THE USE OF PAPER TREATED WITH TRI-*n*-OCTYLPHOSPHINE OXIDE FOR THE CHROMATOGRAPHIC SEPARATION OF METAL IONS

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Recent work has shown that paper[1,2] or cellulose powder[3] treated with tri-*n*-octylamine are very effective for the chromatographic separation of many chemical elements.

The use of tri-*n*-octylphosphine oxide (TOPO) as a highly selective extractant has of late increased considerably in analytical chemistry and, particularly, in nuclear chemistry. It was, therefore, our purpose to investigate the chromatographic behaviour of many metal ions on paper treated with a solution of tri-*n*-octylphosphine oxide. Chloride, nitrate and sulphate systems were investigated.

EXPERIMENTAL

Reagents and equipment

Paper was treated with a 0.025 *M* solution of TOPO in cyclohexane. TOPO (chemical composition $(C_8H_{17})_3PO$; mol. wt. 386.65; m.p. 54–55°), was supplied by Eastman Organic Chemicals, New York, U.S.A. All the acids, salts and organic compounds used in the experiments were analytical grade and were obtained from the following suppliers: Carlo Erba (Milan, Italy); Merck (Darmstadt, W.Germany); B.D.H. (London, England); Fluka (Buchs SG, Switzerland); Light's (Colnbrook, England) and Johnson, Matthey & Co. (London, England).

The chromatographic paper Whatman No. 1, type CRL/1, was used for basic experiments. Each paper sheet (21.3 × 11 cm) consisted of twelve parallel strips, 1.5 cm wide, separated by gaps 3 mm in width. The apparatus shown in Fig. 1 was designed in such a way that, after the spots had been deposited, the chromatogram folded in a cylindrical shape could be attached to the lid of the device. The eluting solution was introduced into the container by means of a pipette, and twelve ascending chromatograms could be simultaneously carried out in a closed atmosphere.

An ordinary chromatographic column and 4 × 35 cm Whatman No. 1 paper strips were used for the other ascending or descending chromatograms mentioned in this paper.

Treatment of the paper and chromatographic procedure

The TOPO–cyclohexane solution was shaken for 10 min with twice the volume of a 1 : 1 solution of the acid that was to be used as the eluent. The organic phase was then

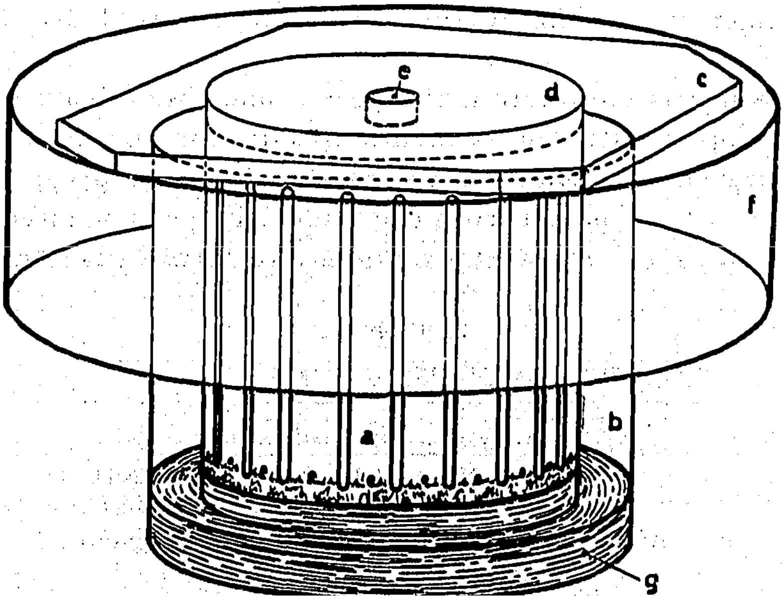

Fig. 1. Apparatus for ascending chromatography. (a) Chromatographic paper CRL/1 type; (b) glass container; (c) perspex lid; (d) internal plate of the lid; (e) central hole; (f) glass crystallizing dish; (g) eluent solution.

collected after percolation through cotton lint to eliminate any trace of the inorganic solution. The equilibrated TOPO solution was transferred to a glass container with a rectangular cross-section of 22 × 14 cm. The level of the solution was about 1 cm from the bottom. The paper sheets were immersed for 10 to 15 sec and then removed and allowed to drip. The organic solvent was eliminated by blowing warm air onto the partially dried strips. The spots (0.01 to 0.05 ml) were deposited as aqueous or slightly acidic solutions containing $5 \cdot 10^{-6}$ equiv./ml of the metal ion. Larger quantities were used for alkali metals and alkaline earths.

After the spots had been deposited, the paper sheet was fixed to the lid of the apparatus shown in Fig. 1. By putting the paper into the hole in the lid and fixing the internal plate, the sheet formed a cylinder which was inserted into the glass container. By means of a glass pipette the eluent solution was added through the central hole in the lid till the lower 0.5 cm of the paper was immersed. Then the apparatus was covered by an inverted crystallizing dish. The elution time for a 9 cm run ranged from 35 to 70 min, depending on the type and molarity of the acid used.

The eluting solutions used in all the experiments are given in Table I.

TABLE I

LIST OF THE ELUENTS

Acid	*Molarities*
HCl	0.1; 0.5; 1; 2; 4; 6; 8; 10; 12
HNO_3	0.5; 1; 2; 6; 10; 14
H_2SO_4	0.1; 0.5; 1; 2; 4

Solutions stronger than 4 M H_2SO_4 could not be used because they attacked the paper.

When the elution was completed, the paper sheet was dried with warm air and the spots were developed with the reagents specific for the metal ions examined. A list of the ions examined, together with their developers is given in Table II.

The R_F values were evaluated from the barycentre of the spots. Some ions, such as Te^{4+}, Ru^{3+}, Zr^{4+} and Hf^{4+}, showed a tendency to form tails when eluted with HCl of low molarity; Zn^{2+} and Sb^{5+} behaved likewise with HCl, and so did Zr^{4+}, Hf^{4+} and Sb^{5+} with H_2SO_4. Other elements, such as Cr, V, Sb, As which exhibit more than one valency state, sometimes formed double spots.

TABLE II

LIST OF IONS EXAMINED AND THEIR DEVELOPERS

Ions	*Developers*
Ag^+, Tl^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Pd^{2+}, As^{3+}, Au^{3+}, Bi^{3+}, Fe^{3+}, Sb^{3+}, Te^{4+}, Ir^{4+}, Pt^{4+}, Se^{4+}, As^{5+}, Sb^{5+}.	$(NH_4)_2S$ aqueous solution
Be^{2+}, Mg^{2+}, Mn^{2+}, Sn^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, Nb^{5+}, Sn^{4+}, Cr^{6+}, Mo^{6+}, W^{6+}.	Quercetin 0.1 % in alcohol
La^{3+}, Th^{4+}, Zr^{4+}, Hf^{4+}, U^{6+}.	Morin 0.1 % in alcohol
Li^+, K^+, Cs^+, Sr^{2+}, Ca^{2+}.	Chloranilic acid 1 % in ethyl ether
Ti^{4+}, V^{5+}.	H_2O_2 3.5 % aqueous solution
Re^{7+}.	8-Hydroxyquinoline 0.5 % in alcohol
Ru^{3+}.	Thiourea 1 % in 5 M HCl

RESULTS AND DISCUSSION

In Figs. 2, 3 and 4, the results obtained by means of the procedure described above are shown. The three figures refer to elutions with HCl, HNO_3 and H_2SO_4 respectively. In consequence of the large number of determinations (about one thousand values) the data have been presented as the curve of the R_F value *versus* the acid molarity. Thus a general and complete picture of the behaviour of each ion can be drawn.

The higher the extraction coefficient E_a°, the lower are the R_F values, when TOPO is used, under the same conditions of acidity. This was also shown in two previous papers[1,2] which dealt with the use of tri-*n*-octylamine (TNOA). Therefore, the present rapid chromatographic procedure can give very useful indications about the extraction behaviour of TOPO with respect to a large number of different ions, except for some particular cases which will be discussed below. For instance, the type and molarity of the acid that is likely to give the best extraction of an ion, can be quickly derived from the lowest value of R_F.

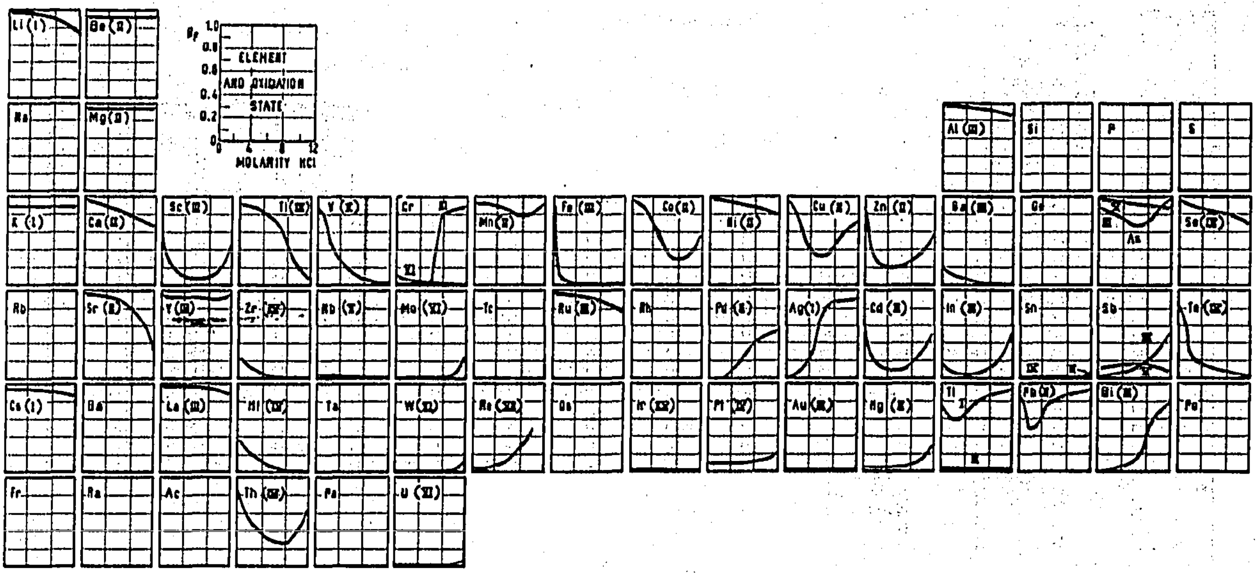

Fig. 2. R_F values as functions of HCl molarity for several metal ions. Paper treated with 0.025 *M* TOPO in cyclohexane.

On the other hand, the general shape of the R_F curve for the different ions in various acids can be anticipated from the extraction data reported in the literature[4–14].

In order to deduce from the data reported in Figs. 2, 3 and 4, all the chromatographic separations that are possible with this method, one must select the type and molarity of the acid in which the R_F values of the elements to be separated differ by at least about 0.20. This fact was experimentally confirmed by obtaining the chromatographic separation of two, three or four elements by either descending or ascending elution on 4 × 35 cm paper sheets.

The curves obtained often showed good agreement with the distribution curves

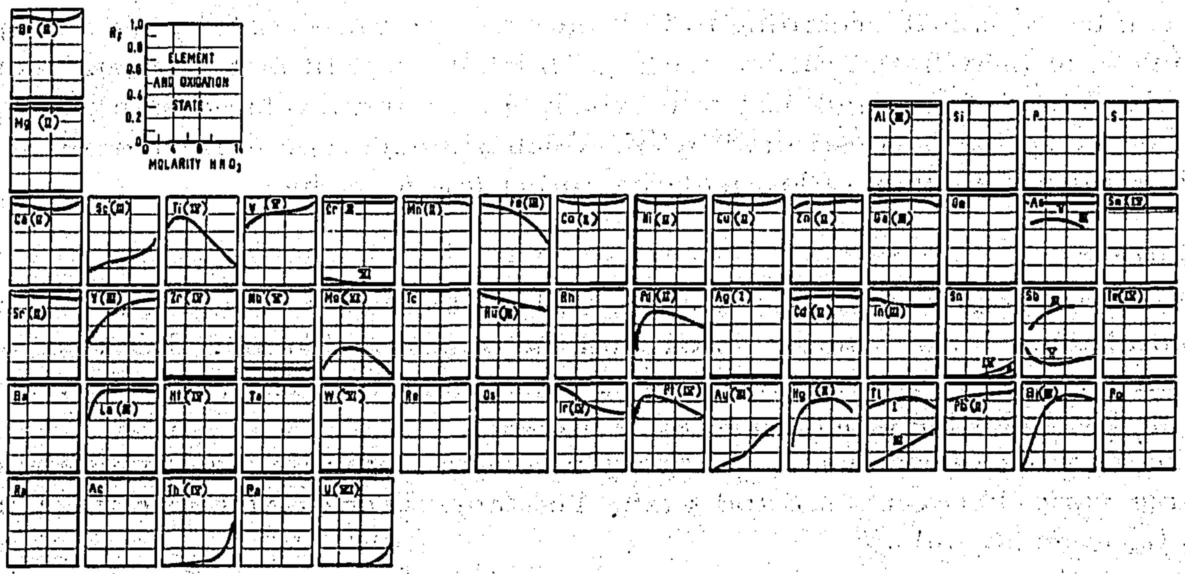

Fig. 3. R_F values as functions of HNO_3 molarity for several metal ions. Paper treated with 0.025 *M* TOPO in cyclohexane.

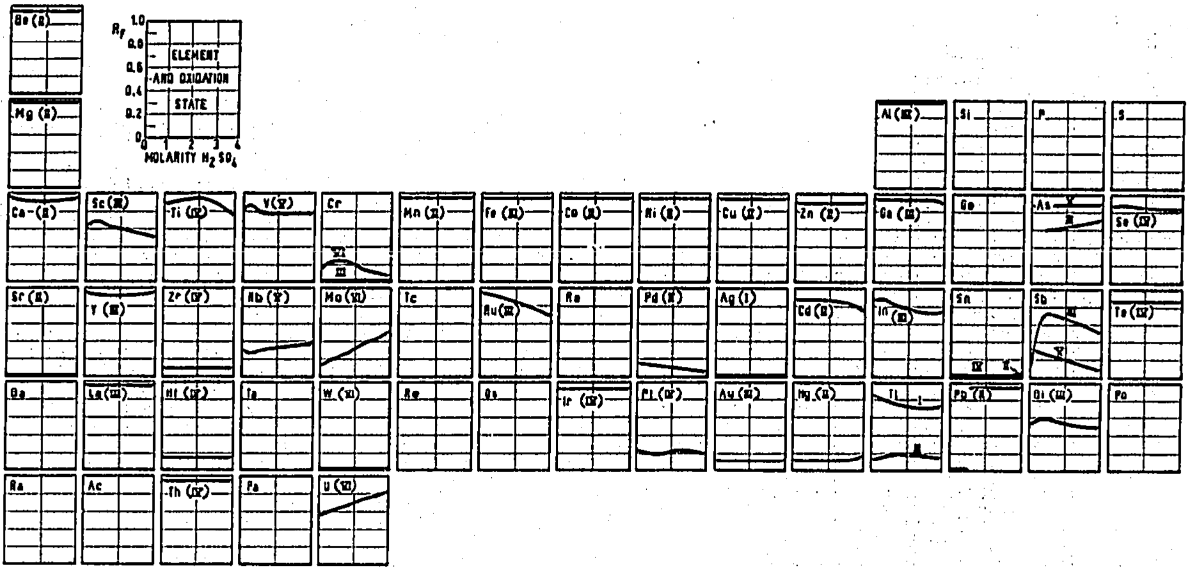

Fig. 4. R_F values as functions of H_2SO_4 molarity for several metal ions. Paper treated with 0.025 M TOPO in cyclohexane.

reported by KRAUS AND NELSON[14] for anionic resins. This was to be expected because TOPO, as well as TNOA, behave like anionic exchangers.

The exceptional behaviour of some of the ions examined depends on different factors. In fact, besides the exchange property of TOPO, additional phenomena such as the precipitation of salts, ion exchange on cellulose, complex formation[15], and adsorption of some metal ions by highly concentrated electrolytes[16], play an important role. Thus the exceptionally low R_F values of Ag, Pb and Sr with H_2SO_4 are not caused by the extraction of these elements with TOPO, because no extraction takes place, but by the formation of insoluble salts with H_2SO_4. Furthermore, the R_F values of Ca and Sr with concentrated HCl, which are appreciably lower than unity, can be explained, according to FOUARGE AND DUYKAERTS[16], by the adsorption by cellulose of dehydrated cations with small ionic radii. In fact, the same authors report R_F values of 0.65 and 0.45 respectively for Ca and Sr eluted with 12 M HCl. A further exception is constituted by Y, which although not extracted by TOPO[4] gives in a nitrate medium of low molarity rather low R_F values.

Other factors

The influence of some additional factors, such as treatment time of the paper, experimental temperature, elution speed, and the concentration of TOPO used for the treatment, was also investigated by using the system U^{6+}, Th^{4+}, La^{3+} in 2 M HCl medium. The following conclusions can be drawn:

The R_F value of each ion is practically unaffected when the time of imbibition of the paper varies between 5 sec and 5 min. The same is the case for operating temperatures between 20 and 40°.

The elution speed proved to have a great influence on the R_F value; in fact, when chromatography was carried out in an open atmosphere, the elution speed was considerably decreased owing to the continuous evaporation of some of the solvent, and the R_F values correspondingly increased.

Gradually decreasing R_F values for U^{6+} and Th^{4+} were obtained by treating the paper with TOPO solutions varying from zero to 0.4 *M*, as shown in Fig. 5.

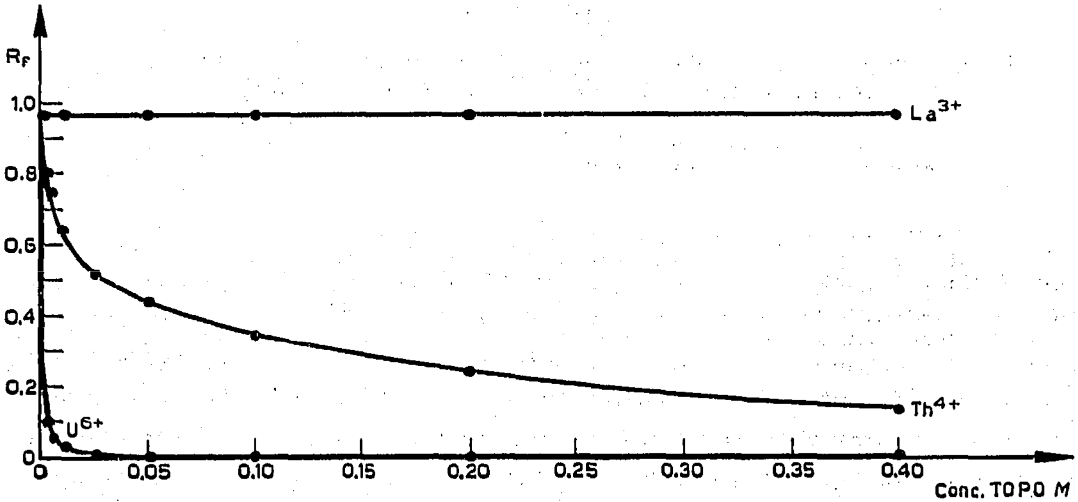

Fig. 5. R_F values for La^{3+}, Th^{4+} and U^{6+} as functions of molarity of TOPO used for treatment of the paper.

Generally, the R_F value can be suitably varied by treating the paper with TOPO of the appropriate molarity, but the greatest effect is to be expected with partially retained elements (*e.g.* Th), an appreciably smaller effect with strongly retained elements (*e.g.* U), and no effect with elements that are not retained (*e.g.* La).

SOME EXAMPLES OF CHROMATOGRAPHIC SEPARATIONS

Some separations of two or more elements were carried out to check the practical usefulness of the method. Whatman No.1 4 × 35 cm paper strips, treated with 0.025 *M* TOPO were used. TOPO had been pre-equilibrated with the various acids.

The separations obtained by using HCl as the eluent are reported in Table III.

TABLE III

CHROMATOGRAPHIC SEPARATIONS ON PAPER TREATED WITH 0.025 *M* TOPO IN CYCLOHEXANE

Room temperature (22 ± 1°). Eluent: HCl

Elements to be separated	*Type of chromatog.*	*Eluent M HCl*	*Run cm*	*Time min*	R_F			
Fe^{3+}–Cu^{2+}–Co^{2+}–Ni^{2+}	ascending	4	25	270	$Fe^{3+} = 0$	$Cu^{2+} = 0.28$	$Co^{2+} = 0.72$	$Ni^{2+} = 0.89$
Ga^{3+}–Th^{4+}–Tl^{+}–Al^{3+}	ascending	4	25	270	$Ga^{3+} = 0$	$Th^{4+} = 0.26$	$Tl^{+} = 0.57$	$Al^{3+} = 0.98$
Fe^{3+}–Cu^{2+}–Ni^{2+}	descending	5	17.5	180	$Fe^{3+} = 0$	$Cu^{2+} = 0.19$	$Co^{2+} = 0.37$	$Ni^{2+} = 0.93$
U^{6+}–Th^{4+}–La^{3+}	descending	5	19	195	$U^{6+} = 0$	$Th^{+} = 0.21$	$La^{3+} = 0.93$	—
Sn^{2+}–Sb^{3+}–Bi^{3+}–As^{3+}	descending	12	25.5	330	$Sn^{2+} = 0.02$	$Sb^{3+} = 0.23$	$Bi^{3+} = 0.67$	$As^{3+} = 0.92$
Au^{3+}–Pt^{4+}–Pd^{2+}–Ag^{+}	descending	12	20	270	$Au^{3+} = 0$	$Pt^{4+} = 0.18$	$Pd^{2+} = 0.59$	$Ag^{+} = 0.80$
Sn^{2+}–In^{3+}–Ca^{2+}–Mg^{2+}	descending	12	28	360	$Sn^{2+} = 0$	$In^{3+} = 0.13$	$Ca^{2+} = 0.69$	$Mg^{2+} = 0.69$

The separations obtained with HNO_3 as the eluent are shown in Table IV. All these, except the separation Sr–Y which was carried out on a 1.5 × 11 cm strip, were performed on 4 × 35 cm paper strips.

In Table V the separations obtained by eluting with H_2SO_4 are presented.

TABLE IV

CHROMATOGRAPHIC SEPARATIONS ON PAPER TREATED WITH 0.025 *M* TOPO IN CYCLOHEXANE

Room temperature (22 ± 1°). Eluent: HNO_3

Elements to be separated	*Type of chromatog.*	*Eluent M* HNO_3	*Run cm*	*Time min*	R_F			
Sr^{2+}–Y^{3+}	ascending	0.5	9	30	Y^{3+} = 0.32	Sr^{2+} = 0.95	—	—
Bi^{3+}–Hg^{2+}–Pt^{4+}	descending	0.5	25	160	Bi^{3+} = 0.03	Hg^{2+} = 0.20	Pt^{4+} = 0.67	—
U^{6+}–Mo^{6+}–Y^{3+}–La^{3+}	descending	2	25	175	U^{6+} = 0.02	Mo^{6+} = 0.32	Y^{3+} = 0.63	La^{3+} = 0.86
Th^{4+}–Y^{3+}–La^{3+}–Ca^{2+}	descending	0.5	26	175	Th^{4+} = 0	Y^{3+} = 0.20	La^{3+} = 0.65	Ca^{2+} = 0.84
U^{6+}–Tl^{3+}–Fe^{3+}–Ga^{3+}	descending	6	30	240	U^{6+} = 0	Tl^{3+} = 0.07	Fe^{3+} = 0.80	Ga^{3+} = 0.98
W^{6+}–U^{6+}–Au^{3+}–In^{3+}	descending	12	29	300	W^{6+} = 0	U^{6+} = 0.11	Au^{3+} = 0.45	In^{3+} = 0.81
Zr^{4+}–Th^{4+}–Sc^{3+}–Y^{3+}	descending	12	29	300	Zr^{4+} = 0	Th^{4+} = 0.17	Sc^{3+} = 0.30	Y^{3+} = 0.90

TABLE V

CHROMATOGRAPHIC SEPARATIONS ON PAPER TREATED WITH 0.025 *M* TOPO IN CYCLOHEXANE

Room temperature (22 ± 1°). Eluent: H_2SO_4

Elements to be separated	*Type of chromatog.*	*Eluent M* H_2SO_4	*Run cm*	*Time min*	R_F			
Zr^{4+}–U^{6+}–Th^{4+}	descending	0.5	26	135	Zr^{4+} = 0.11	U^{6+} = 0.33	Th^{4+} = 0.87	—
W^{6+}–Sc^{3+}–Y^{3+}	descending	0.5	26	135	W^{6+} = 0.03	Sc^{3+} = 0.68	Y^{3+} = 0.93	—
Hg^{2+}–In^{3+}–Bi^{3+}–Ga^{3+}	descending	2	26	160	Hg^{2+} = 0.08	Bi^{3+} = 0.67	In^{3+} = 0.89	Ga^{3+} = 0.99

CONCLUSIONS

The selectivity of TOPO as an extractant for many cations can be transferred to paper by immersing it in a TOPO–cyclohexane solution.

Generally, the higher the extraction coefficients E_a° for a given acid and for the majority of the elements examined, the lower are the R_F values. Some special cases do not follow this general rule. The nature and molarity of the acid suitable for the separation of two or more elements can be selected from the curves presented in Figs. 2, 3 and 4. The same curves can give all the basic indications for the separation of appreciable amounts of elements. In fact, beds of cellulose powder treated with TOPO can be used for column chromatography. Some preliminary experiments have shown that TOPO, like TNOA[3], can be strongly fixed on cellulose powder.

A large amount of chromatographic data can easily be obtained in a short time by using Whatman CRL/1 paper. Each paper sheet permits the simultaneous chromatography of twelve elements which can be developed with the appropriate reagents on the respective strip.

The R_F value of an element can be influenced by the type of acid, its molarity, the elution time and the concentration of the solution used for the treatment. Often, the conditions giving optimal separation can be selected.

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SUMMARY

A systematic study of chromatography with paper treated with 0.025 *M* tri-*n*-octylphosphine oxide (TOPO) in cyclohexane has been described. Curves of the R_F values as functions of the acidity of the eluent, are given for about fifty metal ions. The acids used were HCl, HNO_3 and H_2SO_4.

Some parameters, such as temperature, imbibition time of the paper, elution time, and molarity of the TOPO solution have been considered.

Examples of separations of two or more elements are given to show the practical application of the proposed chromatographic technique.

Generally, the higher the extraction coefficient E_a° of TOPO for a given element at the selected acidity, the lower the R_F value. The possibility of treating chromatographic cellulose powder with TOPO to obtain column separation of appreciable quantities of substances, is suggested.

REFERENCES

[1] C. TESTA, *J. Chromatog.*, 5 (1961) 236.
[2] E. CERRAI AND C. TESTA, *J. Chromatog.*, 5 (1961) 442.
[3] E. CERRAI AND C. TESTA, *J. Chromatog.*, 6 (1961) 443.
[4] J. C. WHITE, *Oak Ridge Natl. Laboratory ORNL*, CF -56-9-18 (1956).
[5] J. C. WHITE, *ASTM Spec. Tech. Publ.*, No. 238 (1958) 27.
[6] J. P. YOUNG AND J. C. WHITE, *Anal. Chem.*, 31 (1959) 393.
[7] J. C. WHITE, *U.S. Atomic Energy Comm.*, TID-7555 (1957) 247.
[8] C. K. MANN AND J. C. WHITE, *Anal. Chem.*, 30 (1958) 989.
[9] C. A. HORTON AND J. C. WHITE, *Anal. Chem.*, 30 (1958) 1779.
[10] J. P. YOUNG AND J. C. WHITE, *Talanta*, 1 (1958) 263.
[11] W. J. ROSS AND J. C. WHITE, *Anal. Chem.*, 31 (1959) 1847.
[12] J. O. HIBBITS, W. F. DAVIS AND M. R. MENKE, *Talanta*, 6 (1960) 28.
[13] R. A. ZINGARO AND J. C. WHITE, *Inorg. & Nuclear Chem.*, 12 (1960) 315.
[14] K. A. KRAUS AND F. NELSON, *Proc. First. Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, 1955, Vol. 7, 1956, p. 113.
[15] M. LEDERER, *Lecture at the VII Rassegna Int. Elettronica e Nucleare, Roma*, June 1960.
[16] J. FOUARGE AND G. DUYCKAERTS, *J. Chromatog.*, 3 (1960) 48.

J. Chromatog., 7 (1962) 112–119