tb and the second, Er. No attempt had been made to determine quantitatively the yield of the microcomponent and the purity of the fractions*. Preliminary experiments carried out with U have, however, shown that the presence of a macroamount of U affects the elution of trace amounts of rare earths and good separation can be obtained only under special conditions of temperature and flow rate. This phenomenon was studied very thoroughly with the pair Tb–U(VI).

When Tb alone is introduced into the column it can be eluted with 1.5 M HNO$_3$ as a sharp peak after the first free volume, disregarding the initial acidity of the column. The situation is quite different when a tracer amount and U in an amount corresponding to 50% of the total column capacity are present together. When such a mixture of Tb and U(VI) is introduced into the column conditioned with 0.1 M HNO$_3$ and elution is carried out with 1.5 M HNO$_3$, the Tb peak is very broad with a long tail. Only a small part of the total Tb activity can be recovered in the main peak,

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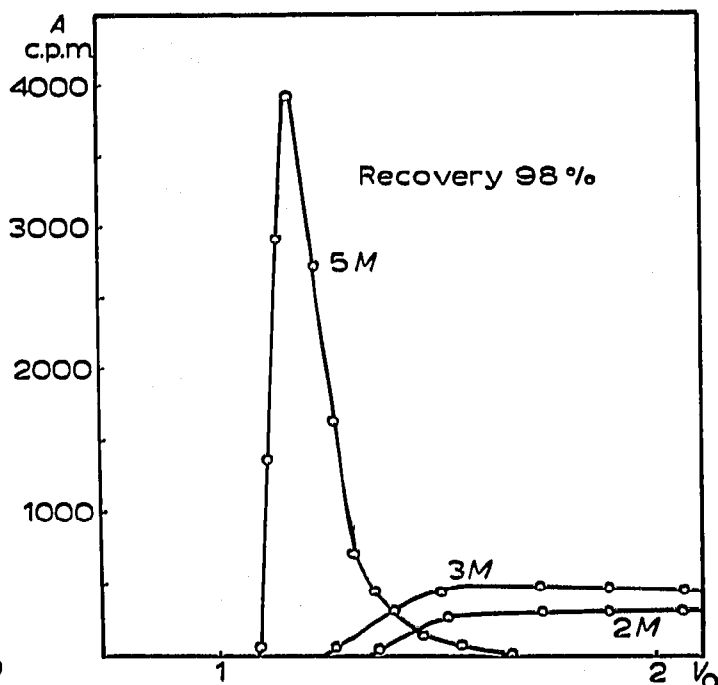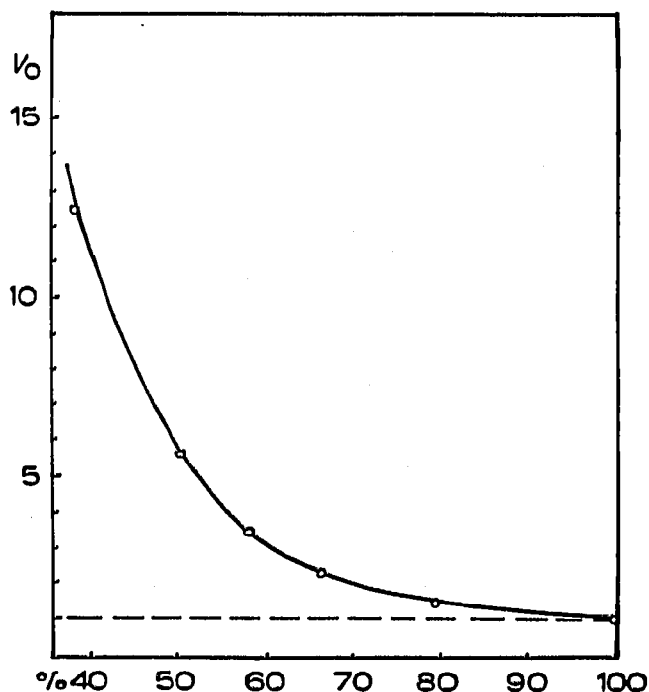
Fig. 1. The appearance of U in eluate as a function of the percentage saturation of the column. Eluant: 5 M HNO$_3$. Flow rate: 1.1 ml·cm^{-2}·min^{-1}. Temperature: 25°.

Fig. 2. The elution of Tb from the mixture U–Tb with nitric acid of varying concentrations. Flow rate: 1.1 ml·cm^{-2}·min^{-1}. Temperature: 25°.
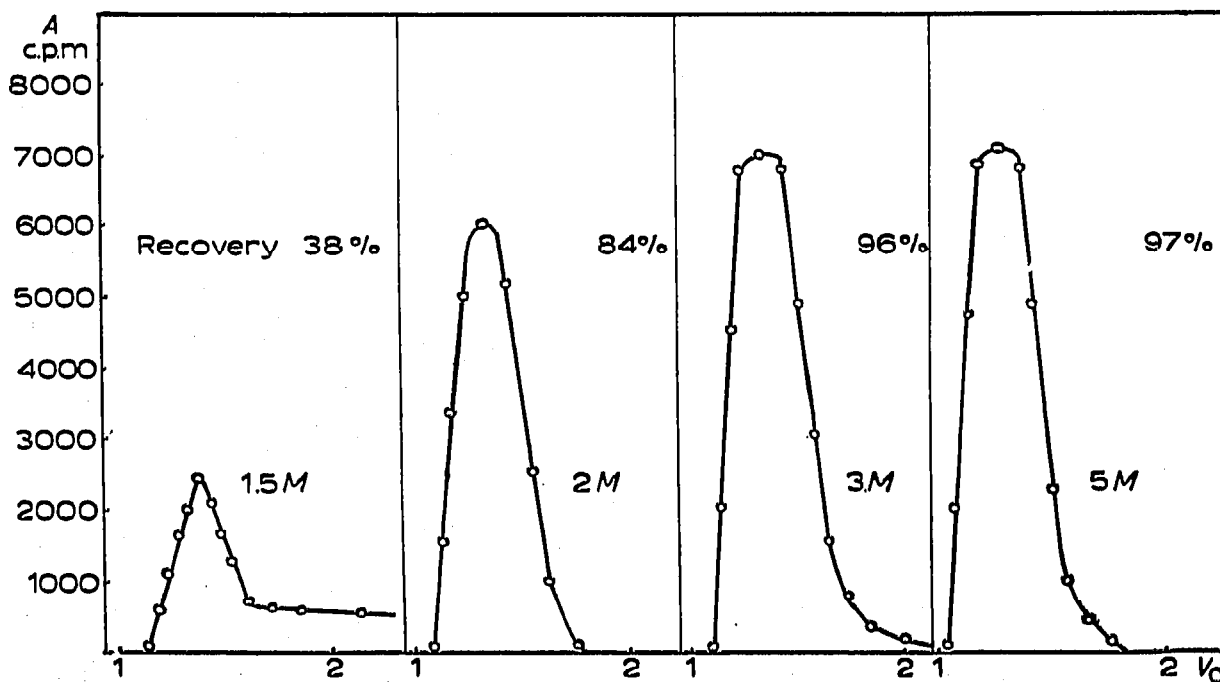
Fig. 3. The elution of Tb from the mixture U–Tb with nitric acid of varying concentrations. Flow rate: 1.1 ml·cm^{-2}·min^{-1}. Temperature: 25°.

even with HNO_3 of higher concentrations (Fig. 2). In the next series of experiments the column was always acidified with the eluting agent and the mixture was dissolved in acid of the same concentration. Elution with 1.5 M HNO_3 gave a better defined Tb curve, but still only 38 % of the total Tb activity was eluted in the main peak, the rest being strongly held on the column. An increase in the concentration of the eluting acid increased the amount of Tb in the main peak (Fig. 3). These results show that the distribution coefficient for the Tb introduced into the column is increased in the presence of a macroamount of U in contrast to previous experience with micro–macro separations.

In order to study this phenomenon in more detail, the influence of flow rate and temperature on the percentage recovery of Tb in the main peak has been investigated. The column was first conditioned with 1.5 M HNO_3, then an acidified (1.5 M HNO_3) mixture of U–Tb was introduced and eluted with 1.5 M HNO_3 at different temperatures and flow rates. The results are shown in Fig. 4, where it can be seen that increased temperature and decreased flow rate improve the separation, thus indicating that the observed effect can be attributed to a slow step in the kinetics of the distribution of Tb between the two phases in the presence of U. It was thought that the increased extraction of Tb in the presence of U could be explained by assuming that the complex between U and HDEHP behaves as a new sorbent which has a higher distribution coefficient for Tb than the HDEHP alone. This assumption has been disproved by an experiment in which Tb was introduced into a column previously saturated with U. No extraction of Tb was observed under these circumstances.

For practical purposes, it is important to know conditions for the separation of a multicomponent mixture when both the column and the mixture are only slightly acidic. In Fig. 5 the separation of Tb from U is presented as a function of the acidity of the eluting agent. The initial acidity of the column was 1.5 M HNO_3, the mixture was 0.1 N in HNO_3, the flow rate was 0.2 $ml \cdot cm^{-2} \cdot min^{-1}$ and the temperature 77°. It can be concluded that the lowest nitric acid concentration necessary for the efficient separation of Tb from U under these conditions is 1.5 M.

It is noteworthy that the elution curve for Tb is rather narrow but has a tail when the mixture and the column are only slightly acidic. When the mixture introduced into the column and the solution in the column are more acidic, the curve becomes broader but tailing is less pronounced. This difference can be attributed to selfsharpening of the front boundary. At the initial low acidity of the column the Tb is sorbed in a thin layer on the top of the column: this layer is eluted down the column by more concentrated HNO_3. The concentration of HNO_3 in the front of the layer is nevertheless always lower than in the rear, and, since the distribution coefficient of Tb increases with decreasing acid concentration, the selfsharpening of the front boundary occurs.

Separation of other pairs

The presence of macroamounts of U in a mixture also causes some difficulties in the separation of microamounts of other ions. This is demonstrated by the occurrence of tailing and incomplete elution of various ionic species from the column. Elution with a rather strong acid offers good separation but is useless for the group separation of a multicomponent mixture. Increasing the temperature and decreasing the flow
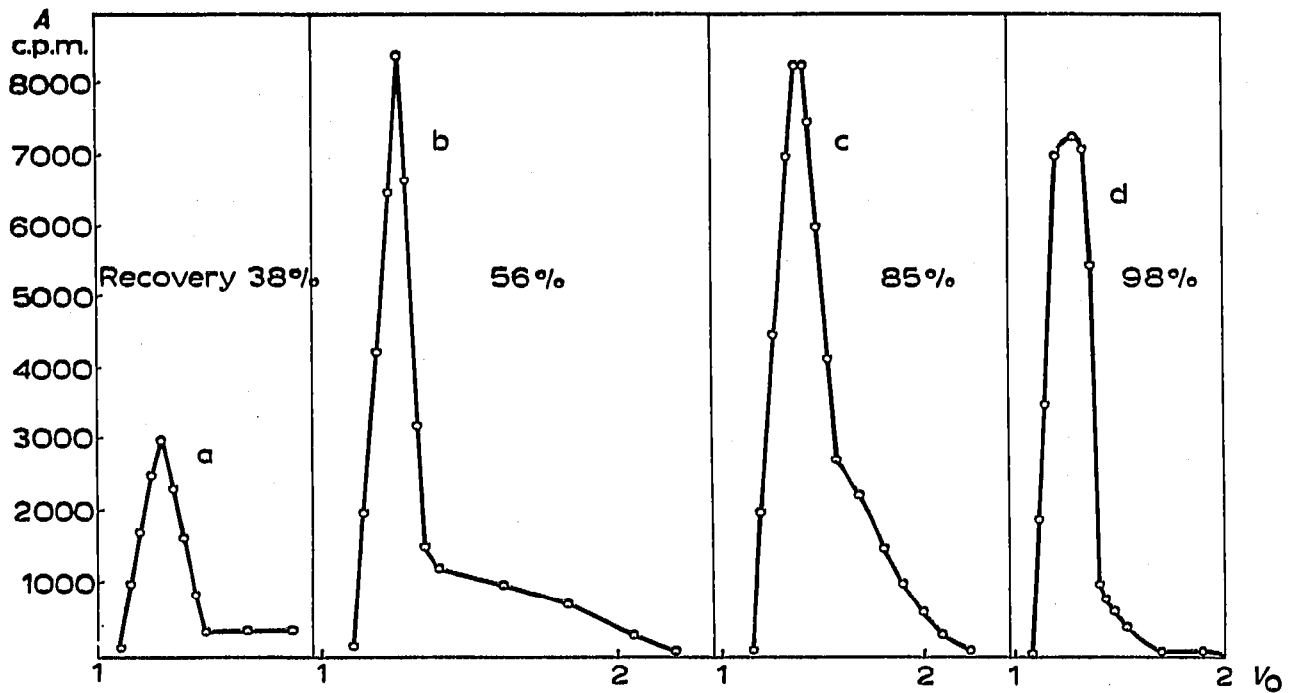
Fig. 4. The influence of temperature and flow rate on the separation of Tb from U. (a) Flow rate: 1.1 ml·cm^{-2}·min^{-1}. Temperature: 25°. (b) Flow rate: 0.2 ml·cm^{-2}·min^{-1}. Temperature: 25°. (c) Flow rate: 1.1 ml·cm^{-2}·min^{-1}. Temperature: 77°. (d) Flow rate: 0.2 ml·cm^{-2}·min^{-1}. Temperature: 77°.
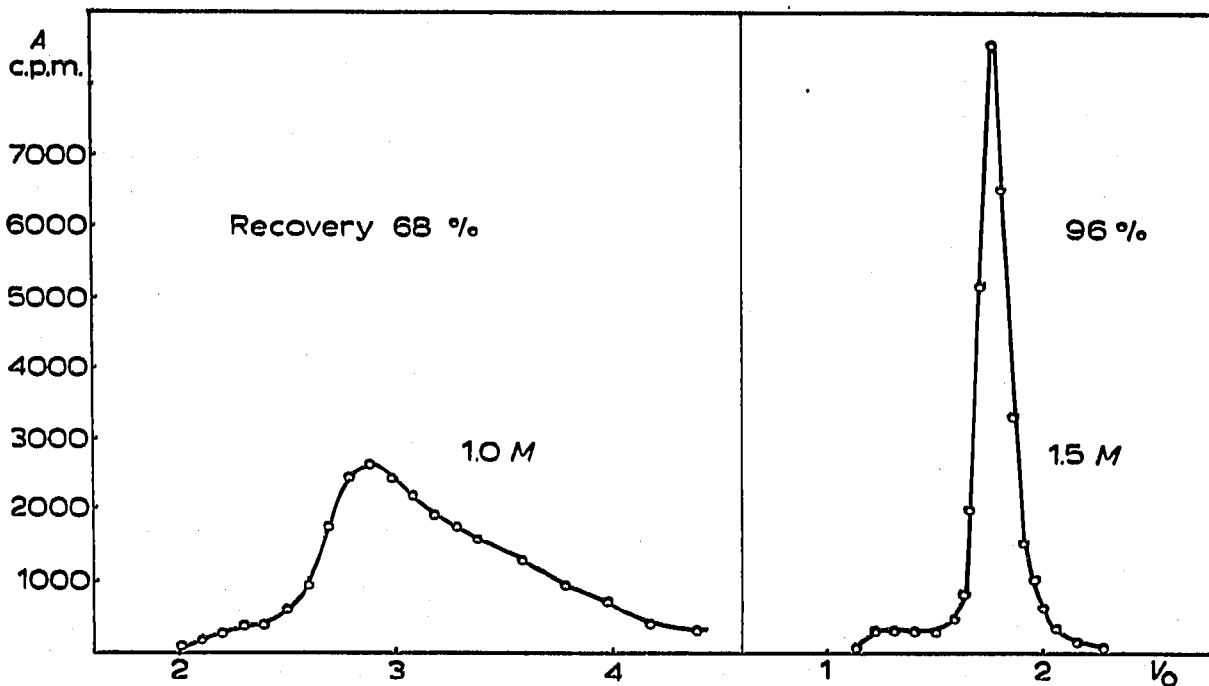
Fig. 5. The influence of the concentration of HNO$_3$ on the separation of Tb from U. Flow rate: 0.2 ml·cm^{-2}·min^{-1}. Temperature: 77°.

rate improve the separation so that more than 95 % of the species is eluted in the main peak even with dilute acid as eluant. The effect of temperature, flow rate and the concentration of the acid on the efficiency of the separation is shown in Table I. It is interesting to note that about 5 % of Cs remains on the column after elution with 0.1 M HNO_3. This is independent of the flow rate and the temperature even in the absence of U. Since Cs is not extracted with HDEHP one can conclude that retention of Cs on the column is due to physical adsorption.

TABLE I

THE SEPARATION OF MIXTURES: URANIUM(MACROAMOUNT)–METAL(TRACE)
50 % of the column capacity occupied by uranium.

Metal	Molarity of HNO_3			Flow rate ($ml \cdot cm^{-2} \cdot min^{-1}$)	Temperature (°C)	Eluted activity (%)
	Used for column conditioning	Used to dissolve the mixture	Used for elution			
Cs	0.1	0.1	0.1	1.1	25	95
Cs	0.1	0.1	0.1	1.1	77	95
Sr	0.1	0.1	0.1	1.1	25	96
Sr	0.1	0.1	0.1	1.1	77	98
Ba	0.1	0.1	0.1	1.1	25	72
Ba	0.1	0.1	0.1	1.1	77	98
La	0.32	0.1	0.32	1.1	25	72
La	0.32	0.1	0.32	1.1	77	96
Ce	0.32	0.1	0.32	1.1	25	70
Ce	0.74	0.1	0.74	1.1	25	77
Ce	0.32	0.32	0.32	1.1	25	93
Ce	0.32	0.32	0.32	1.1	77	93
Ce	0.32	0.1	0.32	0.2	77	96
Eu	0.16	0.16	1.008	1.1	25	56
Eu	1.008	1.008	1.008	0.2	77	96
Eu	0.16	0.16	4.0	0.2	77	98
Tb	1.495	1.495	1.495	1.1	25	38
Tb	2.0	2.0	2.0	1.1	25	84
Tb	3.0	3.0	3.0	1.1	25	96
Tb	1.495	1.495	1.495	0.2	77	98
Tb	0.1	0.1	2.0	0.2	77	80
Tb	0.1	0.1	5.0	0.2	77	98
Y	1.495	0.1	1.495	0.2	77	75
Y	2.0	0.1	2.0	0.2	77	89
Y	5.0	0.1	5.0	0.2	77	100

Group separation of a multicomponent mixture

Using data from Table I a group separation of the mixture containing Cs, Sr, Ba, La, Ce(III), Eu, Tb, Y, Zr and U was carried out. This mixture can serve as a model for the group separation of some fission products from irradiated U. The sample containing radioisotopes and U in a amount equivalent to 50 % of the column capacity was dissolved in 0.1 M HNO_3, introduced into the column, rinsed with 0.1 M HNO_3, and eluted with HNO_3 of varying concentrations. The flow rate at 77° was 0.2 $ml \cdot cm^{-2} \cdot min^{-1}$. Results are shown in Fig. 6. There are three peaks: the first containing Cs, Sr and Ba, the second containing La and Ce, and the third containing Eu, Tb and Y. The U can be stripped from the column with concentrated HCl,
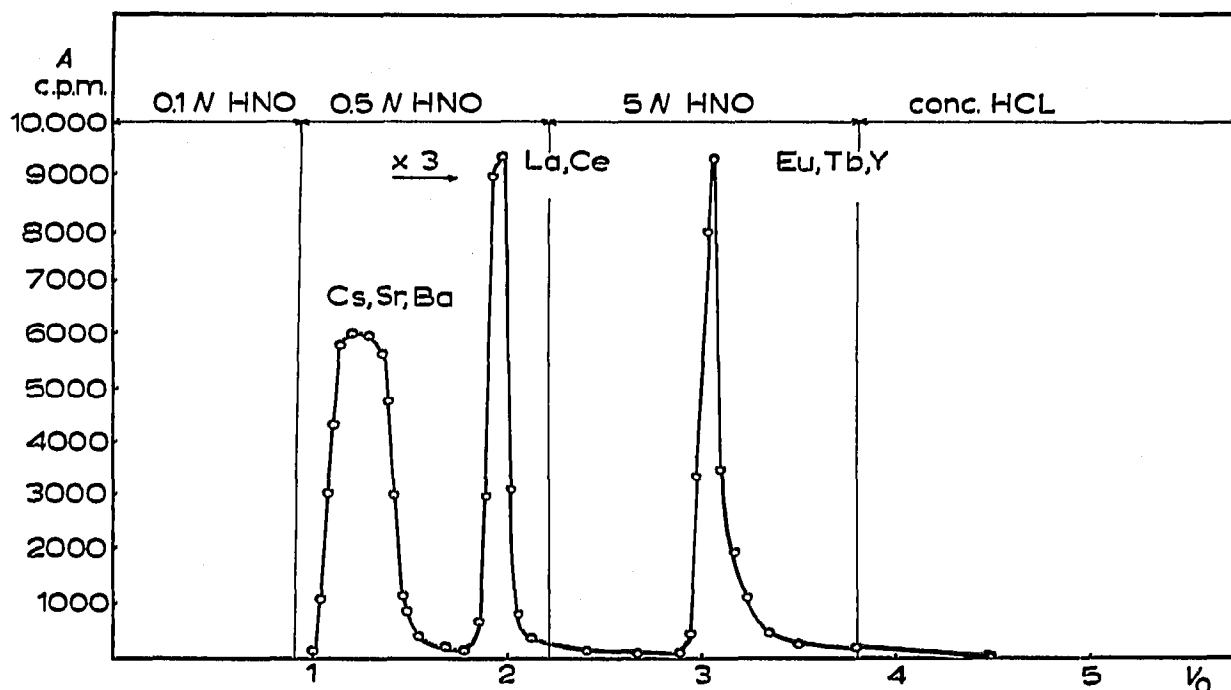
Fig. 6. Group separation of the mixture Cs–Sr–Ba–La–Ce(III)–Eu–Tb–Y–Zr–U using different concentrations of nitric acid. Flow rate: 0.2 ml·cm^{-2}·min^{-1}. Temperature: 77°.

while the Zr remains on the column. Each fraction was recovered with a yield greater than 95 %.

SUMMARY

Reversed-phase partition chromatography with di-(2-ethylhexyl) orthophosphoric acid (HDEHP) retained on kieselguhr as the stationary phase was used for the separation of some fission products in trace amounts from macroamounts of U. The presence of U on the column causes incomplete elution of radiotracers under the usual experimental conditions. Increasing the temperature and decreasing the flow rate improve the separation.

Group separation was performed of the synthetic mixture Cs–Sr–Ba–La–Ce(III)-Eu–Tb–Y–Zr–U. The elutions were carried out with nitric acid of varying concentrations. Applying a flow rate of 0.2 ml·cm^{-2}·min^{-1} at 77°, 95% recovery of the constituents of the mixture was achieved.

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