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## SEPARATION OF METAL IONS USING AN AROMATIC *o*-HYDROXY-OXIME RESIN

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### SUMMARY

A chelating ion exchanger has been synthesized in which an *o*-hydroxypropiophenoneoxime group is attached chemically to the benzene ring of a divinylbenzene resin. On a short column of such resin, copper(II) is selectively adsorbed from pH 3.5 acetate solution or from pH 5 tartrate solution and can be subsequently eluted sharply by 0.1 *M* hydrochloric acid. Molybdenum(VI) is sorbed selectively from 0.1 *N* sulfuric acid solution and is eluted in a narrow band by aqueous sodium hydroxide. Numerous rapid column-chromatographic separations are reported using the resin, including some used in the analysis of NBS standard samples.

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### INTRODUCTION

Several hydroxyoximes have found use as analytical chelating reagents. Benzoin  $\alpha$ -oxime and, more recently, two aliphatic  $\alpha$ -hydroxyoximes<sup>1</sup> were used as selective reagents for solvent extraction of molybdenum(VI) from acid solution and of copper(II) from basic or weakly acid aqueous solution. Copper(II) has been extracted from acidic leach liquors by a commercial product that contains mixed aliphatic  $\alpha$ -hydroxyoximes and *o*-hydroxybenzophenoneoximes<sup>2</sup>. Poddar studied *o*-hydroxyacetophenoneoxime as a reagent for copper and nickel<sup>3,4</sup>, and Gupta and Malik<sup>5</sup> used this compound as a reagent for molybdenum(VI).

A resin containing an  $\alpha$ -hydroxyoxime functional group might be expected to sorb copper(II) and molybdenum(VI) selectively at suitable pH values. Goodkin<sup>6</sup> synthesized such a resin [*Res*-CH(OH)C(=NOH)C<sub>6</sub>H<sub>5</sub>, where *Res* represents a polymeric divinylbenzene]; her resin was fairly selective for copper(II) at a pH of 5 or greater and for molybdenum(VI) over the pH range 1 to 4.

Here, we describe the synthesis and analytical properties of a chelating resin in which *o*-hydroxypropiophenoneoxime is chemically bonded to the polydivinylbenzene resin XAD-4. The resulting chelating resin is used for the separation and quantitative determination of both copper and molybdenum by high-performance liquid chromatography (HPLC). To check the practical applicability of this method, several NBS standard samples have been analyzed.

## EXPERIMENTAL

*Liquid chromatograph*

A liquid chromatograph has been constructed that is more compact and easier to operate than the apparatus used in previous studies<sup>7</sup>. The entire unit is self-contained in a steel cabinet (14 in. × 14 in. × 14 in.). A schematic diagram of the unit is shown in Fig. 1, and some of the main features of the chromatograph are listed below.

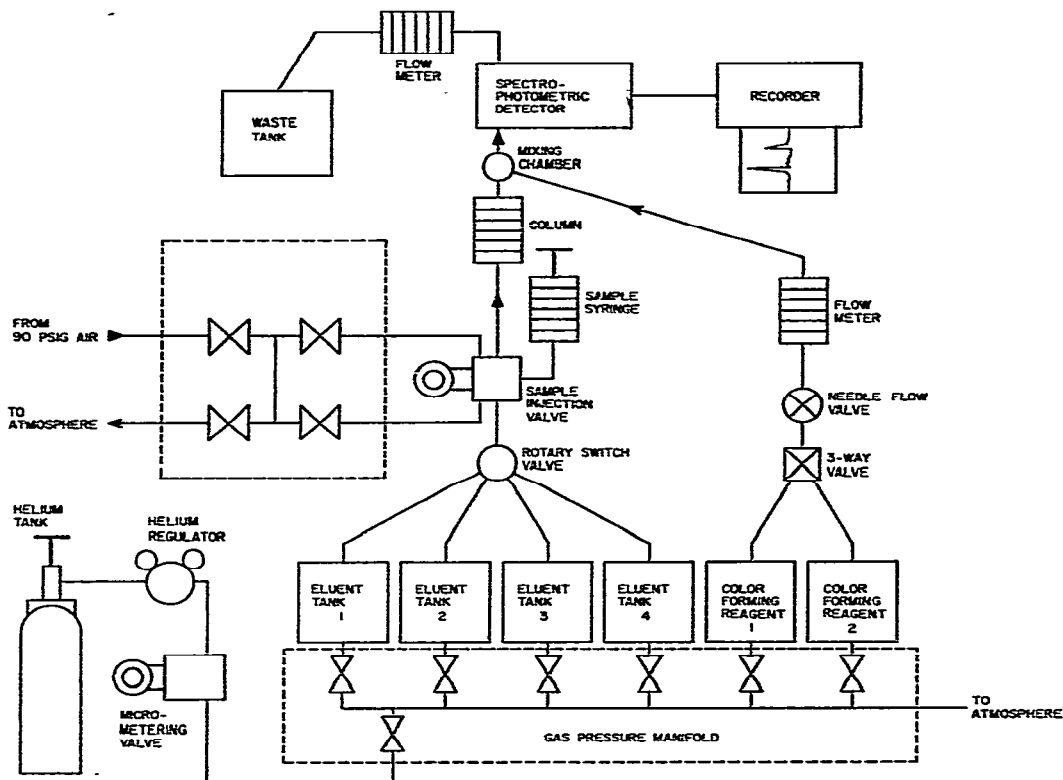


Fig. 1. Schematic diagram of the liquid chromatograph.

(1). The four eluent reservoirs are 500-ml glass reagent bottles with a 24/40 standard taper joint. The stoppers for the bottles are machined from Kel-F and are held in place by No. 35 Thomas clamps. The bottles can withstand pressures up to 90 p.s.i. without danger of explosion. With this system, eluent bottles can be changed in less than 1 min.

(2). Eluent selection is effected by a 6-way rotary selector valve (Altex 202-01), which allows quick selection of any of the eluents with a minimum amount of mixing.

(3). There are two reservoirs that contain dye. Either of the two dyes may be used by switching a 3-way valve (Altex 201-51): this makes it possible to use both dyes in the same run without having to stop operation, change the dye bottle, and start again. The dye flow-rate is regulated by a chemically inert needle valve placed after the 3-way valve.

### *Detector*

A Tracor 970 variable-wavelength detector was used for continuous spectrophotometric monitoring of the column effluent. All chromatograms were recorded on a Houston Instruments Omniscrite recorder.

### *Column*

The analytical column was constructed from two Altex 200-28 glass connectors fused together. The column had an I.D. of 2 mm and an over-all length of 70 mm; a helium pressure of 26 p.s.i. was required to attain a flow-rate of 2 ml/min.

### *Synthesis of the resin*

$\alpha$ -Bromo-2-hydroxypropiophenone was prepared by the method of Buu-Hoi and Lavit<sup>8</sup>. *o*-Hydroxypropiophenone (20 g) in 200 ml of glacial acetic acid was cooled in an ice bath, and bromine (22 g) in 30 ml of the same solvent was added dropwise, with stirring. After complete decolorization, the mixture was diluted with water, and the yellow oil formed was dissolved in chloroform. The chloroform layer was dried over magnesium sulfate and vacuum distilled,  $\alpha$ -bromo-2-hydroxypropiophenone being collected at 145–155°/15 mm. (Caution, this compound is lachrymatory and should be handled with care.)

XAD-4, a macroporous styrene-divinylbenzene copolymer, was obtained from the Rohm & Haas Co. The beads were extracted overnight with methanol in a Soxhlet apparatus, dried, ground and sifted; the 250–325 mesh fraction was further dried in a vacuum oven at 110° to ensure complete removal of water and methanol. The reaction vessel consisted of a 500-ml 3-neck-flask equipped with a mechanical stirrer, reflux condenser, dropping-funnel and nitrogen inlet. XAD-4 (5 g) was slowly added to 33 g of anhydrous aluminium chloride suspended in 100 ml of dichloroethane, and 17 g of  $\alpha$ -bromo-2-hydroxypropiophenone in 25 ml of dichloroethane were added (dropwise, with stirring) to the mixture. After complete addition (0.5 h), the mixture was heated gently under reflux for 4 h. The entire reaction was performed under a nitrogen atmosphere to exclude water. The resin was hydrolyzed by being poured into an ice-hydrochloric acid mixture, and was then washed with water, 1 *M* hydrochloric acid and acetone, and dried. The product was oximated by being heated under reflux for 2 g with 15 g of hydroxylamine hydrochloride in 50 ml of absolute ethanol. Upon cooling, the resin was washed several times with water, then with methanol, then with acetone, and dried.

### *Color-forming reagents*

PAR[4-(2-pyridylazo)resorcinol] was used for the detection of manganese(II), iron(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and uranium(VI); these species were all monitored at 495 nm. The PAR solution was prepared by dissolving 121.1 g of THAM (Tris) in *ca.* 750 ml of distilled water, then adding PAR (0.125 g) and adjusting the pH to 9.0 with concentrated hydrochloric acid. The final solution was diluted to 1 l with distilled water. A red precipitate formed after several days, which necessitated filtering the solution; a corresponding loss in dye strength was also evident after filtering.

Arsenazo I was used for the detection of calcium, magnesium, thorium and

copper(II), all of which were monitored at 590 nm. The arsenazo I solution was prepared as described above for PAR.

Fritz and Sutton<sup>9</sup> have shown that bis-(2-hydroxyethyl) dithiocarbamate will form a water-soluble yellow complex with copper(II). This reagent was easily prepared by adding 0.82 g of carbon disulfide to 105 g of diethanolamine, diluting to 750 ml with distilled water, adjusting the pH to 9.5 with hydrochloric acid, and diluting the solution to 1 l. Copper(II) was detected at 433 nm, at which wavelength the molar absorptivity is 11,400.

Thiolactic (2-mercaptopropionic) acid was used for detection of molybdenum<sup>10</sup>. The reagent was prepared by adding 57.5 ml of glacial acetic acid to 900 ml of water and adjusting the pH to 4.0 with 20% sodium hydroxide solution. Then 1.90 g of thiolactic acid were added, and the solution was diluted to 1 l. Molybdenum was detected at 365 nm with this reagent.

#### *Separation procedure*

*Copper.* The following procedure was used to separate copper from non-interfering metal ions.

(1) Before application of the sample to the column, allow 0.1 M tartrate buffer (pH 5) to flow through the column at 2 ml/min for 5 min.

(2) Inject the sample on to the column.

(3) Allow pH 5 tartrate buffer to flow through the column at 2 ml/min for 5 min to separate the non-interfering ion from copper.

(4) Change the eluent to 0.1 M hydrochloric acid at a flow-rate of 2 ml/min for 5 min to elute copper.

When NBS standards were analyzed, steps 1 and 3 were shortened to 2.5 min each; this allowed an analysis to be completed in 10 min.

*Molybdenum.* The following procedure was used to separate molybdenum from non-interfering metal ions.

(1) Before application of the sample to the column, allow 0.05 M sulfuric acid to flow through the column at 2 ml/min for 5 min.

(2) Inject the sample on to the column.

(3) Allow 0.05 M sulfuric acid to flow through the column at 2 ml/min for 5 min to separate the non-interfering ion from molybdenum.

(4) Change the eluent to 0.1 M sodium hydroxide at a flow-rate of 2 ml/min for 5 min to elute molybdenum.

When NBS standards were analyzed steps 1 and 3 were shortened to 2.5 min; this allowed the analysis to be completed in 10 min.

#### *Analysis of NBS standards*

*Copper.* Approximately 0.15 g of NBS sample 94A, a nickel-copper alloy, was dissolved in 5 ml of aqua regia, and the solution was transferred to a 500-ml volumetric flask, diluted to the mark with pH 5 tartrate buffer and then analyzed for copper as described in the previous section.

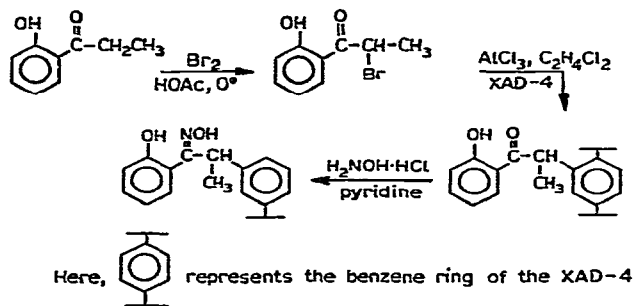
*Molybdenum.* Approximately 0.95 g of NBS sample 160, a chromium-nickel-molybdenum steel, was dissolved in 50 ml of sulfuric acid (1:6). The solution was cooled, transferred to a 250-ml volumetric flask, diluted to the mark with distilled water, then analyzed for molybdenum as described in the previous section.

Approximately 0.35 g of NBS sample 132 A, a tungsten–chromium–molybdenum–vanadium steel, was dissolved in 5 ml of concentrated hydrofluoric acid and 4 ml of concentrated nitric acid in a platinum dish. After cooling, the solution was transferred to a 250-ml volumetric flask containing 50 ml each of saturated sodium borate solution and 0.5 M sodium tartrate. The resulting mixture was diluted to the mark with distilled water; this gave a solution of pH between 2 and 3, in which molybdenum was determined as described in the previous section.

## RESULTS AND DISCUSSION

### Resin synthesis

To produce a chelating resin with favorable kinetics that can be used in column chromatography, it is necessary to start with a resin matrix that is rigid and highly porous; previous experience had shown Rohm and Haas XAD-4 to be an excellent starting material. Several synthetic routes were tried in an attempt to introduce a hydroxyoxime functional group into this resin in high yield. The Friedel–Crafts reaction was first tried, using  $\alpha$ -bromo-2-hydroxyacetophenone. However, Trahanovsky<sup>11</sup> pointed out that this would involve the formation of a primary carbonium ion, which would make the reaction very unfavorable. For this reason,  $\alpha$ -bromo-2-hydroxypropiophenone was chosen as the reagent. The addition of a methyl group in a position *alpha* to the bromine allowed a secondary carbonium ion to form, thus making the reaction more favorable.



Elemental analysis gave an average nitrogen content of 1.77%. Assuming that all of the nitrogen is from the oxime, 1 g of resin should contain 1.26 mequiv. of the desired functional group.

The IR spectra of XAD-4 and of the hydroxyoxime resin are shown in Fig. 2. A large hydroxyl stretch from the phenol, and an oxime C=N stretch evident at  $1700\text{ cm}^{-1}$ , are evident.

### Copper(II) sorption

Previous studies by Fritz *et al.*<sup>1</sup> and Goodkin<sup>6</sup> have shown that *o*-hydroxyoximes can form complexes with copper in basic or slightly acidic (pH 5) medium. In both of these studies, the hydroxyl functional group was an alcohol, which is a much weaker acid than a phenol. The resin used in our work contains a phenolic group and would therefore be expected to sorb copper at a lower pH; this proved to be the case.

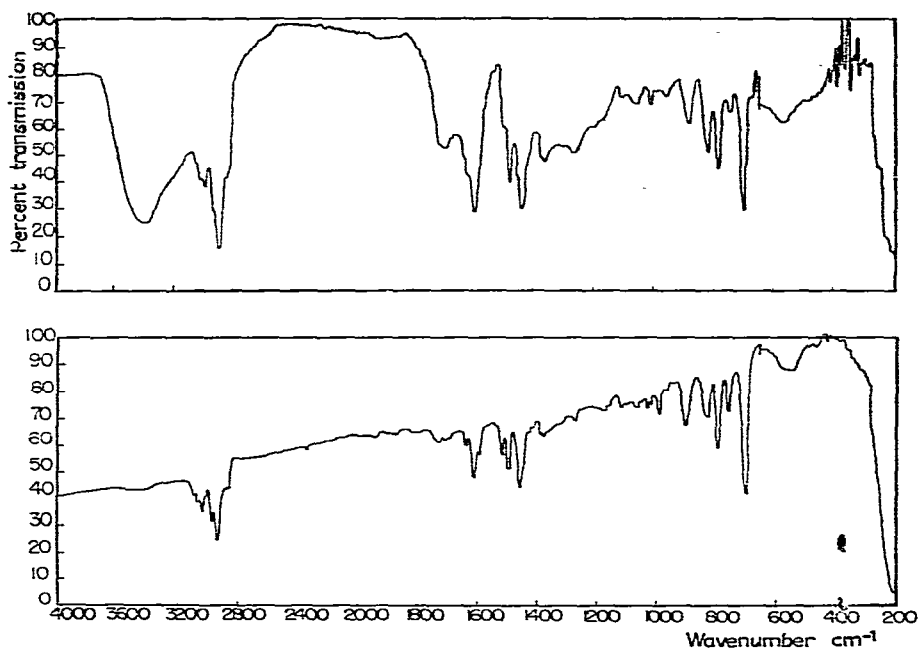


Fig. 2. Infrared spectra. Top: *o*-Hydroxypropiophenone oxime resin. Bottom: XAD-4 resin.

The resin will retain copper completely from a column in a 0.1 *M* acetate buffer down to pH 3.5; below this pH, the copper bleeds off the column. The resin will also completely retain copper from 0.1 *M* tartrate buffer at the same pH. Goodkin found that, when using a tartrate buffer with the  $\alpha$ -hydroxyoxime resin, it was necessary to raise the pH from 5 to 10 to retain copper completely. This is further evidence that the *o*-hydroxyxyoximes are stronger complexers for copper. There was no advantage in working at pH 3.5, so all separations were performed using 0.1 *M* tartrate buffer at pH 5. Higher acid concentrations were tried, but the slight increase in peak height was more than offset by the larger base-line shift. A typical elution of copper is shown in Fig. 3.

Attempts to construct a calibration graph for copper(II) using PAR as color-forming reagent in the detector gave a non-linear curve with a very limited copper range (Fig. 4). A reagent with better selectivity for copper, bis-(2-hydroxyethyl) dithiocarbamate, was then tried. This reagent is easy to prepare and works very well for copper(II), as shown in Fig. 4.

Copper(II) can be sorbed selectively on column of resin from aqueous solution of pH 3.5 or higher, or from tartrate solution of pH 5. The latter condition permits separation of copper(II) from a large number of other metal cations. In the tartrate buffer, the resin had essentially no affinity for zinc(II), nickel(II), cobalt(II) or manganese(II), these species being eluted completely from the column in less than 2 min. Fig. 5 shows the separation of copper from equimolar amounts of zinc and nickel. It is of interest to note that copper and nickel, metals whose chemistry is similar, are completely separated into sharp bands.

Quantitative studies in tartrate solution of pH 5 showed that copper(II) could

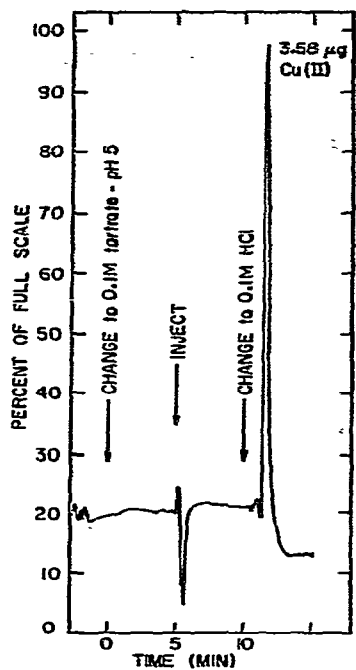


Fig. 3. Sorption and subsequent elution of copper(II).

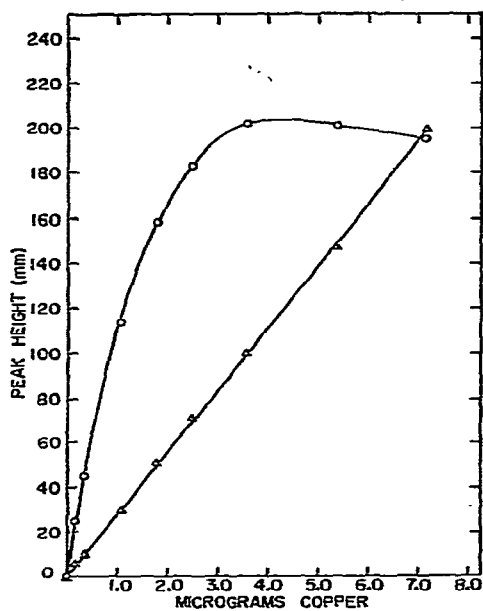


Fig. 4. Comparison of calibration graphs for determination of copper. ○, with PAR; △, with bis-(2-hydroxyethyl)dithiocarbamate.

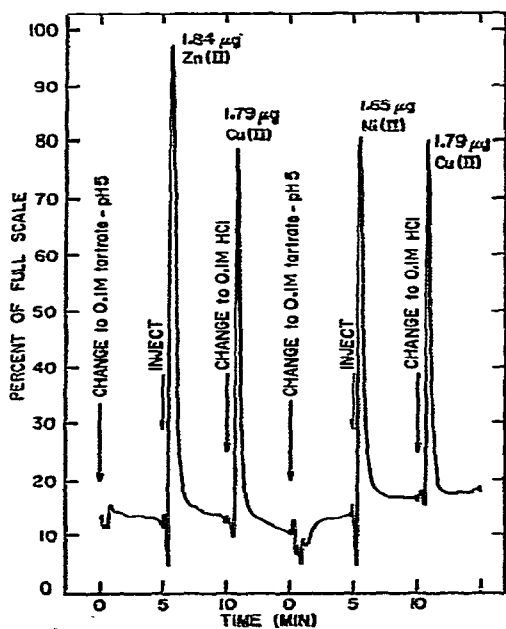


Fig. 5. Separation of copper(II) from equimolar amounts of zinc(II) and nickel(II).

TABLE I  
INTERFERENCE STUDY OF FOREIGN IONS ON DETERMINATIONS OF COPPER(II)  
AND MOLYBDENUM(VI) (EACH 0.0005 M)

Ion	Concn. (M)	Copper determination*	Molybdenum determination*
Acetate	0.10	±	±
Aluminium(III)	0.0005	±	±
Cadmium(II)	0.0005	±	±
Calcium(II)	0.005	±	±
Chloride	0.10	±	±
Chromium(III)	0.0005	±	±
Citrate	0.10	—	
Cobalt	0.001		±
Copper(II)	0.005		±
Fluoride	0.10	—	±
Iron(III)	0.001	+	±
Lead(II)	0.0005	±	±
Magnesium(II)	0.05	±	±
Manganese(II)	0.0005	±	±
Mercury(II)	0.0005	±	±
Molybdenum(VI)	0.0005	±	
Nickel(II)	0.0005	±	±
Nitrate	0.10	±	±
Phosphate	0.10	±	±
Sulfate	0.10	±	±
Thorium(IV)	0.0005	±	±
Tungsten(VI)	0.001		±
Uranium(VI)	0.0001	+	±
Vanadium(V)	0.001		±
Zinc(II)	0.0005	±	±

\* ± means that the peak height deviated by ±3% or less from that on a calibration graph; + indicates high results and — indicates low results.

be separated from many foreign metal ions and anions (see Table I). Of the metals studied, only iron(III) and uranium(VI) are taken up by the resin under the same conditions as copper(II); these, like copper, are eluted with 0.1 M hydrochloric acid. After sorbing both copper(II) and uranium(VI) from tartrate solution of pH 5, the copper can be eluted with 0.01 M EDTA (pH 6.0), leaving the uranium intact; then the uranium can be stripped with 0.1 M hydrochloric acid. However, this separation does not lend itself well to automatic chromatic detection.

Iron(III) is by far the most important practical interference. Fluoride was tried unsuccessfully as a masking agent, and attempts to avoid interference by reduction to iron(II) with ascorbic acid also failed. Some iron is eluted from pH 5 tartrate solution, but some is retained and subsequently eluted with the copper.

#### *Molybdenum(VI) sorption*

Studies by Gupta and Malik<sup>5</sup>, Fritz *et al.*<sup>1</sup> and Goodkin<sup>6</sup> have shown that hydroxyoximes form complexes with molybdenum(VI) in acidic media, the actual complexing species being the molybdyl ion, MoO<sub>2</sub><sup>+2</sup>.

A series of eluents was prepared in which the pH was varied from 0 to 5, and retention of molybdenum by the resin in each of these eluents was determined.



Molybdenum was completely retained on the column at pH values between 1 and 4, but below and above this range the element slowly bled off the column. The eluent used throughout this work to load the column with molybdenum was 0.1 *M* sulfuric acid.

The molybdenum could be stripped from the column in a narrow band by switching to 0.1 *M* sodium hydroxide. Various concentrations of ammonium hydroxide were also tried as stripping eluents; each of these gave a peak with considerable tailing, indicating that the resin-molybdenum complex was not being broken up as readily as with the sodium hydroxide eluent.

With 0.1 *N* sulfuric acid as eluent, molybdenum(VI) was successfully separated from 17 other metal ions (see Table I); no foreign metal ion investigated interfered. As copper(II) was sorbed by the resin only at a higher pH, molybdenum could also be separated from copper (see Fig. 6). Thiolactic acid is an excellent and delective color-forming reagent for molybdenum(VI). With thiolactic acid, the calibration graph of peak height vs. molybdenum content is rectilinear for 1 to 11  $\mu\text{g}$  of molybdenum.

The best proof of any method of analysis is how well actual samples can be analyzed. Results of three independent analyses for each of three NBS standard samples are shown in Table II; these results are in excellent agreement with the certified values.

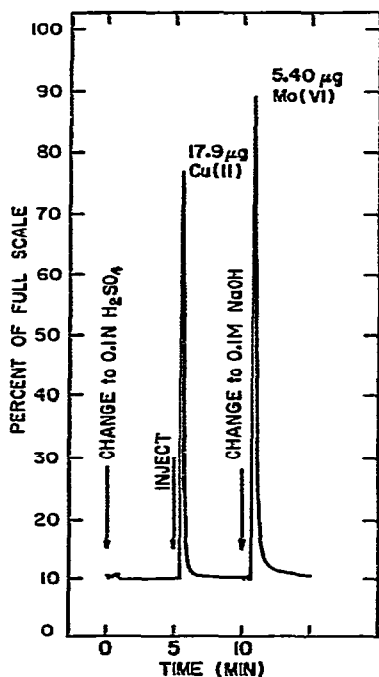


Fig. 6. Separation of molybdenum(VI) from a fivefold molar excess of copper(II).

TABLE II  
ANALYSIS OF NBS STANDARDS

Sample number	Element present	Content present (%)	Content found (%)	Standard deviation
94A	Ni	66.38		
	Cu	28.93	28.94	0.171
	Mn	2.34		
	Si, Co, Fe, Cr	<1		
	Al, Ti, C, S	<1		
160	Cr	19.12		
	Ni	8.91		
	Mo	2.95	2.96	0.074
	Si	1.13		
	Mn	<1		
	C, P, S, Cu	<0.1		
132A	V, Co, N	<0.1		
	W	6.20		
	Mo	4.51	4.53	0.055
	Cr	4.21		
	V	1.94		
	C, Mn, Si, Cu, Ni	<1		
	P, S	<0.1		

#### ACKNOWLEDGMENT

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