

## SEPARATION AND CONCENTRATION OF MOLYBDENUM(VI) AND TUNGSTEN(VI) WITH CHELATING ION-EXCHANGE RESINS CONTAINING SULPHUR LIGANDS

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**Summary**—Three chelating ion-exchange resins based on macroreticular polyacrylonitrile-divinylbenzene copolymers with thioglycolic acid and cysteine as functional groups have been tested for separation of molybdenum(VI) and tungsten(VI). On a short column of the thioglycolic acid resin, molybdenum(VI) and tungsten(VI) can be selectively sorbed from pH-4.3 acetate buffer and eluted with 2*M* hydrochloric acid and a mixture of 0.1*M* sodium hydroxide and 0.1*M* sodium chloride, respectively, with quantitative recovery even at very low concentrations. Simulated sea-water samples have been analysed.

The synthesis and characterization of chelating ion-exchange resins containing thioglycolic acid and cysteine as functional groups, and their analytical applications to noble metals, have been described.<sup>1,2</sup> As part of a systematic survey of the behaviour of metal ions with these resins, the chromatography of molybdenum(VI) and tungsten(VI) species has now been studied.

### EXPERIMENTAL

#### Instrumentation

A Radiometer pH-meter was used with saturated calomel (Type K 401) and glass (Type G 202 B) electrodes, and calibrated with Beckman standard buffers of pH 4.00 and 7.00. A Hitachi model 624 digital spectrophotometer connected to a Hitachi model QD<sub>15</sub> recorder was used, with 10-mm quartz cells.

#### Reagents

Previously published procedures were used to synthesize the macroreticular polyacrylonitrile—divinylbenzene copolymers.<sup>1,2</sup> The nitrile groups were hydrolysed to carboxylic acid groups. The carboxylic acid resin (200 g) was mixed with 600 g of molten 1,6-hexanediol (m.p. 41°) or 500 g of ethylene glycol, and 40 ml of concentrated sulphuric acid (as catalyst), and kept at 70° for 30 hr for the first esterification. Then a mixture of 150 g of this product with 460 g of thioglycolic acid and 40 ml of concentrated sulphuric acid was reacted at 70° for 30 hr for the second esterification. The 1,6-hexanediol or ethylene glycol served both as linking agent and reaction medium, the products being Resins I and II respectively.<sup>1</sup> The carboxylic acid resin was similarly treated with 1,6-hexanediol and L-cysteine in a two-step esterification to give Resin III.<sup>2</sup> The final product was collected by filtration under suction and washed sequentially with water, concentrated hydrochloric acid, water and acetone.

#### Spectrophotometric determination of molybdenum(VI) and tungsten(VI)

The procedures used were essentially those reported by Sandell.<sup>3</sup> Maximum colour development and stability were obtained with ascorbic acid as reducing agent for the determination of molybdenum(VI). The sensitivity was increased by extraction of the molybdenum(V) and tungsten(V) thiocyanate complexes into *n*-butyl acetate.

#### Sorption by the batch method

Exactly 0.3 g of dry polymer was pre-equilibrated with 20 ml of 1*M* sodium perchlorate–0.5*M* sodium acetate mixture, the pH being periodically adjusted to the required value with perchloric acid or sodium hydroxide until it had remained constant for 6 hr. The solution was removed by filtration. The metal ion solution (10 ml, 0.062*M*) was then added to 10 ml of 2*M* sodium perchlorate and 10 ml of 1*M* sodium acetate, and the pH adjusted to the required value. The prepared metal ion solution, diluted to 50 ml, was added to the pre-equilibrated polymer and stirred for 18 hr. The pH was then checked for constancy, and the resin was filtered off and washed with the appropriate acetate buffer. The filtrate and washings were combined and analysed for molybdenum(VI) or tungsten(VI).

The distribution coefficient for molybdenum(VI), as a function of hydrochloric acid concentration, was also determined by a batch equilibrium method; 25 ml of a mixture containing various amounts of acid and 0.4 mmole of metal ion were stirred with 0.2 g of air-dried resin for 18 hr at 25°. The resin was filtered off and washed, and the molybdenum(VI) in the filtrate was determined.

#### Equilibration rates

From the capacity studies, the total capacity of each resin for molybdenum(VI) and tungsten(VI) at the optimal pH was known. Twice the quantity of molybdenum(VI) or tungsten(VI) corresponding to saturation of 0.3 g of resin at pH 4.3 was diluted in the appropriate buffer to give 0.03*M* metal ion concentration. Then 0.3 g of the air-dried resin was introduced into this solution and equilibrated. Samples of solution were removed at intervals and their metal ion content was determined.

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### Separation of molybdenum(VI) and tungsten(VI)

Resin I was packed into a glass tube ( $10 \times 0.6$  cm) and conditioned with 20 ml of 1M acetate buffer (pH 4.3). After conditioning, 9.3  $\mu$ moles each of molybdenum(VI) and tungsten(VI) were loaded on to the column, and molybdenum(VI) was eluted with 2M hydrochloric acid at 0.5 ml/min. Tungsten(VI) was retained on the column and then eluted with 0.1M sodium hydroxide-0.1M sodium chloride mixture at the same flow-rate.

### Concentration of trace metals

Portions (500 ml) of water containing various amounts of molybdenum(VI) or tungsten(VI) were adjusted to pH 4.3 and passed at 0.5 ml/min through a preconditioned  $7.0 \times 0.6$  cm resin column, and the molybdenum(VI) and tungsten(VI) eluted as above and determined. Recovery of 9.70  $\mu$ g of molybdenum(VI) and 0.01  $\mu$ g of tungsten(VI) from 1 litre of simulated sea-water<sup>4</sup> was similarly determined.

## RESULTS AND DISCUSSION

The pH-dependence of the sorption behaviour of Resins I-III towards molybdenum(VI) and tungsten(VI) was tested by the batch equilibrium method. Table 1 shows the distribution coefficients obtained. Resins I and II, which contained the same functional groups but different linking agents, behaved similarly. The length of the linking agent slightly influenced the capacity. The similarity of the distribution coefficients for molybdenum(VI) and tungsten(VI) at pH 2-7 prevents simple separation of the metals in this pH range. The distribution coefficients for molybdenum(VI) between hydrochloric acid and Resins I-III are shown in Table 2. Tungsten(VI) precipitated from the acid solution, so could not be studied. Molybdenum(VI) or tungsten(VI) at pH 4.3 was used to assess the kinetics of sorption, 50% of the

Table 2. Distribution coefficients of molybdenum(VI) on the three resins in hydrochloric acid

Resin	Concentration of HCl, M							
	0.1	0.5	1	2	4	5	6	7
I	75	25	16	1	27	43	38	30
II	56	19	12	2	31	49	36	29
III	64	82	72	62	42	42	41	40

available sites of Resin I being occupied by molybdenum(VI) and tungsten(VI) in 12 min and 21 min, respectively. From the results of the batch equilibrium study, the possibility of separating molybdenum(VI) and tungsten(VI) by using a Resin I column was obvious. The molybdenum(VI) and tungsten(VI) sorbed can be easily stripped quantitatively from the resin column in succession by 2M hydrochloric acid and 0.1M sodium hydroxide-0.1M sodium chloride mixture, respectively. Figure 1 shows such a separation.

The effect of foreign ions on the recovery of molybdenum(VI) and tungsten(VI) with Resin I was studied. The results are reported in Table 3. Since the sulphur content of Resin I was 1.56 mmole/g, the silver(I) capacity was 1.52 mmole/g, the mercury(II) capacity was 0.80 mmole/g, the molybdenum(VI) capacity was 0.75 mmole/g, and the tungsten(VI) capacity was 0.35 mmole/g, silver(I) and mercury(II) interfered severely, even if the mole ratio to molybdenum or tungsten was reduced to 1, whereas copper(II), zinc(II) and tin(IV) did not interfere at this concentration ratio. The resin exhibited no affinity for the alkali and alkaline-earth metals studied. Small quantities of the resin can therefore be used to concentrate trace metals from samples with a high electrolyte content, such as sea-water and biological

Table 1. Distribution coefficients for molybdenum(VI) and tungsten(VI) on the three resins

pH	Resin I		Resin II	Resin III	
	Mo	W	Mo	Mo	W
1.60				166	
2.20			11		
2.25	11				
2.28					47
3.40	65		49	18	47
3.70		25			
3.80	71		94	17	
4.10	73		100	18	
4.28		35			
4.30	71		97	26	55
4.40			90		
4.80	60	35	60	11	
4.86					51
4.95		36			
5.15	53		40	4	
5.25			26		
5.95	11				
6.05					26
6.12	26				
6.58		37			
7.10			26		
7.30				11	

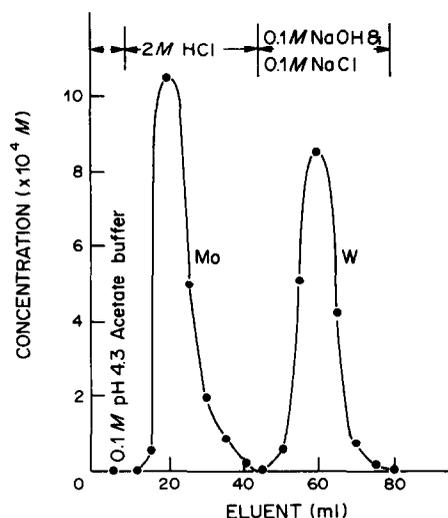


Fig. 1. Separation of molybdenum(VI) and tungsten(VI) with Resin I: (Column  $10.0 \times 0.6$  cm bore, flow-rate 0.5 ml/min; 9.3  $\mu$ mole of each metal absorbed).

Table 3. Effects of foreign ions on the recovery of molybdenum(VI) and tungsten(VI) (35  $\mu\text{g}$  each) respectively, with Resin I

Foreign metal	Amount added, mg	Molybdenum found, $\mu\text{g}$	Tungsten found, $\mu\text{g}$
Ag <sup>+</sup>	0.04	6.0	5.1
K <sup>+</sup>	5	35.0	35.0
Na <sup>+</sup>	5	35.0	35.0
Ca <sup>2+</sup>	2	35.0	35.0
Co <sup>2+</sup>	1	35.0	37.3
Cu <sup>2+</sup>	0.02	33.6	33.0
Hg <sup>2+</sup>	0.07	17.4	15.1
Mg <sup>2+</sup>	1	35.0	35.1
Mn <sup>2+</sup>	1	35.0	34.9
Ni <sup>2+</sup>	1	35.0	38.1
Pb <sup>2+</sup>	0.07	33.1	30.1
Zn <sup>2+</sup>	0.02	24.9	35.0
Al <sup>3+</sup>	1	34.9	34.9
Fe <sup>3+</sup> *	10	35.0	36.1
Sn <sup>4+</sup>	0.04	34.9	33.0
U(VI)	1	34.8	35.0
W(VI)†	1	35.0	

\* In the presence of 5 drops of 10% ascorbic acid solution.

† In the presence of 5 drops of 10% sodium tartrate solution.

Table 5. Preconcentration and determination of molybdenum(VI) and tungsten(VI) in simulated sea-water\*

Metal ion	Amount added, $\mu\text{g}$	Amount found, $\mu\text{g}$	Recovery of total metal, %
Mo(VI)†	0.0	9.4	97
	10.2	19.9	100
W(VI)§	10.3	11.1	98
	10.3	11.1	98

\* Metal content in original sample: Mo = 9.70  $\mu\text{g/l}$ , W = 0.10  $\mu\text{g/l}$ .

† Sample 1 litre.

§ Sample 10 litres.

fluids, since the resin would not become saturated by the alkali or alkaline-earth metals present.

Very low concentrations of molybdenum(VI) and tungsten(VI) in pure water and simulated sea-water can be concentrated with Resin I before their determination. Tables 4 and 5 show the recoveries.

Table 4. Recovery of metal ions from very dilute solution with Resin I

Metal ion	Amount added* $\mu\text{mole}$	Eluent	Amount found, $\mu\text{mole}$	Recovery, %
Mo(VI)	0.37	2M HCl	0.37	100
Mo(VI)	0.104	2M HCl	0.100	96
W(VI)	0.37	0.1M NaOH-0.1M NaCl	0.37	100
W(VI)	0.37	0.5M NaOH-0.5M NaCl	0.37	100
W(VI)	0.025	0.1M NaOH-0.1M NaCl	0.021	84

\* In 500 ml of pH-4.3 0.1M acetate buffer.

Table 6. Colour imparted to the solution by the three resins with excess of molybdenum ions

pH or acidity	Colour		
	Resin I	Resin II	Resin III
7M HCl	green	green	pale yellow
6M HCl	green	green	pale yellow
5M HCl	brown	brown	pale yellow
3M HCl	brown	brown	pale yellow
2M HCl	yellow-brown	yellow-brown	pale yellow
1M HCl	yellow-brown	yellow-brown	pale yellow
0.5M HCl	yellow-brown	yellow-brown	pale yellow
0.1M HCl	blue	blue	blue
pH 1.60	—	—	blue
pH 2.20	—	blue	—
pH 2.25	blue	—	—
pH 3.80	—	—	colourless
pH 4.00	green	—	—
pH 4.10	—	green	—
pH 4.30	—	—	colourless
pH 4.40	—	green	—
pH 4.80	yellow-green	—	—
pH 5.15	—	—	colourless
pH 5.25	—	pale green	—
pH 5.95	yellow-green	—	—
pH 6.12	colourless	—	—
pH 7.10	—	colourless	—
pH 7.30	—	—	colourless

Molybdenum(VI) can be reduced to molybdenum(V) in 2*M* hydrochloric acid and to molybdenum(III) at higher acid concentrations.<sup>5</sup> The colours imparted to the solution by the chelating ion-exchange resins in presence of molybdenum(VI) species are listed in Table 6. The colours, taken in conjunction with those of chemical forms of molybdenum(V) at various concentrations of hydrochloric acid,<sup>5</sup> suggest that molybdenum(VI) is reduced by the resins, *e.g.* to molybdenum(V) in 0.5*M* hydrochloric acid. Because of this reductive behaviour of the resin, the possibility of using the Mo–thioglycollic acid and Mo–cysteine resin systems for catalysing hydrogenation reactions is obvious. Investigation of the

catalytic behaviour of these systems in the nitrogenase reaction as model are in progress.

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