SEPARATION OF METAL IONS USING
AN O-HYDROXYPROPIOPHENOXIME RESIN

MASTER

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M. S. Degree Submitted to Iowa State University

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Separation of metal ions using
an o-hydroxypropiophenoxime resin

by

Jeffrey North King

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INTRODUCTION

The evolution of modern liquid chromatography over the past decade has made possible the analysis of very complex mixtures. Commercial instrumentation in the way of high-pressure pulseless pumps, sophisticated liquid chromatographs, and highly sensitive detectors has made high-speed liquid chromatography the technique of choice for many analyses. Much of the work accomplished in this area has been in the separation and determination of organic molecules. The use of high-speed liquid chromatographic techniques employing automatic detection for the analysis of inorganic ions has only recently come into common practice.

In recent years much of the interest in inorganic chromatographic analysis has been with chelating resins chemically bound to a polymer matrix. Resins of this type exhibit greater selectivity and faster kinetics than simple ion exchangers. Since the functional group is chemically bonded to the polymer matrix the problems associated with phase bleeding are also eliminated.

Interest in o-hydroxyoximes dates back to 1930 when Ephrain (1) proposed the use of salicylaldoxime as a precipitating agent for the gravimetric determination of copper. Simonsen and Burnett (2) used a 0.02 M solution of

salicylaldoxime in n-amyl acetate to quantitatively extract copper in the pH range 3.5 - 9.5. They applied this to the colorimetric determination of copper in aluminum alloys.

More recently salicylaldoxime has been found to react with a variety of metal ions. It has found uses in the determination of iron (3), nickel (4), lead (5), palladium (6), bismuth, and vanadium (7). A detailed review of all of its analytical applications is given by Welcher (8).

While salicylaldoxime has enjoyed a great deal of attention as an analytical reagent, its methyl derivative, o-hydroxyacetophenoxime, has endured benign neglect. Most of the work involving this reagent has come out of the laboratory of Poddar in India. In a series of papers he describes the conditions necessary for the gravimetric determination of copper, nickel (9,10), titanium (11), palladium (12), and vanadium (13). o-Hydroxyacetophenoxime has also been used as a colorimetric reagent for the spectrophotometric determination of uranium (14), vanadium (15), and iron (16). Gupta and Malik (17) observed that o-hydroxyacetophenoxime reacted with molybdenum (VI) in acidic media to form a highly stable, bright yellow, soluble complex. They studied the composition, stability, and structure of the complex and found that the phenolic hydrogen is replaced by MoO_2^{++} which, in turn, is coordinated to the nitrogen of the oxime group to give a molecular formula of $(\text{C}_8\text{H}_8\text{O}_2\text{N})_2 \text{MoO}_2$.

The first major use of hydroxyoximes outside of the analytical laboratory was for the specific extraction of copper from acidic leach liquors (18). General Mills produces a series of substituted 2-hydroxybenzophenoximes and markets them under the trade name LIX (Liquid Ion Exchanger). These reagents have found wide acceptance in the mining industry for the recovery of copper from low grade ores. Comprehensive reviews on their uses, composition, structure, spectra, and properties have been compiled by Ashbrook (19-21). One of these reagents, LIX-64, was used by Cerrai and Ghersini (22) for reversed-phase extraction chromatography. They were able to separate copper from iron (II), cobalt (II), nickel (II), manganese (II), and chromium (III) using a pH 3 ammonium sulfate buffer as eluent. Iron (III) was separated from copper when the eluent contained ammonium hydrogen difluoride.

Recently Beuerman and Fritz synthesized two aliphatic α -hydroxyoximes. These compounds, termed HEO and DHDO, were used for the separation of copper from seventeen other metal ions by extraction chromatography (23). These reagents were also found to be selective for molybdenum (VI) in the pH range 0 - 2 (24). A resin similar in structure to α -benzoin oxime was synthesized by Goodkin (25). It was prepared by reacting anhydrous phenyl glyoxal with XAD-4, a macroporous styrene - divinylbenzene copolymer, in the presence of

anhydrous aluminum trichloride. The resin was used to separate copper and molybdenum from other metals and from themselves.

The present work involves the synthesis of a chelating resin in which o-hydroxypropiophenoxime is chemically bonded to XAD-4. This resin is used for the separation and quantitative determination of both copper and molybdenum by high-speed liquid chromatography. To check the applicability of the method to real samples several NBS samples are analyzed.

EXPERIMENTAL

Apparatus

Liquid chromatograph

A new liquid chromatograph has been constructed. This model is more compact and is easier to operate than the chromatograph used in previous studies (26). The entire unit is self-contained in a 14" X 14" X 14" cabinet fabricated from steel. A schematic diagram of the unit is shown in Figure 1. Some of the main features of the new chromatograph are listed below:

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 number 35 Thomas clamps. The bottles can withstand pressures up to 90 p.s.i. without any danger of explosion. With this system eluent bottles can be changed in less than a minute.

2. Eluent selection is effected by a 6-way rotary selector valve (Altex 202-01). This 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 two dyes in the same run without having to stop operation, change the dye bottle, and start up again. The dye flow is regulated by a

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Figure 1. Schematic diagram of the liquid chromatograph.

chemically inert needle valve placed after the 3-way valve.

Detector

A Tracor 970 Variable Wavelength Detector was used for the continuous spectrophotometric monitoring of the column effluent. All chromatograms were recorded on a Houston Instrument Omniscribe Recorder.

Column

The analytical column was constructed of two Altex 200-28 glass connectors fused together. The column had an i.d. of 2 mm and an overall length of 70 mm. A helium pressure of 26 p.s.i. was required to attain a flow of 2 ml/min.

Miscellaneous equipment

All pH measurements were made with an Orion Model 701 Digital pH Meter.

The resin was ground with a Model 4-E Quaker City Mill and sieved with a Tyler Portable Sieve.

All atomic absorption analyses were performed using a Perkin--Elmer 303 Atomic Absorption Spectrophotometer.

Reagents

Copper standard solution was prepared by dissolving 6.354 g of copper metal in a minimum amount of nitric acid and diluting to 1.000 l with distilled, deionized water. Molybdenum standard solution was prepared by dissolving 14.394 g of molybdenum trioxide in a minimum amount of

ammonium hydroxide and diluting to 1.000 l with distilled, deionized water.

Stock solutions of 0.001 M metal ion were prepared from reagent grade chloride or nitrate salts. All stock metal solutions, with the exception of lead and mercury, were in a 0.1 M tartaric acid - sodium tartrate buffer with pH 5.0. Lead and mercury were prepared in a 0.1 M acetic acid - sodium acetate buffer with pH 5.0. The lead and mercury solutions were prepared in acetate buffer because insoluble salts were formed when they were prepared in the tartrate buffer.

The tartrate buffer eluent was prepared by dissolving 15 g of tartaric acid in approximately 900 ml of distilled water and adjusting the pH to 5.0 with 20% sodium hydroxide. The solution was then diluted to 1.000 l with distilled water.

The preparations of the various color - forming reagents are described in detail further in this work. All of the dyes were used as received with no further purifications. Acids, bases, and all other chemicals used to prepare various solutions were reagent grade or better and were used as received.

Synthesis

α-Bromo-2-hydroxypropiophenone was prepared by the method of Buu-Hoi and Lavit (27). 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 taken up in chloroform. The chloroform layer was dried over magnesium sulfate and vacuum distilled, α-bromo-2-hydroxypropiophenone being collected at 145-55°/15 mm. (Caution, this compound is a lachrymer and should be handled with care.)

The NMR and infrared spectra are shown in Figures 2 and 3. The peak integration gives a proton ratio of 4:1:3. The multiplets at δ 7.10 and δ 6.90 correspond to the phenyl

Figure 2. NMR spectrum of α -bromo-2-hydroxypropiophenone.

Figure 3. Infrared spectrum of α -bromo-2-hydroxypropiophenone.

hydrogens; the quartet at δ 5.30 corresponds to the methine hydrogen; and the doublet at δ 1.82 corresponds to the methyl group. The hydroxyl stretch at 3200 cm^{-1} on the IR is weaker than would normally be expected from a phenol because of strong intramolecular hydrogen bonding with the carbonyl.

XAD-4, a macroporous styrene - divinylbenzene copolymer, was obtained from the Rohm and Haas Co. The beads were Soxhlet extracted overnight with methanol, dried, ground, and sieved. The 250 - 325 mesh fraction was collected and further dried in a vacuum oven at 110° to ensure complete removal of water and methanol. The reaction vessel consisted of a 500-ml three-neck flask equipped with a mechanical stirrer, reflux condensor, addition funnel, and nitrogen inlet. XAD-4 (5 g) was slowly added to 33 g of anhydrous aluminum chloride suspended in 100 ml of ethylene dichloride. To this mixture 17 g of α -bromo-2-hydroxypropiophenone in 25 ml of ethylene dichloride was added dropwise with stirring. After complete addition (0.5 hour) the mixture was gently refluxed for four hours. The entire reaction was performed under a nitrogen atmosphere to exclude water. The resin was hydrolyzed by pouring into an ice-hydrochloric acid mixture. It was then washed with water, 1 M hydrochloric acid, acetone, and dried.

The final oximated resin was prepared by refluxing for two hours with 15 g of hydroxylamine hydrochloride in 50 ml

of absolute ethanol. Upon cooling, the resin was washed several times with water, then methanol, then acetone, and dried.

Characterization

Hydrogen capacity

A direct titration of the resin with tetrabutylammonium hydroxide in dimethylformamide solvent was attempted (28). However, the phenol group on the resin proved to be too weak an acid and did not give a discernible endpoint. Therefore, an indirect titration was performed. The resin (1.360 g) in the hydrogen form was added to 15.00 ml of standard sodium hydroxide and allowed to equilibrate for one hour. The excess base was filtered off and titrated to a phenolphthalein endpoint.

Copper and Molybdenum capacity

Batch capacities of the resin were obtained for copper (II) from 0.1 M tartrate -pH 5 and for molybdenum (VI) from 0.1 N sulfuric acid. These conditions are identical to those used in the separation procedures described later. The resin (0.3 g) was added to 10.00 ml of 0.002 M metal ion in the appropriate buffer and allowed to equilibrate for two hours with shaking. The solution was filtered off and analyzed for metal content by atomic absorption.

Spectroscopic and elemental analyses

An infrared spectrum was taken using a solid potassium bromide disc.

The CHN content of the resin was obtained using a Perkin-Elmer 240 Elemental Analyzer.

Choice of Color - Forming Reagents

Arguello (29) has recently pointed out several characteristics that a color-forming reagent should exhibit when it is used for the continuous spectrophotometric analysis of forced-flow chromatographic effluent. A variety of dyes were used in this work to detect many different metal ions. Each dye was mixed 1:2 (dye:effluent) on-stream with the column effluent.

PAR

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 ions were all monitored at 495 nm. The PAR solution was prepared by dissolving 121.1 g of THAM (tris(hydroxymethyl)aminomethane) in approximately 750 ml of distilled water. PAR (0.125 g) was then added and the pH was adjusted to 9.0 with concentrated hydrochloric acid. The final solution was diluted to 1.000 l with distilled water. Contrary to what Arguello found (29), 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

Arsenazo I was used for the detection of calcium (II), magnesium (II), thorium (IV), and copper (II). These were all monitored at 590 nm. The Arsenazo I solution was prepared by the same procedure as that already described earlier for PAR.

Hydrochloric acid

Goodkin (30) has shown that hydrochloric acid may be used for the detection of many metal ions by the ultraviolet absorbance of their chloride complexes. The elution of lead (II) and copper (II) was detected by mixing the column effluent with 12 M hydrochloric acid and monitoring at 271 nm. The use of hydrochloric acid as a dye in this work was limited to wavelengths above 250 nm because of the large background ultraviolet absorbance of the tartrate buffer used.

Bis(2-hydroxyethyl)dithiocarbamate

Many times a dye that is non-specific does not give adequate results when quantitative work is performed. This was found to be the case when PAR was used for the quantitative determination of copper (II). Fritz and Sutton (31) have shown that bis(2-hydroxyethyl)dithiocarbamate will form a yellow complex with copper that is water soluble. The dye is also easy to prepare and will work over a wide pH range.

For these reasons this reagent was studied to determine if it would be a suitable substitute for PAR in the quantitative determination of copper by forced-flow chromatography.

The reagent was prepared by adding 0.82 g of carbon disulfide to 105 g of diethanolamine. This was then diluted to 750 ml with distilled water and the pH adjusted to 9.5 with concentrated hydrochloric acid. The final solution was diluted to 1.000 l with distilled water. As reported by Fritz and Sutton (31) a slight cloudiness appeared after several hours. This cloudiness did not increase over the course of several weeks and appeared to have no effect upon the performance of the dye. The large excess of amine present acts as a buffer for the solution.

The absorption spectra of the copper - carbamate complex is shown in Figure 4. The wavelength maximum is at 433 nm with a molar absorptivity of 11,400. A comparison of the carbamate dye with PAR was made by preparing separate calibration curves. The calibration curves were constructed by injecting standards containing known amounts of copper and plotting the resulting peak heights versus the amount of copper injected. This is shown graphically in Figure 5. PAR gives a fairly linear response for low (0-1.5 μg) amounts of copper but reaches a limit (3.5 μg) where there is no further increase in peak height with increasing amounts of copper. This is apparently due to the low solubility of PAR in

Figure 4. Absorption spectrum of copper-bis-(2-hydroxyethyl) dithiocarbamate complex.

Figure 5. Comparison of calibration curves for the quantitative determination of copper.

aqueous solutions. The carbamate dye gave a linear response from 0 to 7 μg copper. A 56.3- μl sample loop was used so that the copper concentrations ranged from $5 \times 10^{-5} \text{ M}$ to $2 \times 10^{-3} \text{ M}$. The carbamate dye was subsequently used for all quantitative work involving copper.

Thiolactic acid

The use of thiolactic acid for the spectrophotometric determination of molybdenum (VI) was first reported by Fritz and Beuerman (32). The yellow molybdenum - thiolactic acid complex was formed at pH 1.0 - 1.6 and the absorbance was read at 365 nm. The absorbance was also shown to be constant within a pH range of 3 - 5. For the continuous spectrophotometric analysis of molybdenum the higher of the two pH ranges appeared to be more suitable. The reagent was prepared by mixing 57.5 ml of glacial acetic acid in approximately 900 ml of distilled water and adjusting the pH to 4.0 with 20% sodium hydroxide. Thiolactic acid (1.90 g) was added and the solution was diluted to 1.000 l with distilled water. A calibration curve was constructed by injecting standards containing known amounts of molybdenum and plotting the resulting peak heights versus the amount of molybdenum injected. This is shown in Figure 6. A range of 0.5 to 11 μg of molybdenum gave a linear response. With a 56.3 μl sample loop this corresponds to molybdenum concentrations of $5 \times 10^{-5} \text{ M}$ to $2 \times 10^{-3} \text{ M}$. Thiolactic acid buffered to pH 4.0 was

Figure 6. Calibration curve for the quantitative determination of molybdenum using thiolactic acid.

subsequently used for the quantitative determination of molybdenum.

Separation Procedures

Copper

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

1. Prior to introduction of the sample onto the column allow pH 5 tartrate buffer to flow through the column at a flow rate of 2 ml/min for five minutes.
2. Inject the sample onto the column.
3. Allow pH 5 tartrate buffer to flow through the column at a flow rate of 2 ml/min for five minutes 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 five minutes to elute copper from the column.

When NBS standards were analyzed steps one and three were reduced to 2.5 minutes each. This allowed an analysis to be completed in ten minutes.

Molybdenum

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

1. Prior to introduction of the sample onto the column allow 0.1 N sulfuric acid to flow through the column at a

flow rate of 2 ml/min for five minutes.

2. Inject the sample onto the column.

3. Allow 0.1 N sulfuric acid to flow through the column at a flow rate of 2 ml/min for five minutes 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 five minutes to elute molybdenum from the column.

When NBS standards were analyzed steps one and three were reduced to 2.5 minutes. This allowed the analysis to be completed in ten minutes.

Analysis of NBS Standards

Copper

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

Molybdenum

Approximately 0.95 g of NBS sample number 160, a chromium - nickel - molybdenum steel, was dissolved in 50 ml of 1:6 sulfuric acid. The solution was cooled, transferred to a 250-ml volumetric flask, and diluted to the mark with

distilled water. The solution was then analyzed for molybdenum content by the procedure described in the previous section.

Approximately 0.35 g of NBS sample number 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 that contained 50 ml of a saturated sodium borate solution and 50 ml of a 0.5 M sodium tartrate solution. The resulting solution was diluted to the mark with distilled water. The final pH of the solution was between two and three. The molybdenum concentration was then determined by the procedure described in the previous section.

RESULTS AND DISCUSSION

Characterization of the Resin

Several synthetic routes were attempted during the course of this work. The procedure described in the experimental section gave the highest yield with the lowest possibility of side reactions.

The Friedel - Crafts reaction was first tried using α -bromo-2-hydroxyacetophenone. However, it was pointed out by Trahanovsky (33) that this would involve the formation of a primary carbonium ion, which would make the reaction very unfavorable. For this reason α -bromo-2-hydroxypropioophenone was chosen as the reagent. The addition of a methyl group alpha to the bromine allowed a secondary carbonium ion to form, thus making the reaction more favorable.

Ethylene dichloride was chosen as solvent because of its ability to partially swell the resin, which leads to higher yields (25).

The resin is light tan in acid and dark brown in base. It is stable to dilute acids and bases under mild conditions. The resin decomposes to a black substance when exposed to 6 M nitric acid.

As stated in the experimental section the phenol group proved to be too weak an acid to titrate directly. The hydrogen capacity of the resin as determined by the procedure

given in the Experimental section was found to be 0.84 meq/g.

The CHN analysis gave an average nitrogen content of 1.77%. Assuming all of the nitrogen is from the oxime this would give a capacity of 1.26 meq/g. There is no readily apparent explanation for the different capacities by the two methods.

The infrared spectra of XAD-4 and of the *o*-hydroxypropio-phenoxime resin are shown in Figure 7. A large hydroxyl stretch from the phenol and oxime functional groups is present from 3200 - 3600 cm^{-1} . The oxime C=N stretch is also evident at 1700 cm^{-1} .

Investigation of Copper

Choice of conditions

Previous studies by Fritz et al. (23) and Goodkin (25) have shown that α -hydroxyoximes can form copper complexes from basic or slightly acidic (pH 5) solutions. In both of these studies the hydroxyl functional group was an alcohol, which is a much weaker acid than a phenol. It has also been reported that the 2-hydroxybenzophenoximes can form copper complexes at pH values as low as 1.4 (34). Since the resin used in this work is a 2-hydroxypropio-phenoxime it was thought that it should form a copper complex at a lower pH than the α -hydroxyoximes and a higher pH than the 2-hydroxybenzophenoximes. This in fact proved to be the case.

Figure 7. (Bottom) Infrared spectrum of XAD-4 resin.
(Top) Infrared spectrum of o-hydroxypropio-
phenoxime resin.

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The resin will completely retain copper (II) on the column in a 0.1 M acetate buffer down to pH 3.5. Below this pH the copper will bleed off the column. The resin will also completely retain copper from a 0.1 M tartrate buffer at the same pH. Goodkin found that when using a tartrate buffer with the α -hydroxyoxime resin it was necessary to raise the pH from five to ten to completely retain copper. This is further evidence that the o-hydroxyoximes are stronger complexers for copper. No advantage could be found for working at pH 3.5 so all separations were performed using a 0.1 M tartrate buffer at pH 5.

Copper can be stripped off the column in a tight band by 0.1 M hydrochloric acid. Stronger 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 Figure 8.

Capacity

The batch capacity of the resin was found to be 0.0315 meq copper per gram of resin from 0.1 M tartrate - pH 5. The capacity was determined under these conditions because they duplicate those used in the separation procedures. The maximum capacity is probably much higher at higher pH values. However, no advantage could be found for determining it at higher pH values since it would not be used under those conditions.

Figure 8. Elution of copper (II).

Column: 7 cm X 0.2 cm

Detection: PAR color-forming reagent, 1.4 ml/min;
495 nm; 1.28 absorbance units full scale

Sample: 65.3 μ l

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Separations

The conditions described above were used to separate copper from 13 other metal ions. Two metal ions, uranium (VI) and iron (III), were found to interfere and will be discussed in detail in a later section.

In the pH 5 tartrate buffer the resin had essentially no affinity for zinc (II), nickel (II), cobalt (II), and manganese (II). These ions were eluted completely in less than two minutes from the column. Figure 9 shows the separation of copper from equimolar quantities of zinc and nickel. Figure 10 shows the separation of copper from equimolar quantities of cobalt and manganese. It is interesting to note that copper and nickel, two metals whose chemistry is quite similar, are separated completely into two sharp bands.

The separation of copper from equimolar quantities of cadmium (II) and lead (II) are shown in Figures 11 and 12, respectively. Cadmium is eluted as a very sharp peak with no tailing. Lead shows some tendency to tail, although it is completely eluted within the five minute wash time. Figure 13 shows the separation of copper from an equimolar quantity of thorium (IV). Arsenazo I proved to be a poor choice of color - forming reagent because of low sensitivity and large baseline shifts with solvent change. Its use here was limited to qualitative information concerning the separations of copper from thorium, calcium, and magnesium.

Figure 9. Separation of Copper (II) from equi-molar quantities of Zinc (II) and Nickel (II).

Column: 7 cm X 0.2 cm

Detection: PAR color-forming reagent, 1.4 ml/min;
495 nm; 1.28 absorbance units full scale

Sample: 65.3 μ l

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Figure 10. Separation of Copper (II) from equi-molar quantities of Cobalt (II) and Manganese (II).

Column: 7 cm X 0.2 cm

Detection: PAR color-forming reagent, 1.4 ml/min;
495 nm; 1.28 absorbance units full scale

Sample: 65.3 μ l

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Figure 11. Separation of Copper (II) from an equimolar quantity of Cadmium (II).

Column: 7 cm X 0.2 cm

Detection: PAR color-forming reagent, 1.4 ml/min;
495 nm; 1.28 absorbance units full scale

Sample: 65.3 μ l

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Figure 12. Separation of Copper (II) from an equimolar quantity of Lead (II).

Column: 7 cm X 0.2 cm

Detection: Concentrated hydrochloric acid, 1.4 ml/min;
271 nm; 0.16 absorbance units full scale

Sample: 65.3 μ l

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Figure 13. Separation of Copper (II) from an equimolar quantity of Thorium (IV).

Column: 7 cm X 0.2 cm

Detection: Arsenazo I color-forming reagent, 1.4 ml/min;
590 nm; 0.08 absorbance units full scale

Sample: 65.3 μ l

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As expected, the resin showed no affinity for calcium (II) or magnesium (II). A 5×10^{-4} M copper sample was successfully isolated from a ten-fold molar excess of calcium and a one-hundred-fold molar excess of magnesium. These separations are shown in Figure 14.

The resin was also able to separate copper from equimolar quantities of aluminum (III), chromium (III), mercury (II), and molybdenum (VI). The separation of these ions from copper was established by collecting fractions of the pH 5 tartrate buffer after injecting the ions onto the column and analyzing each fraction by atomic absorption for the ion of interest.

Interferences

Of the metal ions studied iron and uranium were found to interfere in the determination of copper.

Uranium Uranium (VI) is taken up by the resin under the same conditions as copper. It can be eluted with 0.1 M hydrochloric acid. However, under these conditions the copper is also eluted. Klygin and Smirnova (35) have shown that uranium will form a strong complex with carbonate ions. Therefore, a 1 M sodium bicarbonate - sodium carbonate solution at pH 9 was used as an eluent to try and selectively elute the uranium. This was unsuccessful and led to attempts to selectively elute the copper. It was found that a 0.01 M EDTA solution at pH 6 will elute copper from the column and

Figure 14. Separation of copper (II) from a ten-fold excess of Calcium (II) and a one-hundred molar excess of magnesium (II).

Column: 7 cm X 0.2 cm

Detection: Arsenazo I color-forming reagent, 1.4 ml/min;
590 nm; 0.08 absorbance units full scale

Sample: 65.3 μ l

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leave the uranium intact. The uranium can then be stripped off the column with 0.1 M hydrochloric acid. This scheme does not lend itself to quantitative work because the copper is taken off as a broad peak with tailing. The EDTA also competes with the color-forming reagent to such an extent that PAR gives a negative peak and the bis(2-hydroxyethyl) dithiocarbamate dye gives a much smaller peak than usual. This separation scheme could possibly be investigated as a quantitative method for uranium. This idea was not pursued in the present work.

Iron In terms of occurrence in real samples iron (III) is by far the major interference in this method. Several attempts were made to overcome the interference of iron. In their work on LIX-64 as a stationary phase in column chromatography Cerrai and Ghersini (22) found that iron (III) could be eluted from the column when the eluent was 0.18 M in ammonium hydrogen difluoride. Several solutions were prepared with various fluoride concentrations and pH values. All of these were successful at eluting iron from the column. However, in all cases copper was also eluted at the same time.

It was thought that if the iron (III) was reduced to iron (II) it would behave as other divalent metal ions and not be retained by the resin. A 1×10^{-3} M solution of iron (III) was reduced to iron (II) by the addition of ascorbic

acid. An aliquot of this was then injected onto the column. Results of this are shown in Figure 15. The iron (II) was not retained by the resin and was eluted with the pH 5 tartrate buffer. However, the resin was able to provide enough of a driving force to oxidize part of the iron (II) to iron (III) and complex it. This was then eluted with 0.1 M hydrochloric acid. Part of the iron was retained even when there was a one-hundred-fold molar excess of ascorbic acid in the sample.

Anions Several anions were tested with copper to determine if they interfered in the method. Of those tested fluoride and citrate were found to give low results for copper. Apparently when these ions are present they prevent the entire copper sample from being sorbed onto the resin.

A summary of the ions tested with copper and those which were found to interfere is shown in Table 1.

Investigation of Molybdenum

Choice of conditions

Previous studies by Gupta and Malik (17), Fritz and Beuerman (24), and Goodkin (25) have shown that hydroxyoximes will form a complex with molybdenum (VI) in acidic media. The actual complexing ion is the molybdate ion MoO_4^{2-} .

Figure 15. Interference of Iron (III).

Column: 7 cm X 0.2 cm

Detection: PAR color-forming reagent, 1.4 ml/min;
495 nm; 1.28 absorbance units full scale

Sample: 65.3 μ l

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Table 1. Interference^a of foreign ions with the determination of copper^b

Ion	Concentration, <u>M</u>	Copper Peak Height ^c
acetate	0.10	0
aluminum (III)	0.0005	0
cadmium (II)	0.0005	0
calcium (II)	0.005	0
chloride	0.10	0
chromium (III)	0.0005	0
citrate	0.10	-
cobalt (II)	0.0005	0
fluoride	0.10	-
	0.05	-
	0.01	-
iron (III)	0.001	+
lead (II)	0.0005	0
magnesium (II)	0.05	0
manganese (II)	0.0005	0
mercury (II)	0.0005	0
molybdenum (VI)	0.0005	0
nickel (II)	0.0005	0
nitrate	0.10	0
phosphate	0.10	0
sulfate	0.10	0
thorium (IV)	0.0005	0
uranium (VI)	0.0001	+
zinc (II)	0.0005	0

^a The ion was deemed an interference if the copper peak deviated more than $\pm 3\%$ from a calibration curve.

^b Copper concentration is 5×10^{-4} M.

^c 0 : peak height within tolerances of calibration curve
 - : peak height gives low results
 + : peak height gives high results.

A series of eluents were prepared in which the pH was varied from 0 to 5. The retention of molybdenum by the resin in each of these eluents was then determined. Molybdenum is completely retained on the column between pH 1 and 4. Below and above this range the molybdenum slowly bleeds off the column. The eluent used throughout this work to load the column with molybdenum was 0.1 N sulfuric acid.

The molybdenum can be stripped off the column in a tight 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.

Capacity

The batch capacity of the resin was found to be 0.042 meq molybdenum per gram of resin from 0.1 N sulfuric acid. As with copper, the maximum resin capacity for molybdenum was not determined. The total loading of the column with molybdenum never exceeded 1% of the total capacity throughout this work.

Separations and Interferences

When 0.1 N sulfuric acid is used as an eluent it is possible to separate molybdenum from seventeen other commonly occurring metal ions. These ions and their respective

concentrations are summarized in Table 2. Of all the metal ions tested only molybdenum was taken up by the resin in 0.1 N sulfuric acid. The other metals were eluted from the column in a tight band immediately after injection. The separation of molybdenum from a five-fold molar excess of copper is shown in Figure 16. Goodkin (25) reported interferences from chromium, titanium, and vanadium in the determination of molybdenum when using an α -hydroxyoxime resin prepared from phenyl glyoxal. This imposes serious restrictions on the method since at least one of these ions is present in most molybdenum steel samples.

Analysis of NBS Standards

The proof of any new method of analysis is not how well it performs under controlled conditions in "distilled, deionized water", but how accurately real samples can be analyzed for copper or molybdenum content. The results of three independent determinations are shown in Table 3.

The elution of a molybdenum standard followed by the separation and determination of molybdenum in NBS sample 160 is shown in Figure 17.

Table 2. Interference^a of foreign ions on the determination of molybdenum^b

Ion	Concentration, <u>M</u>	Molybdenum Peak Height ^c
acetate	0.10	0
aluminum (III)	0.001	0
cadmium (II)	0.001	0
calcium (II)	0.005	0
chloride	0.10	0
chromium (III)	0.001	0
cobalt (II)	0.001	0
copper (II)	0.005	0
fluoride	0.10	0
iron (III)	0.001	0
lead (II)	0.001	0
magnesium (II)	0.05	0
manganese (II)	0.001	0
mercury (II)	0.001	0
nickel (II)	0.001	0
nitrate	0.10	0
phosphate	0.10	0
thorium (IV)	0.001	0
tungsten (VI)	0.001	0
uranium (VI)	0.001	0
vanadium (V)	0.001	0
zinc (II)	0.001	0

^a The ion was deemed an interference if the molybdenum peak deviated more than $\pm 3\%$ from a calibration curve.

^b Molybdenum concentration is 5×10^{-4} M.

^c 0 : peak height within tolerances of calibration curve.

Figure 16. Separation of molybdenum (VI) from a five-fold molar excess of Copper (II).

Column: 7 cm X 0.2 cm

Detection: Thiolactic acid 1.4 ml/min; 365 nm; 0.32
absorbance units full scale

Sample: 65.3 μ l

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Table 3. Analysis of NBS Standards

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

Figure 17. Elution of molybdenum (VI) standard followed by the determination of molybdenum (VI) in NBS sample 160.

Column: 7 cm X 0.2 cm

Detection: Thiolactic acid, 1.4 ml/min; 365 nm; 0.32
absorbance units full scale

Sample: 65.3 μ l

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CONCLUSIONS

A chelating ion-exchange resin incorporating an o-hydroxypropiophenoxime functional group onto an XAD-4 polymer matrix has been synthesized. This resin has been used for the separation and quantitative determination of both copper and molybdenum by high-speed liquid chromatography. Iron, uranium, citrate, and fluoride were found to interfere in the determination of copper. Of the ions tested, none were found to interfere with the determination of molybdenum. Several NBS Standard samples were successfully analyzed for copper and molybdenum. The new method is both accurate and fast. Most samples can be analyzed in less than ten minutes.

Bis(2-hydroxyethyl) dithiocarbamate was shown to be superior to PAR as a color-forming reagent for the continuous spectrophotometric detection of copper. Thiolactic acid was shown to be adaptable to the continuous spectrophotometric detection of molybdenum. Both dyes gave linear responses when peak height was plotted against micrograms of metal.

FUTURE WORK

There is a vast number of chelating resins that can be synthesized. Almost any organic functional group shows some affinity for certain metals or groups of metals. The discussion here will be limited to one such resin.

It has recently been shown in this laboratory (36) that n-heptaldoxime will extract copper from acidic chloride solutions. The exact nature of the complex is not fully understood as yet. It is suspected that the complex has the formula $\text{Cu}(\text{oxime})_2\text{Cl}_2$. Of several metals tested thus far only nickel and palladium are partially extracted. This same functional group could be immobilized onto a polystyrene matrix by the following reactions.

A resin of this type should exhibit properties similar to those of heptaldoxime. One advantage this resin would have over the hydroxy-oxime resins prepared previously would be the elimination of the interference of iron. Under

conditions that will give quantitative extraction of copper by heptaldoxime iron is not extracted at all. A resin of this type has already been prepared by Farrall and Frechet (37). They used Bio - Beads SX1 as a polymer matrix and achieved a capacity of 2.3 meq/g. No applications of the resin were reported.

LITERATURE CITED

1. F. Ephrain, Ber., 63, 1928 (1930).
2. S. H. Simonsen and H. M. Burnett, Anal. Chem., 27, 1336 (1955).
3. D. E. Howe and M. G. Mellon, Ind. Eng. Chem., Anal. Ed., 12, 448 (1940).
4. H. L. Riley, J. Chem. Soc., 895 (1933).
5. W. D. Liggett and L. P. Biefeld, J. Ind. Eng. Chem., Anal. Ed., 13, 813 (1941).
6. H. Holzer, Z. Anal. Chem., 95, 392 (1933).
7. J. F. Flagg and N. H. Furnam, J. Ind. Eng. Chem., Anal. Ed., 12, 529 (1940).
8. F. J. Welcher, "Organic Analytical Reagents," Van Nostrand Co., New York, N. Y., 1947, Vol. 3.
9. S. N. Poddar, Z. Anal. Chem. 154, 254 (1957).
10. S. N. Poddar, Z. Anal. Chem., 155, 327 (1957).
11. S. N. Poddar, Ind. J. App. Chem., 26, 153 (1963).
12. S. N. Poddar, Anal. Chem. Acta, 28, 586 (1963).
13. S. N. Poddar, J. Ind. Chem. Soc., 40, 706 (1963).
14. S. N. Poddar, J. App. Chem., 27, 67 (1964).
15. S. N. Poddar, Ind. J. Chem., 1, 537 (1963).
16. S. N. Poddar, Ind. J. Chem., 1, 496 (1963).
17. B. D. Gupta and W. U. Malik, J. Less - Common Met., 17, 277 (1969).
18. R. R. Swanson, U. S. Patent 3,224,873 (1965).
19. A. W. Ashbrook, Coord. Chem. Rev., 16, 285 (1975).
20. A. W. Ashbrook, J. Chrom., 105, 141 (1975).

21. A. W. Ashbrook, Hydrometallurgy, 1, 5 (1975).
22. E. Cerrai and G. Ghersini, Analyst, 94, 599 (1969).
23. J. S. Fritz, D. R. Beuerman, and J. J. Richard, Talanta, 18, 1095 (1971).
24. J. S. Fritz and D. R. Beuerman, Anal. Chem., 44, 692 (1972).
25. L. Goodkin, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1974.
26. M. D. Seymour, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1972.
27. N. P. Buu-Hoi and D. Lavit, J. Chem. Soc., 18 (1955).
28. J. S. Fritz, "Acid-Base Titrations in Nonaqueous Solvents," Allyn and Bacon, Boston, Massachusetts, 1973.
29. M. D. Arguello, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1977.
30. L. Goodkin, Talanta, 22, 245 (1975).
31. J. S. Fritz and S. A. Sutton, Anal. Chem., 28, 1300 (1956).
32. J. S. Fritz and D. R. Beuerman, Talanta, 19, 336, (1972).
33. W. S. Trahanovsky, Chemistry Department, Iowa State University, personal communication (1976).
34. General Mills Inc., French Patent No. 1,467,504, (1966).
35. A. E. Klygin and I. D. Smirnova, Zh. Neorgan. Khim., 4, 42 (1959).
36. J. N. King and J. S. Fritz, Chemistry Department, Iowa State University, unpublished data (1977).
37. M. J. Farrall and J. M. Frechet, J. Org. Chem., 41, 3877 (1976).

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