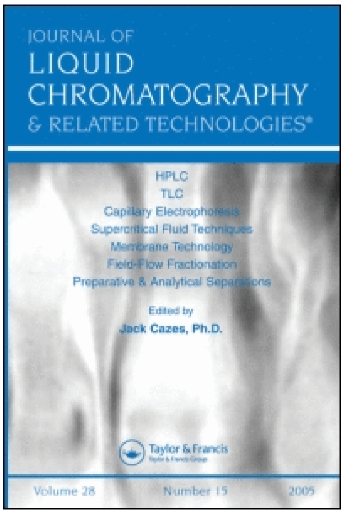

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REVERSED PHASE CHROMATOGRAPHIC SEPARATION OF MOLYBDENUM AND TUNGSTEN USING ORGANOPHOSPHINES

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ABSTRACT

The reversed phase chromatographic behaviour of Mo(VI) and W(VI) along with other associated metal ions using Cyanex 301, 302, and 925 impregnated on a silica gel column is presented. The optimum condition for the separation has been developed and almost quantitative separation of Mo(VI) from W(VI), V(V), Al(III), Cr(III), Fe(III), Mn(II), Co(II) and Ni(II) and W(VI) from Fe(III), Mn(II), Zn(II), Cd(II), and Pb(II) achieved.

INTRODUCTION

Molybdenum and tungsten, both are important strategic metals for the industrial sector. Due to their widespread use, the natural resources are being depleted. There is a need to develop extraction procedures for their recovery from low grade ores and spent catalysts. The purity of these metals for technology is of paramount importance.

Under certain experimental conditions Cyanex 301, 302, and 925 were found to be fairly selective extractants for Mo(VI) and W(VI), respectively.[1-3] They were employed for achieving separations involving the two elements and their recovery from low grade ores and spent catalysts.

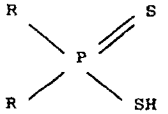
Liquid-liquid extraction has added a new dimension to separations science in the form of extraction chromatography wherein the extraction data help to develop reverse phase chromatographic procedures. Reversed phase extraction chromatography (RPEC), sometimes offers the advantages of both solvent extraction and ion exchange chromatography under favourable conditions. The separations of similar metal ions which are normally not easily achieved by single stage liquid-liquid extraction can be obtained with better resolution by multistage reversed phase partition chromatography. Moreover, the yields are more quantitative.

Not much literature is available on the RPEC behaviour of Mo(VI) and W(VI). Some high molecular weight amines[4-7] have been explored as an impregnant for attaining their separation. In view of the success of alkylphosphine extractants for the liquid-liquid extraction separation of Mo(VI) and W(VI), it could be beneficial to explore their use for the reverse phase column chromatographic separation. These extractants have the added advantages of much lower aqueous solubility compared to high molecular weight amines, thereby reducing the extractant loss from the column on repeated use.

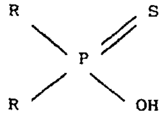
The liquid-liquid extraction behaviour of different metal ions including Mo(VI) and W(VI) in Cyanex 301, 302, and 925[1-3] provided useful guidelines to study the retention behaviour and develop reversed phase chromatographic separation procedures. It has been possible to separate Mo(VI) from W(VI), V(V), Al(III), Cr(III), Fe(III), Mn(II), Co(II), and Ni(II) on Cyanex 301 and 302 columns and W(VI) from Fe(III), Mn(II), Zn(II), Cd(II), and Pb(II) using Cyanex 925 columns. The regeneration capacity of the column was tested up to ten cycles and there was practically insignificant change in the retention and elution behaviour up to six cycles.

EXPERIMENTAL

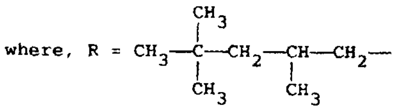
Cyanex 301, 302, and 925 were obtained form American Cyanamid Company, USA and used as received. Cyanex 301 (I) and 302 (II) arebis(2,4,4-trimethylpentyl)dithio-phosphinic acid and bis(2,4,4- trimethylpentyl) monothiophosphinic acid, respectively.



(I)



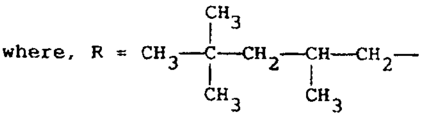
(II)



$$\text{where, } R = CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_2-$$

Cyanex 925 is a mixture of two compounds which have the following structure:

$R_3P(O)$ (III) $R_2R'P(O)$ (IV)



$$\text{where, } R = CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_2-$$

$R' = CH_3(CH_2)_7$

Component IV predominates representing approximately 85% of the mixture.

Binder free silica gel (80-100 mesh) used for column extraction chromatography was procured from CDH (India) and was silianized by following a literature.[8] Silica gel (10 gm), washed with dilute hydrochloric acid, was added to 50 mL solution of 5% dimethylchlorosilane (DMCS). The resulting slurry was heated to gentle boiling with continuous stirring and subsequently allowed to stand and cool. Silica gel was then filtered through a Whatman No.1 paper without vacuum and washed with sufficient amount of toluene. The resulting solid was again washed with methanol, transferred to a beaker, slurried and heated to boiling. After cooling, the support was filtered and washed again with methanol. The treated silica gel was dried overnight at at 120°C. Dry silanized silica gel was slurried with 15 and 20 mL of 0.10 M toluene solution of Cyanex 301 and 302 and Cyanex 925, respectively. The toluene was evaporated by gentle stirring. The loaded silica gel containes 0.15 mmoles of Cyanex 301 and 302 and 0.20 mmoles of Cyanex 925 per gram of silica gel. At different steps, care was taken to avoid vigorous mixing so that there is no change in the particle size of the support. The loaded silica gel was left overnight in the required concentration of the acid and then transferred to a glass column of 1 cm internal diameter so as to obtain a length of 10 cm. The flow rate of the column was adjusted to 0.5 mL/min.

For separations, the column was loaded with a mixture containing equimolar amounts 1.0×10^{-4} M of the metal ions and eluted with appropriate concentration of the eluant. Equal fractions of the eluants, with respect to volume, were collected and assayed by ICP-AES. The ammonical column was regenerated by washing it thrice with 1.0 M HCl and subsequently with water till the eluant was almost neutral.

The recycling capacity of Cyanex 301 and 302 for Mo(VI) and Cyanex 925 for W(VI) was checked up to ten cycles. The per cent recovery for each step was calculated from the amount which was retained on the column in that particular cycle.

The results reported are the average of two determinations. All chemicals used were of analytical purity.

RESULTS AND DISCUSSION

The retention behaviour of the Mo(VI), W(VI), Al(III), Cr(III), Fe(III), Mn(II), Co(II), and Ni(II) was studied from hydrochloric acid solutions on silanized columns loaded with Cyanex 301 and that of Mo(VI) and V(V) using Cyanex 302 columns. Employing 0.10 M Cyanex 925 as a stationary phase the retention behaviour of W(VI), Fe(III), Mn(II), Zn(II), Cd(II), and Pb(II) was investigated.

Mo(VI) is strongly retained at Cyanex 301 column from 1.0×1.0^{-3} to 1.0 M HCl whereas W(VI), Cr(III), Mn(II), and Ni(II) are easily eluted with 1.0×10^{-3} M HCl and Al(III) and Co(II) with 1.0 M HCl. Fe(III) is strongly adsorbed from 1.0×10^{-3} M HCl, while its retention at 1.0 M HCl is not that strong. The separation of Mo(VI) from Fe(III) is achieved by retaining both of them on Cyanex 301 column and then successively eluting Mo(VI) and Fe(III) with 5% NH_4Cl in 1:20 NH_3 and 6.0 M HCl.

Using Cyanex 302 column, Mo(VI) is retained from 10×10^{-2} M HCl, whereas V(V) is easily eluted out. Mo(VI), strongly retained at Cyanex 301/302 column, is easily eluted out with 5% NH_4Cl in 1:20 NH_3.

Table 1

Separation Conditions and Recovery of Mo(VI) or W(VI) From Other Metal Ions

Metal Ions Separated	Aqueous Phase HCl(M)	Cyanex	Eluant	Recovery (%)
W(VI)-Mo(VI)	1.0×10^{-3}	301	1.0×10^{-3} M HCl-5% NH_4Cl in 1:20 NH_3	91-95
V(V)-Mo(VI)	1.0×10^{-2}	302	1.0×10^{-2} MHCl-5% NH_4Cl in 1:20 NH_3	88-85
Al(III)-Mo(VI)	1.0	301	1.0 M HCl-5% NH_4Cl in 1:20 NH_3	92-95
Cr(III)-Mo(VI)	1.0×10^{-3}	301	1.0×10^{-3} M Hcl-5% NH_4Cl in 1:20 NH_3	99-95
Mo(VI)-Fe(III)	1.0×10^{-3}	301	5% NH_4Cl-6.0 MHCl in 1:20 NH_3	93-95
Mn(II)-Mo(VI)	1.0×10^{-3}	301	1.0×10^{-3} M HCl-5% NH_4Cl in 1:20 NH_3	99-95
Co(II)-Mo(VI)	1.0	301	1.0 M HCl-5% NH_4Cl in 1:20 NH_3	98-95
Ni(II)-Mo(VI)	1.0×10^{-3}	301	1.0×10^{-3} M HCl-5% NH_4Cl in 1:20 NH_3	90-95
W(VI)-Fe(III)	1.0×10^{-3}	925	1.0×10^{-3} MHCl-0.10M oxalic acid	94-99
Mn(II)-W(VI)	0.10	925	0.10 M HCl-5% $(NH_4)_2CO_3$ in 1:20 NH_3	95-90
Zn(II)-W(VI)	0.10	925	0.10 M HCl-5% $(NH_4)_2CO_3$ in 1:20 NH_3	99-90
Cd(II)-W(VI)	0.10	925	0.10 M HCl-5% $(NH_4)_2CO_3$ in 1:20 NH_3	96-90
Pb(III)-W(VI)	0.10	925	0.10 M HCl-5% $(NH_4)_2CO_3$ in 1:20 NH_3	98-90

Conditions: Metal Ion = 1.0×10^{-4} M. Cyanex 301 and 302 = 0.15 mmoles. Cyanex 925=0.20 mmoles

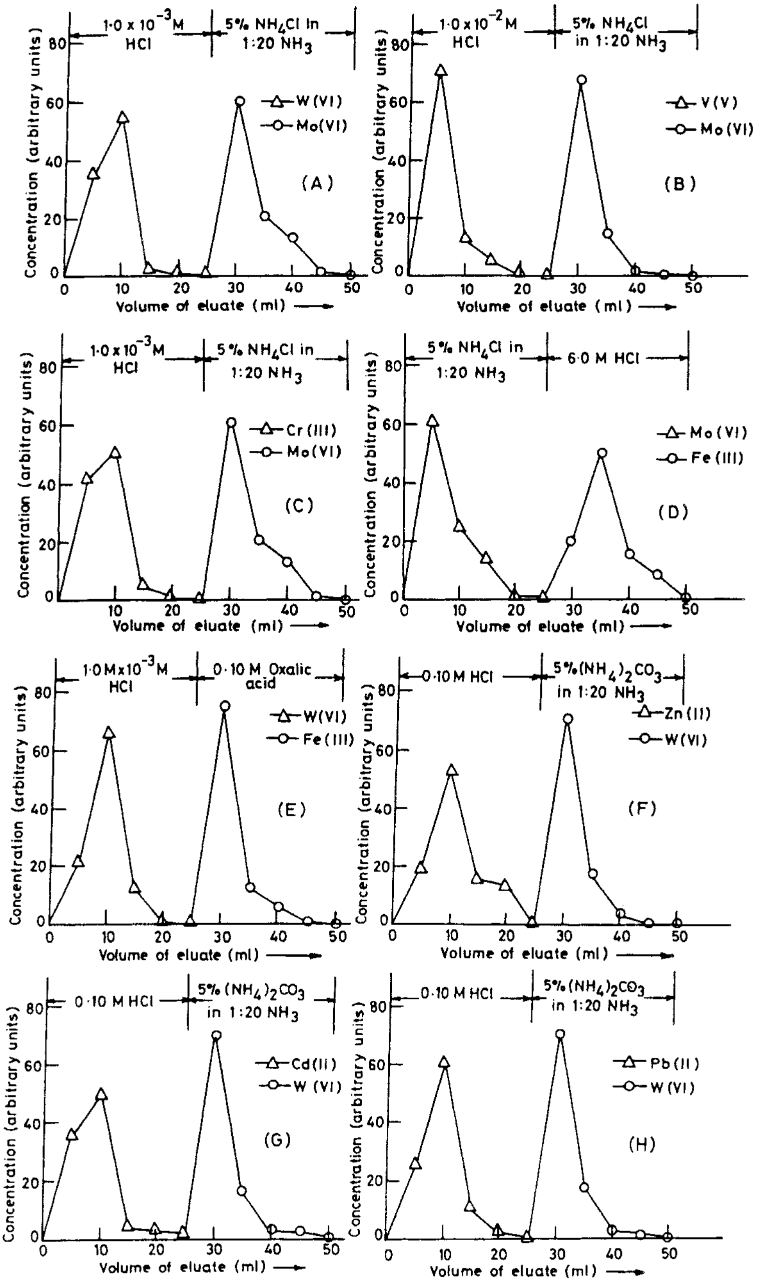


Figure 1. Elution curves of separations.

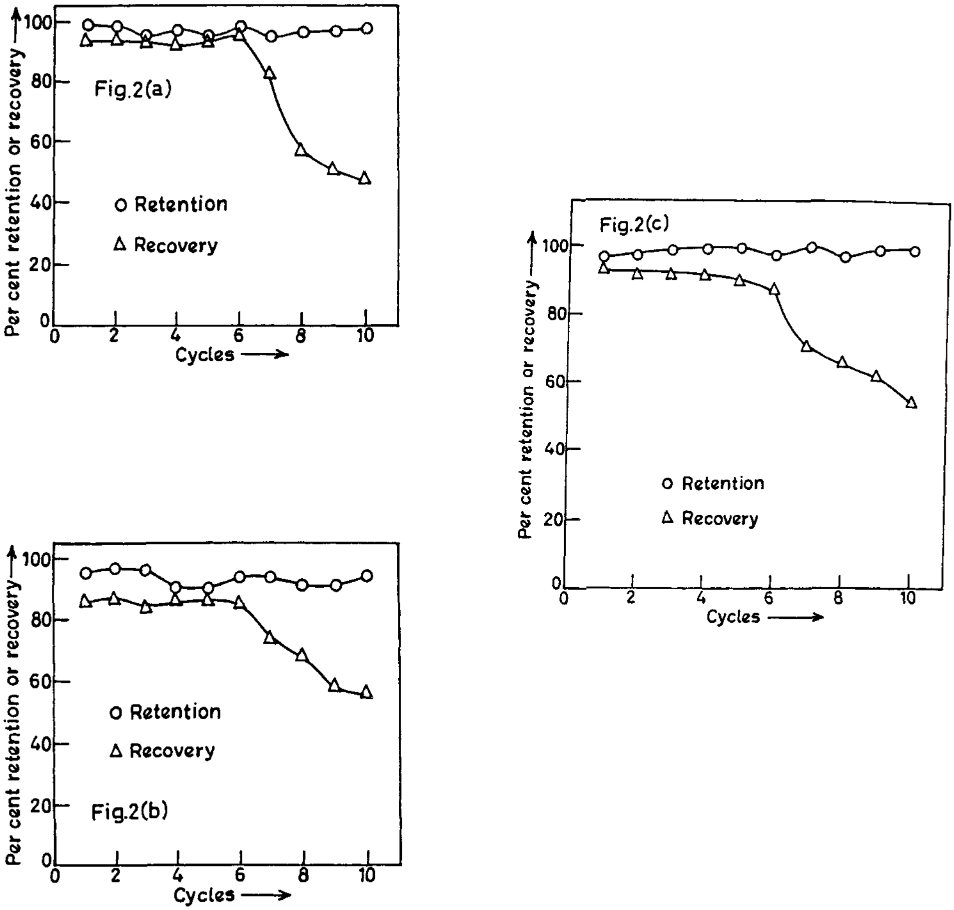


Figure 2. (a) Variation in the retention or recovery of Mo(VI) using Cyanex 301 column in successive cycles. (b) Variation in the retention or recovery of Mo(VI) using Cyanex 302 column in successive cycles. (c) Variation in the retention or recovery of W(VI) using Cyanex 925 column in successive cycles.

On Cyanex 925 column W(VI) is retained from 0.10 M HCl whereas Mn(II), Zn(II), Cd(II) and Pb(II) easily come out at this molarity. W(VI) can be eluted from the column using 5% $(NH_4)_2CO_3$ in 1:20 NH_3. At 10×10^{-3} M HCl Fe(III) is retained on the column but W(VI) elutes out. Fe(III) is recovered from column using 0.10 M oxalic acid. The conditions of separations and percentage recovery are summarised in Table 1. It may be noted that on changing the acid from HCl to HNO_3 no change in the retention and elution behaviour of the metal ion is observed. Some of the typical elution curves are shown in Figure 1 (a-h).

The retention and elution of the Cyanex columns for Mo(VI) and W(VI) in successive cycles is shown in Figure 2 (a-c). It is apparent that up to six cycles there is no significant change in the amount of Mo(VI) and W(VI) retained and eluted. In the subsequent cycles there is a decrease in the amount of metal ion eluted and visually the column is disturbed with pockets in it.

The above investigations clearly demonstrate the potential of Cyanex 301, 302 and 925 for achieving reversed phase column separations of Mo(VI) or W(VI) from many closely associated metal ions. The elution curves are invariably sharp because of the availability of the extractant molecules at the surface. The separations have been possible by using simple eluting agents which may facilitate subsequent processing/estimation of the metal ions. The utility of these reversed phase materials for repeated use cannot be comparable to conventional organic resinous ion exchangers. However, these reversed phase columns can be used up to six cycles without any significant change in their behaviour.

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