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Characterization and analytical application of an α-hydroxy oxime resin for chromatography

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Characterization and analytical application of

an α-hydroxy oxime resin for chromatography

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INTRODUCTION

Modern liquid chromatography is a rapidly growing field within analytical chemistry. New instrumentation has taken a lot of the blood, Tswett, and tears out of the experimental procedures and has greatly extended the scope of liquid chromatography. However, use of modern instrumentation has led to the need for new column packings which operate without loss of efficiency at high pressures. Typically, in liquid-liquid chromatography, the stationary liquid phase will bleed off the inert support when eluent under pressure is forced through the column. Besides the obvious problem of loss of column efficiency, there is the problem of interference with detection. One solution to the problem of phase bleeding has been the development of bonded stationary phases in which the stationary liquid is chemically bound to an inert support (1). Another possible solution, especially for the separation of metal ions, seems to be resins with complex- or chelate-forming functional groups bound directly to a polymeric matrix. The evaluation of one such resin having α-hydroxy oxime groups bound to a polystyrene-divinylbenzene matrix is reported here.

Complex-forming resins have some advantages over conventional ion exchange resins in that (1) complex-forming resins are generally more selective than ion exchange resins because the mode of interaction with metal ions includes formation of

coordinate as well as ionic bonds (2), and (2) complex-forming resins can be used in solutions having high concentrations of salt, whereas with ion exchange resins, the mass action effect of large amounts of salt renders them ineffective.

α-Benzoinoxime has long been known to be a selective reagent for copper (3) and for molybdenum (4). Recently, two aliphatic α-hydroxy oximes have been used to separate copper (II) and molybdenum(VI) from other metal ions (5). The demonstrated selectivity of α-hydroxy oximes for copper and molybdenum, coupled with the straightforward synthetic route to a resin containing that group, is the basis for the choice of that resin for synthesis and evaluation.

The resin is synthesized by reacting XAD-2 a macroporous, polystyrene-divinylbenzene copolymer, with anhydrous phenylglyoxal and anhydrous aluminum trichloride in carbon disulfide. The product is oximated with hydroxylamine hydrochloride giving a resin with the structure

$$\text{Res} - \underset{\underset{OH}{|}}{CH} - \underset{\underset{NOH}{\|}}{C} - \bigcirc$$
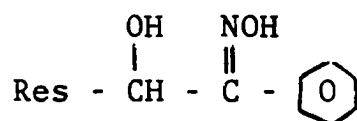
where <u>Res</u> represents the polystyrene-divinylbenzene matrix.

The resin is found to sorb copper(II) and molybdenum(VI) under conditions similar to those found with other α-hydroxy oximes, i.e., copper(II) is sorbed from solutions having a pH of 5 or more, and molybdenum(VI) is sorbed over the pH range 1 to 4. Although several metals are found to interfere with

the determination of copper or molybdenum, good results are obtained for the analysis of a zinc-base and an aluminum alloy for copper.

Since Skogseid's preparation in 1946 of what is generally considered to be the first chelating resin (6), many such resins have been synthesized. Blasius and Brozio (7), Schmuckler (8), Myasoedova, Eliseeva, and Savvin (9), and Saldadze and Kopylova (2) have reviewed much of the work on chelating resins. Marhol (10) has reviewed work on ion exchange materials containing phosphorus, arsenic, or antimony in the functional group.

Blasius and co-workers have synthesized several chelating resins which have proven to be selective for various metal ions. A resin based on 2,6-pyridinecarboxylic acid is selective for alkaline earth metals (11,12). Hydrazide resins based on cyclic maleic hydrazide and on dimalyl succinic dihydrazide are selective for mercury(I) and mercury(II) and for copper(II), respectively (13). Resins with polyaminepolycarboxylate functional groups have been used to separate binary mixtures of first row transition metals (14). Two resins which are selective for zirconium have been synthesized. One is based on catechol-O,O-diacetic acid (15), and the other has 1,8-dihydroxynaphthalene-O,O-diacetic acid as the functional group (16). A resin based on o-(hydroxyphenylazo) benzoic acid has been prepared (17) and used to separate calcium(II) from strontium(II), traces of alkaline earths from

solutions having high alkali metal content (18), traces of iron from concentrated salt solutions (19), and beryllium(III) from aluminum(III) (20). Traces of iron have also been separated from concentrated salt solutions with a resin having maleic hydroxamic acid as the functional group (21).

Myasoedova, Eliseeva, Savvin, and co-workers have prepared chelating resins from several different polymeric matrices. Phenol-formaldehyde resins have been used to sorb germanium, tantalum, and tungsten from acidic media, and uranium, thorium, and tungsten from imitation sea water (22). The resins have also been used to concentrate microamounts of niobium, tantalum, and beryllium (23). Several resins based on cross-linked dextrans have been synthesized (24,25). Some show promise for the concentration of palladium, platinum, and gold and for their separation from base metals (26).

A series of resins has been prepared from aminopoly-styrene which is diazotized and coupled to a variety of reagents. The functional groups of these resins include resorcinol azo derivatives (27), the o'-hydroxy-o'-aminoazo group (28), several derivatives of chromotropic acid (29,30), and the quinolylazoamino group (31). Resins of that type have been applied to the selective sorption of protactinium (32), concentration of americium and curium and their separation from plutonium and fission products (33), and to the separation of microamounts of tantalum from niobium (34).

Two series of resins having polystyrene-divinylbenzene matrices have functional groups analogous to Arsenazo I, o,o'-dihydroxyazobenzene, 8-hydroxyquinoline, hydroxyphenylarsonic acid (35), and to rhodanine, 8-aminoquinoline, 5-amino-8-mercaptoquinoline, 8-mercaptoquinoline, thiourea (36). Several of the resins in the latter group are selective for palladium, platinum, rhodium, and gold and can be used to concentrate those elements from highly acidic solutions containing large amounts of copper, iron, and nickel.

Chelating resins containing organo-phosphorus groups (37), α-dioxime groups (38), diphenylcarbazide groups (39), and pyridylazoresorcyl groups (40) have been synthesized by Szczepaniak. The α-dioxime resin is a copolymer of α-furildioxime, phenol, and formaldehyde. It sorbs all cations which are complexed by α-furildioxime. The diphenylcarbazide resin has been used to separate rhenium(VII) from molybdenum(VI), tungsten(VI), vanadium(V), iron(III), and copper(II). The pyridylazoresorcinol resin is quite selective for palladium(II) and copper(II). It forms weaker complexes with mercury(II), calcium(II), zinc(II), cadmium(II), nickel(II), cobalt(II), aluminum(III), iron(III), zirconium(IV), and thorium(IV).

Marhol's work has been mainly with phosphorus-containing resins and their application to the separation of uranium from other metals (41-44).

Saldadze and co-workers have worked mainly with cation

exchangers of the phosphoric acid type (45-47) and with anion exchangers of the vinylpyridine type (48-53), and of the poly-ethylenepolyamine type (54-60).

Several groups of workers have concerned themselves with the theoretical aspects of chelating resins as well as with the synthesis and application of that type of resin. Theo-retical work has been done by Gregor, by Hering, by Schmuck-ler, by Saldadze, by Eger, by Luttrell, and by Brajter.

Gregor, et al., have put forth four criteria that they feel must be met by a chelating group to make it suitable for incorporation into a resin (61).

Hering has proposed a theory of complexation of an imino-diacetic acid resin and has developed an equation for calcu-lating dissociation constants of resin-metal complexes for divalent metal ions (62). He has suggested that K_d is a function of the acid dissociation constants of the resin and the decomplexing pH, i.e., the pH at which the metal ion dis-sociates from the resin. The decomplexing pH for 22 metal ions has been determined for an iminodiacetic acid resin (63).

Saldadze, et al., have determined the stability of resin-metal complexes by potentiometric titration of the resin both in the presence and in the absence of metal ions (50,54,57,59). It has been found that, in general, the stability of the resin-metal complexes is in agreement with the stability of the metal complexes with the monomeric reagents.

The structure of resin-metal complexes has been studied

both by potentiometric titration and by infrared spectroscopy
(45,50,58-60). Kinetics of formation of resin-metal complexes
has also been studied (55,56), as has the effect of the struc-
ture of the macromolecular framework on the complexing proper-
ties of some of the resins (46,48,52).

Schmuckler has studied the sorption of lead and copper by
Dowex A-1, an iminodiacetic acid resin, from various media
(64). It is found that the presence of complexing agents in
solution exerts a marked effect on the sorption of metal ions
by the resin. She suggests that the effect is similar to com-
peting equilibria in homogeneous medium when two or more com-
plexing agents are present. Moreover, she feels that the
scope of metal separations can be widened by judicious choice
of complexing agent in an eluent.

Lowenschuss and Schmuckler have studied the properties of
Dowex A-1 in contact with aqueous solutions containing metal
ions complexed with aminocarboxylate ligands. They have
determined the stability of the resin-metal complexes and the
structures of the complexes formed by the resin, metal, and
ligand (65).

Eger, et al., have studied the coordination behavior of
cobalt, nickel, copper, and zinc on Dowex A-1 by potentio-
metric titration (66,67). Luttrell, Moore, and Kenner have
determined the effect of pH and ionic strength on the ion
exchange and chelating properties of Dowex A-1 with alkaline
earth ions (68). Brajter has compared the complexing proper-

ties of Chelex 100, an iminodiacetic acid resin, with those of iminodiacetic acid towards cadmium, zinc, and lead (69).

Schmuckler, in addition to theoretical work with chelating resins, has been concerned with the synthesis of chelating resins and their application to the solution of analytical problems. A guanidine resin has been used to separate palladium(II) and platinum(II) chlorides (70), and the platinum metals and gold have been separated from base metals by means of a benzylisothiouronium resin (71).

In addition to the concentrated work on chelating resins being done by some groups, there is work with such resins going on on a more modest scale in a number of other laboratories. Hirsch, Gancher, and Russo have synthesized a macroreticular iminodiacetic acid resin (72). Davankov has used a vinylpyridine copolymer with triethyleneglycol dimethacrylate as the basis for preparation of nitrogen-, phosphorus-, and sulfur-containing resins having high selectivity for heavy metals (73). Egawa and Saeki have synthesized several polyamine resins and found that some have high affinity for gold (III), mercury(II), and copper(II) (74). Egawa and Takahara have prepared chelating resins from methyl methacrylate-divinylbenzene copolymers (75). A resin with a styrene-divinylbenzene matrix to which salicylic acid has been bound by an azo linkage is found to have a greater affinity for copper(II) than for zinc(II) and for zinc(II) than for lead (II) (76). Phenolic resins capable of boron complexation have

been reported by Kessick (77). Resins selective for silver, platinum, palladium, and gold have been prepared by diazotizing polyaminostyrene and coupling it with rhodanine or thiorhodanine (78). Rogozhin, Davankov, and Yamskov have synthesized a series of chelate-forming resins from α-amino acids (79). The effects of pH, equilibration time, crosslinking, and monomer units have been studied for copper, zinc, and nickel on several polyamine-polyurea resins (80). Dithiocarbamate resins have been used to concentrate traces of silver(I), mercury(II), copper(II), antimony(III), lead (II), and cadmium(II) (81).

To date, iminodiacetic acid resins, of all chelating resins synthesized, have found the widest applicability. They have been used for the determination of trace elements in sea water (82-84), for the separation of uranium(VI) from other metal ions (85), and for the determination of low levels of cadmium in foods (86). Chelex 100 has been used as a medium for concentrating traces of some elements and, subsequently, as a sample matrix for the determination of those elements by X-ray fluorescence (87,88).

Recently, Koster and Schmuckler synthesized a resin which can be used to separate noble metals from base metals (71). The resin is now commercially available and has been used in the determination of gold (89) and for the collection of methyl mercury and inorganic mercury (90).

EXPERIMENTAL

Apparatus

Figure 1 is a schematic diagram of the liquid chromato-
graph used in this work. The eluent delivery system has been
described previously (91). The detector is a Heath Model 701
spectrophotometer equipped with a Heath Model Eu-703-01 photo-
metric readout, a Model EU-200-01 potentiometric amplifier,
and a Model EU-205-11 strip chart recorder. The sample com-
partment of the spectrophotometer is modified so that the
photomultiplier tube is mounted next to the flow-through cell
in the sample compartment (92). That modification is neces-
sary to cut decreases in the signal caused by dispersion of
visible or ultraviolet radiation in passing through the sample
compartment from the monochromator to the photomultiplier
compartment.

Reagent Addition for Detection

For eluent systems in which the metal ions under study
do not absorb visible or ultraviolet radiation, a reagent may
be mixed with the eluate to impart "color" to the metal ion.
So called "color-forming" reagents may range from 4-(2-
pyridylazo) resorcinol and Arsenazo I to hydrochloric acid.
The eluate and reagents are mixed in a mixing chamber of the
whirlpool, divided tangential entry type (93). The relative
flow rates of eluate and reagent are adjusted by varying the
lengths of 0.012-in. i.d. Teflon tubing placed in each
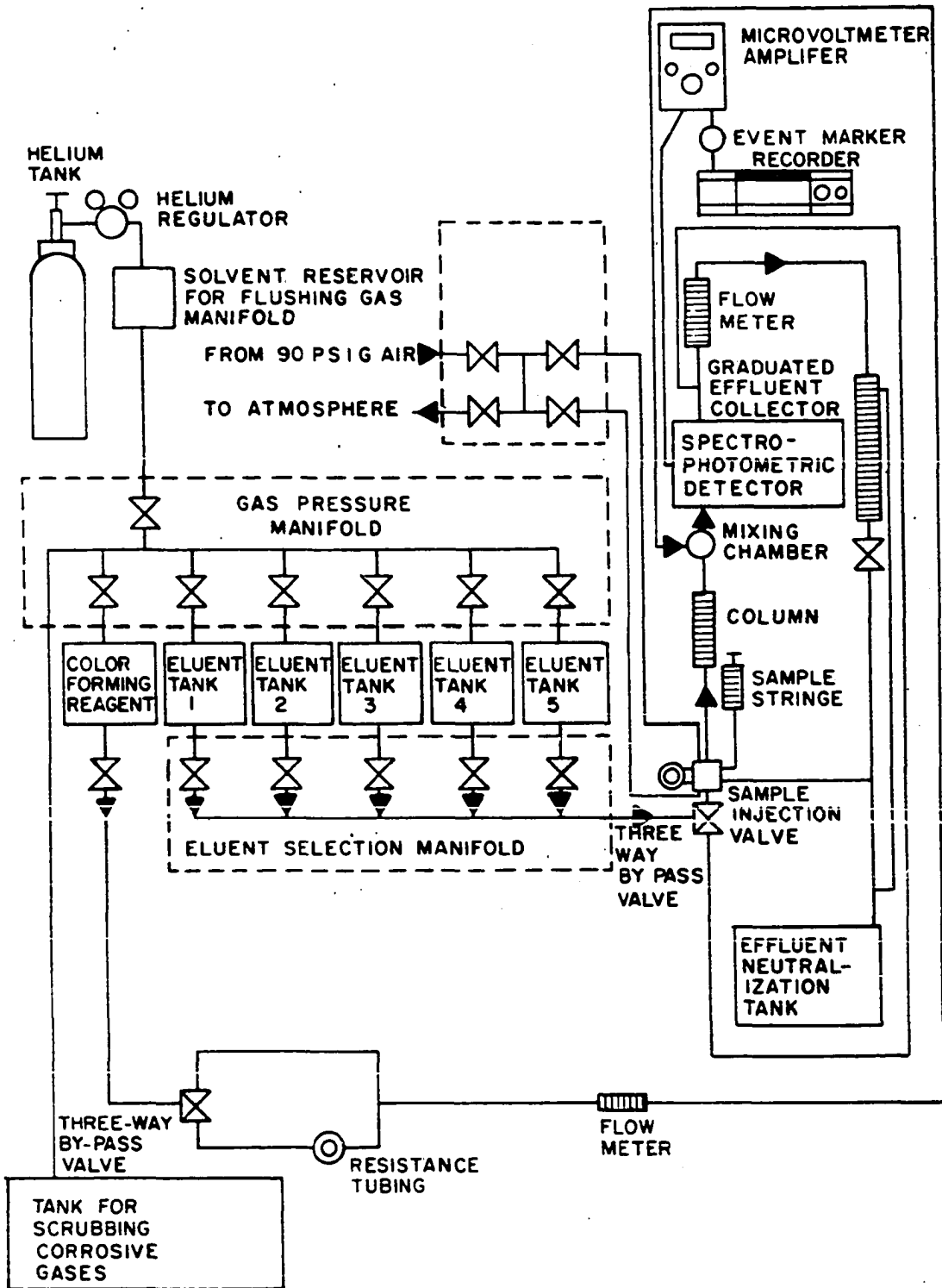
Figure 1. Schematic diagram of the liquid chromatograph

stream. The system may be represented as in Figure 2.

By analogy with an electrical circuit, one could write "Ohm's law" for the system. Pressure would correspond to electromotive force, flow rate to current, and resistance to liquid flow to electrical resistance. Therefore

$$E = iR$$

would become

$$P = fR$$

The branch of the circuit having the column and tubing is analogous to an electrical circuit having resistors in series. The equivalent resistance would be

$$R_e = R_c + R_t'.$$

The circuit containing R_e and R_r is analogous to an electrical circuit having resistors in parallel. The relationships among flow rates, pressures, and resistances for the circuit may be expressed as follows:

$$P_e = f_e R_e$$

$$P_r = f_r R_r$$

But,

$$P = P_r = P_e$$

Therefore,

$$f_e R_e = f_r R_r$$

$$\frac{f_e}{f_r} = \frac{R_r}{R_e}$$
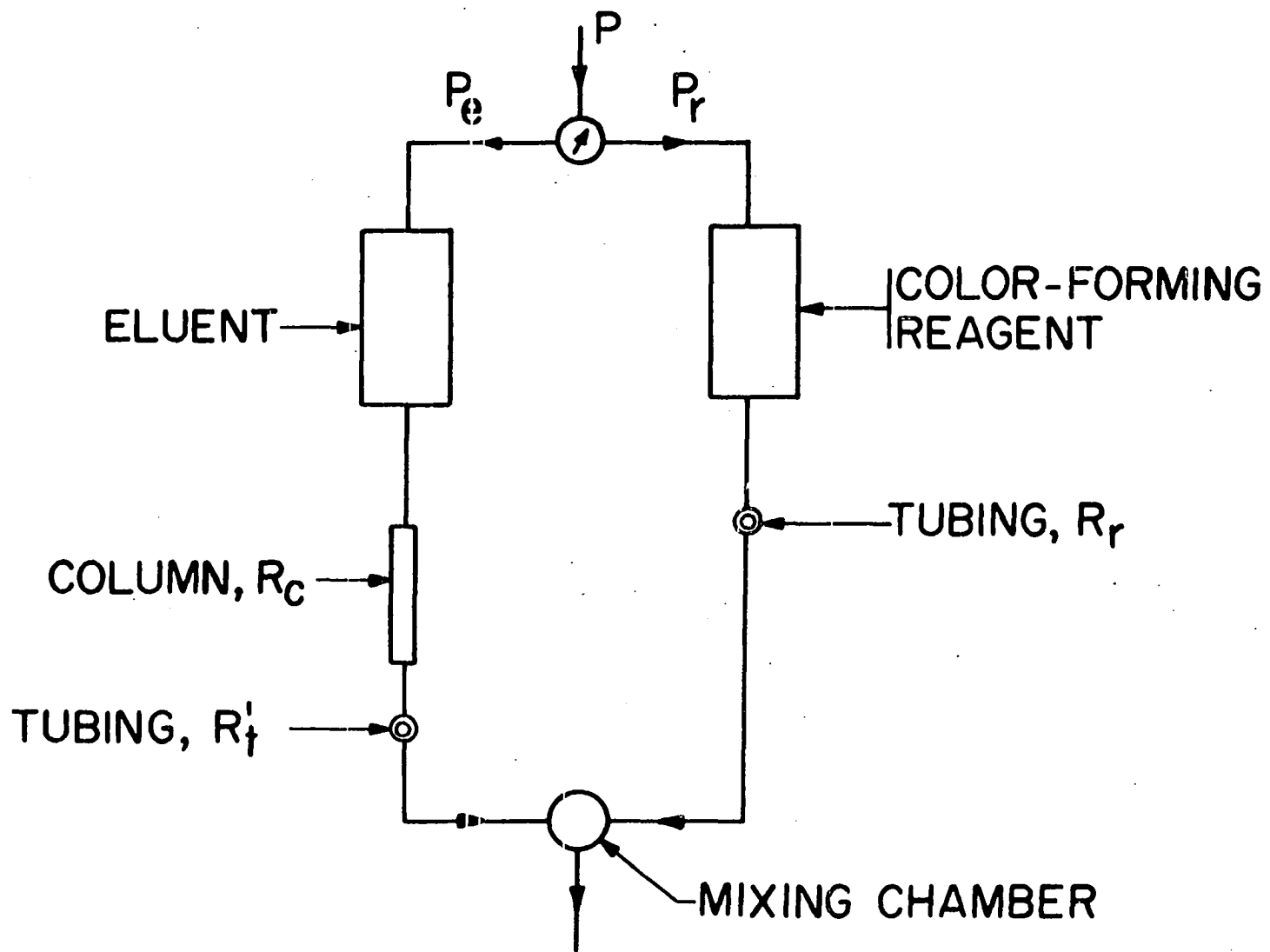
Figure 2. Schematic diagram of system for reagent addition for detection

The resistance of the column and of the tubing is determined by measuring the flow rate through the column or tubing as a function of applied pressure. Assuming that the diameter of the tubing is uniform, the resistance of the tubing per unit length can be calculated. The length of tubing in the reagent stream needed to give a certain ratio of flow rates can be calculated from the measured values of R_e and R_r.

Tubing is sometimes added to the eluate stream to increase the pressure needed to force eluent through the column at a given flow rate. That is done because, for the system being used, it is difficult to regulate the pressure when it is less than 15 p.s.i.g.

Using the system described, the eluate and reagent streams can be mixed in any ratio needed. By use of a 6-way valve, a range of mixing ratios can be achieved without interrupting operation of the chromatograph.

Preparation of the α-Hydroxy Oxime Resin

The resin was prepared by John J. Richard according to the procedure of Arnold and Fuson (94).

Phenylglyoxal hydrate, obtained from Columbia Organic Chemicals, Inc., was converted to the anhydrous compound by distillation. XAD-2, a macroporous, polystyrene-divinylbenzene copolymer, obtained from the Rohm and Haas Co. was ground and sieved. The 250-325 mesh fraction was used in the syntheses.

A solution containing 0.8 g of anhydrous phenylglyoxal in 25 ml of carbon disulfide was added dropwise with stirring to 13.3 g of anhydrous aluminum trichloride and 5.2 g of XAD-2 suspended in 50 ml of carbon disulfide in a 200 ml round-bottomed flask equipped with a dropping funnel and a reflux condenser. After addition was completed the mixture was re-fluxed with stirring for 24 hours. The reaction mixture was hydrolyzed by pouring it with stirring over an ice-hydro-chloric acid mixture. The resin was washed with water then with methanol to remove residual aluminum salts and any unre-acted starting material.

The resin was oximated by refluxing it overnight with 11 g of hydroxylamine hydrochloride, 50 ml of pyridine and 50 ml of absolute ethanol. Upon completion of reaction, the solvent was decanted, and the resin was washed 5 times with water, with dilute hydrochloric acid, 5 times with water, and 5 times with methanol. A small sample of the resin was dried at 105°C and analyzed for nitrogen content. The amount of nitrogen found was 1.1%. The theoretical value is 5.5%.

A second batch of resin was prepared in the same way as the first. Nitrogen analysis gave 1.2% nitrogen.

A third batch of resin was prepared using ethylene di-chloride in place of carbon disulfide as the solvent for the first reaction. The resin was allowed to swell in ethylene dichloride for 24 hours prior to carrying out the first step of the synthesis. The amount of nitrogen found in the third

batch of resin was 3.3%.

Infrared spectra of the 3 batches of resin were run by Tom Lyttle of the Chemistry Department. The spectra are shown in Figure 3. The spectra of Batches 1 and 2 of the resin are consistent with an aromatic α-hydroxy oxime. The poor resolution in the spectrum of Batch 3 makes it difficult to draw conclusions about the structure.

Columns

Chromatronix Model LC-6M-23 columns having an i.d. of 6.3 mm were used. The columns were packed with methanol slurries of the resin from which fines had been decanted. The resin was washed free of methanol by passing 50 ml of 0.1M acetic acid through the columns.

Reagents

All chemicals used were reagent grade or better. Solutions of metal ions were prepared from the metal chlorides, oxides, or nitrates. The standard stock solutions of copper and molybdenum were prepared from 99.99 percent pure metals.

Evaluation of the Resin

Distribution coefficients

Distribution coefficients may be calculated from the following equation:

$$D = \frac{V_R - V_M}{w}$$

Figure 3.   Infrared spectra of α-hydroxy oxime resin, Batches 1, 2 and 3, top to bottom

PERCENT TRANSMISSION

WAVENUMBER cm⁻¹
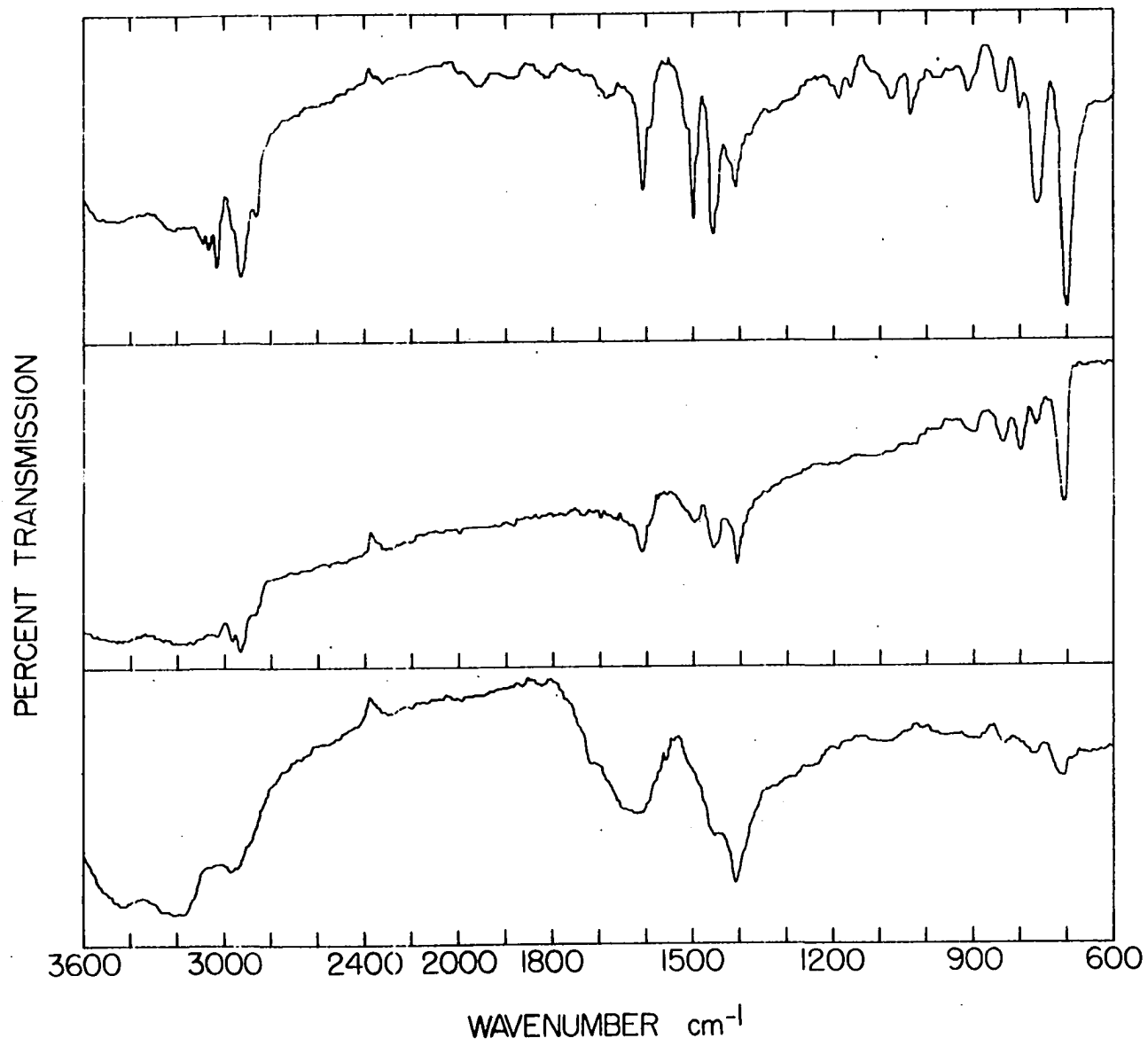
where V_R is the total retention volume, i.e., the volume of eluent entering the column between injection and peak maximum; V_M is the hold-up volume of the column, i.e., the volume of eluent necessary to elute an unretained component; and w is the weight of resin in the column.

V_R was measured for copper(II) and molybdenum(VI) in various media. V_M was determined by measuring V_R for chromium(III) and iron(III) which should not be retained by the resin. The average of the 20 lowest V_R values for copper(II), chromium (III), molybdenum(VI), and iron(III) was taken as V_M. For determination of distribution coefficients on columns containing Batch 2 or Batch 3 of the resin, V_M was taken as the average of V_R values for chromium(III) and iron(III) with 1M perchloric acid as the eluent.

After measurements of V_R were completed, the resin was removed from the column and washed with water, 4M hydrochloric acid, water, 0.1M sodium hydroxide, water, and acetone. It was dried under vacuum for 48 hours over anhydrous calcium chloride. The dried resin was then weighed.

For the determination of distribution coefficients 51.4 µl aliquots of 4×10^{-3} M solutions of metal ions were used. The composition of the solvent for each solution was the same as that of the eluent flowing through the column. Copper(II), chromium(III), and iron(III) were detected by mixing 10M hydrochloric acid with the eluate. Iron(III) and chromium(III)

were monitored at 225 nm and copper(II) at 275 nm. Molybdenum(VI) was monitored at 250 nm with no addition of reagent.

Capacity of resin

The capacities of the 3 batches of resin were determined by stirring a weighed portion of each resin with 60 ml of a solution containing copper(II) or molybdenum(VI) and then measuring the amount of copper(II) or molybdenum(VI) remaining in solution. The resin and solution were equilibrated for 12 hours. For copper the solution with which the resin was equilibrated was an $0.1M$ acetate solution, pH 4.5, containing 0.894 mmole of copper(II). The experiment was repeated using a solution containing 1.471 mmole of copper(II). The medium for molybdenum(VI) was $0.1M$ acetic acid and contained 0.892 mmole of molybdenum(VI). The amount of copper(II) or molybdenum(VI) remaining in solution was determined spectrophotometrically using a Cary Model 16 spectrophotometer.

After each solution was freed of resin by filtration, an aliquot was diluted so that the absorbance of the resulting solution fell in the range 0.2-0.8. The composition of the solvent for copper(II) was 60 percent $0.1M$ acetate and 40 percent concentrated hydrochloric acid. For molybdenum(VI) the solvent was $0.1M$ acetic acid. Both metal ions were measured at 250 nm.

Interference studies

Interference studies for copper(II) were done using a 5.3

cm column containing Batch 1 of the resin. For molybdenum(VI) a 6.0 cm column of Batch 2 of the resin was used. Solutions of copper(II) or molybdenum(VI) plus a test metal ion were injected onto the column. Copper(II) or molybdenum(VI) was then eluted, and the percentage recovery was determined from a calibration curve. If the test metal was found to interfere, the concentration was cut by a factor of 10, and the experiment was repeated.

For the interference studies the concentrations of copper (II) and molybdenum(VI) were $2x10^{-4}\underline{M}$, and a sample loop with a volume of 0.969 ml was used. Test solutions for copper(II) were in 0.25$\underline{M}$ tartrate, pH 10, and for molybdenum(VI) in 1$\underline{M}$ hydrochloric acid.

For copper, samples were injected onto a column which had been pre-equilibrated for 3 minutes with 0.1$\underline{M}$ acetate, pH 7. That eluent was allowed to flow through the column for 3 minutes after injection at which time the eluent was changed to 4$\underline{M}$ hydrochloric acid to elute the copper. The same time sequence was used for molybdenum, but the initial eluent was 0.1$\underline{M}$ acetic acid, pH 2.9, and the second eluent was 0.1$\underline{M}$ sodium hydroxide. The flow rates were 1.5 ml/min.

Preparation and Analysis of NBS Samples

Samples of NBS materials 85A, aluminum alloy, and 94A, zinc-base alloy, were dissolved in 20 ml of concentrated hydrochloric acid. When dissolution was complete, the solu-

tions were diluted to 100 ml and 2 ml of 30% hydrogen peroxide was added to ensure complete oxidation of copper. The solutions were boiled to destroy excess peroxide. Fifty ml of 1$\underline{M}$ sodium tartrate was added to the solutions which were then adjusted to pH 10 with sodium hydroxide and diluted to 200 ml with water.

A 5.3 cm column of Batch 1 of the resin was used for the analyses. A 0.969 ml sample loop was used. The elution sequence was the same as described above for interference studies. The percentage of copper in each sample was calculated from data obtained from a calibration curve prepared by sorbing and eluting standard samples of copper using the same sequence as for the NBS materials.

RESULTS AND DISCUSSION
Choice of Resin

Complex-forming resins may be prepared from monomeric materials or by attaching a complex-forming functional group to a polymeric matrix. The first route involves more variables than the second, but often is easier in terms of synthetic procedure. However, by using the second method, one can take advantage of well-characterized, commerically available polymeric materials with good physical properties. The disadvantage of the second method is that, although it is easy to think of groups to attach to the matrix, it is often difficult to find a suitable synthetic route to accomplish that.

For this work, the choice of an α-hydroxy oxime resin is based on the straightforward synthesis coupled with knowledge of the selectivity of monomeric α-hydroxy oximes for copper and molybdenum.

The matrix to which α-hydroxy oxime groups are added is a macroporous, polystyrene-divinylbenzene copolymer. Macroporous resins are generally more suitable than gel-type resins for use in high pressure systems. The gel-type resins are subject to large changes in volume in going from one ionic form to another, whereas macroporous resins show very little change in volume under similar conditions. In some cases, too, macroporous resins have better kinetic characteristics than gel resins, i.e., sorption and desorption are more rapid

with the macroporous materials.

Evaluation of the Resin

Distribution coefficients

The work of Beuerman (5) indicates that a resin with α-hydroxy oxime functional groups might be applicable to the separation of copper and molybdenum from other metals. The approach to evaluating the resin was to determine distribution coefficients for copper(II) and molybdenum(VI) in various media, from that data to choose suitable conditions for separations, and then by analysis of actual samples and by interference studies to test the applicability of the resin.

Distribution coefficients for Batch 1 of the resin are shown in Table 1. The data indicate that, in the absence of other complexing agents, copper(II) is strongly sorbed by the resin from solutions having a pH of 5 or greater and that molybdenum(VI) is strongly sorbed over the pH range 1 to 4.

Table 2 shows a comparison of the distribution coefficients for the resin with the distribution coefficients for 5,8-diethyl-7-hydroxydodecanone-6-oxime (DHDO) and 10-hydroxy-eicosan-9-oxime (HEO) at approximately the same pH values (5). It can be seen that for copper, the trend in distribution coefficients is the same with the resin as with DHDO and HEO. For molybdenum, the maximum distribution coefficient comes at a higher pH with the resin than with HEO.

Table 1. Distribution coefficients for copper(II) and molybdenum(VI) on an α-hydroxy oxime resin

Eluent	Copper(II)	Molybdenum(VI)
pH 10, 0.25M tartrate	4.3	0.3
pH 8, 0.25M tartrate	4.8	0
pH 6, 0.25M tartrate	2.8	0
pH 7, 0.1M acetate	>25	0
pH 6, 0.1M acetate	>25	0
pH 5, 0.1M acetate	>25	1.7
pH 4, 0.1M acetate	2.0	15.5
0.1M acetic acid	0.5	32.5
0.01M hydrochloric acid	0	21.7
0.1M hydrochloric acid	0	17.8
1M hydrochloric acid	0	1.5
2M hydrochloric acid	0	1.9
4M hydrochloric acid	0.5	3.9
6M hydrochloric acid	0.6	2.4
0.01M perchloric acid	0	13.6
0.1M perchloric acid	0	6.2
1M perchloric acid	0	1.2
2M perchloric acid	0	0.9
4M perchloric acid	0	0.8
6M perchloric acid	0	2.1

Table 2. Comparison of distribution coefficients for copper and molybdenum for an α-hydroxy oxime resin and for DHDO and HEO

Eluent	pH	Distribution coefficient Resin	DHDO	HEO
		Copper		
acetate	2.87		0.3	0.2
0.1M acetic acid	2.87	0.5		
acetate	4.0		43	39
0.1M acetate	4.0	2.0		
acetate	4.7		174	151
0.1M acetate	5.0	>25		
		Molybdenum		
6M H$^+$				10
6M hydrochloric acid		2.4		
4M hydrochloric acid		3.9		
1M H$^+$				500
1M hydrochloric acid		1.5		
0.1M H$^+$				351
0.1M hydrochloric acid		17.8		
0.01M H$^+$				34
0.01M hydrochloric acid		21.7		
0.1M acetic acid	2.87	32.5		
0.1M acetate	4.0	15.5		

Because copper is taken up from alkaline or slightly acidic solution, it is necessary to have a complexing agent in solution to prevent hydrolysis of most metal ions. Tartrate is often used for that purpose and is used in this work. In the presence of tartrate, copper is not held as strongly by the resin as without tartrate. It is, therefore, necessary to work at a higher pH with tartrate present. In solutions containing 0.25$\underline{M}$ tartrate, it is found that if the pH is adjusted so that it falls in the range 8 to 10, analyses for copper will give the same results.

As an alternative to tartrate, citrate is found to be too strong a complexing agent for use with the resin. Even at pH 10 copper(II) is not held on the column long enough to allow ether metal ions to be separated from it.

Capacity

For complex-forming resins, the capacity is a function of pH and of the presence of complexing agents in solution. For the α-hydroxy oxime resin, it would be difficult to determine the capacity for copper(II) under optimum conditions, i.e., where copper(II) is sorbed most strongly, because in that pH range copper(II) will precipitate in the absence of a complexing agent in solution. Therefore, capacity is determined in a solution having a pH of 4.5.

The capacities of Batches 1, 2, and 3 of the resin are found to be 0.058, 0.159, and 0.305 mmole copper(II) per gram

of resin, respectively, when the solution with which the resin
is equilibrated contains 0.894 mmole of copper(II). For a
solution containing 1.471 mmole of copper(II), the capacities
are 0.119, 0.312, and 0.548 mmole/g. Presumably, upon further
increase in the initial amount of copper(II) in solution, the
capacity will increase until the maximum capacity of the resin
at pH 4.5 is reached. However, that capacity has not been
determined.

The capacities of Batches 1, 2, and 3 of the resin are
found to be 0.159, 0.269, and 0.369 mmole molybdenum(VI) per
gram of resin, respectively. However, the resin turns blue
under the conditions used for the experiment indicating either
reduction of molybdenum(VI) to molybdenum(V) or formation of a
blue resin-molybdenum(VI) complex. In his work with α-ben-
zoinoxime, Knowles reported some reduction of molybdenum(VI)
by the reagent (4). Beuerman also reported some reduction of
molybdenum by DHDO, but not by HEO (5).

A second experiment run under the same conditions gives
capacities of 0.098, 0.162, and 0.266 mmole/g, thus indicating
that some reaction of the resin with molybdenum(VI) does
occur. The capacity of each batch of resin is decreased by
approximately the same amount. For Batch 1, the capacity
determined in the second experiment is 60 percent of that
found in the first experiment. For Batch 2, it is 62 percent,
and for Batch 3, it is 72 percent.

In column operation over a 2 month period of time, no obvious change in column behavior is observed. Therefore, it can be assumed that the reaction of molybdenum(VI) with the resin occurs only when they are in contact for prolonged periods of time.

From the distribution coefficients in Table 3, it can be seen that the distribution coefficient is a function of capacity. That situation is analogous to the increase in distribution coefficient with the increase in percentage loading of the stationary liquid phase in liquid-liquid partition chromatography.

Choice of Operating Conditions

Initial eluents are chosen so that copper(II) or molybdenum(VI) is strongly sorbed by the resin. For copper(II), the initial eluent is 0.1$\underline{M}$ acetate, pH 7, and for molybdenum, it is 0.1$\underline{M}$ acetic acid, pH 2.9.

From distribution coefficients it seems that once copper is sorbed by the resin, it should be eluted by lowering the pH of the eluent to 2 or 3. However, it is found experimentally that 4$\underline{M}$ hydrochloric acid is needed to elute copper rapidly and in a tight band. With a solution having a pH of 2, with 1$\underline{M}$ hydrochloric acid, or with 2$\underline{M}$ hydrochloric acid as the eluent, the peak height for copper is less than with 4$\underline{M}$ hydrochloric acid as the eluent. The peak is also broader and has a shoulder, possibly indicating the presence of more than one

Table 3. Distribution coefficients for copper(II) and molybdenum(VI) on different batches of an α-hydroxyoxime resin

Eluent	Batch 1	Batch 2	Batch 3
Copper(II)			
pH 7, 0.1$\underline{M}$ acetate	> 25	> 25	> 25
pH 4, 0.1$\underline{M}$ acetate	2.0	2.6	> 25
0.1$\underline{M}$ acetic acid	0.5	0.7	> 25
2$\underline{M}$ hydrochloric acid	0	0.4	9.8
4$\underline{M}$ hydrochloric acid	0.5	1.0	> 25
pH 10, 0.25$\underline{M}$ tartrate	4.3	14.9	> 25
Molybdenum(VI)			
pH 7, 0.1$\underline{M}$ acetate	0	0	0
pH 5, 0.1$\underline{M}$ acetate	1.7	6.6	> 40
pH 4, 0.1$\underline{M}$ acetate	15.5	> 40	> 40
0.1$\underline{M}$ acetic acid	32.5	> 40	> 40
2$\underline{M}$ hydrochloric acid	1.9	8.3	> 25
4$\underline{M}$ hydrochloric acid	3.9	18.0	> 25

complex of copper on the resin, or, alternatively, that there is a minimum concentration of acid below which the resin-copper complex is not broken up rapidly.

For molybdenum(VI), 0.1$\underline{M}$ sodium hydroxide is found to be a suitable eluent. Eluents having pH values of 6 and 7 do not elute molybdenum as rapidly or in as tight a band as 0.1$\underline{M}$ sodium hydroxide. Even with 0.1$\underline{M}$ sodium hydroxide as the eluent, molybdenum peaks have a slight shoulder. Considering the complex chemistry of molybdenum(VI), the shoulder might be attributable to equilibria among various molybdenum(VI) species in different media.

Distribution coefficients for copper on Batch 1 and Batch 2 of the resin do not indicate any particular advantage in using one batch over the other. Because preliminary work was done using Batch 1, analyses were carried out using that material. Distribution coefficients for molybdenum, on the other hand, indicate that by using Batch 2, operation in more acidic solution should be possible than with Batch 1. That would be desirable because of hydrolysis problems. However, when 1 $\underline{M}$ hydrochloric acid is used as the initial eluent, part of the molybdenum injected is not held by the resin. If 0.1$\underline{M}$ acetic acid is used as the initial eluent, but samples are dissolved in 1$\underline{M}$ hydrochloric acid, all of the molybdenum sticks to the column until eluted with 0.1$\underline{M}$ sodium hydroxide.

Although the distribution coefficients for Batch 3 of the resin indicate that it should be useful for separations of

copper and of molybdenum, Batch 3 was not available until most of the work with the resin was completed. A few experiments with Batch 3 indicated that $0.1\underline{M}$ sodium hydroxide would not elute molybdenum(VI) rapidly and in a narrow band nor would $4\underline{M}$ hydrochloric acid elute copper rapidly and in a narrow band.

The 3 minute time span (1.5 ml/min) between injection and elution is found to be sufficient to allow several test elements to pass through the column. For times as long as 8 minutes between injection and elution, the peak height for copper or molybdenum is the same upon elution.

Detection of copper(II) directly in $4\underline{M}$ hydrochloric acid is possible, but it is found that peak height on elution for repeated injections of the same sample is not very reproducible. By mixing the eluate with $10\underline{M}$ hydrochloric acid in a 3:2 ratio, good reproducibility of peak height is achieved.

Chromatograms showing the separation of copper(II) from molybdenum(VI) and of molybdenum(VI) from copper(II) using the conditions described above are shown in Figures 4 and 5, respectively.

Linear calibration curves are obtained for copper over the concentration range from $1\times10^{-4}\underline{M}$ to $4\times10^{-4}\underline{M}$ and for molybdenum over the range from $2\times10^{-4}\underline{M}$ to $8\times10^{-4}\underline{M}$.

Analysis of NBS Materials

Results of the analyses of 2 NBS materials are shown in Table 4. The results are based on the average of three independent determinations for each sample. NBS 85A contains
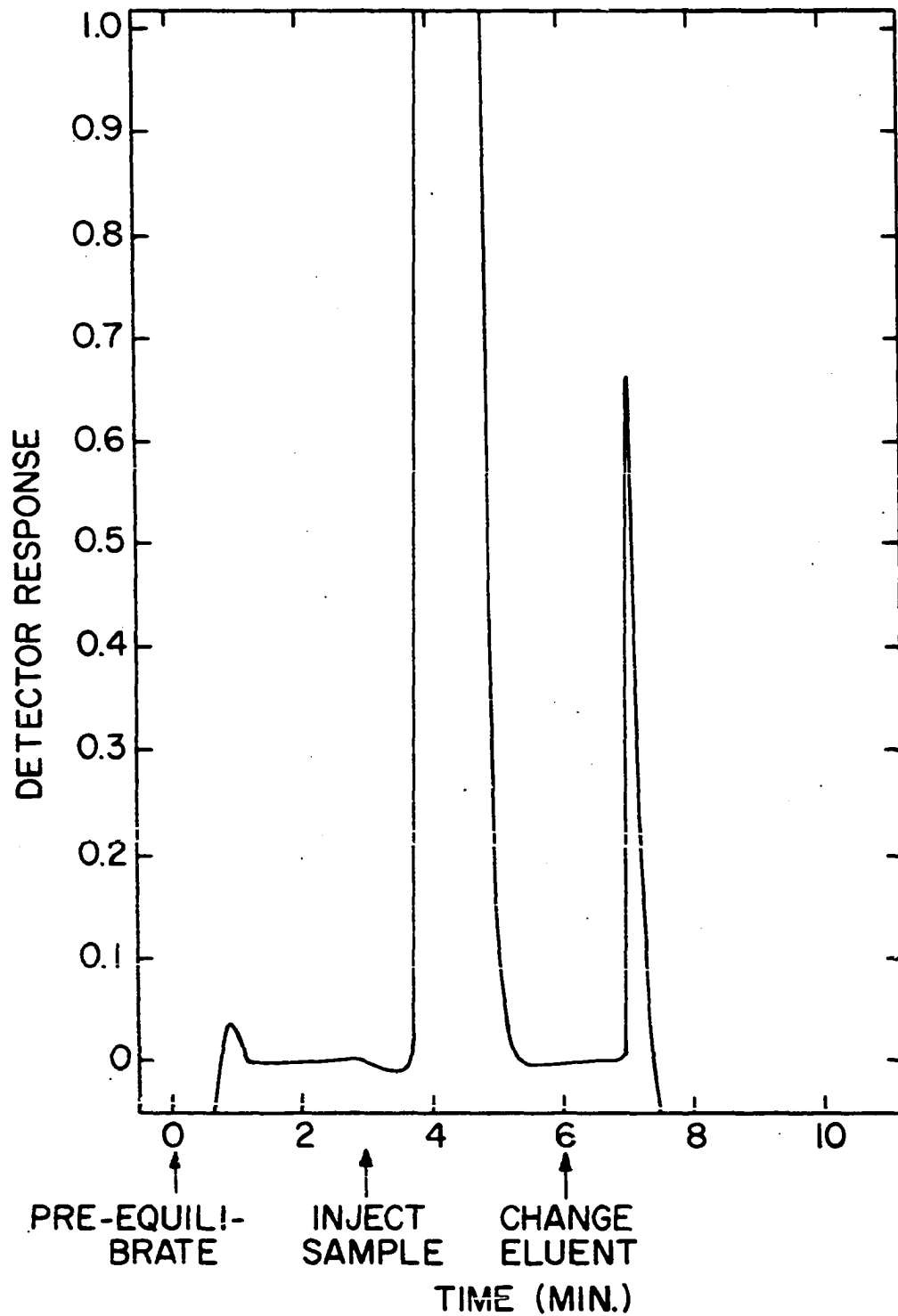
Figure 4. Separation of molybdenum from copper on a 5.3 cm column containing Batch 1 of the α-hydroxy oxime resin

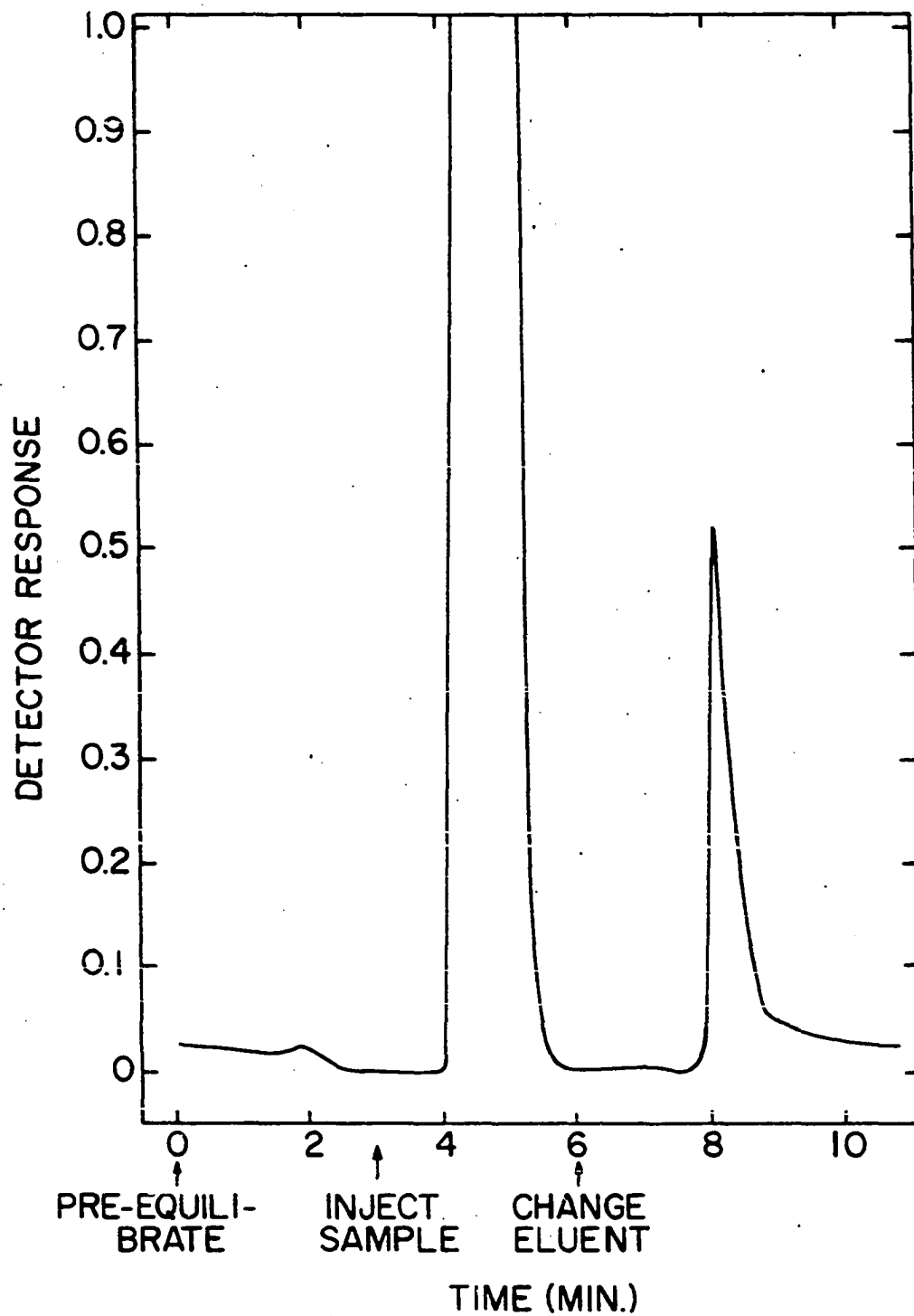Figure 5. Separation of copper from molybdenum on a 6.0 cm
column containing Batch 2 of the α-hydroxy oxime
resin

Table 4. Analysis of NBS alloys for copper

Sample	% Copper, NBS	% Copper, found	Relative error, %
NBS 85A, aluminum alloy	2.48	2.47 ± 0.01	-0.40
NBS 94A, zinc-base alloy	1.08	1.07 ± 0.02	-0.93

aluminum (94 percent), magnesium (1.6 percent), manganese, chromium, nickel, silicon, iron (less than 1 percent each), and zinc, titanium (less than 0.1 percent each). NBS 94A contains zinc (95 percent), aluminum (3.9 percent), and magnesium, manganese, iron, lead, nickel, tin, cadmium (less than 0.1 percent each).

A third sample, NBS 54D, tin-base bearing metal, having 3.62 percent copper, was also analyzed. The small amount of lead, 0.6 percent, in the sample caused an error of +20 percent.

Molybdenum is found in some iron alloys at a level of 1 or 2 percent. Analysis of several molybdenum steels of that type was attempted. The results were neither accurate nor reproducible. Both iron and chromium, which is sometimes found in such samples, interfere in the determination of molybdenum.

Interferences

Tables 5 and 6 summarize the interference studies for copper and molybdenum. It is apparent that a number of metals would interfere in the determination of copper or molybdenum. In terms of occurrence, iron is the most serious interference for both metals. Chromium, titanium, and vanadium which are often found in molybdenum steels are major interferences in the determination of molybdenum. Lead is a major interference in the determination of copper.

Table 5. Interference of metal ions with the determination
of copper[a]

Metal ion	Concentration, $\underline{M}$	% Recovery of Cu
Aluminum(III)	2×10^{-2}	90.5
	2×10^{-2}	101.0[b]
Cadmium(II)	2×10^{-3}	104.5
	2×10^{-4}	102.5
Calcium(II)	2×10^{-3}	99.0
Chromium(III)	2×10^{-4}	94.0
Cobalt(II)	2×10^{-2}	101.0[c]
	2×10^{-3}	88.0
	2×10^{-4}	103.5
Iron(III)	2×10^{-3}	114.0
	2×10^{-4}	107.0
Lead(II)	2×10^{-4}	162.5[d]
	2×10^{-4}	153.5[e]
	2×10^{-4}	162.0[f]
Lithium(I)	2×10^{-2}	101.0
Magnesium(II)	2×10^{-2}	99.5
Manganese(II)	2×10^{-3}	102.0
Mercury(II)	2×10^{-3}	135.0[d]
	2×10^{-4}	105.0
Molybdenum(VI)	2×10^{-2}	99.0

[a]Concentration of copper(II) is $2 \times 10^{-4} \underline{M}$. Column is 5.3
cm and contains Batch 1 of the resin.

[b]$2\underline{M}$ hydrochloric acid added before adjusting pH.

[c]Sorbed from pH 5.5, $0.1\underline{M}$ acetate medium.

[d]Sorbed from pH 8, $0.25\underline{M}$ tartrate medium.

[e]Sorbed from pH 10, $0.5\underline{M}$ tartrate medium.

[f]Sorbed from pH 7, $0.1\underline{M}$ acetate medium.

Table 5. (Continued)

Metal ion	Concentration, $\underline{M}$	% Recovery of Cu
Nickel(II)	2×10^{-3}	90.0^d
	2×10^{-4}	103.5
Potassium(I)	2×10^{-2}	101.5
Sodium(I)	2×10^{-2}	99.5
Thorium(IV)	2×10^{-3}	38.0
	2×10^{-4}	69.5
Tin(IV)	2×10^{-2}	100.5
Uranium(VI)	2×10^{-3}	116.0^d
	2×10^{-4}	105.0
Zinc(II)	2×10^{-2}	52.0
	2×10^{-2}	64.0^b

Table 6. Interference of metal ions with the determination of molybdenum[a]

Metal ion	Concentration, $\underline{M}$	% Recovery of Cu
Aluminum(III)	2×10^{-2}	112.5
	2×10^{-3}	102.5
Bismuth(III)	2×10^{-2}	108.5[b]
Cadmium(II)	2×10^{-2}	118.5
	2×10^{-3}	99.0
Calcium(II)	2×10^{-2}	98.5
Chromium(III)	2×10^{-2}	118.5
	2×10^{-4}	102.0
Cobalt(II)	2×10^{-2}	99.5
Copper(II)	2×10^{-2}	102.5
Iron(III)	2×10^{-2}	138.0
	2×10^{-4}	103.0
Lithium(I)	2×10^{-2}	99.5
Lead(II)[c]	2×10^{-2}	98.0
Magnesium(II)	2×10^{-2}	100.0
Manganese(II)	2×10^{-2}	104.5
	2×10^{-4}	106.5
Mercury(II)	2×10^{-2}	248.0
	2×10^{-3}	99.0
Nickel(II)	2×10^{-2}	102.5
Potassium(I)	2×10^{-2}	99.5
Sodium(I)	2×10^{-2}	99.5
Thorium(IV)	2×10^{-2}	98.5

[a]Concentrationoof molybdenum(VI) is $2\times10^{-4}\underline{M}$. Column is 6.0 cm and contains Batch 2 of the resin.

[b]Bled off column slowly under conditions used. Column washed with $4\underline{M}$ hydrochloric acid to remove bismuth completely.

[c]Lead(II) sorbed from $1\underline{M}$ nitric acid.

Table 6. (Continued)

Metal ion	Concentration, $\underline{M}$	% Recovery of Cu
Tin(IV)	2×10^{-2}	197.5
	2×10^{-4}	129.5
Titanium(IV)	2×10^{-2}	220.0
	2×10^{-4}	108.5
Vanadium	2×10^{-2}	198.0
	2×10^{-4}	142.0
Uranium(VI)	2×10^{-2}	132.5
	2×10^{-4}	104.0
Zinc(II)	2×10^{-2}	99.0

Although the data for zinc(II) in Table 5 indicate that it would cause low results in the determination of copper, that is not found to be the case. NBS 94A has a zinc/copper ratio of 95/1, but the results for copper are both accurate and precise.

Beuerman reports no interference from cobalt(II), nickel (II), chromium(III), iron(III), zinc(II), cadmium(II), tin(IV), molybdenum(VI), palladium(II), lead(II), bismuth(III), thorium (IV), mercury(II), vanadium(IV), titanium(IV), antimony(III), uranium(VI), and tungsten(VI) in the liquid-liquid chromatographic determination of copper when HEO is used as the stationary liquid phase. Of these metal ions, only titanium(IV) interferes when DHDO is used. Iron(III), nickel(II), cobalt (II), zinc(II), copper(II), tin(IV), tungsten(VI), cadmium(II), mercury(II), and thorium(IV) do not interfere in the determination of molybdenum when HEO is used. However, in the interference studies with HEO and DHDO, copper(II) or molybdenum (VI) and the other metal ion are present in approximately the same amount. No data are available for the case where a metal ion may be present in an amount in large excess of copper(II) or molybdenum(VI).

With removal of the constraints imposed by seeking a general method, it may be possible to analyze specific samples containing copper or molybdenum using conditions different from those described here. Thereby, interference from some metals may be eliminated. An example can be seen in Table 5.

Cobalt(II) in 0.25$\underline{M}$ tartrate, pH 10 interferes in the determination of copper when present at 10 times the concentration of copper. However, in 0.1$\underline{M}$ acetate, pH 5.5, cobalt(II) does not interfere when present at 100 times the concentration of copper.

CONCLUSIONS

The synthesis and characterization of an α-hydroxy oxime complex-forming resin have been described. Favorable conditions exist for the sorption by and elution from the resin of copper(II) and molybdenum(VI). However, under the conditions used, several commonly occurring metals interfere in the determination of copper or molybdenum, thus limiting the utility of the resin. Some alteration of conditions for specific samples is indicated as a method for overcoming some of the interferences.

Because alkali metals do not inhibit the sorption of copper or molybdenum by the resin, possible applications of the resin would be to the removal of traces of copper or molybdenum from solutions having a high content of alkali metals, and to the concentration of traces of copper or molybdenum from solutions with a high salt content. For copper, however, the α-hydroxy oxime resin would be no better than Dowex A-1.

The similarity in trends for distribution coefficients with the resin and with DHDO and HEO is evidence that the resin does, indeed, have α-hydroxy oxime functional groups. Further characterization of the resin might include determination of the structure and composition of resin-copper and resin-molybdenum complexes. Beuerman (5) has found that copper can form two complexes with DHDO, a brown complex having a ligand:

copper ratio of 2:1 and a green complex with a 1:1 ratio.
Molybdenum apparently forms only a 1:1 complex. For this
resin, formation of a 2:1 resin:metal complex would be un-
likely because the low capacity of the resin indicates that
no two functional groups would be close enough to each other
to coordinate with copper at the same time.

In theory, information pertaining to the nature of the
bonding, i.e., formation of metal-oxygen bonds and/or metal-
nitrogen bonds, should be available from comparison of infra-
red spectra of the resin alone and of the resin-metal com-
plexes.

An approach to determining the composition of sorbed
species is indicated by Lowenschuss and Schmuckler (65) who
have demonstrated the formation of mixed ligand complexes of
copper(II) and nickel(II) with Dowex A-1 and aminocarboxylate
ligands. One would expect, then, that in the case where the
coordination sphere of the metal is not filled by the func-
tional groups of the resin some other species in solution,
e.g., water, acetate, tartrate, chloride, will also be coor-
dinated with the metal. Thus, the composition of the eluent
would be expected to have an important effect on the distribu-
tion of metal ions between the resin and eluent.

Two effects which have to be taken into account with
complex-forming resins are the effect of sorption by the
matrix and the steric effect resulting from the functional

groups being immobilized on the matrix. XAD-2 shows no tendency to sorb ionic species, so for the α-hydroxy oxime resin, one would expect no contribution to sorption by the polymeric matrix. It is assumed that the functional groups of the α-hydroxy oxime resin are located on the styrene rings para to the vinyl groups. Presumably, if the functional groups are ortho to the vinyl groups, no complexation could take place. Saldadze et al. (48) have shown that to be the case for vinyl-pyridine resins.

A theoretical approach, rather than a practical one, to the evaluation of complex-forming resins would, in the long run, be more fruitful. By determining stability constants and the structure of resin-metal complexes, by studying the effects of the matrix and of solution composition on complex formation, and by devising experiments to elucidate the mechanism(s) of sorption, the theory of complex-forming resins can be modified and extended. On theoretical grounds, then, one would be better able to predict which complex-forming resins, i.e., which matrix and which functional group, would have utility.

FUTURE WORK

Among compounds that have been used as extractants for metal ions, those containing both phosphorus and sulfur are found to be quite selective. Handley and Dean have done extensive work with trialkyl thiophosphates (95), dialkyl phosphorothioates (96), and dialkyl phosphorodithioates (97).

Cerrai and Ghersini have described a paper chromatographic system in which methyl and ethyl derivatives of p-nitrophenyl thiophosphate are used as stationary phases (98). They are found to extract palladium, silver, cadmium, mercury, and gold from nitric acid.

Elliott and Banks have found tri-n-octylphosphine sulfide to be a selective extractant for gold(III), mercury(II), silver(I), and palladium(II) (99).

Solvent extraction data indicate that resins with functional groups analogous to those mentioned above should be selective for heavy metals. Moreover, because of the insolubility of the polymeric matrix, studies can be done to determine the effect of the size of the alkyl groups on the selectivity of the resins. In extraction systems the size of the alkyl groups is often dictated by the solubility of the extractant in the aqueous phase. With resins the effects of small groups such as methyl and ethyl groups as well as of large alkyl groups can be tested.

With complex-forming resins of any type, theoretical

studies should be at least as important as the empirical determination of the applicability of the resin. Much needs to be learned about how complex-forming resins function, i.e., about the mechanism(s) of sorption, about the effects of the polymeric matrix, about the effects of solution composition, and about steric effects.

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