Ugovor SKNE : br. 04 - 1 / 33
Šifra Instituta : 3.16
Nosilac ugovora : Dr. Ivan Gal

PRERADA ISLUŽENOG NUKLEARNOG GORIVA
/ Izveštaj za 1963 g. /

Prilog 7 : CHROMATOGRAPHIC SEPARATION OF METAL IONS BY MEANS OF PAPER TREATED WITH TRIOCTYL - PHOSPHATE

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V I N Č A
1963

BULLETIN OF THE BORIS KIDRIČ INSTITUTE OF NUCLEAR SCIENCES
Vol. 14, № 2, P/302, April 1963.

CHROMATOGRAPHIC SEPARATION OF METAL IONS BY MEANS OF PAPER TREATED WITH TRIOCTYL-PHOSPHATE

by

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The chromatographic behavior of uranium, thorium, and some other metal ions and long-lived fission products was investigated on paper treated with trioctyl-phosphate. Hydrochloric, nitric, sulphuric and perchloric acids in concentrations of 0.1-10 N were used as the elution agents. The R_f values of the ions investigated, which show the possibility of the interseparation of some cations, are given as a function of the concentration of acids.

Many interesting achievements in chemical separation have recently been made by using cellulose powder or chromatographic paper treated with tri-n-octylamine (TNOA) (1, 2, 3, 4),tri-n-octyl-phosphine oxide (TOPO) (5, 6), and di(2-ethyl-hexyl) phosphate (HDEHP) (7, 8, 9). The selectivity of the separation of different elements in corresponding media is connected with the properties of these extragents, which either act as anion exchangers (TNOA), or form neutral additional compounds with extracting elements (TOPO), or behave like cation exchangers (HDEHP).

The purpose of our investigations was to study the behavior of metal ions on paper treated with tri-n-octylphosphate; we were especially interested in uranium,thorium and some long-lived fission products, and we wanted to determine the relationships between the R_f values and concentration of the eluting agents, and the concentration of the organic solvent used for the treatment of the paper. When all these factors were known, it was necessary to find the best conditions for separating the investigated elements by descending chromatography.

Experimental procedure

Materials and reagents

The chromatographic paper was treated with an 0.1 M solution of tri-n-octylphosphate in carbon tetrachloride. Tri-n-octylphosphate

(Fluka, Buchs SG, Switzerland), chemical composition $(C_8H_{17})_3PO_4$, mol. weight 434.63, ρ = 0.92 at 23°C was used. We mainly used the nitrate and chloride solutions of the elements investigated. The radioisotopes were supplied by the Isotope Production Department of the Boris Kidrič Institute; the fission products were supplied by the radiochemical centers Amersham (England) and Saclay (France).

All the investigations were performed on Whatman No. 4 paper. The bandwidth was 28 x 2.5 cm. The dimensions of the glass cells were 24 x 12 x 8 cm, and the glass cylinders were 40 cm long.

Treatment of the paper and the procedure

The TOP/CCl_4 solution was equilibrated for 5 minutes with the same amount of acid with the highest normality used for elution. The organic phase was then passed through a filter paper so as to eliminate any traces of the inorganic phase. The chromatographic paper was impregnated by dipping the band (57 x 2.5 cm) into the solution for 30 seconds. The paper bands were then dried for 10 hours in air. When 0.1 M TOP in carbon tetrachloride was used, the amount fixed on the paper was 1.2 mg/cm^2, determined by weighing the paper before and after the treatment. Neutral and weak acid solutions of metal ions in amounts of 0.005-0.020 ml, i.e., 5-50 μg of each ion, were put on the paper thus treated. The amount of radioactivity during the investigation of the active substance was 0.5-5 μC. The paper bands were put into glass cells or cylinders and the descending chromatographic method was used in a closed atmosphere. The elution time for 20 cm front runs ranged from 35 to 90 min. depending on the kind and normality of the acid used.

Table I shows the concentrations of the acids used.

Table I

Eluents	
Acid	Normality
HCl	0.5; 1; 2; 4; 6; 8; 10
HNO_3	0.5; 1; 2; 4; 6; 8; 10
H_2SO_4	0.1; 0.5; 1; 2; 4;
$HClO_4$	0.1; 0.5; 1; 1.5; 2

Concentrations of H_2SO_4 stronger than 4 N and concentrations of $HClO_4$ stronger than 2 N attacked the paper, so they could not be used.

After the paper had been eluted and dried, the ions were identified with specific reagents for the cations examined (5, 10). The identification of ^{51}Cr, ^{90}Sr-^{90}Y, ^{95}Zr-^{95}Nb, ^{106}Ru, ^{137}Cs, ^{144}Ce was done ra-

diometrically, by measuring the activity along the chromatogram with a GM counter, using an automatic recorder, or by measuring strips of the chromatogram on the scintillation counter.

Results and discussion

In this way the behavior of about 30 elements was investigated, taking the above concentrations of HCl, HNO_3, H_2SO_4, and $HClO_4$ as the elution agents. Figures 1, 2, 3, and 4 show the results obtained which are presented as the curve of the R_f values versus the normality of the eluting agent. The R_f values were calculated from the center of the spot.

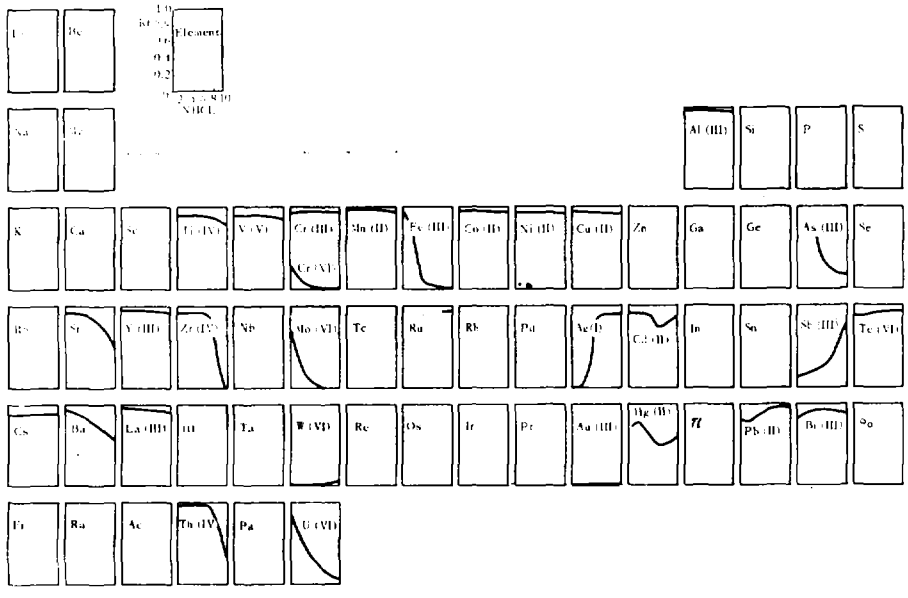

Fig. 1. - The R_f values of the investigated ions as functions of the HCl normality

The higher the extraction coefficient E_a° in case of TOP, the lower the R_f value under the same conditions of acidity, i.e., $R_f \to 0$ if $E_a^\circ \to \infty$, and $R_f \to 1$, if $E_a^\circ \to 0$. This was also the case when the paper was treated with TNOA, TOPO and HDEHP (1, 2, 5, 9). The R_f values obtained give an insight into the extraction properties of TOP for a larger number of metal ions, with the exception of some few cases; it also gives an insight into the type and normality of the acid most sui-

table for the extraction of an element under given conditions.

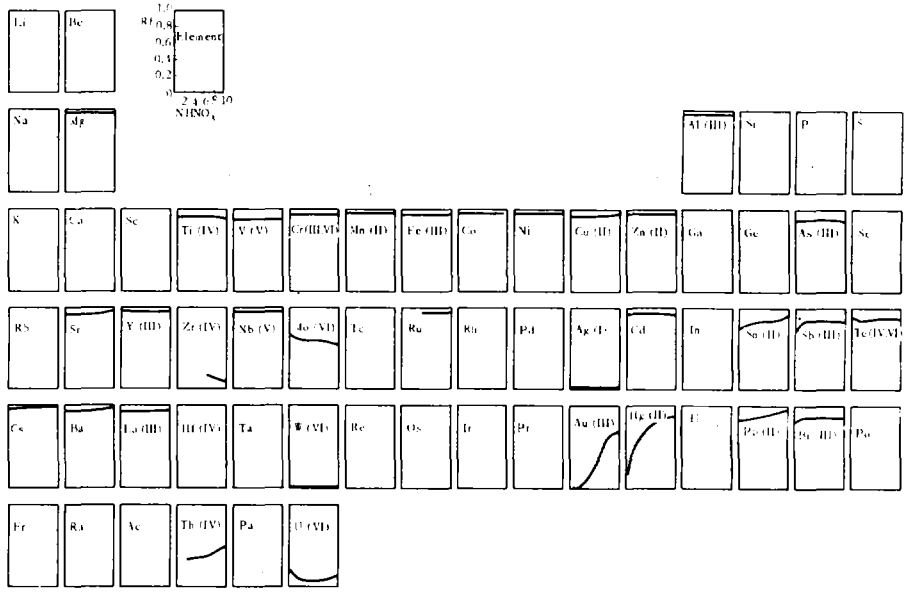

Fig. 2. - The R_f values of the investigated ions as functions of the HNO_3 normality

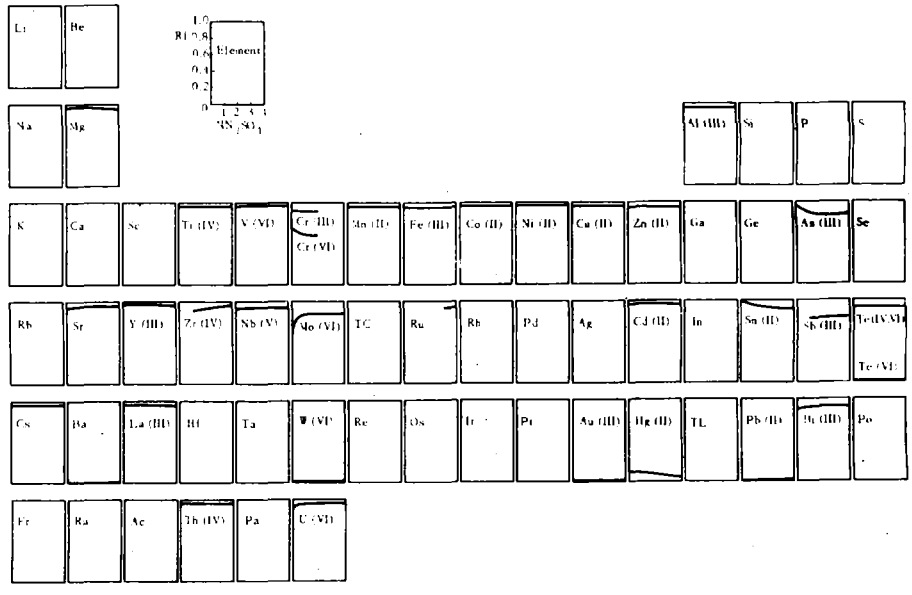

Fig. 3. - The R_f values of the investigated ions as functions of the H_2SO_4 normality

From the data presented, conditions for the separation of two or more elements or different oxidation states of an element can be found.

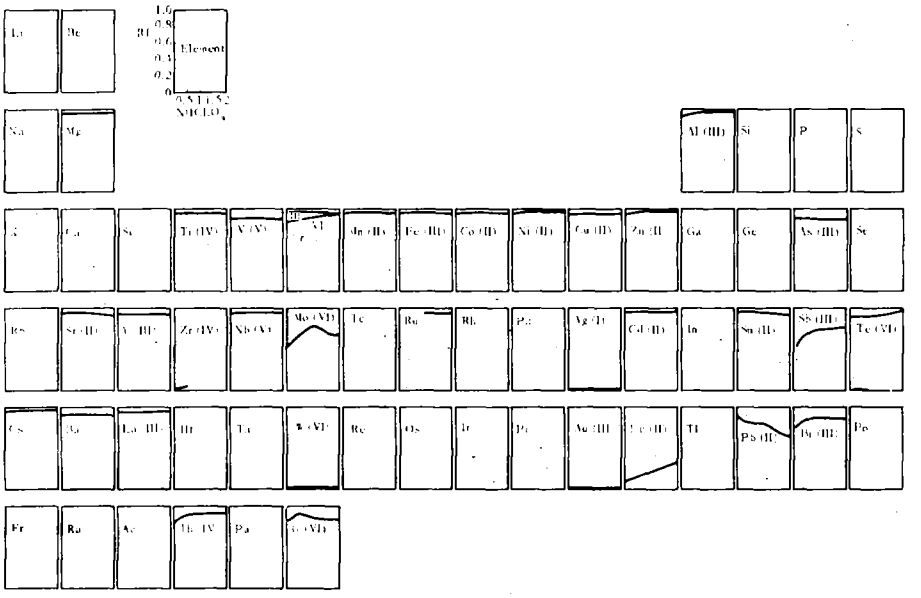

Fig. 4. - The R_f values of the investigated ions as functions of the $HClO_4$ normality

The exceptional behavior of some cations has been observed here too. The low R_f values obtained for Pb, Ag, and Ba by elution with H_2SO_4 were not the result of the extraction of these elements with TOP, but of the formation of insoluble salts with the acids mentioned. The R_f values for Sr and Ba which are obtained by elution with HCl and are considerably lower than 1, are a result (5) by the adsorption by cellulose of dehydrated cations with a small ion radius. In the case of some elements such as Te and Sb which have several valence forms with some concentrations of the acids mentioned above, double spots were obtained. In the investigation of ^{106}Ru as a RuNO-complex by elution with acids of low concentrations, three maximums of the distribution of the activity were found. With 8 and 10 N HCl and HNO_3 only one maximum was obtained with $R_f \sim 1$. The behavior of ^{144}Ce was similar to lanthanum.

The influence of some other factors

The influence of some other factors was also investigated, such as the time, temperature, another organic solvent and the TOP con-

centration used for the treatment of the paper when Ti, U and Fe were investigated by elution with 4 N HCl.

The R_f values of metal ions and the amount of TOP on the paper did not change when the treatment of the paper varied from 30 seconds to 5 minutes. The temperature variation of 20 - 30°C did not influence the R_f values either. The same values were obtained when benzene was used as the solvent instead of carbon tetrachloride.

The influence of the concentration of TOP of 0 - 0.3 M on the R_f values of Fe, U and Ti obtained by elution with 4 N HCl is shown in Fig. 5.

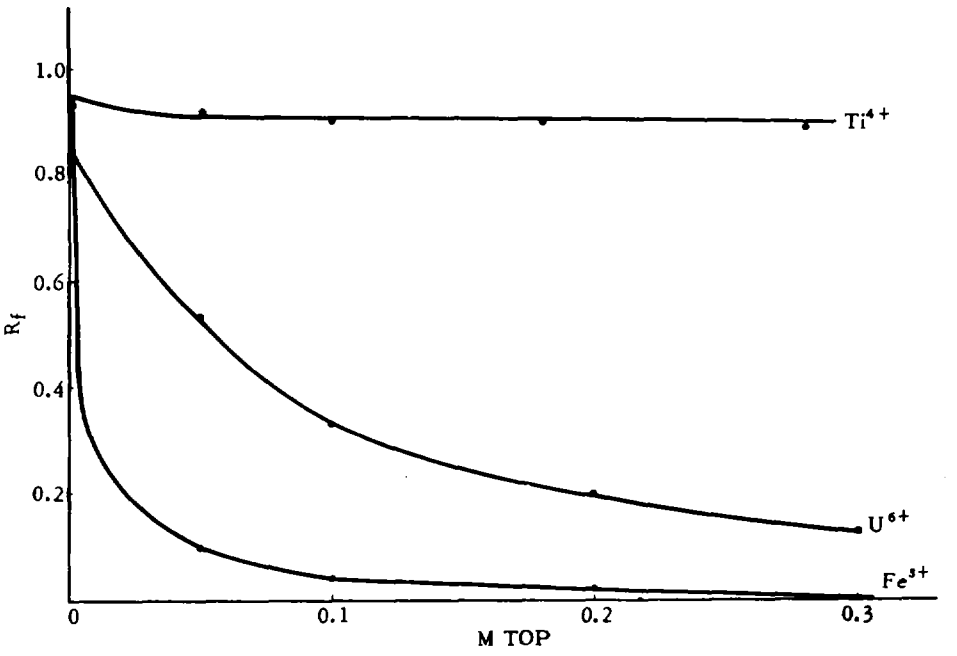

Fig. 5. - The R_f values for Fe^{3+}, U^{6+} and Ti^{4+} in dependence on the TOP concentration used for the treatment of the paper

The increase in the TOP concentration exerted an influence on the decrease of the R_f values of uranium and iron; in the case of titanium which is not retained the effect was negligible.

The application of paper treated with 0.1 M TOP for some separations of metal ions.

On the basis of the experiments described above, the separation of two or more elements from mixtures was performed by choosing suitable concentrations of the acids.

The separation is shown in Tables II, III, IV and V.

Table II

Chromatographic separation on paper treated with 0.1 M TOP/CCl_4
Room temperature 23 ± 1°C; *eluent* HCl

Elements	Eluent N HCl	Solvent front cm	R_f			
W^{6+}-Mo^{6+}-U^{6+}-V^{5+}	2	22.6	W^{6+}=0	Mo^{6+}=0.30	U^{6+}=0.66	V^{5+}=0.89
Cr^{6+}-Mo^{6+}-U^{6+}-Ti^{4+}	2	22.6	Cr^{6+}=0.05	Mo^{6+}=0.30	U^{6+}=0.63	Ti^{4+}=0.88
Mo^{6+}-U^{6+}-Hg^{2+}-Bi^{3+}	4	22.6	Mo^{6+}=0.03	U^{6+}=0.33	Hg^{2+}=0.68	Bi^{3+}=0.91
Fe^{3+}-U^{6+}-Ti^{4+}	4	22.3	Fe^{3+}=0.04	U^{6+}=0.33	Ti^{4+}=0.90	
Fe^{3+}-U^{6+}-Zr^{4+}	4	23.0	Fe^{3+}=0.04	U^{6+}=0.33	Zr^{4+}=0.88	
Sb^{3+}-As^{3+}-Bi^{3+}	4	21.9	Sb^{3+}=0.22	As^{3+}=0.74	Bi^{3+}=0.92	
Au^{3+}-Hg^{2+}-Cu^{2+}	6	22.4	Au^{3+}=0	Hg^{2+}=0.48	Cu^{2+}=0.89	
$^{51}Cr^{6+}$-$^{51}Cr^{3+}$	6	22.5	Cr^{6+}=0	Cr^{3+}=0.94		
U^{6+}-Th^{4+}-La^{3+}	10	22.3	U^{6+}=0.09	Th^{4+}=0.30	La^{3+}=0.89	
^{90}Sr-^{90}Y	10	22.4	^{90}Sr=0.56	^{90}Y=0.91		

The separation of $^{51}Cr^{6+}$ - $^{51}Cr^{3+}$ and ^{90}Sr - ^{90}Y is shown in Figs. 6 and 7.

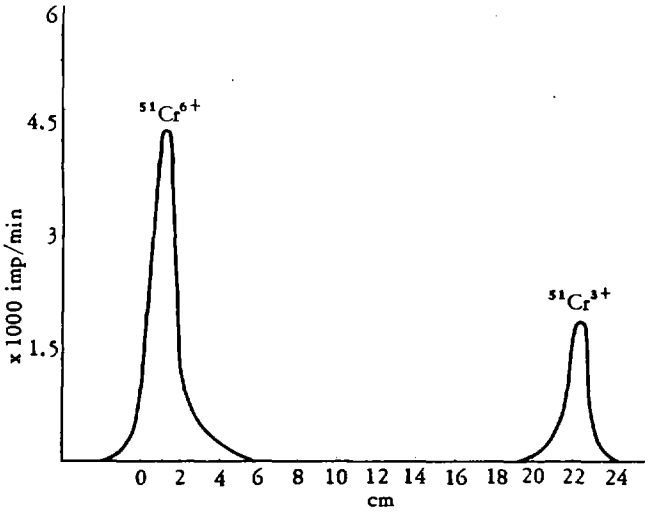

Fig. 6. - The separation of $^{51}Cr^{6+}$ - $^{51}Cr^{3+}$ on paper treated with 0.1 M TOP/CCl_4

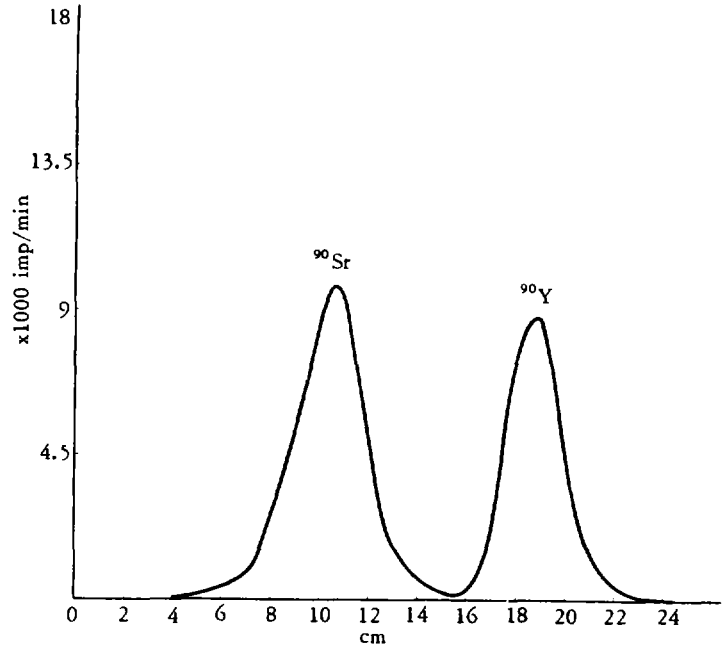

Fig. 7. - The separation of ^{90}Sr - ^{90}Y on paper treated with 0.1 M TOP/CCl_4

Table III

Chromatographic separation on paper treated with 0.1 M TOP/CCl_4
Room temperature 23 ± 1°C; eluent HNO_3

Elements	Eluent N HNO_3	Solvent front cm	R_f			
Au^{3+}-Sb^{3+} As^{3+}	0.5	22.3	Au^{3+}=0	Sb^{3+}=0.73	As^{3+}=0.89	
Ag^{+}-Hg^{2+}-Pb^{2+}-Cu^{2+}	0.5	21.0	Ag^{+}=0	Hg^{2+}=0.16	Pb^{2+}=0.84	Cu^{2+}=0.98
Ag^{+}-Hg^{2+}-Bi^{3+}-Cd^{2+}	2	22.0	Ag^{+}=0	Hg^{2+}=0.45	Bi^{3+}=0.84	Cd^{2+}=0.95
U^{6+}-Mo^{6+}-Bi^{3+}-Fe^{3+}	2	21.1	U^{6+}=0.1	Mo^{6+}=0.68	Bi^{3+}=0.84	Fe^{3+}=0.97
Ag^{+}-Au^{3+}-Pb^{2+}	6	20.9	Ag^{+}=0	Au^{3+}=0.42	Pb^{2+}=0.89	
W^{6+}-U^{6+}-Th^{4+} Y^{3+}	8	23.0	W^{6+}=0	U^{6+}=0.13	Th^{4+}=0.40	Y^{3+}=0.93
Zr^{4+}-Th^{4+}-Ti^{4+}	10	20.5	Zr^{4+}=0.1	Th^{4+}=0.40	Ti^{4+}=0.91	
^{95}Zr-^{95}Nb	10	22.0	^{95}Zr=0.1	^{95}Nb=0.97		

The separation of ^{95}Zr - ^{95}Nb is shown in Fig. 8.

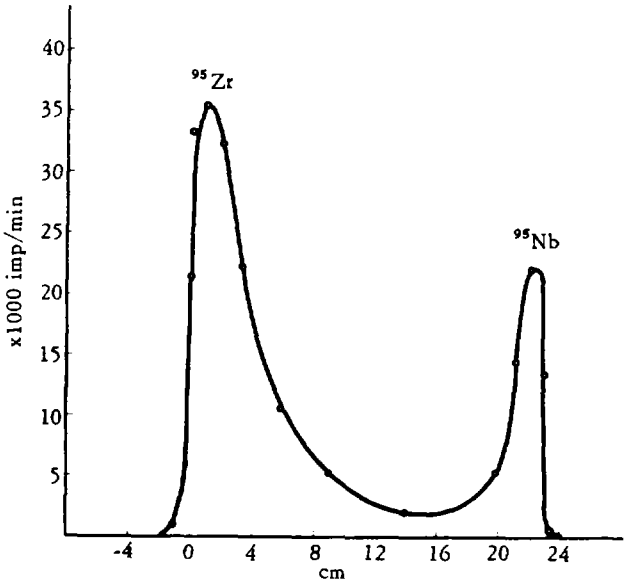

Fig. 8. - The separation of ^{95}Zr - ^{95}Nb on paper treated with 0.1 M TOP/CCl_4

Table IV

Chromatographic separation on paper treated with 0.1 M TOP/CCl_4
Room temperature 23 ± 1°C; eluent H_2SO_4

Elements	Eluent N H_2SO_4	Solvent front cm	R_f
Pb^{2+}-Mo^{6+}-Fe^{3+}	0.1	21.1	Pb^{2+}=0 Mo^{6+}=0.52 Fe^{3+}=0.95
W^{6+}-Cr^{6+}-Mn^{2+}	0.5	20.3	W^{6+}=0 Cr^{6+}=0.60 Mn^{2+}=0.98
Au^{3+}-Hg^{2+}-As^{3+}-Cd^{2+}	2	20.8	Au^{3+}=0 Hg^{2+}=0.1 As^{3+}=0.88 Cd^{2+}=0.98

Table V

Chromatographic separation on paper treated with 0.1 M TOP/CCl_4
Room temperature 23 ± 1°C; eluent $HClO_4$

Elements	Eluent N $HClO_4$	Solvent front cm	R_f
W^{6+}-Mo^{6+}-Th^{4+}	0.1	19.4	W^{6+}=0.03 Mo^{6+}=0.62 Th^{4+}=0.94
Ag^{+}-Hg^{2+}-Pb^{2+}-Zn^{2+}	1	21.5	Ag^{+}=0 Hg^{2+}=0.37 Pb^{2+}=0.75 Zn^{2+}=0.95
Au^{3+}-Sb^{3+}-Te^{6+}	1.5	22.1	Au^{3+}=0 Sb^{3+}=0.77 Te^{6+}=0.93

Conclusion

The experimental data show that a good separation of many metal ions on paper treated with tri-n-octylphosphate can be made. If the extraction coefficient E_a^o is higher, the R_f values are lower for almost all the ions investigated, when TOP is used under the same conditions of acidity.

The most favorable conditions for the separation of two or more ions can be found from the curves which represent the dependence of the R_f values on the concentration of the acids.

With the choice of the corresponding concentration of HCl and HNO_3 the separation of U and Th and their separation from other elements has been achieved. Satisfactory separation of some long-lived fission products has also been achieved.

Similar investigations on paper treated with dibutyl-phosphate are in progress.

Acknowledgements

We wish to express our thanks to D. Nemoda and J. Mitrović for their help in carrying out the measurements.

Résumé

SEPARATION CHROMATOGRAPHIQUE DES IONS METALLIQUES SUR LE PAPIER TRAITE AVEC LE TRIOCTYLE PHOSPHATE

Il a été examiné le comportement de l'uranium, du thorium, de quelques autres ions métalliques et des produits de fission de longue période, sur le papier traité avec le trioctyle phosphate. Les acides chlorydrique, azotique, sulfurique et perchlorique aux concentrations de 0,1 - 10 N ont été utilisés comme éluant. Les valeurs R_f données en fonction de la concentration des acides pour les ions examinés montrent la possibilité de l'interséparation de certains cathions.

Резюме

ХРОМАТОГРАФИЧЕСКОЕ ОТДЕЛЕНИЕ МЕТАЛЛИЧЕСКИХ ИОНОВ НА БУМАГЕ ОБРАБОТАННОЙ ТРИ-ОКТИЛ ФОСФАТОМ

Изучено поведение, урана, тория, прочих металлических ионов и долгоживущих продуктов деления на бумаге обработанной три-ок-

тил фосфатом. Элюентами служили соляна, азотная, серная и хлорная кислоты в концентрациях от 0,1 - 10 N.

Для исследования ионов даны R_f величины в зависимости от концентрации кислоты, на основании которых можно сделать заключение о возможности взаимного отделения некоторых катионов.

REFERENCES:

1. C. T e s t a, J. Chromatog., 5, 236 (1961).

2. E. C e r r a i and C. T e s t a, J. Chromatog., 5, 442 (1961).

3. E. C e r r a i and C. T e s t a, J. Chromatog., 6, 443 (1961).

4. C. T e s t a, Anal. Chem., 34, 1556 (1962).

5. E. C e r r a i and C. T e s t a, J. Chromatog., 7, 112 (1962).

6. E. C e r r a i and C. T e s t a, Energia nucleare, 8, 510 (1961).

7. E. C e r r a i and C. T e s t a, J. Chromatog., 8, 232 (1962).

8. E. C e r r a i, C. T e s t a, and C. T r i u l z i, Energia nucleare 9, 193 (1962).

9. E. C e r r a i C. T e s t a, and C. T r i u l z i, Energia nucleare 9, 377 (1962).

10. F. F e i g l, Spot tests, Inorganic Applications, Elsevier Publishing Company, Amsterdam, 1954.

February, 1963.