

## THE CHROMATOGRAPHIC SEPARATION OF URANIUM, THORIUM AND RARE EARTHS BY MEANS OF PAPER TREATED WITH A LIQUID ANION EXCHANGER

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Recently, the interest in chemical separation methods based on the use of suitably treated chromatographic papers has increased considerably. Many examples are reported in the literature, and lately, the problem of a quick and dependable method for the preparation of amine-containing papers has been solved in our laboratory<sup>1</sup>. Such papers, which contain an anion exchanger (tri-*n*-octylamine), were successfully applied to the resolution of some mixtures of chemical elements that are very similar. As described, a hydrochloric medium was used as the eluent, because the various elements differ in their ability to form hydrochloric complexes.

The separation of uranium, thorium and rare earths, which is of considerable interest in the field of nuclear chemistry, cannot be adequately performed by conventional paper chromatography since the  $R_F$  values of thorium and the rare earths are very similar<sup>2</sup>.

Furthermore, thorium and rare earths do not form hydrochloric complexes<sup>3</sup>, and hence thorium cannot be separated from rare earths even by the above-mentioned method of elution from aminated paper with hydrochloric acid. Similarly, as is well known, these elements in hydrochloric solution are not retained by anion exchange resins or extracted by liquid anion exchangers. On the other hand, the behaviour of uranium, thorium and the rare earths in nitrate solutions is dissimilar<sup>4-7</sup>, their distribution coefficients being very different, so that it is possible to obtain a good separation of the elements from each other.

Since it was shown<sup>1</sup> that paper treated with a liquid anion exchanger (tri-*n*-octylamine) acts very much like a film of an anionic resin, it was decided to investigate the chromatographic separation of uranium, thorium and rare earths by paper chromatography on aminated paper in a nitrate system.

### EXPERIMENTAL AND RESULTS

#### *Preparation of the paper*

For all the experiments described below, Whatman No. 1 paper was used. The tri-*n*-octylamine (Fluka and Light's) was applied by dipping square or rectangular sheets of paper into a solution of the amine in benzene. This solution was prepared by adding

sufficient amine to benzene to obtain the required molarity, and then shaking for 5 min with three times the volume of nitric acid or nitrate of a given concentration in water. In this way the amine is converted into the nitrate salt; this makes the elution more regular and the solvent front well-defined. Then the organic phase was separated and freed from residual droplets of the aqueous phase by passing it through cotton lint. After soaking the paper, it was allowed to drip and then dried with warm air to remove the excess of benzene. The amount of amine fixed on the paper was determined by weighing a  $15 \times 15$  cm sheet of paper before and after treatment. When using a 0.1 *M* solution of amine in benzene the amount fixed proved to be 0.55 mg/cm<sup>2</sup>. Obviously, by using more concentrated solutions, this amount can be considerably increased. After the paper was ready for use it was cut partly into 10 cm diameter discs for circular chromatography, and partly into  $5 \times 30$  cm strips for descending chromatography.

#### *Solutions of the elements*

The solutions of the elements were prepared from  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  (B.D.H.),  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck). Since in the first experiments, cerium (III) and lanthanum behaved in the same fashion, only lanthanum was used subsequently.

#### *Circular chromatography*

A drop of about 10  $\mu\text{l}$ , containing 25–50  $\mu\text{g}$  of each element, was deposited at the center of the disc and immediately dried. The spot was then developed at room temperature (20°) by slowly dropping 2 or 3 ml of the appropriate eluent at the center of the disc with a micropipette, till the diameter of the wet surface was about 7 cm.

The elution time ranged from 10 to 20 min according to the viscosity and density of the eluent solution and the permeability of the paper. The permeability of the paper in turn depends on the molarity of the amine solution used for the treatment.

After the elution was completed, the paper was dried and the zones developed by means of a 0.1 % solution of morin in alcohol; uranium and thorium are revealed at once, whereas lanthanum (or Ce (III)) appear only after the paper has been exposed to ammonia vapour.

#### *Elution with $\text{HNO}_3$*

The  $R_F$  values for uranium, thorium and lanthanum were measured as functions of the molarity of the nitric acid used as eluent. In this experiment the paper was treated with an amine solution which had been pre-equilibrated with 10 *M*  $\text{HNO}_3$ , and the elution was performed with  $\text{HNO}_3$  in the range from 1 *M* to 10 *M*. The experimental results reported in Fig. 1 show that in the whole range of  $\text{HNO}_3$  molarities, thorium is retained more strongly than uranium, while lanthanum always moves with the solvent front. When the  $\text{HNO}_3$  molarity of the eluent increases from 1 to 6, both thorium and uranium become progressively more complexed and hence their  $R_F$  values become lower and lower. From 6 *M* to 10 *M*, however, the  $R_F$  values rise again.

This fact is probably due to anion exchange between the nitric acid and the anionic complex fixed by the aminated paper. Analogous behaviour was found during the adsorption of thorium and uranium from nitric acid solutions on anionic resins<sup>5-6</sup> or by extraction with tri-*n*-octylamine<sup>7</sup> and tri-iso-octylamine<sup>8</sup>.

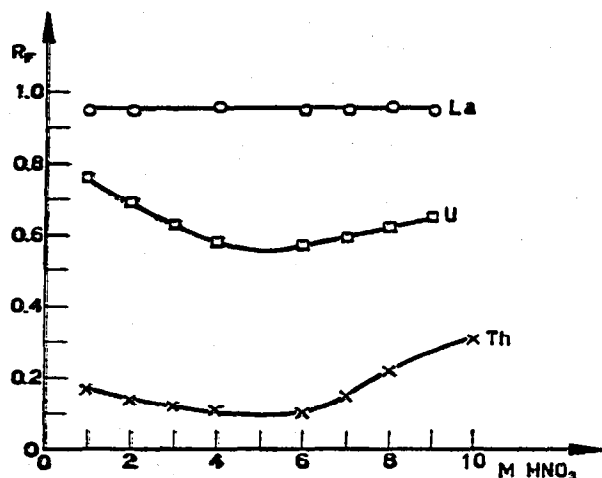


Fig. 1.  $R_F$  values on paper treated with 0.1 M TNOA in benzene vs. molarity of  $\text{HNO}_3$  in the eluent.

The  $R_F$  values of the three elements (U, Th and La) were compared with the values of the extraction coefficient  $E_a^0$ , by shaking 10 ml of 0.2 M tri-*n*-octylamine (TNOA) for 10 min with 10 ml of a 0.01 M solution of each element, containing different amounts of  $\text{HNO}_3$ .

Thorium and lanthanum were determined by complexometry, and uranium by colorimetry. The results are shown in Fig. 2; in Fig. 2a the values of  $1/R_F - 1$  are given and in Fig. 2b the extraction coefficients  $E_a^0$ . From the plots it is clear that lanthanum is always very poorly extracted ( $E_a^0 = 0.01$  and  $R_F = 0.96$ ) and that both uranium and thorium show the highest extraction between 6 M and 7 M  $\text{HNO}_3$ .

The shape of the curves is very similar for the quantities  $1/R_F - 1$  and  $E_a^0$ , and under the above conditions the extraction coefficients of uranium are quite close to those of thorium. This fact does not account for the considerable difference in the  $R_F$  values that was found in our experiments, but the effect of the amine concentration must also be considered. In fact, as shown in Fig. 3, the extraction of thorium is increased much more than that of uranium when the amine concentration is raised. These experiments were carried out by shaking 10 ml of a 3 M  $\text{HNO}_3$  solution 0.01 M in uranium or thorium, with 2 mmoles of TNOA diluted with varying amounts of benzene. By changing the amine concentration from 0.1 M to 2.3 M, the extraction coefficient of thorium is increased about 1,000 times, whereas that of uranium is increased only 80 times.

It can be inferred that the amine fixed on the paper behaves as if it were in a concentrated solution, since the solvent is completely removed during the preparation; this would enhance the difference between the  $R_F$  of uranium and that of thorium.

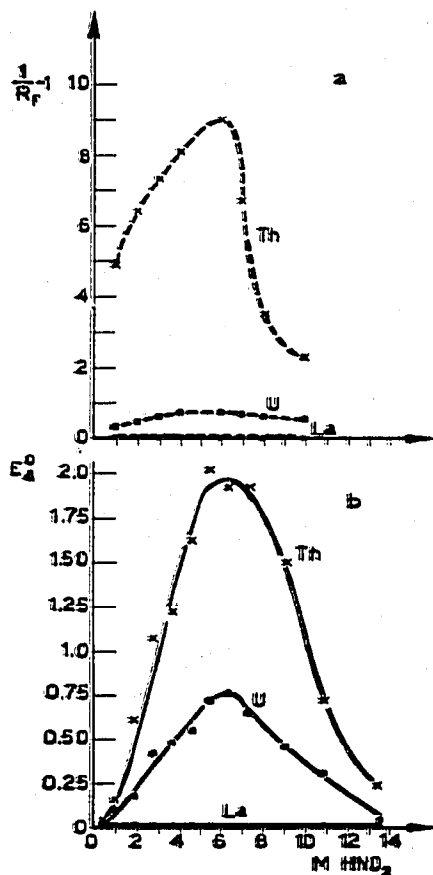


Fig. 2. Comparison of (a)  $D_r$  vs. the molarity of HNO<sub>3</sub> in the eluent and (b) the extraction coefficient  $E_a^0$ , for 0.2 M TNOA in benzene, vs. the molarity of HNO<sub>3</sub> in the aqueous phase.

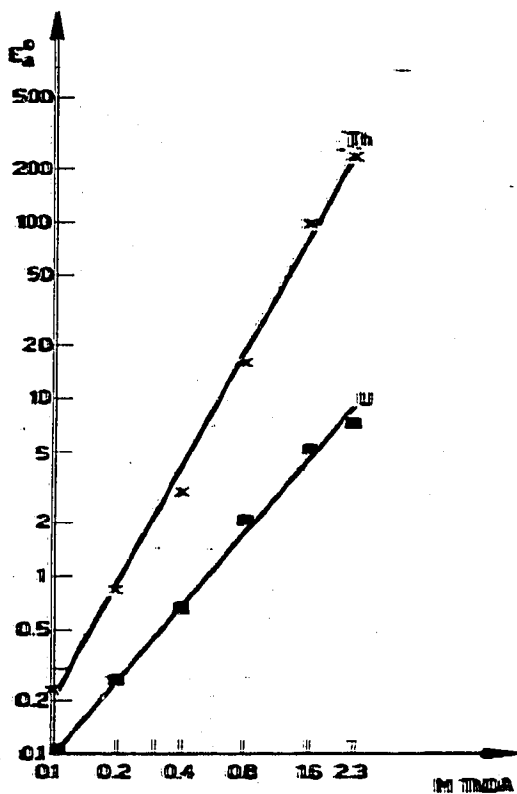


Fig. 3. Effect of the dilution of TNOA (2 mmoles in total) in benzene on the extraction coefficient  $E_a^0$ ; 3 M HNO<sub>3</sub>.

Moreover, by treating the paper with solutions of TNOA in benzene, of molarities ranging from 0.01  $M$  to 0.6  $M$ , the  $R_F$  values were considerably lowered for uranium and thorium, the decrease being greatest for the latter. These results are shown in Fig. 4.

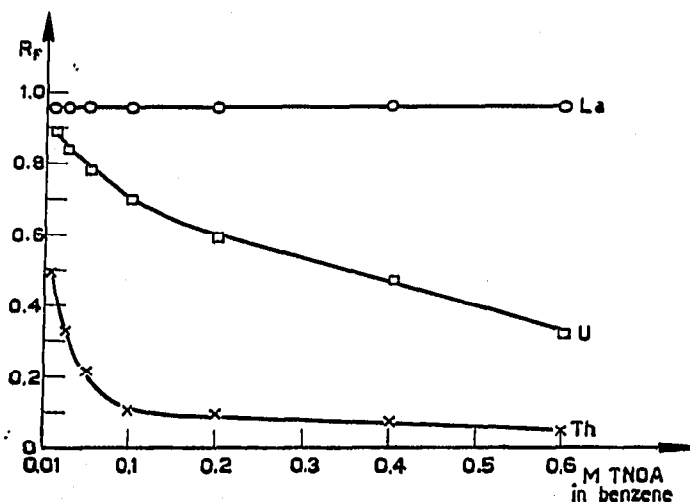


Fig. 4. Effect on  $R_F$  of the molarity of the TNOA used for treatment of the paper; eluent 3  $M$   $HNO_3$ .

Therefore the difference in behaviour of the two elements can be influenced both by the molarity of the eluting acid and by that of the amine used to treat the paper.

#### *Elution with nitrate salts*

Elsewhere<sup>4</sup>, it has been pointed out that the adsorption of uranium on anionic resins can be enhanced by using  $NH_4NO_3$  instead of  $HNO_3$ , at the same molarity. In this case thorium behaves approximately as in a  $HNO_3$  solution, whilst the rare earths, which are not adsorbed from  $HNO_3$  solutions, show sufficient adsorption from ammonium nitrate and lithium nitrate solutions<sup>9</sup>. Furthermore, no re-extraction takes place at higher  $NO_3^-$  molarities. Therefore, the possibility of using solutions of a nitrate salt as the chromatographic eluent was considered.

Lithium nitrate was investigated first. The 0.1  $M$  TNOA was pre-equilibrated with three times its volume of a solution 6  $M$  in  $LiNO_3$  and 0.005  $M$  in  $HNO_3$ . The free acid, which was also present in the eluent, was added in order to prevent hydrolysis of the salts of the elements being investigated. The paper was then prepared in the usual way and chromatography was carried out by eluting with lithium nitrate solution, the molarity of which ranged from 1  $M$  to 6  $M$ . The results given in Fig. 5 show that: (a) the  $R_F$  values of uranium are lower than those obtained with  $HNO_3$  at the same molarity (see Fig. 1); (b) the  $R_F$  values diminish continuously as the molarity of nitrate is increased up to 6  $M$ ; (c) for thorium there is no marked difference between  $HNO_3$  and  $LiNO_3$ ; (d) the  $R_F$  values of lanthanum are slightly lowered. Generally, the picture of this type of ion exchange chromatography is very similar to that of ion exchange on anionic resins.

Fig. 6 shows the experimental results obtained with 3  $M$   $LiNO_3$  and  $HNO_3$

from 0.025 *M* to 1 *M*. These results show that uranium and lanthanum are progressively less retained; in fact, their  $R_F$  values increase, whilst those of thorium remain unaffected. In this case, however, the amine solution had not been pre-equilibrated

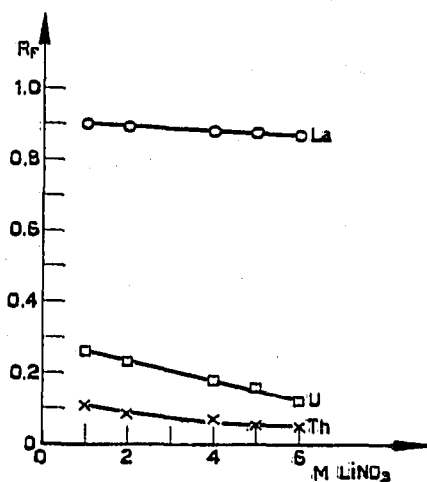


Fig. 5.  $R_F$  values on paper treated with 0.1 *M* TNOA in benzene vs. molarity of  $\text{LiNO}_3$  in the eluent.

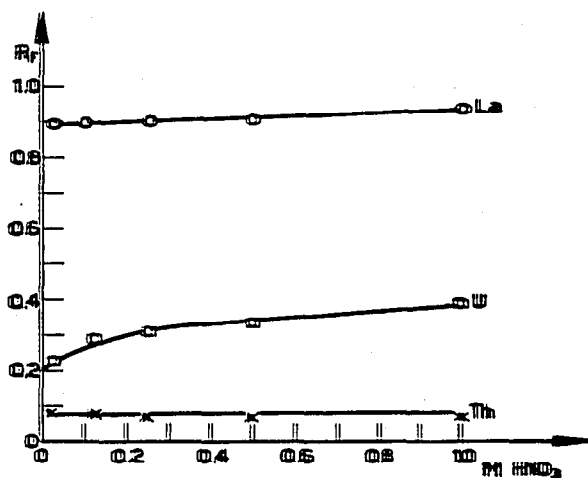


Fig. 6. Effect on  $R_F$  of the molarity of the  $\text{HNO}_3$  present in the 3 *M*  $\text{LiNO}_3$  eluent.

with the nitrate solution. The effect of lithium nitrate is clearly seen in Fig. 7, which shows that by varying the  $\text{LiNO}_3$ - $\text{HNO}_3$  ratio (the total  $\text{NO}_3^-$  molarity being 6 *M*), the  $R_F$  values of uranium are greatly affected. For these experiments the amine solution had been pre-equilibrated with three times its volume of the respective eluent solution.

Some experiments were carried out with  $\text{NaNO}_3$ , the concentration being varied from 1 *M* to 8 *M* ( $\text{HNO}_3$  0.005 *M*). The results plotted in Fig. 8 show that the behaviour of the  $R_F$  values is similar to that found with  $\text{LiNO}_3$ ; moreover no back-extraction was found up to 8 *M*, since the  $R_F$  values decrease progressively as the molarity increases.

Similar experiments were carried out with  $\text{NH}_4\text{NO}_3$  of molarities from 1 *M* to 10 *M* ( $\text{HNO}_3$  0.005 *M*). The paper was treated with amine pre-equilibrated with 10 *M*  $\text{NH}_4\text{NO}_3$  + 0.005 *M*  $\text{HNO}_3$ . As shown in Fig. 9, the  $R_F$  curve of thorium is very similar to that obtained with the other alkali nitrates, while the  $R_F$  values of uranium are lower than those with nitric acid, but higher than with lithium and sodium nitrate. This can be due to the higher acidity arising from free  $\text{HNO}_3$ , which results from the hydrolysis of  $\text{NH}_4\text{NO}_3$  solutions. The behaviour of lanthanum with  $\text{NH}_4\text{NO}_3$  was rather interesting because in this case the  $R_F$  values are considerably lower than in all the experiments discussed above.

With  $\text{NH}_4\text{NO}_3$ , as with  $\text{LiNO}_3$  and  $\text{NaNO}_3$ , no increase of the  $R_F$  values with increasing concentration of nitrate ions was found up to 10 *M*.

The effect of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Al}(\text{NO}_3)_3$  was also investigated. The results plotted in Fig. 10 show that the effect of calcium nitrate is very similar to that of sodium and lithium nitrate, provided that the concentration of nitrate ion is the same. As

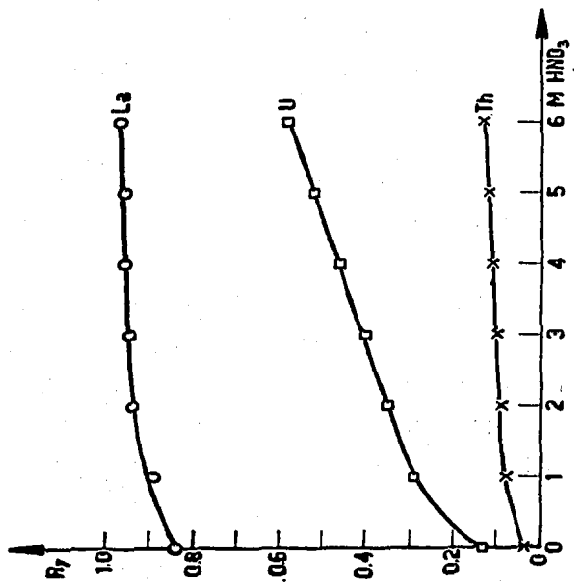


Fig. 7. Effect on  $R_F$  of the ratio  $HNO_3/LiNO_3$  in the eluent; total nitrate ion molarity 6  $M$ .

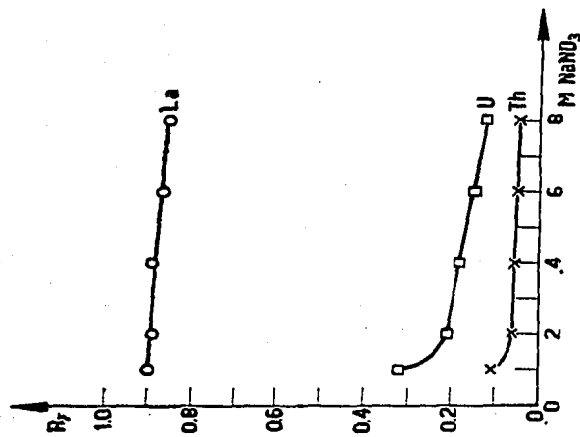


Fig. 8.  $R_F$  values on paper treated with 0.1  $M$  TNOA-benzene vs. molarity of  $NaNO_3$  in the eluent.

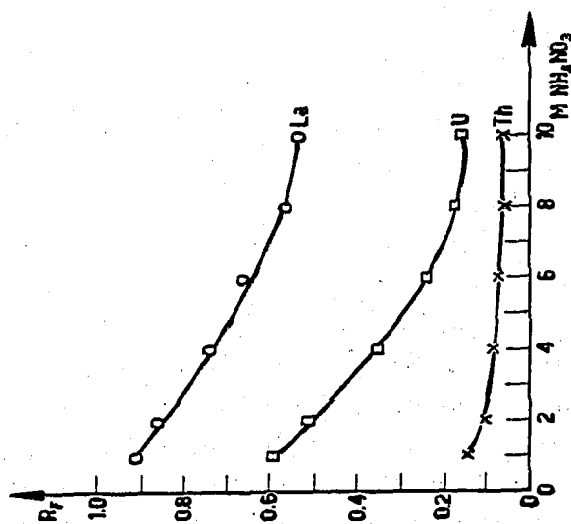


Fig. 9.  $R_F$  values on paper treated with 0.1  $M$  TNOA-benzene vs. molarity of  $NH_4NO_3$  in the eluent.

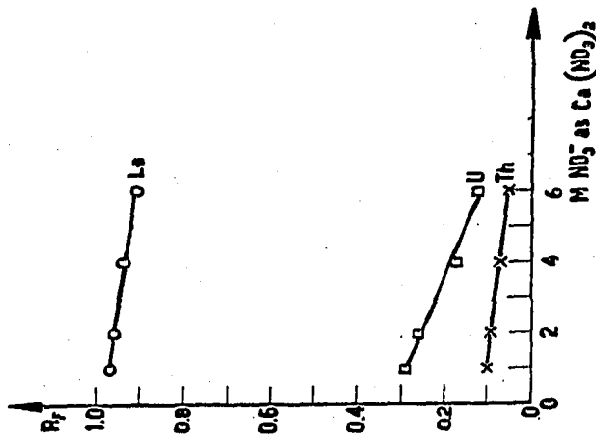


Fig. 10.  $R_F$  values on paper treated with 0.1  $M$  TNOA-benzene vs. nitrate ion molarity of the  $Ca(NO_3)_2$  eluent.

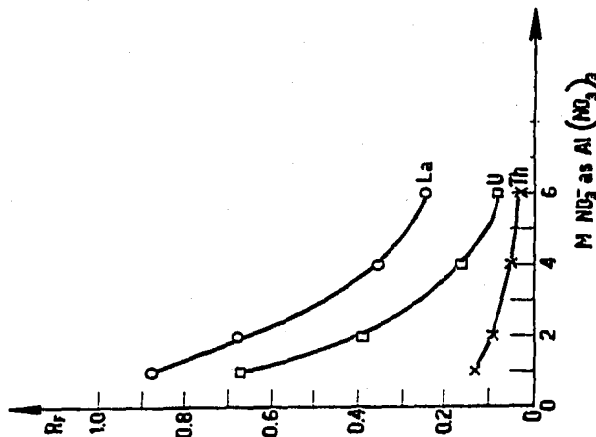


Fig. 11.  $R_F$  values on paper treated with 0.1  $M$  TNOA-benzene vs. nitrate ion molarity of the  $Al(NO_3)_3$  eluent.

shown in Fig. 11, the behaviour of thorium was normal with aluminium nitrate, while the  $R_F$  values of uranium were relatively higher at lower molarities of nitrate, but rapidly reached the normal values as the molarity increased. Similar results were obtained also for lanthanum, which, at higher molarities, has lower  $R_F$  values than with ammonium nitrate.

For the experiments with the calcium and aluminium salts the paper was treated with an amine solution previously equilibrated with the eluting solution containing the highest concentration of the respective salt (6 M and 0.005 M  $\text{HNO}_3$ ).

To facilitate comparison of the experimental data, all the results have been collected in Table I.

TABLE I  
CIRCULAR CHROMATOGRAPHY  
EFFECT OF THE NATURE AND CONCENTRATION OF THE ELUENT ON THE  $R_F$   
Paper treated with 0.1 M TNOA-benzene.

Molarity $\text{NO}_3^-$		1	2	4	6	8	10
$\text{HNO}_3$	Th	0.17	0.14	0.11	0.10	0.22	0.31
	U	0.76	0.69	0.58	0.57	0.62	0.65
	La	0.95	0.95	0.96	0.95	0.95	0.96
$\text{LiNO}_3$	Th	0.11	0.08	0.07	0.05		
	U	0.26	0.23	0.18	0.12		
	La	0.90	0.89	0.88	0.87		
$\text{NaNO}_3$	Th	0.11	0.06	0.05	0.05	0.05	
	U	0.32	0.21	0.18	0.15	0.12	
	La	0.90	0.89	0.89	0.87	0.86	
$\text{NH}_4\text{NO}_3$	Th	0.14	0.10	0.08	0.06	0.05	0.05
	U	0.59	0.51	0.35	0.24	0.17	0.15
	La	0.91	0.86	0.74	0.66	0.56	0.53
$\text{Ca}(\text{NO}_3)_2$	Th	0.10	0.09	0.07	0.05		
	U	0.29	0.26	0.17	0.12		
	La	0.97	0.96	0.94	0.92		
$\text{Al}(\text{NO}_3)_3$	Th	0.13	0.09	0.05	0.03		
	U	0.67	0.39	0.16	0.08		
	La	0.88	0.68	0.36	0.25		

#### *Descending chromatography*

Good results in the separation of uranium, thorium and lanthanum were also obtained with descending chromatography.

From the experimental data, which are reported in Table II, the following observations have been made:

(a) Thorium and uranium present well defined oval spots, while lanthanum, which is not retained by the amine, forms a narrow band extending all along the solvent front.

(b) By lowering the amine concentration on the paper, all the other conditions being equal, the  $R_F$  values of uranium and thorium increase considerably as in the case of circular chromatography.



(c) The  $R_F$  value is unaffected by the distance that the front runs, provided that the other conditions are kept constant.

Some chromatograms were also made by using 0.1 mg and 1 mg of each element. The solution was deposited along a horizontal band at the start; after elution with

TABLE II  
DESCENDING CHROMATOGRAPHY  
Amount of element deposited: 25  $\mu\text{g}$ ; eluent 3 M  $\text{HNO}_3$ .

Front run cm	Molarity of pre-equilibrated amine	$R_F$		
		Th	U	La
24	0.20	0.02	0.23	0.98
18	0.10	0.05	0.42	0.97
16	0.05	0.16	0.68	0.97
28	0.05	0.15	0.68	0.97

5 M  $\text{HNO}_3$  and development, thorium, uranium and lanthanum showed three distinct bands, which differed in width.

Two experiments were performed with  $\text{NH}_4\text{NO}_3$  as the eluent, and in this case also lanthanum formed a distinct spot. The experimental data are given in Table III.

TABLE III  
DESCENDING CHROMATOGRAPHY  
Amount of element deposited: 25  $\mu\text{g}$ ; paper treated with 0.05 M TNOA-benzene.

Front run cm	Molarity of $\text{NH}_4\text{NO}_3$ and $\text{HNO}_3$ in the eluent	$R_F$		
		Th	U	La
32	10 M $\text{NH}_4\text{NO}_3$ 0.02 M $\text{HNO}_3$	0.02	0.20	0.60
29	2 M $\text{NH}_4\text{NO}_3$ 0.1 M $\text{HNO}_3$	0.05	0.70	0.87

### CONCLUSIONS

Good separations of uranium, thorium and rare earths can be obtained by chromatography on paper treated with tri-*n*-octylamine. Nitric acid, or a solution of a nitrate salt, can be used as the eluent. As previously observed for the chloride complexes, in this case also a certain concordance exists between the behaviour of the  $R_F$  and that of both the distribution coefficient of anionic resins and the extraction coefficients of liquid anion exchangers. Treatment of the chromatographic paper with various substances that have a certain degree of selectivity for the different elements (amines, phosphines, organo-phosphoric acids, inorganic exchangers<sup>10</sup>, etc.) appears to be a useful tool for the analytical chemist, and many separation problems can be solved by

selecting both the appropriate substance for the treatment and a suitable eluent. For instance, the separation of uranium, thorium and lanthanum can be carried out also from hydrochloric solutions by using a paper treated with tri-*n*-octyl-phosphine oxide (TOPO). An experiment was made with a solution of 3 *N* HCl and paper treated with 0.05 *M* TOPO in cyclohexane. In this case, as expected from the extraction curves with TOPO<sup>III</sup>, uranium is most strongly retained and presents the smallest  $R_F$  (0.06), followed by thorium ( $R_F = 0.38$ ) and lanthanum ( $R_F = 0.97$ ).

A new series of experiments is now being performed, in which cellulose powder treated with TNOA is used to carry out column chromatography. Good results have been obtained and will be described in a subsequent paper.

#### SUMMARY

The chromatographic separation of uranium, thorium and rare earths was carried out by using a paper treated with tri-*n*-octylamine (TNOA).

Solutions containing HNO<sub>3</sub>, LiNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, NaNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> were used as eluents. This type of chromatographic separation is analogous to ion exchange on anionic resins or with liquid amines.

The effects of the various parameters on the  $R_F$  values are examined.

The separation of thorium, uranium and lanthanum with hydrochloric solutions, on paper treated with tri-*n*-octyl-phosphine oxide was investigated.

The possibility of using columns filled with cellulose powder treated with TNOA, as anionic resin columns is also anticipated.

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