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The use of aliphatic α-hydroxyoximes for the separation of metal ions

by

Donald Roy Beuerman

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INTRODUCTION

It is often necessary to separate the chemical components in a system before a quantitative analysis can be carried out. The purpose of the separation is to isolate the desired component from any interference of the matrix and/or to concentrate a component by removing it from the bulk of the sample.

The techniques of extraction and chromatography are two important methods of separation used in analytical chemistry. The mechanics of these methods differ but both are based on a partitioning of the chemical component between two media. In the extraction method, these media are usually two immiscible liquids. In chromatography, the media may be combinations of solids, liquids or gases. Since both methods are based on the distribution of a constituent between two media, the data obtained from extraction studies can often be applied to liquid-liquid chromatography.

One property of an ideal extractant or chromatographic substrate is specificity. The usefulness of the substrate is enhanced if it will extract a limited number of metal species. In compounds containing an oxime and hydroxyl group in close proximity to each other, a coordinate bond can form between the metal and an unshared pair of electrons from either the nitrogen or the oxygen. The oxime and hydroxyl groups are weakly acidic and can form an anion which neutralizes the charge on the metal. When these groups are in the correct structural positions to form chelate rings, they can form metal complexes. Previous studies of such compounds have involved aromatic structures such as α-benzoinoxime and salicyaldoxime. These form complexes with some 20 metals and therefore are not very selective.

The purpose of this research is to investigate the aliphatic α-hydroxyoximes as selective agents for separating metal ions. It is usually necessary to dissolve the metal alloys or ores in an acid medium. Therefore, this investigation is limited to acidic solutions.

LITERATURE SURVEY

Previous investigations of compounds containing both hydroxyl and oxime groups were concerned with salicylaldoxime [$(OH)C_6H_4CH(NOH)$], α-benzoinoxime [$C_6H_5CH(OH)C(NOH)C_6H_5$] or derivatives of these compounds. This survey will consider each of these separately. Both of these compounds are aromatic and provide only background information for the present research with aliphatic hydroxyoximes.

Salicylaldoxime and Derivatives

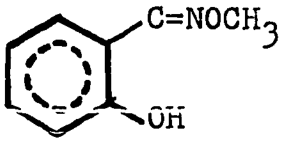
The oximes discussed in this section contain the -CH(OH)CHCH(NOH) group with the oxime and hydroxyl groups not on adjacent carbons. The unassigned valences of the two carbons in the group may be part of a ring system as in salicylaldoxime. Studies of this compound or its derivatives comprise the bulk of the research with compounds containing the hydroxyl and oxime groups. A survey of salicylaldoxime as an analytical reagent is presented by Welcher (94). This work includes discussion and analytical procedures using salicylaldoxime.

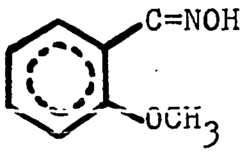
Salicylaldoxime forms precipitates with copper(II) (25) and palladium(II) (46) in acidic solutions. The use of salicylaldoxime as a precipitating agent for copper was proposed by Ephraim (26) in 1928 and modified by other workers (35, 68, 77). Its use was expanded to the determination of iron (26, 47), zinc (26), lead (62), bismuth, vanadium (36), nickel (74) and palladium (46). Reactions with other metals were studied by Flagg and Furman (36) who found that precipitates were formed with 21 metals in neutral or basic solutions.

The green color of the copper compound formed with salicylaldoxime has been used by Benedetti-Pichler and Cefula (6) and Biefeld and Howe (10) to detect the presence of copper in solutions. This was incorporated into a qualitative analysis scheme by Biefeld (9) and used to separate copper from cadmium.

Although this oxime was used primarily in gravimetric analysis, it was tried with other techniques. Its use in an indirect titration method was advanced by Tougarinoff (90) in 1935. The copper precipitate was used to reduce iron(III) to iron(II) which was titrated with potassium permanganate. Neuberger (69) used salicylaldoxime in a direct titration of copper with a potentiometric end point. Finkelshtein (35) adapted it to the nephlometric determination of copper. The color intensity of the iron(III) salicylaldoxime complex has been used to determine small quantities of iron (47). Careful control of the acidity was necessary since the color was reported to change from purple at pH 3 to yellow at pH 10.

Studies of the copper-salicylaldoxime reaction product by Ephraim (25) and Feigl and Bondi (33) show that the phenolic hydrogen is lost in the reaction. Feigl and Bondi investigated the following compounds





and found that only the one with the free phenolic group reacted with copper. Two oximes were associated with each copper ion. The effect of pH on the precipitation of metals by salicylaldoxime was investigated by Jean (50). A table of 14 metals and the conditions under which the precipitate was formed is found in Welcher (94). This table is based on the investigations by Jean.

A number of substituted salicylaldoximes were studied by Flagg and Furman (36). The 5-chlorosalicylaldoxime, p-methylsalicylaldoxime, 5-nitrosalicylaldoxime and 2,4-dihydroxybenzaldoxime, have been used to precipitate bismuth, copper, iron, lead, nickel and zinc. Analytical procedures using these compounds are outlined in Welcher (94).

Other hydroxyoximes having the hydroxyl and oxime groups on an aromatic ring were studied by Ephraim (26) but showed no advantages over salicylaldoxime. These compounds are also listed in Feigl (29) and Welcher (94). According to Feigl (29), hydroxyoximes with the same grouping on an aliphatic skeleton do not react with copper. The above studies indicate that the complexing property of these hydroxyoximes was due to the location of the functional groups on an aromatic ring and was affected very little by any other substituents on the ring.

Acyloin Oximes

This class of oximes contains the oxime and hydroxyl groups on adjacent carbon atoms. The hydroxy ketone starting material can be readily synthesized by the acyloin condensation procedure (19, 42). The oximation of these ketones forms the hydroxyoxime containing the -CH(OH)C(NOH)- group which was reported to be specific for the copper ion (29, 32).

The first investigation of acyloin oximes was reported by Feigl (29) in 1923. Feigl used α-benzoinoxime to detect micro quantities of copper. A green color was formed when oxime and sample solutions were mixed in the presence of ammonia. The presence of 0.2 ppm of copper was detected by this method.

Feigl (29, 32) and Strebinger (80) used α-benzoinoxime for the quantitative precipitation of copper. Azzalin (3) and Shik (76) had difficulty obtaining a suitable precipitate and suggested igniting it to copper(II) oxide before weighing. They reported that the procedure was not specific for copper as previously reported. Iron(III), aluminum(III), lead(II), tin(IV) and zinc(II) gave high results. Riley (74) differed with Azzalin by claiming that the α-benzoinoxime did not precipitate iron(III) or zinc(II). Other workers investigated the reaction of this oxime with other metals and found positive reactions with molybdenum(VI), vanadium(V), chromium(VI) (58), tungsten(VI) (30, 58, 94), nickel(II) (24, 47), gold(III), palladium(II) (46, 52), platinum(IV) (52), cadmium(II) and cobalt(II) (4, 24). Langer (61) used α-benzoinoxime as a reagent for the amperometric titration of copper. He reported this method to be accurate within 1 per cent; however, nickel interfered strongly with this determination.

α-Benzoinoxime appears to be more specific in acidic solutions. In 1932, Knowles (58) published a detailed investigation of its use for precipitating molybdenum from 5-20% solutions of mineral acids. After separating the molybdenum from the other metals, the precipitate was ignited and weighed as molybdenum(VI) oxide. Tungsten(VI), palladium(II), chromium(VI) and vanadium(V) were reported as the only interferences. Chromium(VI) and vanadium(V) decrease the efficiency of the oxime by oxidation. These ions were eliminated in the sample solution by reducing them to chromium(III) and vanadium(IV) with sulfurous acid or iron(II) (58). The reduction products did not interfere with the analysis. A lengthy digestion procedure was used to dissolve the molybdenum(VI) oxide in the precipitate, making it possible to correct for the remaining impurities (principally tungsten).

The molybdenum-α-benzoinoxime complex is said to be soluble in chloroform (94). Therefore, development of uses for α-benzoinoxime changed in the late 1940's from gravimetric procedures to extraction procedures. Jones (53) extracted copper from ammonium tartrate solution and molybdenum from acidic solutions using α-benzoinoxime dissolved in chloroform. The solubility of the complex is questioned by Maeck and co-workers (64) and Phillips (72). Phillips reported that a milky suspension was formed with molybdenum but the separation was effective. Maeck (64) minimized the turbidity problem by adding ethyl acetate to the solution.

The extraction of molybdenum with α-benzoinoxime solution has been adapted for the analysis of fission products (96), alloys (17, 24, 56, 72, 78), hair, wool (44), sea water (93), rocks and ores (51) and plant products (53). This list is not intended to be complete, but to show the versatility of the extraction of different types of material. A brief review of α-benzoinoxime for the separation of molybdenum and tungsten from other metals is presented by Korkisch (59).

A variety of structures have been reported for the α-benzoinoxime-metal complexes. Feigl (28, 34) reported an oxime:copper ratio of 1:1 while Swanson (84) reported the ratio to be 2:1. At first it was believed that the coordination sphere of the metal was satisfied by interaction of the aromatic radical with the metal (28). Peng and Sandell (70) described the complex as an addition compound rather than a coordination complex. The molybdenum-α-benzoinoxime complex was reported to have an oxime:metal ratio of 3:1 (87) and 2:1 (45). Later, investigators suggested that the MoO_2^{++} ion was the metallic species involved in the complex formation (45, 91). The chemistry of molybdenum in acidic solutions is complicated. Molybdenum has been reported as a variety of cationic complexes (18, 45, 52, 54, 57, 91) and anionic complexes (13, 63) including MoO_2^{++} and its dimer. Most of the above reported species are polymeric in nature. Kraus, Nelson and Moore (60) report that multiple complexes are formed in 1 M hydrochloric acid but the equilibrium between the species is very slow.

The use of aliphatic α-hydroxyoximes as extracting agents was not stressed until the mid 1960's when Swanson was granted a series of patents for their use in commercial hydrometallurgical processes. These patents included the use of branch chain acyloin oximes for the extraction of copper (83, 84), vanadium (82) and molybdenum (86) from leach liquors of low grade ores. His work also included the use of unsaturated aliphatic acyloin oximes (85) and substituted benzophenone oximes (81). The claims in these patents are designed to include a wide range of conditions, some of which were not presented in his experimental data. This work by Swanson specifically applies to recovery of metals in a commercial operation. The conditions reported in these patents are not necessarily those required for quantitative removal of the metals from samples in an analytical laboratory. In the industrial process, the organic oxime solutions can be recycled through the process without being stripped completely of the metal content. Swanson (84) reported that straight chain acyloin oximes did not extract copper from aqueous solutions, but the work reported in this thesis indicates that his conclusions were not based on a complete investigation.

A series of liquids for large scale extractions is produced by General Mills under the trademark LIX (1, 2). The use of this liquid ion exchanger (LIX-64) for the separation of copper in commercial operations was publicized in 1965 (1) and 1967 (2). Cerrai and Ghersini (15) studied some analytical applications of LIX-64 and speculated that it was a mixture of substituted hydroxybenzophenone oximes and 5,8-diethyl-7-hydroxy-6-dodecanone oxime. They employed a column containing LIX-64 on a solid support to separate copper(II) from five other metal ions. With a 0.5 M ammonium sulfate eluent, considerable tailing was observed with iron(III), manganese(II), chromium(III) and vanadium(V). Except for iron(III), the use of 0.5 M ammonium chloride reduced this tailing. Ammonium hydrogen fluoride was finally used to complex iron(III) and eliminate the tailing problem.

The composition of LIX-64 has not been published. It is known to contain hydroxyoximes along with other constituents but the hydroxyoximes have not been identified. Two samples of LIX-64 examined by this author had different copper(II) capacities and different physical properties. Fractionation under reduced pressure and gas chromatographic analysis indicated the presence of at least 9 constituents.

A brief study of LIX-64 for separating metals was made by this author. Copper(II) was separated from seven metals by a chromatographic column containing LIX-64 on an inert support. Iron(III) created a severe tailing problem while molybdenum(VI) and silver(I) were not quantitatively retained by the column. The observations regarding molybdenum and silver differ from the results presented later in this thesis using pure α-hydroxyoximes.

The impure nature of LIX-64 and the uncertainty regarding its composition, led to abandoning its study in favor of pure α-hydroxyoximes synthesized and characterized in this laboratory.

THEORY AND BACKGROUND

Solvent extraction and reversed-phase paper and column chromatography were the basic separation techniques used in this research. The principle of these methods is based on a partitioning of the metal ions between two media. Therefore, the data from extraction studies often indicate the action of metal ions in reversed-phase paper or column chromatography.

The following discussion is not intended to be a rigorous presentation of the topics. It is presented to show the relationship between these techniques and is limited to the action of metal ions. A theoretical and detailed treatment of solvent extraction is presented by Fomin (37), Berg (7), Morrison and Freiser (67), and Irving and Williams (48). Partition chromatography is discussed by Giddings (40) and Heftman (44) and reviewed by Testa (89). A bibliography of reversed-phase paper chromatography, including abstracts, has been prepared by Eschrich and Drent (27). The relationship of extraction to reversed-phase paper chromatography was developed by Kabasakalian (55). Reversed-phase chromatography has been reviewed by Peppard (71) and Cerrai and Ghersini (14, 16).

Solvent Extraction of Metals

Liquid-liquid solvent extraction is a process of partitioning the metal species between two immiscible liquids. When an aqueous phase containing the metal comes in contact with an organic phase, the two liquids compete for the metal species. The metal may be a complexed species which is more soluble in the organic phase or it may form a stronger complex with the organic phase and distribute itself accordingly to attain equilibrium. One phase has a greater affinity for the metal species and causes the distribution.

The ratio of the metal concentration in each layer at equilibrium is expressed as the distribution ratio (D).

$$D = \frac{[M]_o/V_o}{[M]_a/V_a} \quad \text{or} \quad D = \frac{[M]_o}{[M]_a} \times \frac{V_a}{V_o} \tag{1}$$

where $[M_o]$ and $[M_a]$ are the analytical concentrations of metal species in the organic and aqueous layers and V_o and V_a are the respective volumes of the layers. When $V_a = V_o$, equation (1) reduces to equation (2).

$$D = \frac{[M]_o}{[M]_a} \tag{2}$$

A high D value indicates that the metal species will be extracted into the organic phase in an efficient manner. The distribution ratio can also be applied to liquid-liquid chromatography since the metal is partitioned between the layers.

This distribution ratio is of practical interest and is related to the percentage extracted as follows:

$$\%E = \frac{100\,D}{D + V_a/V_o} \tag{3}$$

If the volumes of the layers are equal, this relationship becomes:

$$\%E = \frac{100\ D}{D + 1} \qquad (4)$$

Therefore a D value of 99 indicates 99% of the metal is removed from the aqueous layer in a one step extraction process.

The distribution ratios may be related to the composition of the complex. Assuming a complex contains one metal ion, the formation reaction is expressed as follows:

$$M^{+n} \ + \ mH_2Ox \ \mathrm{---->} \ M(H_{2-n/m}Ox)_m \ + \ nH^+ \qquad (5)$$

The formation constant is expressed as:

$$K = \frac{[M(H_{2-n/m}Ox)_m]\ [H^+]^n}{[M^{+n}]\ [H_2Ox]^m} \qquad (6)$$

If the concentration of the metal in the organic and aqueous layers is in the complexed and ionic forms respectively, and the volumes of the phases are equal, equation (2) becomes:

$$D = \frac{[M(H_{2-n/m}Ox)_m]}{[M^{+n}]} \qquad (7)$$

Substituting equation (7) into equation (6) and rearranging the terms,

$$D = \frac{K[H_2Ox]^m}{[H^+]^n} \qquad (8)$$

or $\log D = \log K + m \log [H_2Ox] - n \log [H^+]$. (9)

If the pH is held constant while the oxime concentration is varied, equation (9) becomes:

$$\log D = \log K + m \log [H_2Ox] \qquad (10)$$

and a graph of log D vs log $[H_2Ox]$ will yield a slope equal to m, the number of oximes associated with each complex.

If the pH is varied while the oxime concentration remains constant, equation (9) becomes:

$$\log D = \log K - n \log [H^+] \qquad (11)$$

and a graph of log D vs log $[H^+]$ will yield a slope equal to -n, the number of protons lost per complex. Since the value of m was determined from equation (10), the number of protons lost per oxime is n/m.

The above discussion is simplified to express these relationships as used in this work. A theoretical and thorough treatment is presented by Irving, Rossotti, and Williams (49), and Schweitzer (75).

Reversed-phase Chromatography

In reversed-phase chromatography the organic, stationary phase is impregnated on an inert supporting solid. The metals are placed on the solid and eluted with some immiscible, mobile phase. As the metals move on the solid support, they partition themselves between the stationary and mobile phases and become separated. In general, a greater difference in the D values of the two metals gives a greater separation on a chromatographic support.

If the above support is paper, the action of the metal species on the impregnated paper is measured by the ratio of the distance the metal moved on the support to the distance the eluent moved. This is known as the R_f value of the metal.

$$R_f = \frac{\text{Distance metal moved}}{\text{Distance eluent moved}} \qquad (12)$$

The R_f values and the distribution values are related. Kabasakalian (55) used the following relationship to equate the R_f values from reversed phase chromatography with the percent extracted to optimize the extraction parameters.

$$\%\ \text{Extracted} = \frac{100\ K}{R_f} \qquad (13)$$

K is a proportionality constant between 0.5 and 2.0. It is not necessary to determine this constant if trends are sought instead of actual numbers.

Soczewinski (79) studied the relationship of R_f values to the behavior of metals on chromatographic columns. He stated that the R_f data indicated trends in column separations but applying the R_f values to the actual distribution of the metal was difficult. Deviations from the theoretical model were due to the interaction between the solute and the support, and slow kinetics between the solute and the stationary phase.

EXPERIMENTAL

Apparatus

pH meter: A Corning model 12 pH meter with a Sargent combination electrode was used to control the pH in all EDTA titrations and determine the acidity of analytical solutions.

Spectrometers: A Bausch and Lomb Spectrophotometer was used for all ultraviolet and visible spectrometric measurements. This instrument was equipped with a deuterium source for use in the ultraviolet region of the spectrum and a tungsten source for use in the visible region of the spectrum. Matched quartz cells (1 cm) were used as sample containers. A VOM-8 recorder and a 1 cm Bausch and Lomb flow-through cell were used in the continuous monitoring of the vanadium-copper separation. All infrared spectra were obtained with a Beckman IR-7 infrared spectrophotometer. The samples were prepared in the form of a KBr pellet. All proton spectra were obtained with a Hitachi Perkin Elmer R-20 B Nuclear Magnetic Resonance Spectrometer with Perkin Elmer accessories. Deuterated chloroform was used as the solvent.

Radiochemical equipment: A Nuclear Chicago Anti-walk, single channel analyzer, model 27352 spectrometer was used to isolate the gamma radiation in all radiometric analysis. A Nuclear Chicago Decade Scaler, Model 27104, was used to count the emissions from the spectrometer. The detector was a 3 x 3 inch NaI scintillation crystal from Harshaw Chemical

Company. The isotopes were either produced by thermal neutron bombardment at the Ames Laboratory Research Reactor or obtained from the Ames Laboratory stock. The gamma spectra were checked with the Ames Laboratory 1600 channel analyzer and associated computer facilities.

Paper chromatographic apparatus: Rectangular glass jars, 4 x 12 x 10 inches, with glass covers were used as chromatographic tanks. Holes were drilled into the sides of the tank, 2.5 cm from the top and 2 cm from the edges. A 7 mm rod was fitted through these holes to support the glass frames which held the chromatographic paper. The paper was fitted onto 21.5 x 20.5 cm rectangular glass frames which had 1.5 cm extensions on the top.

Chromatographic columns: Columns were made of 9 mm pyrex tubing. The top of the column was enlarged to 15 mm to provide a reservoir for the eluent. The bottom of the column was restricted to 2 mm to control the flow of the effluent. A WCLID 1205 series, Automatic Fraction Collector, manufactured by Warner-Chilcott Laboratories Instruments Division, was used to collect portions of effluent from a 3 ml volumetric siphon.

Extraction apparatus: Batch extractions were performed in 16 x 150 mm pyrex culture tubes with plastic screw caps. These were shaken in a horizontal position by a Burrel wrist action shaker.

Reagents and Solutions

Metal salt solutions: The reagent grade metal salts were obtained from commercial sources. The 0.05 M solutions of most metals were made by dissolving the appropriate salts in distilled water. Tartaric acid (approx. 0.05 M) was added to the antimony, tin, titanium and tungsten solutions to prevent hydrolysis at pH 5. Tartaric acid was also added to the iron solution to minimize tailing during the column separations and increase its velocity through the column bed.

Radioactive solutions: The radioactive isotopes were made by irradiating about 1 ml of the salt solution in the Ames Laboratory Research Reactor. The solutions were sealed in 5 ml polyethylene containers and exposed to neutrons in the reactor. The gamma spectra were checked on the 1600 channel analyzer and associated computer facilities. The original solution was adulterated with the radioactive solution to obtain a reasonable amount of gamma activity.

Oxime solutions: The acyloin oximes were dissolved in reagent grade toluene. The solutions used for batch extractions varied in oxime concentration. Unless noted in the discussion section, the solutions used to prepare the chromatographic columns were 20% oxime by weight.

Eluents: Acetate buffer (pH 5) and 6 M and 9 M hydrochloric acid solutions were used for all column separations of copper and silver. Sulfuric acid (0.1 N) and ammonium hydroxide (pH 12) solutions were used for all column separations of molybdenum. The eluents used in the paper chromatography and batch extractions were the same as the column eluents, except for the adjustment of the pH. All of the eluents were equilibrated with toluene by shaking in a separatory funnel and separating the layers.

Chromatographic supports: Whatman No. 1 chromatographic paper was cut into 21 x 20 cm sheets and used in all of the paper chromatography. Amberlite XAD-2, an inert styrene-divinyl-benzene, macroreticular resin from Rohm and Haas Chemical Company, was used for all column supports. The beads were ground and sieved to obtain an 80-100 mesh fraction. The support was backwashed to remove any adhering fines, washed with 6 M hydrochloric acid and rinsed with water and acetone. It was air dried prior to use.

Analytical Procedures

Titration methods

Quantitative determination of many of the metals was accomplished by titration with standardized EDTA using either Xyenol Orange or Napthyl Azoxine S (NAS) as indicators. The special conditions for these determinations are outlined by Fritz, Abbink and Payne (39).

Radiometric methods

Chromium, silver, antimony, iron, tungsten, uranium, tin and trace amounts of copper were determined by counting the gamma emissions from their radioactive isotopes as compared to a standard solution of the activated metal. The nuclides used were Cr^{51}, Cu^{64}, $Ag^{110-110m}$, Sn^{113}, Sb^{125} and W^{187}. Uranium was determined by the activity of its fission products. The solution was allowed to decay for at least 24 hours and its activity compared to a standard solution.

Spot tests

The position of the metal ions on the chromatographic paper was determined by the color of the ions when sprayed with a developing solution. In Table 1, these metals are divided into four groups according to the developing agent used.

Table 1. Developing solutions used to detect metal ions on paper chromatograms

Group	Developing agent	Metals detected
Sulfide	50% $(NH_4)_2S$ solution	Mn(II), Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), As(III), Y(III), Zr(IV), Pd(II), Ag(I), Hg(II), Cd(II), Sb(III), Sb(V), Pt(IV), Au(III), Pd(II), Bi(III)
Alizarin	0.1% ammonical solution of alizarin	Al(III), Sc(III), V(IV,V), Ge(IV), Ga(III), In(III), Sn(II, IV)
Arsenazo	0.1% solution of Arsenazo I	Tl(III), W(VI), La(III), RE(III), Th(IV), U(VI)
Peroxide	3% H_2O_2	Ti(IV), Mo(VI)

Manganese and zinc were visible only on the wet paper. Thiolactic acid was used to detect molybdenum in some experiments. In earlier work, a 0.1% solution of Napthyl Azoxine S (NAS) was used instead of the alizarin solution.

Various spot tests, as outlined by Feigl (31), were used to detect the presence of metal ions in the effluent from the column separations.

Spectrometric methods

Palladium was determined by the intensity of the yellow chloride complex at 290 nm. The solution was 9 N hydrochloric acid and had a molar absorptivity of 5×10^4 l. cm^{-1} $moles^{-1}$ and followed Beer's Law over the range 1 to 3×10^{-5} M.

Small amounts of copper were determined by the intensity of the bathocuproine complex according to the method of Diehl and Smith (22). The sample was treated with 2 ml of 10% hydroxylammonium chloride, 10 ml of 10% ammonium acetate and 1 ml of 0.01 M bathocuproine. The complex had a molar absorptivity of 13,333 l. cm^{-1} $moles^{-1}$ at 479 nm.

In the vanadium-copper separation, the presence of VO^{++} was detected at 670 nm using the Bausch and Lomb spectrometer and flow-through cell. The presence of copper was detected as the yellow chloride complex at 425 nm using the same equipment.

In the early work, molybdenum was measured by absorption of the peroxide complex according to the method of Telep and Boltz (88). In later work, an alternate method was employed using thiolactic acid. The development of this method is described later.

Experimental Procedures

Paper chromatography

Sheets of Whatman No. 1 chromatographic paper were impregnated with the extracting agent by dipping them into a 10% toluene solution of the desired oxime. The papers were fastened to the glass frames with Teflon clamps. The excess solution was allowed to drain from the sheet. After the paper was air dried, spots of the metal ions were placed 1 inch from the bottom edge of the paper by using small wooden applicator sticks. Each sheet could accommodate 10 metals, and 5 sheets could be put into the tank simultaneously. The metal solutions were allowed to dry before placing the sheets in the chromatographic tank.

The eluent (500 ml) was added to the chromatographic tank. The tank was covered and the atmosphere allowed to equilibrate with the solution overnight. The treated papers were suspended in the equilibrated tank and the eluent allowed to ascend the paper by capillary action until it was about 1½ inches from the top of the sheet.

After eluting with the desired buffered eluent, the papers were removed and air dried. Spraying with a color developing reagent revealed the location of the metal ions on the paper. $R_{\underline{f}}$ values were determined by comparing the advance of the metal ions with the advance of the solvent front on the paper sheets.

Distribution ratios

A 5 ml portion of toluene containing a known amount of oxime and 5 ml of an aqueous phase containing a known amount of the desired metal were placed in 16 x 150 mm pyrex culture tubes with screw type plastic caps. These solutions were shaken for 1 hour on a Burrel wrist action shaker to equilibrate the organic and aqueous layers. After the layers were separated, the metal content in the aqueous layer was determined. The metal in the organic layer was calculated by difference. The distribution ratio was calculated according to equation (1).

Column preparation

The sieved and pre-treated XAD-2 support (1.50 grams) was slurried in water and poured into the glass columns (9 x 62 mm) containing a glass wool plug. The column was gently tapped while the excess liquid drained from the column. A small plug of glass wool was placed on top of the resin bed to hold it in place and to prevent disturbing the resin when adding the eluent. This was later replaced by a perforated Teflon disc.

The packing was coated with the oxime by passing a known volume of the oxime-toluene solution through the column to replace the water. The column was allowed to equilibrate for at least one hour before flushing off and measuring the excess toluene. The volume of the toluene phase retained by the column (approximately 1.5 ml) was determined by difference. Eight to ten column volumes of the desired eluent were flushed through the column bed to prepare it for the separation step.

Column separations

A known amount of each metal ion that was to be separated was mixed in the reservoir above the resin bed and allowed to drain onto the column. The sides of the reservoir were rinsed with 1-2 ml of the desired eluent. When this had drained onto the column, the sample was eluted with the required amount of eluent at a flow rate of 4-5 ml per minute. The eluent was changed for the subsequent elution of the metal remaining on the column. These eluents varied according to the metal being studied.

The metals in the National Bureau of Standard samples were separated in a like manner. Details of this work are described in the next section under the appropriate metal.

RESULTS AND DISCUSSION

Synthesis of the α-Hydroxyoximes

The 10-hydroxyeicosan-9-one (I) and 5,8-diethyl-7-hydroxydodecan-6-one (II) needed for the synthesis of the α-hydroxyoximes were prepared according to the procedure of Hansley (42). (I) was purified by vacuum distillation (b.p. 110-115°C at 0.05 mm Hg). The methyl esters used in the preparation of the α-hydroxyketones were prepared by the procedure of Vogel (92).

The α-hydroxyoximes were prepared by the procedure similar to that of Swanson (83). A mixture of 0.2 mole of the 2-hydroxyketone, 0.4 mole hydroxlamine hydrochloride, 125 ml pyridine and 125 ml of absolute ethanol were refluxed for three hours. The reaction mixture was cooled, diluted with about 500 ml of water and extracted with ether. The aqueous layer was discarded. The ether layer was washed 4 times with water, twice with 3% hydrochloric acid and 4 more times with water. The ether layer was dried and the ether removed by evaporation.

Two products were isolated from the residue obtained from the oximation of (I). The residue from the ether evaporation step was dissolved in petroleum ether and cooled in an ice bath. The solid compound had an analysis of C, 70.7%; H, 11.6%; N, 8.1%; calculated C, 70.5%; H, 11.8%; and N, 8.3% for 9,10-eicosandione-dioxime (EDO). The NMR spectrum showed a triplet at δ 1.08, a broad singlet at δ 1.64 and a singlet at δ 4.42. The proton intergration of these peaks gave a ratio of 6:32:2 respectively. The melting point was 151-2°C. This vic-dioxime was a result of the oximation of the vic-diketone by-product of the acyloin condensation (65).

Further cooling of the residue in a dry ice-acetone bath yielded a solid compound having an analysis of C, 73.3%; H, 12.2%; N, 3.9%; calculated C, 73.6%; H, 12.3%; and N, 4.3% for 10-hydroxyeicosan-9-oxime (HEO). The NMR spectrum (Figure 1) had a triplet at δ 1.08, a broad singlet at δ 1.61, a singlet at δ 3.96 and a broad singlet at δ 4.46. The proton integration of these peaks showed a ratio of 6:33:1:1 respectively. The melting point was 48-49°C. The infrared spectrum is shown in Figure 2.

Purification of the oximation product from (II) was obtained by the distillation of the residue from the ether evaporation step. The product, 5,8-diethyl-7-hydroxydodecanone-6-oxime (DHDO), was a viscous liquid having a boiling point of 133-4°C at 0.02 mm Hg. The analysis was C, 70.7%; H, 12.2%; N, 5.2%; calculated C, 70.8%, H, 12.3%; and N, 5.2% for DHDO. The NMR spectrum (Figure 3) had a triplet at δ 1.08, a quintet at δ 1.64, a broad singlet at δ 2.84, and a sharp singlet at δ 4.98. The proton integration of these peaks gave a ratio of 12:19:1:1 respectively. The peak at δ 1.64 is due to the superimposing of the 16 methylene hydrogens upon the 3 methine hydrogens. This explains the additional splitting within the peak. The infrared spectrum is shown in Figure 4.

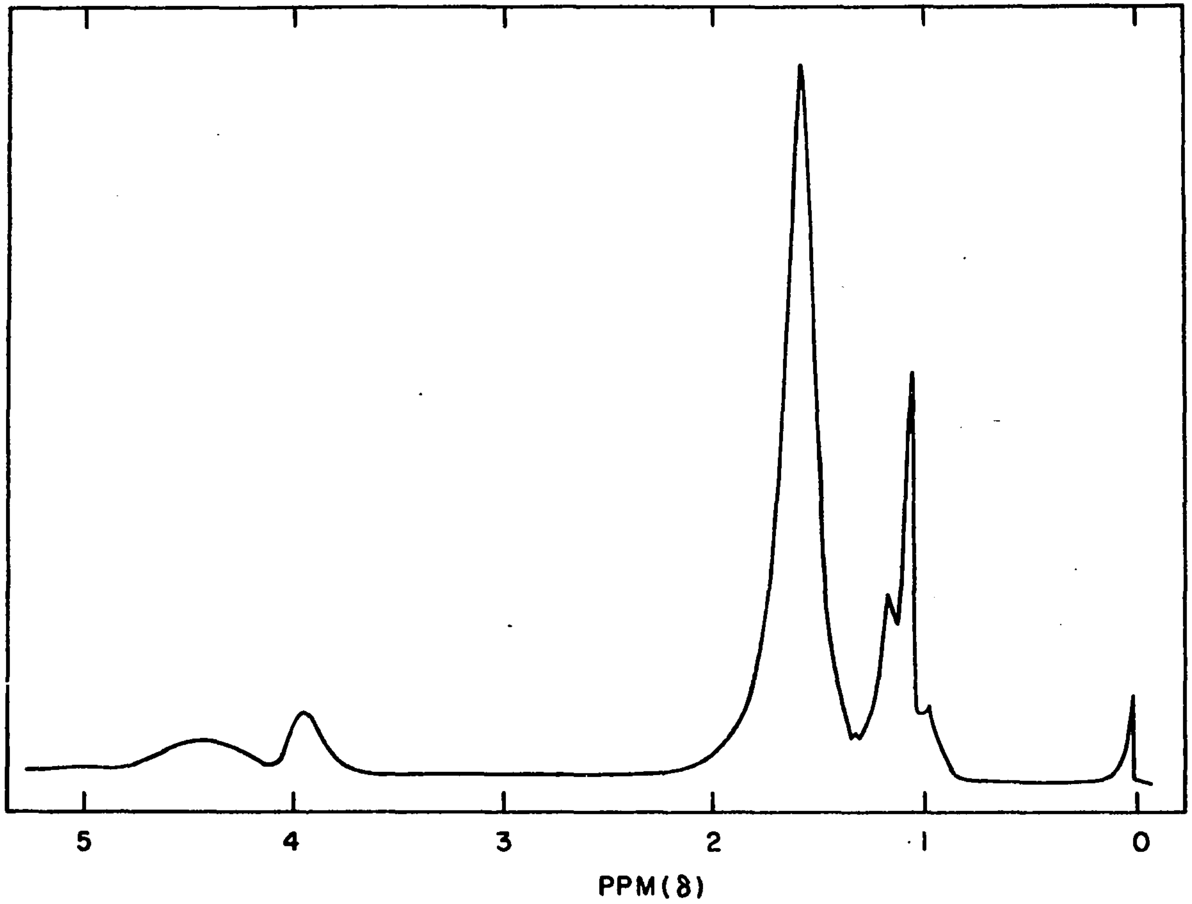


Figure 1. The NMR spectrum of 10-hydroxyeicoxanone-9-oxime (HEO)

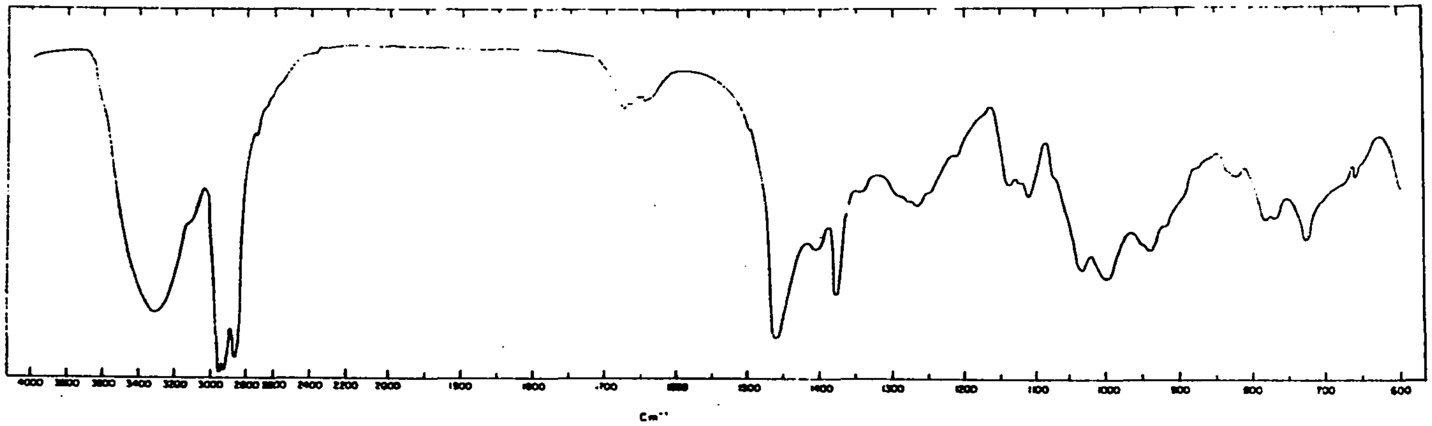


Figure 2. The infrared absorption spectrum of HEO

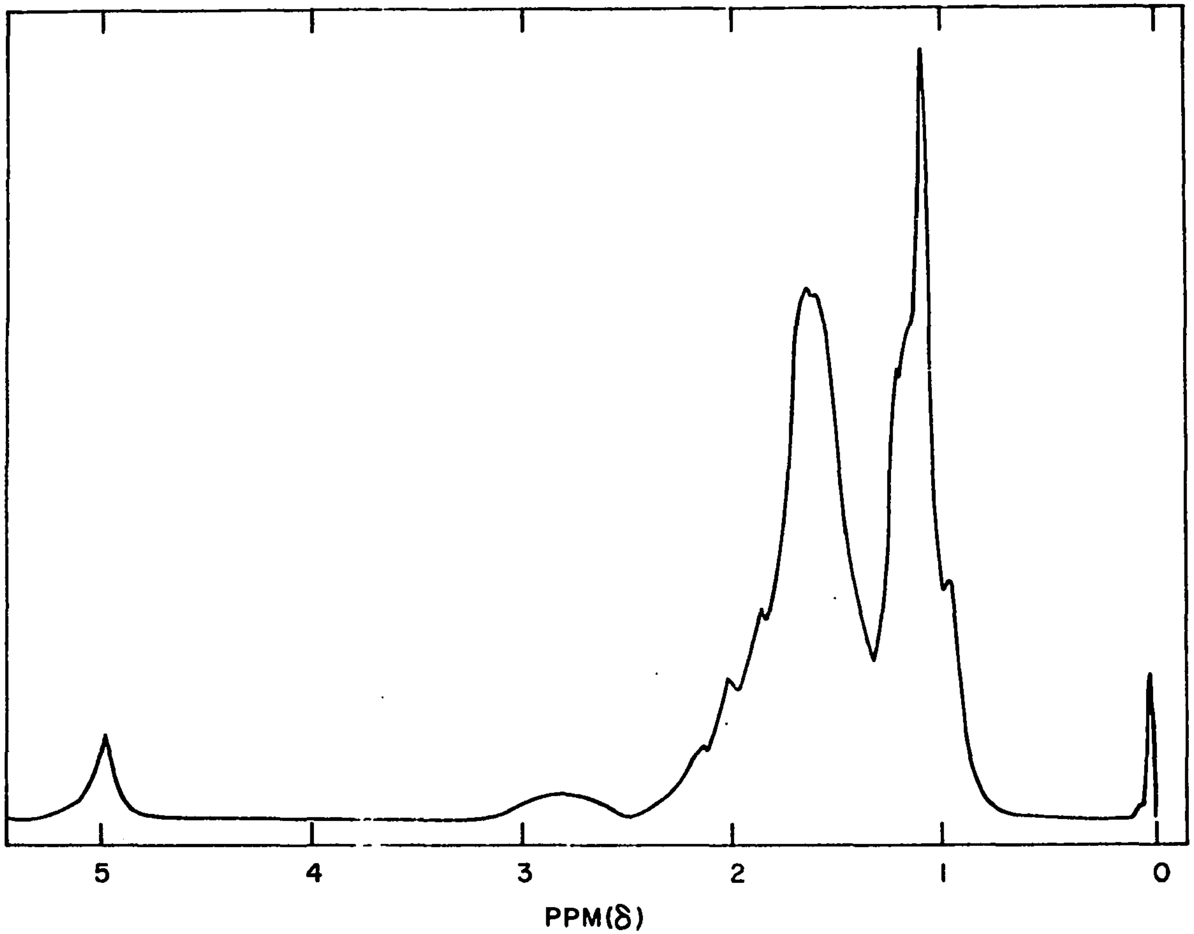


Figure 3. The NMR spectrum of 5,8-diethyl-7-hydroxydodecanone-6-oxime (DHDO)

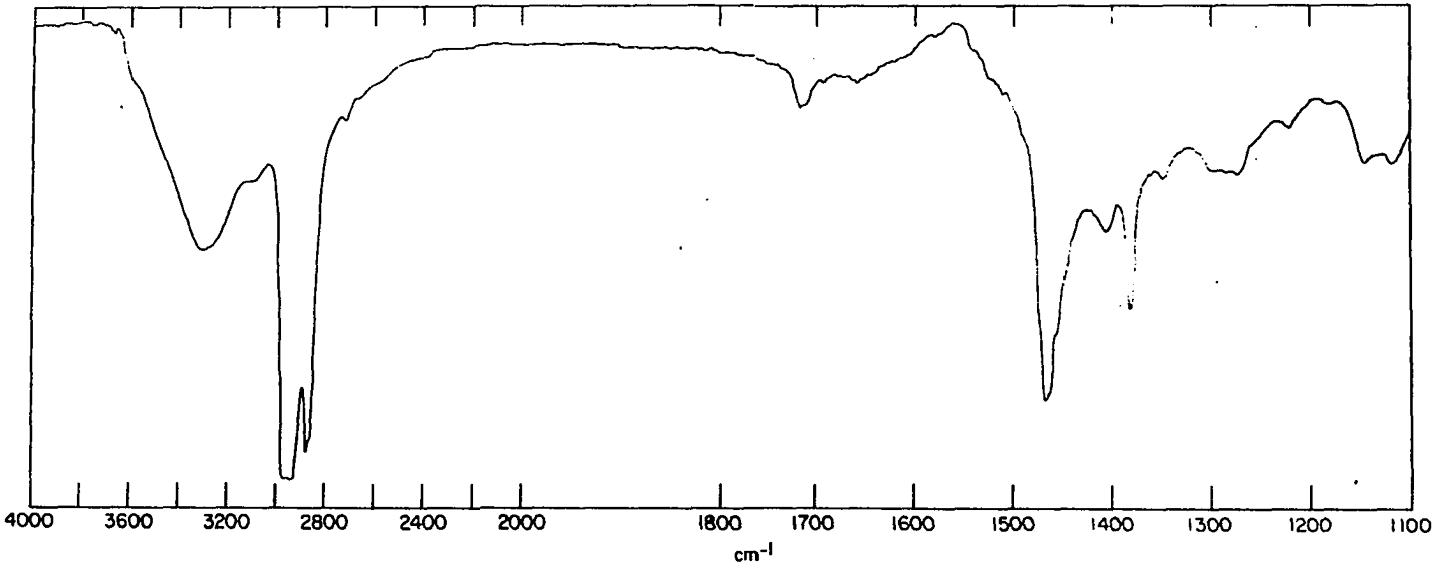


Figure 4. The infrared absorption spectrum of DHDO

The formulas for these compounds are shown below.

HEO

$C_9H_{19}CH(OH)C(NOH)C_9H_{19}$

DHDO

$C_4H_9CH(C_2H_5)CH(OH)C(NOH)CH(C_2H_5)C_4H_9$

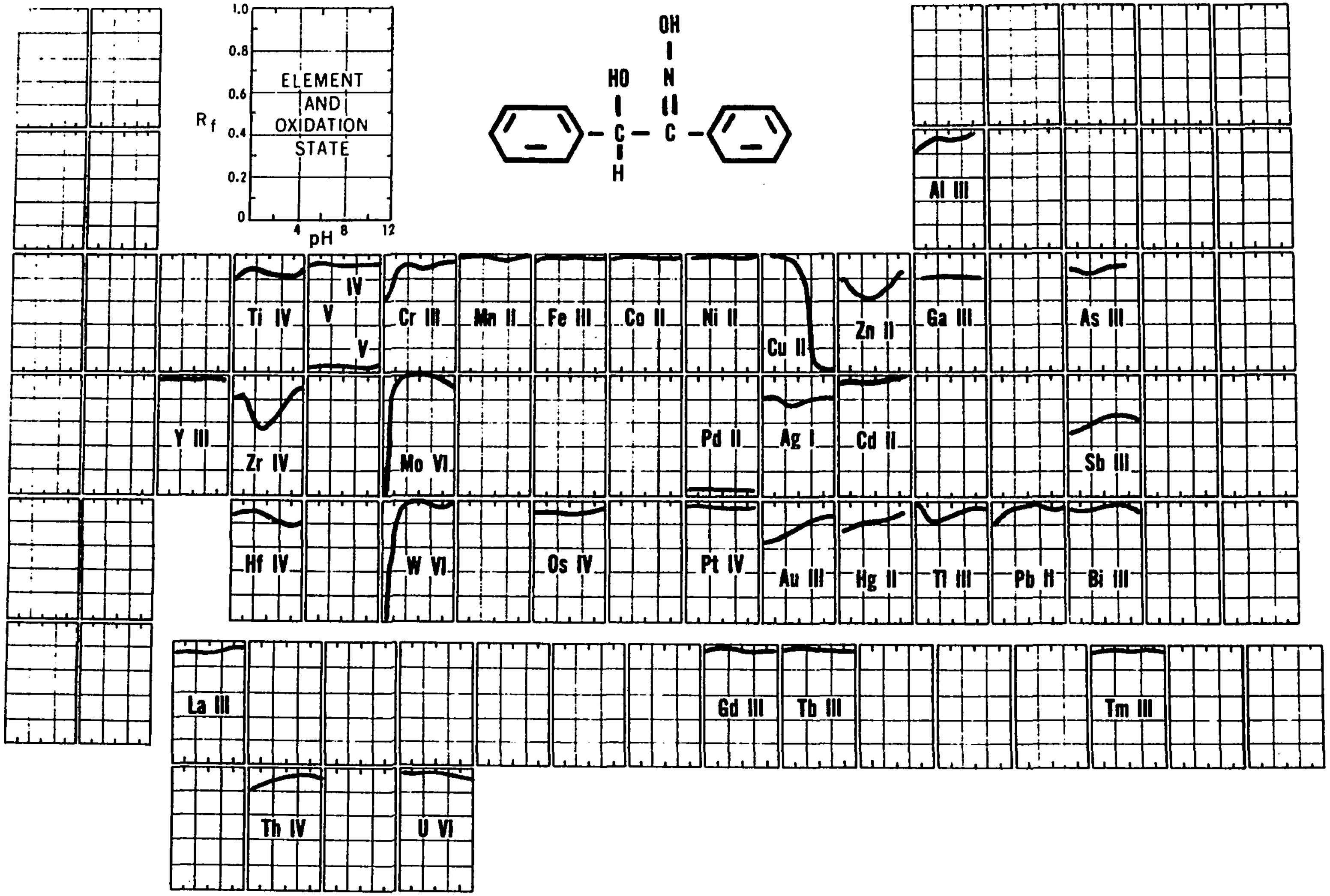
Paper Chromatographic Survey

Series of paper chromatograms were produced to determine the oxime-metal interactions and point out potential separation systems. The oxime impregnated paper retards the movement of metal ions which form strong oxime-metal interactions while allowing the free movement of other metals. The lower R_f values are indicative of strong interactions of the metals with the oxime substrate.

α-Benzoinoxime--acetate buffer

Since α-benzoinoxime is the basic α-hydroxyoxime reported in the literature, a series of chromatograms was made using paper impregnated with it. This was to provide a comparison in the extractive powers of the aromatic and the aliphatic compounds. Figure 5 shows the results of this study. The R_f for copper(II) decreases sharply above pH 8. Molybdenum(VI) and tungsten(VI) are retained by the oxime at pH 0-1. Vanadium(V) and palladium(II) appear to be the only other metals studied that show complete retention by the α-benzoinoxime.

Figure 5. The chromatographic behavior of metal ions on paper impregnated with α-benzoinoxime and eluted with perchloric acid (pH 1-3), acetate solution (pH 3-7) or sodium carbonate solution (pH 7-12)


R$_f$
1.0
0.8
0.6
0.4
0.2
0
4
pH
8
12
ELEMENT AND OXIDATION STATE
OH
N
HO
C
H
Al III
Ti IV
V IV
V V
Cr III
Mn II
Fe III
Co II
Ni II
Cu II
Zn II
Ga III
As III
Y III
Zr IV
Mo VI
Pd II
Ag I
Cd II
Sb III
Hf IV
W VI
Os IV
Pt IV
Au III
Hg II
Tl III
Pb II
Bi III
La III
Gd III
Tb III
Tm III
Th IV
U VI

10-Hydroxyeoicosanone-9-oxime (HEO)--acetate buffer

The chromatographic behavior of metals on paper impregnated with HEO and eluted with acetate buffer solution (pH 3-7) or perchloric acid (pH 1-3), is shown in Figure 6. Copper(II) is completely retained by the substrate at pH 5 compared to pH 8 with benzoinoxime. Iron(III) was partially retained at this acidity and considerable tailing was noticed. This may be caused by incomplete complexing of the metal by the oxime. The tailing and interference of iron(III) was prevented by adding tartrate ions to the sample solution.

Molybdenum(VI) was retained by the oxime at pH 1 while the retention of tungsten(VI) was not complete. The addition of tartrate to the sample solution prevented the hydrolysis of tungsten and did not interfere with the interaction between molybdenum and the oxime.

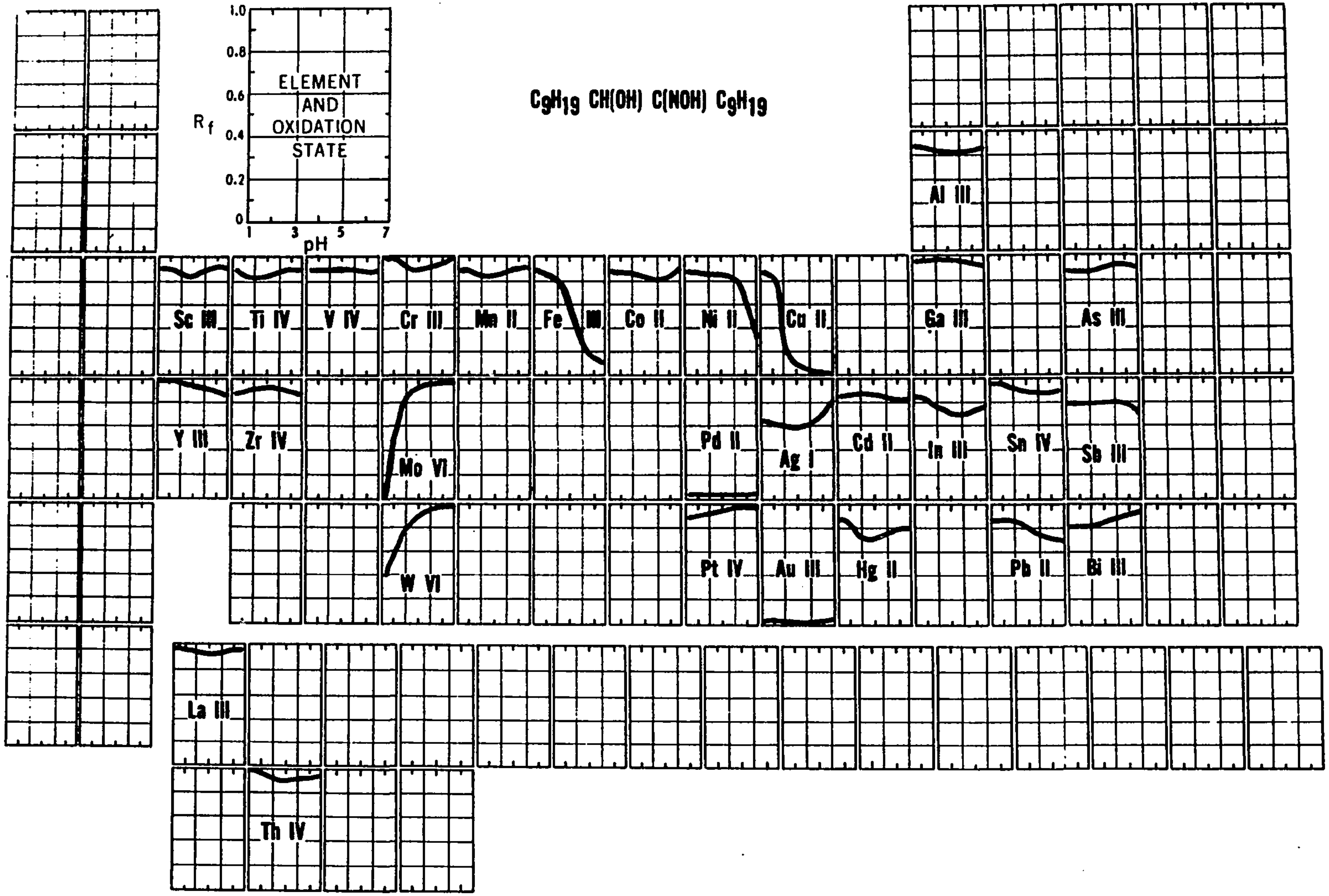
The retention of palladium(II) with HEO is the same as found with α-benzoinoxime. However, gold(III) was retained by HEO but not by α-benzoinoxime.

10-Hydroxyeicosanone-9-oxime (HEO)--tartrate buffer

As stated above, the addition of tartrate to the iron(III) sample prevented the tailing problem. Other metals such as tungsten(VI), antimony(III), tin(IV) and titanium(IV) were prevented from hydrolyzing at decreased acidity by the addition of complexing agents such as tartrate. Feigl (30) separated copper from iron, aluminum and other metals that precipitated in ammoniacal solution by adding tartrate and then forming the

Figure 6. The chromatographic behavior of metal ions on paper impregnated with HEO and eluted with perchloric acid (pH 1-3) or acetate solution (pH 3-7)

$C_9H_{19}\,CH(OH)\,C(NOH)\,C_9H_{19}$

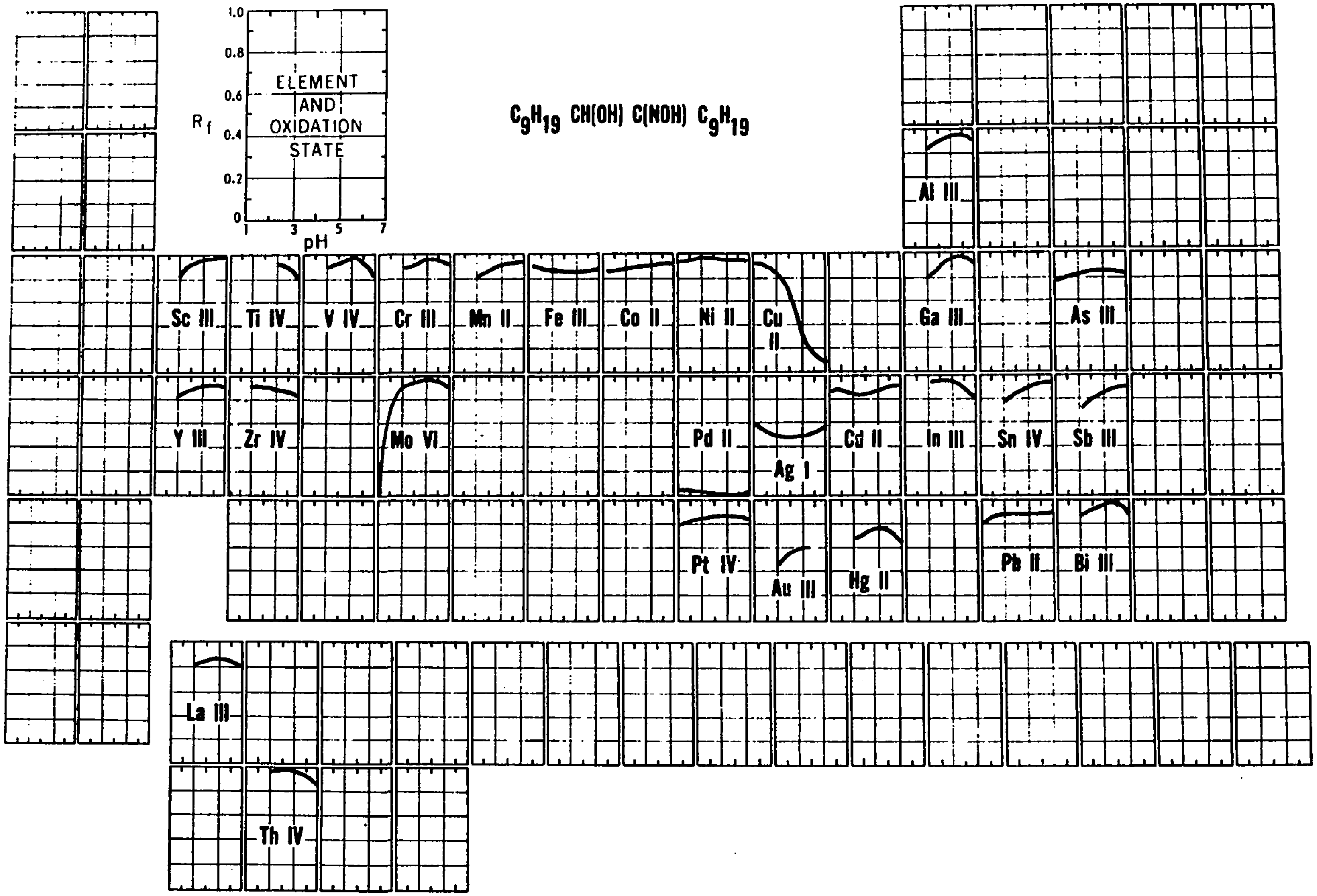


benzoinoxime-copper complex. However, Dubsky (23) states that an excess of tartrate decreased the sensitivity of α-benzoinoxime toward the formation of the copper complex. Since there is an apparent difference in these statements, tartrate buffer (pH 5) was evaluated as an eluent. The results are shown in Figure 7. The number of tartrate ions coming in contact with the copper(II) ions on the paper is greater than when the tartrate is added to the sample solution. The large amount of tartrate ions in the flowing eluent increased the competition for the copper(II) ions by the oxime and the tartrate. A complete retention of the copper was not achieved at pH 5. Small amounts of tartrate ions can be tolerated in the sample solution, but it was not the proper eluent for quantitative retention of copper in acidic solutions. This was verified in later column separations.

5,8-Diethyl-7-hydroxydodecanone-6-oxime (DHDO)--acetate buffer

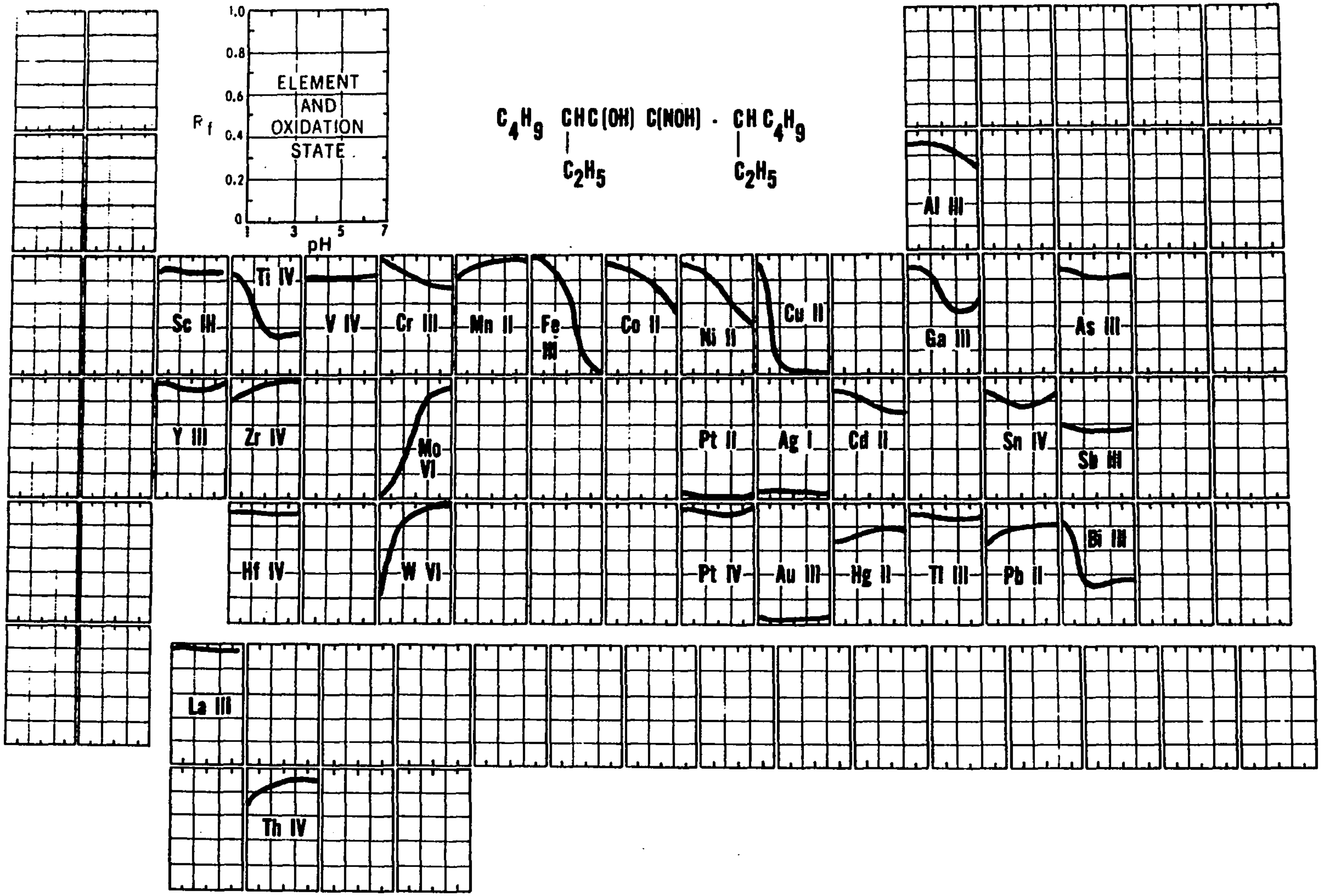
Figure 8 shows the chromatographic behavior of various metals on paper impregnated with DHDO. These results are similar to those reported for HEO (Figure 6) except that silver(II) was strongly retained by DHDO. There appeared to be a weaker interaction of DHDO with titanium(IV) and bismuth(III). Later column separations showed that bismuth(III) did not interfere with the separation of copper while titanium(IV) did interfere. The retention of copper(II) appears to be complete at pH 4 compared to pH 5 with HEO.

Figure 7. The chromatographic behavior of metal ions on paper impregnated with HEO and eluted with perchloric acid (pH 1-3) or tartrate solution (pH 3-7)



C_9H_{19} CH(OH) C(NOH) C_9H_{19}

Figure 8. The chromatographic behavior of metal ions on paper impregnated with DHDO and eluted with perchloric acid (pH 1-3) or acetate solution (pH 3-7)


Rf
1.0
0.8
0.6
0.4
0.2
0
1
3
5
7
pH
ELEMENT AND OXIDATION STATE
C4H9 CHC(OH) C(NOH) · CH C4H9
C2H5
C2H5
Al III
Sc III
Ti IV
V IV
Cr III
Mn II
Fe III
Co II
Ni II
Cu II
Ga III
As III
Y III
Zr IV
Mo VI
Pt II
Ag I
Cd II
Sn IV
Sb III
Hf IV
W VI
Pt IV
Au III
Hg II
Tl III
Pb II
Bi III
La III
Th IV

Suggested separations

The following is a list of some possible separations based on the paper chromatographic results.

a. Copper(II) from many metals using acetate buffer (pH 5) as eluent and HEO or DHDO substrate.

b. Molybdenum(VI) from many metals using hydrochloric or sulfuric acid eluent (pH 1).

c. Silver(I) from other metals, except copper, using acetate eluent (pH 5) and DHDO substrate.

d. Palladium(II) and gold(III) from other metals using acetate eluent (pH 3) and HEO or DHDO substrate.

Investigation of Copper(II)

Batch distribution ratios

The distribution ratios for copper(II) were determined by batch extractions according to the general procedure described previously. The percentage of copper extracted into the organic phase at various DHDO:copper ratios and pH values are presented graphically in Figure 9. This figure shows that the extracting ability of the oxime depends upon the ratio of oxime to copper and the pH of the aqueous phase. Data for HEO was similar to that for DHDO.

The D values of copper as a function of the oxime concentration at pH 4 are presented in Table 2. The effect of hydrogen iron concentration of the aqueous phase on the distribution ratio of copper at constant oxime concentration is presented in Table 3.

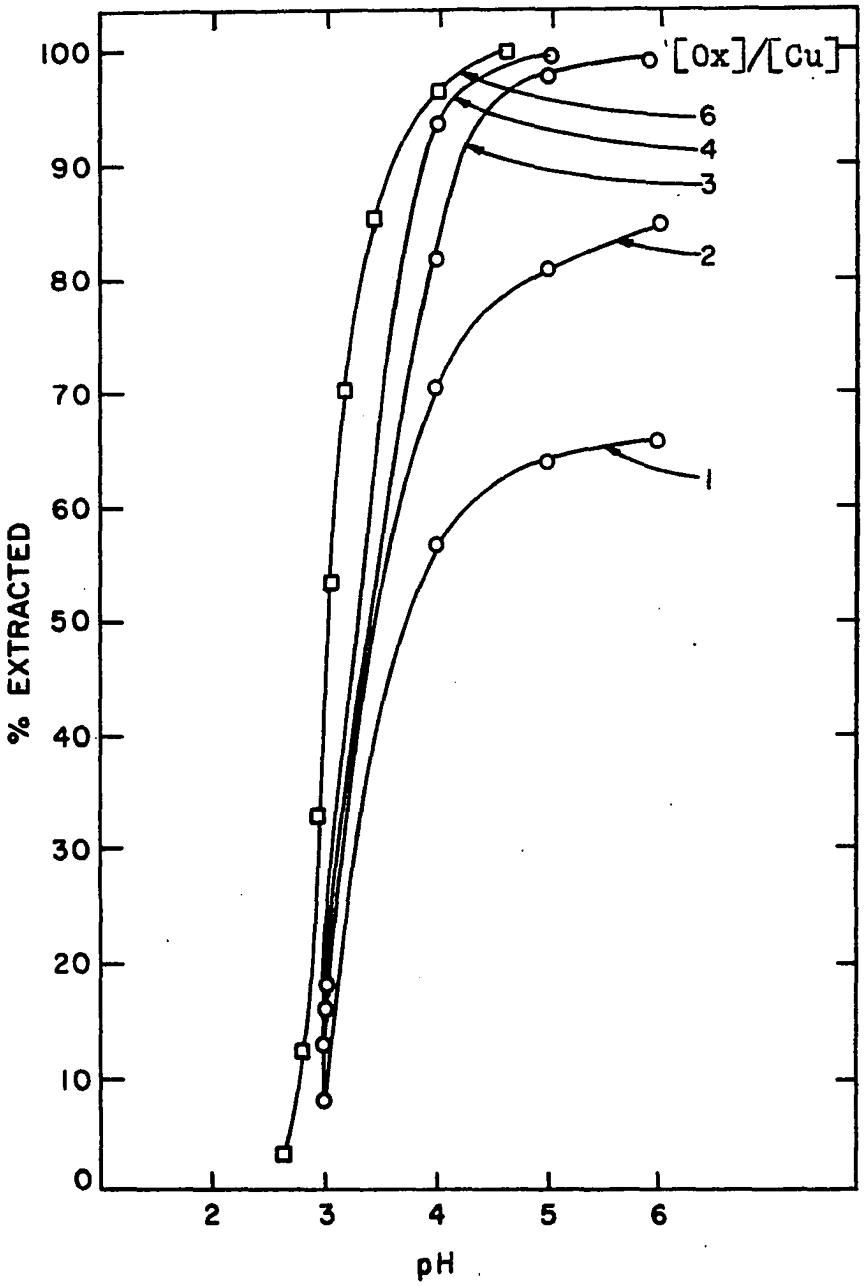


Figure 9. The dependence of extraction efficiency for copper(II) upon the pH at various ratios of copper to oxime

Table 2. Distribution ratios of copper(II) between acetate buffer (pH 4) and toluene solutions of hydroxyoximes as a function of the oxime concentration (Cu=0.0052 M)

pH	M oxime	Distribution ratio HEO	DHDO
4	0.0052	4.3	1.4
4	0.0104	10	3
4	0.0211	-	7
4	0.0500	17	20
4	0.1000	42	53
4	0.1500	81	123
4	0.2000	-	261
4	0.2500	162	409

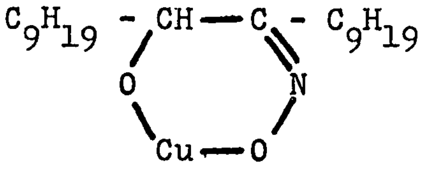
Table 3. Distribution ratios of copper(II) between an acetate solution and toluene solution of hydroxyoximes as a function of the hydrogen ion concentraction (Cu=0.0263 mmoles, oxime=0.1560 mmoles)

(H^+)	Distribution HEO	Ratio DHDO
1.3×10^{-3}	0.2	0.3
4.0×10^{-4}	2.4	3.3
2.0×10^{-4}	9.7	10.2
1.0×10^{-4}	39	43
5.0×10^{-5}	151	174

Characterization of copper(II)--oxime complex

HEO-Cu complex: Extraction of copper(II) in aqueous solution with a toluene solution of HEO produces a green complex in the toluene layer. Figure 10 shows that log D is a straight line function of the log of the oxime concentration. The slope of this line indicates the number of oxime molecules associated with each metal ion in the complex. The value of 0.98 indicates the presence of one oxime per copper in the complex.

To obtain charge neutralization in the complex, the HEO must lose two hydrogens, or some anion in the solution must be associated with the complex. A plot of log D as a function of the log hydrogen ion concentration at constant oxime and copper concentrations of 0.0312 M and 0.0052 M, respectively, is shown in Figure 11. The slope of -1.96 indicates that two hydrogens are lost from each oxime. The NMR spectrum (Figure 12) confirms the loss of the oxime hydrogen and hydroxyl hydrogen at δ 3.96 and δ 4.46 ppm respectively. A structure that is consistent with these data is as follows:



A complex having a copper to α-benzoinoxime ratio of 1:1 was reported by Feigl (32). He claimed that the coordination sphere of the metal was saturated by interaction with the pi

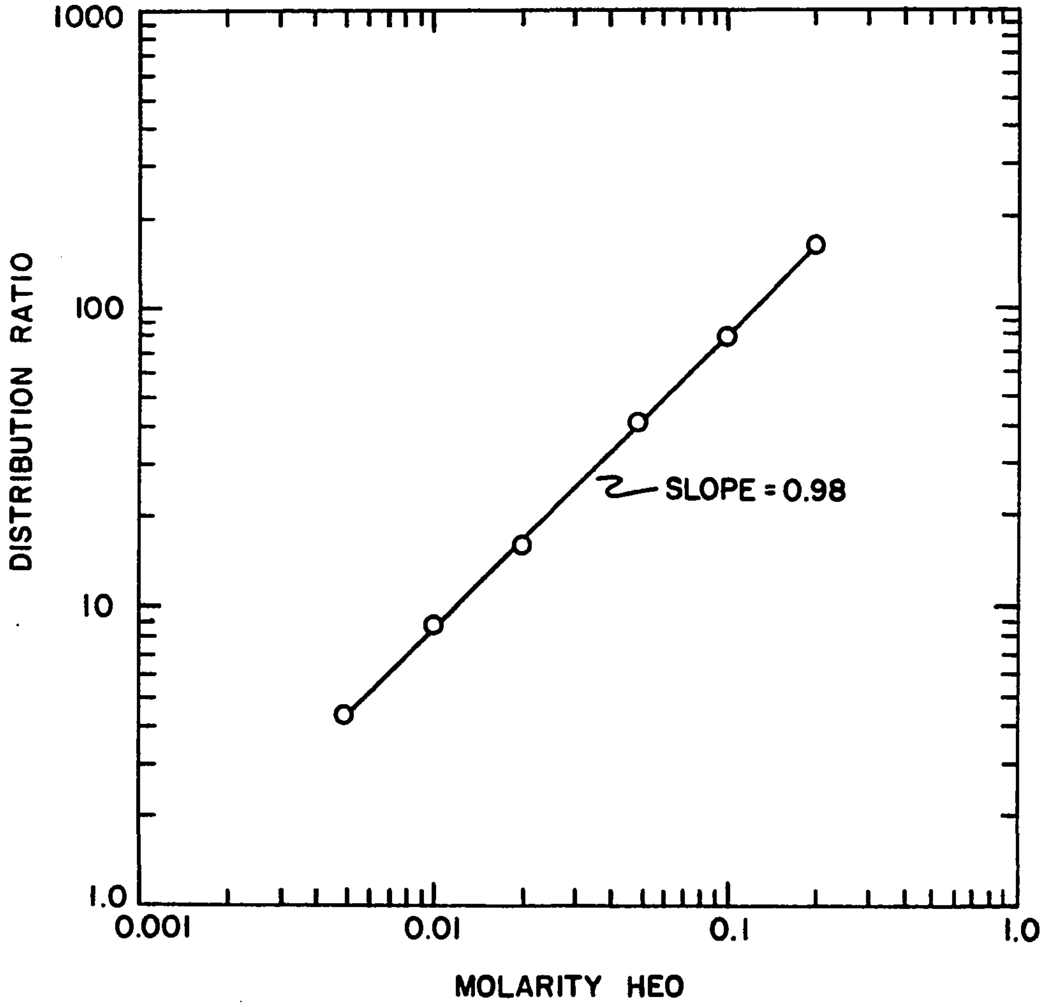


Figure 10. The distribution ratio of copper(II) extracted from an acetate solution (pH 4) as a function of the concentration of HEO in the organic phase

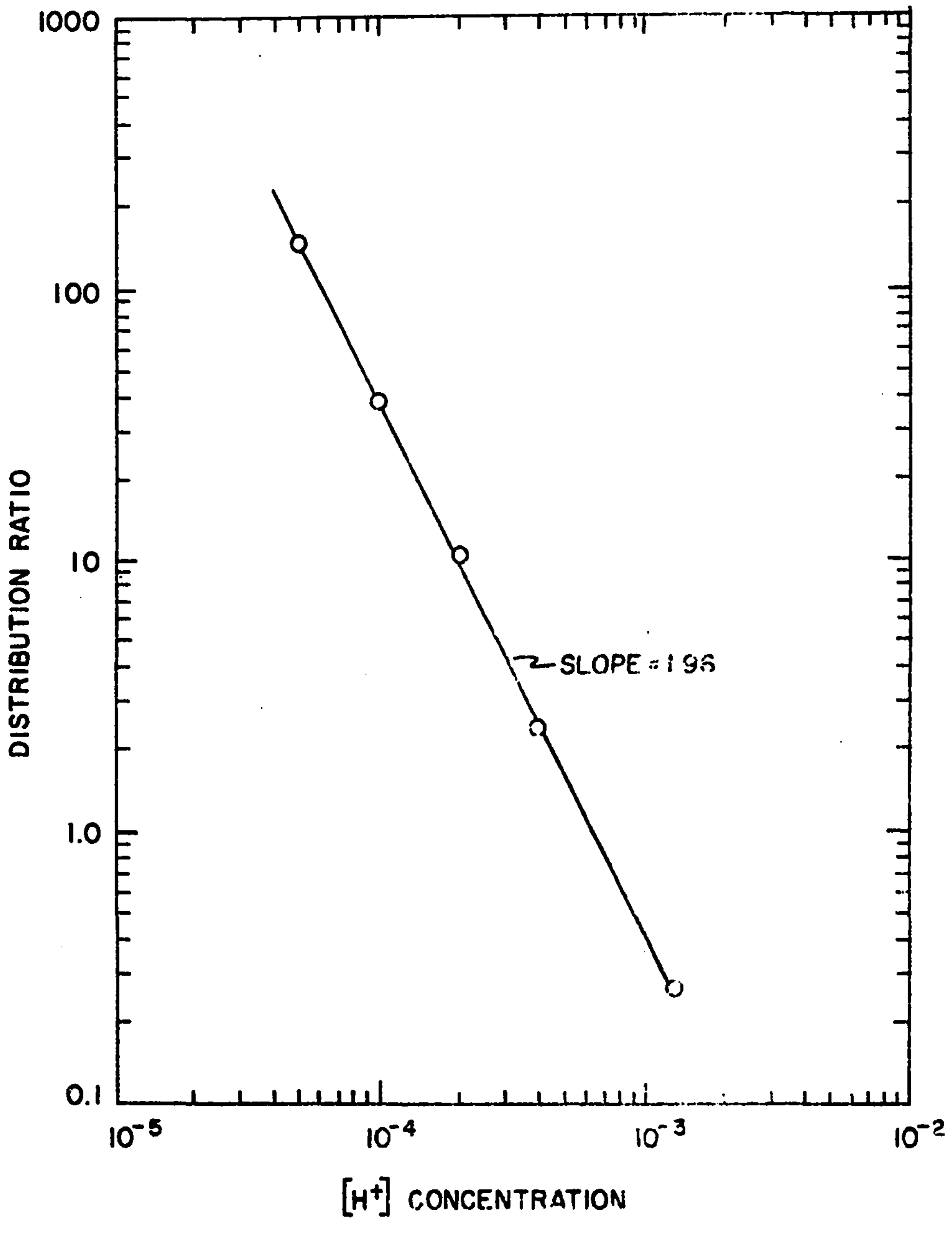


Figure 11. The distribution ratio of copper(II) between an acetate solution and a toluene solution of HEO as a function of the hydrogen ion concentration (HEO:Cu = 6:1)

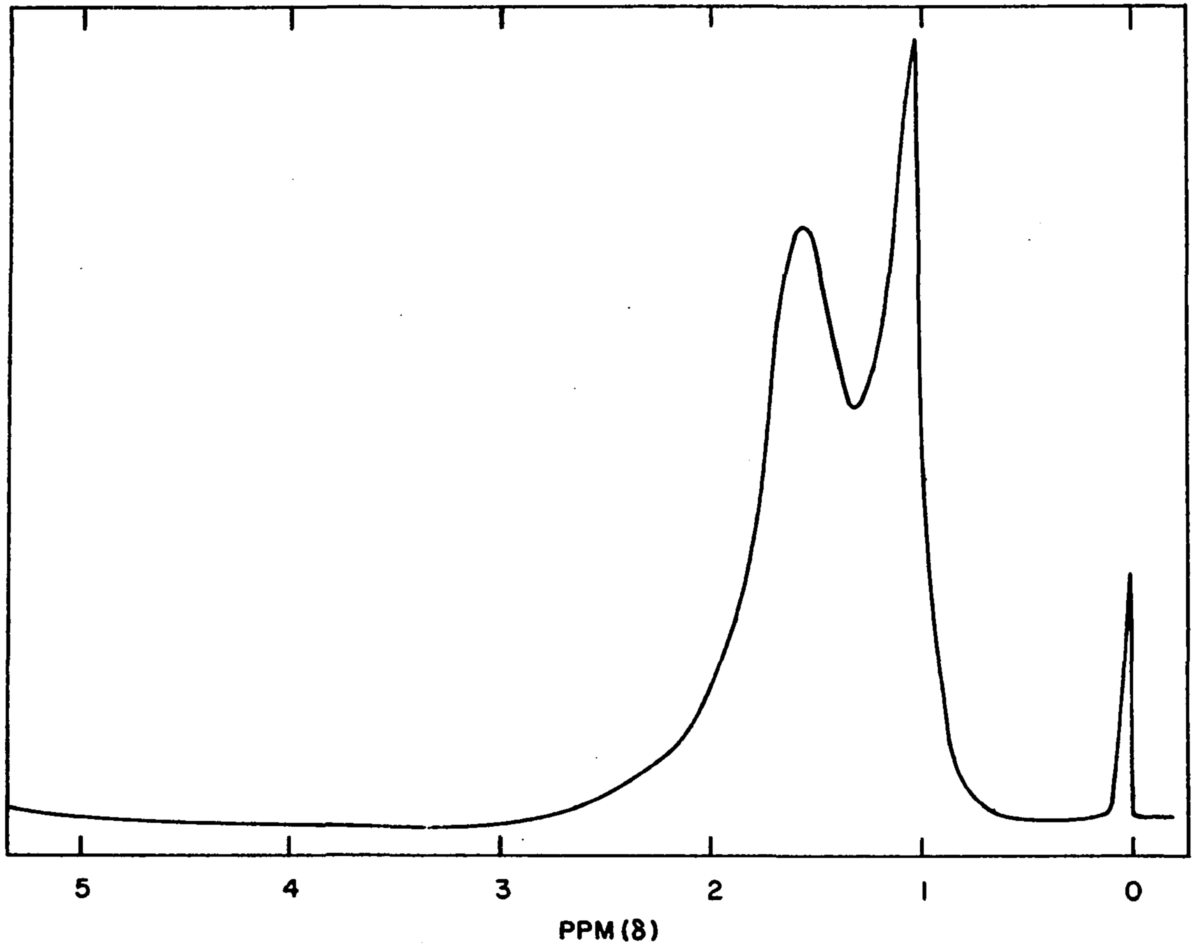


Figure 12. The NMR spectrum of the HEO-Cu complex

clouds of the benzene ring. The fact that a similar complex has now been formed with an aliphatic hydroxyoxime suggests that the complex is formed as a salt.

DHDO-Cu complex: The batch extractions of copper(II) with toluene solutions of DHDO produces a green complex at low oxime concentrations and a brown complex at higher oxime concentrations. The green complex yields a slope of 1.11 when log D is plotted against the log DHDO concentration (Figure 13). This represents one oxime molecule associated with each copper ion. A slope of -1.98 is obtained by plotting the log D against the log of the hydrogen ion concentration (Figure 14). This represents a loss of 2 hydrogens during the formation of the complex. The NMR spectrum (Figure 15) shows no hydroxyl or oxime hydrogens present at δ 2.97 and δ 4.42 respectively. The infrared spectrum (Figure 16) indicates no OH stretching around 3400 cm^{-1}. The residual absorption is greatly reduced from the parent oxime (Figure 4) and probably due to contamination by excess DHDO. These results indicate that the complex is similar to that obtained with HEO.

The brown complex exhibits a slope of 2.03 when log D is plotted against log oxime concentration (Figure 13) indicating a 2:1 ratio of DHDO:Cu. The NMR spectrum (Figure 17) shows the presence of an oxime hydrogen at δ 2.48 but no hydroxyl hydrogen at δ 4.49.

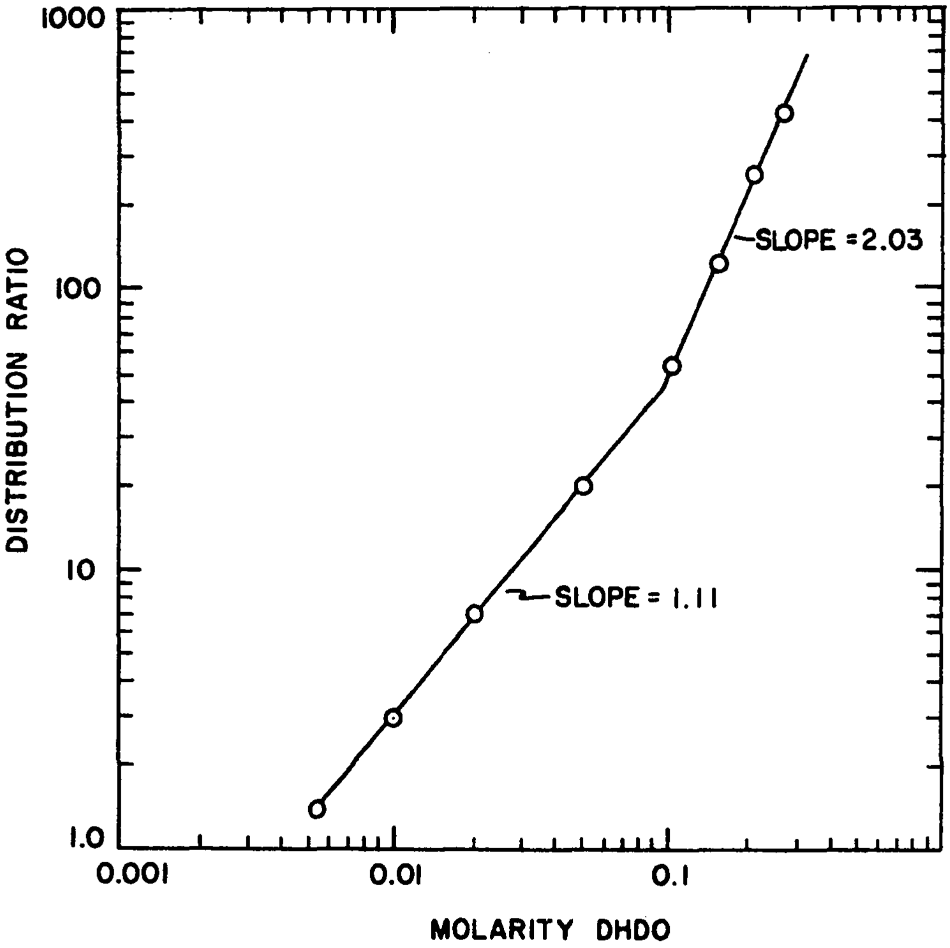


Figure 13. The distribution ratio of copper(II) extracted from an acetate solution (pH 4) as a function of the concentration of DHDO in the organic phase

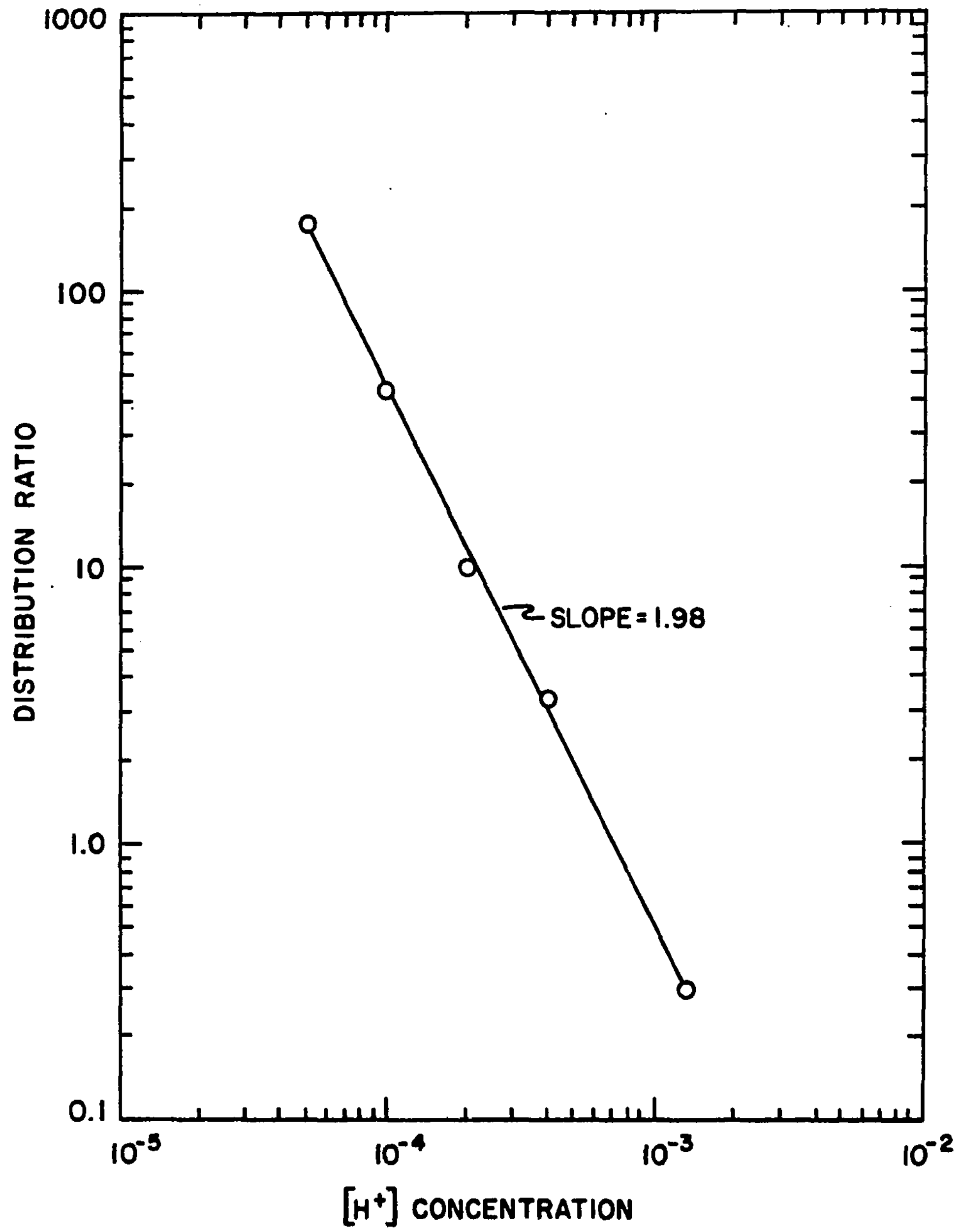


Figure 14. The distribution ratio of copper(II) between an acetate solution and a toluene solution of DHDO as a function of the hydrogen ion concentration (DHDO:Cu = 6:1)

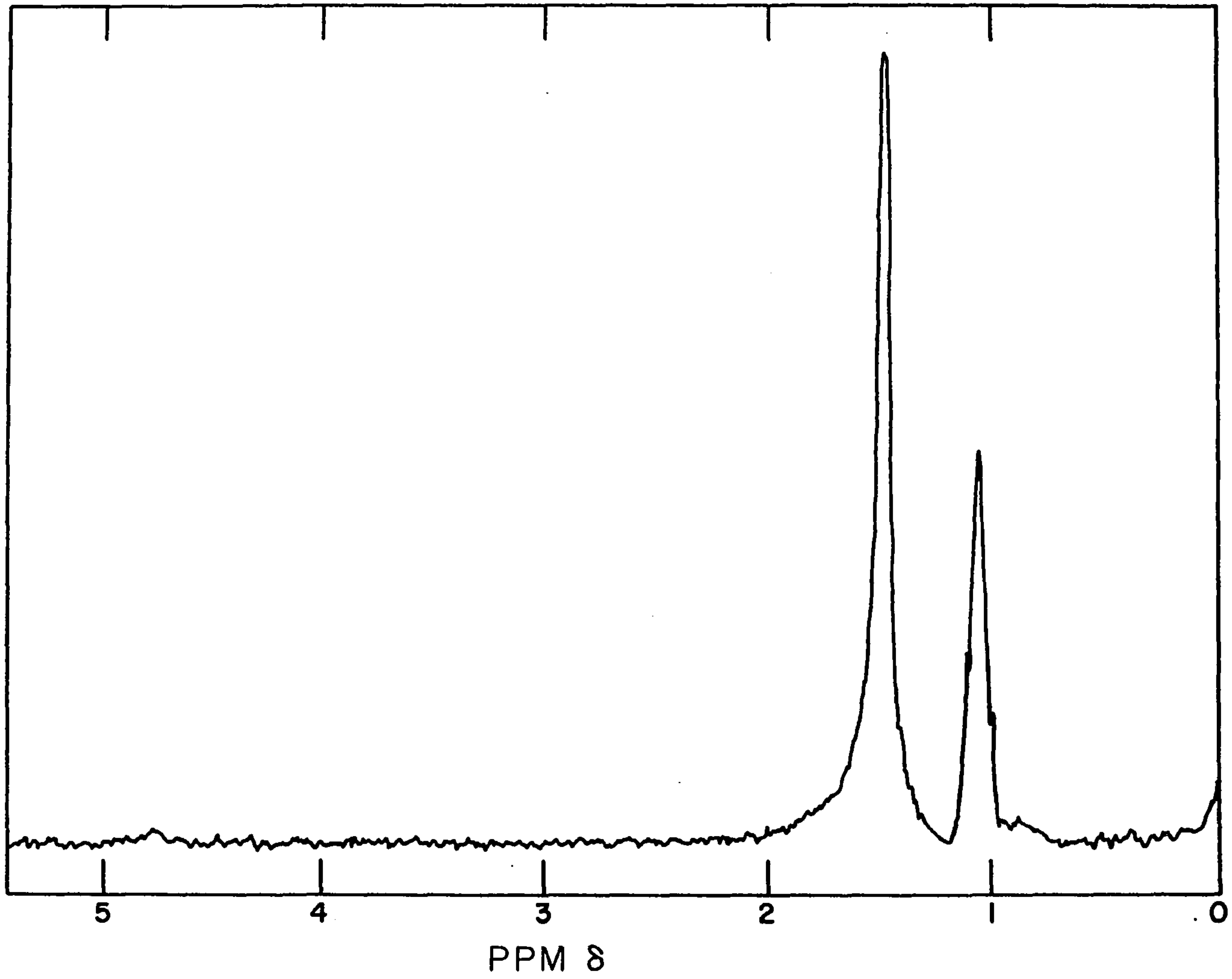


Figure 15. The NMR spectrum of the DHDO-Cu complex

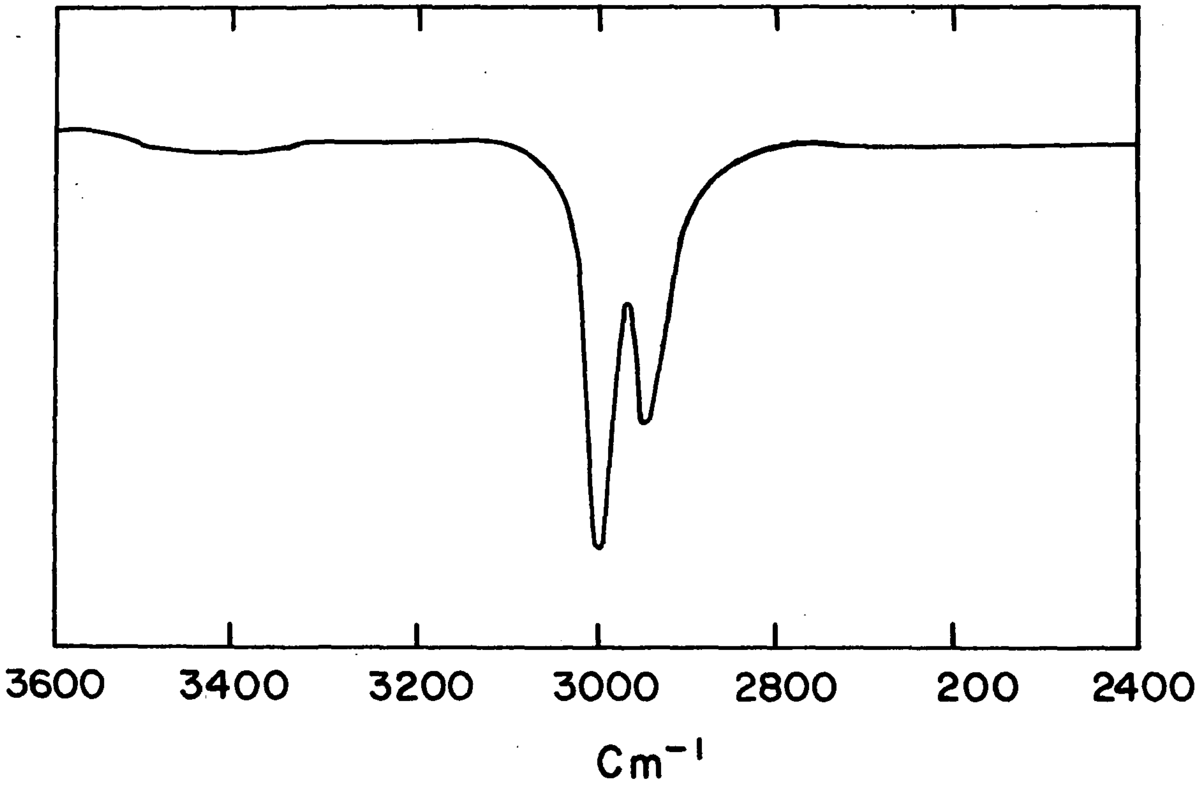


Figure 16. The infrared spectrum of the DHDO-Cu complex

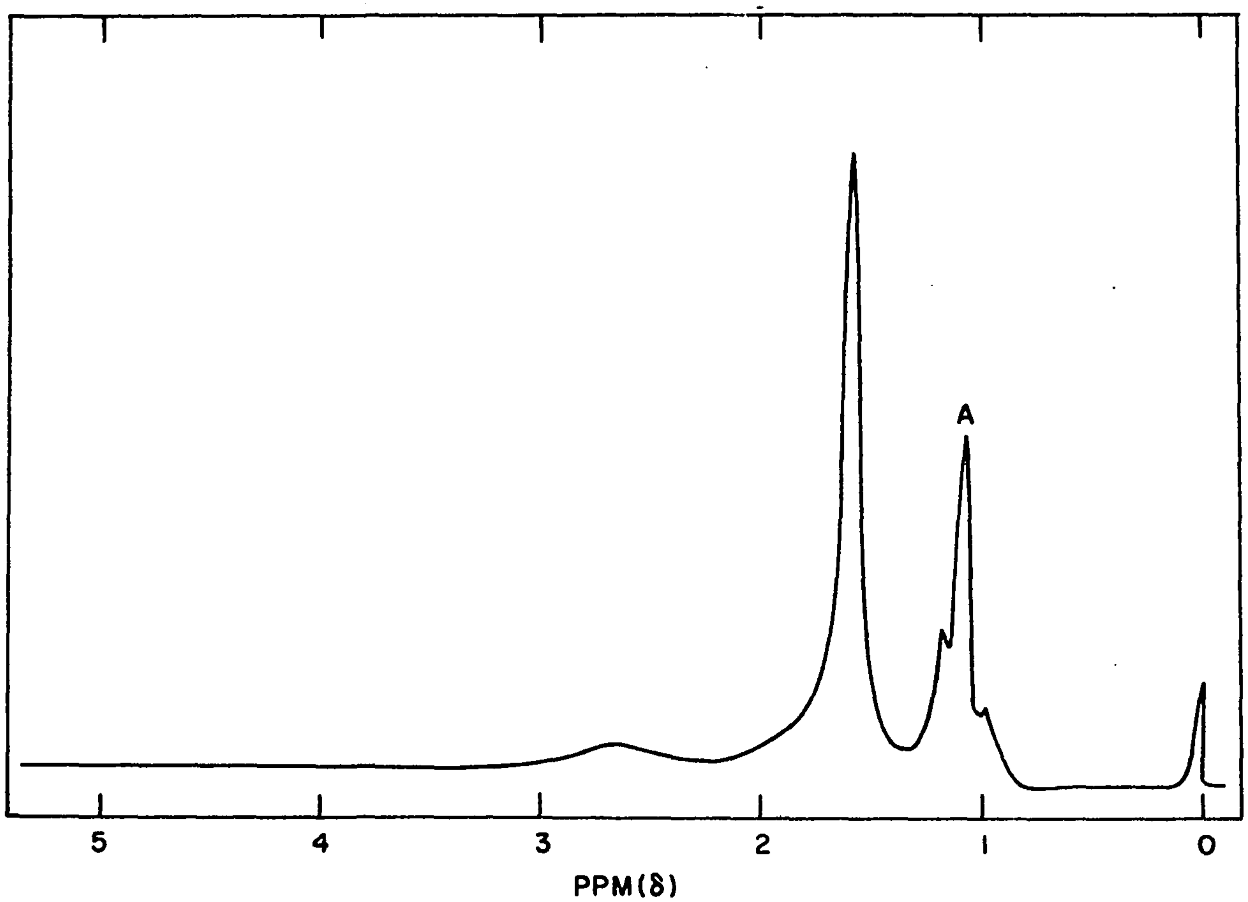
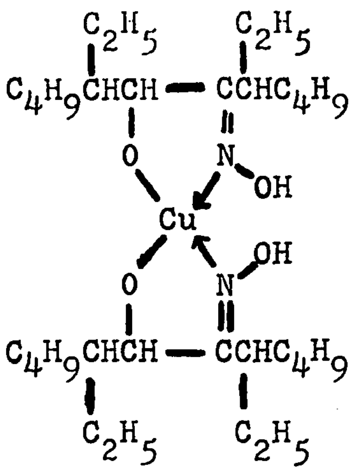


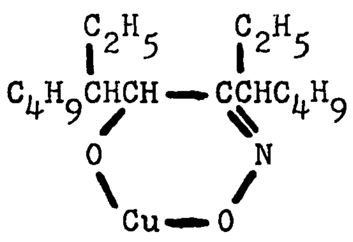
Figure 17. The NMR spectrum of the $(DHDO)_2Cu$ complex

The infrared spectrum indicates a reduction of the OH stretching frequency. In the spectrum of the parent oxime (Figure 18), the ratio of percent transmittance of the OH stretching mode at 3380 cm^{-1} to the CH stretch at 2869 cm^{-1} is 0.527. This ratio is reduced to 0.263 in the complex (Figure 19). The decrease in the amount of stretching by one-half indicates the loss of one of the two OH groups.

Structures which are consistent with these data are presented below:



brown complex



green complex

The remaining sites in the coordination sphere can be occupied by solvent molecules and no distinction was made between possible cis and trans isomers in the brown complex. A mixture of these probably exist in equilibrium.

Column separations

Column separations were made according to the general procedure outlined previously using columns of 20% (w/w) HEO

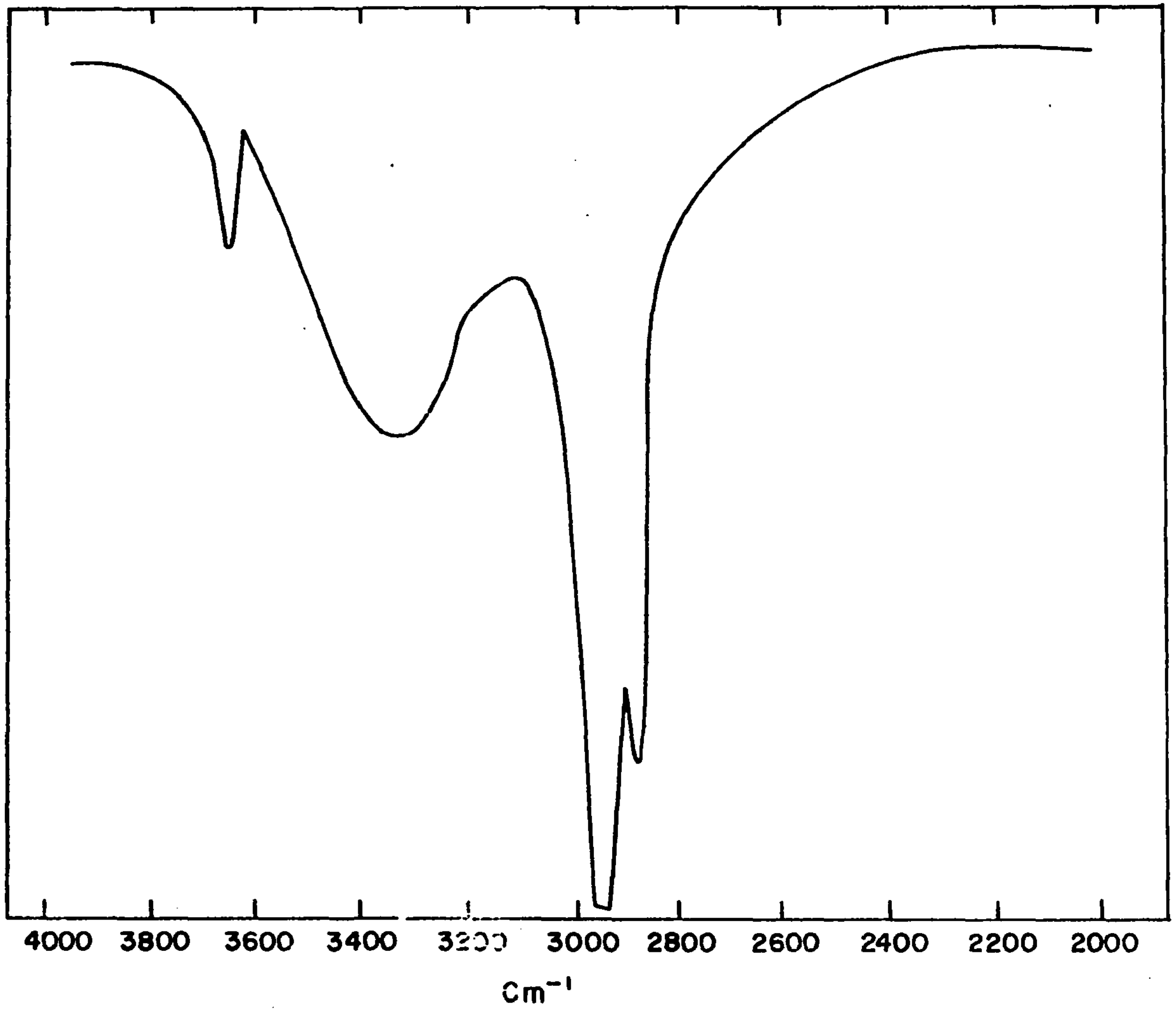


Figure 18. The infrared spectrum of DHDO

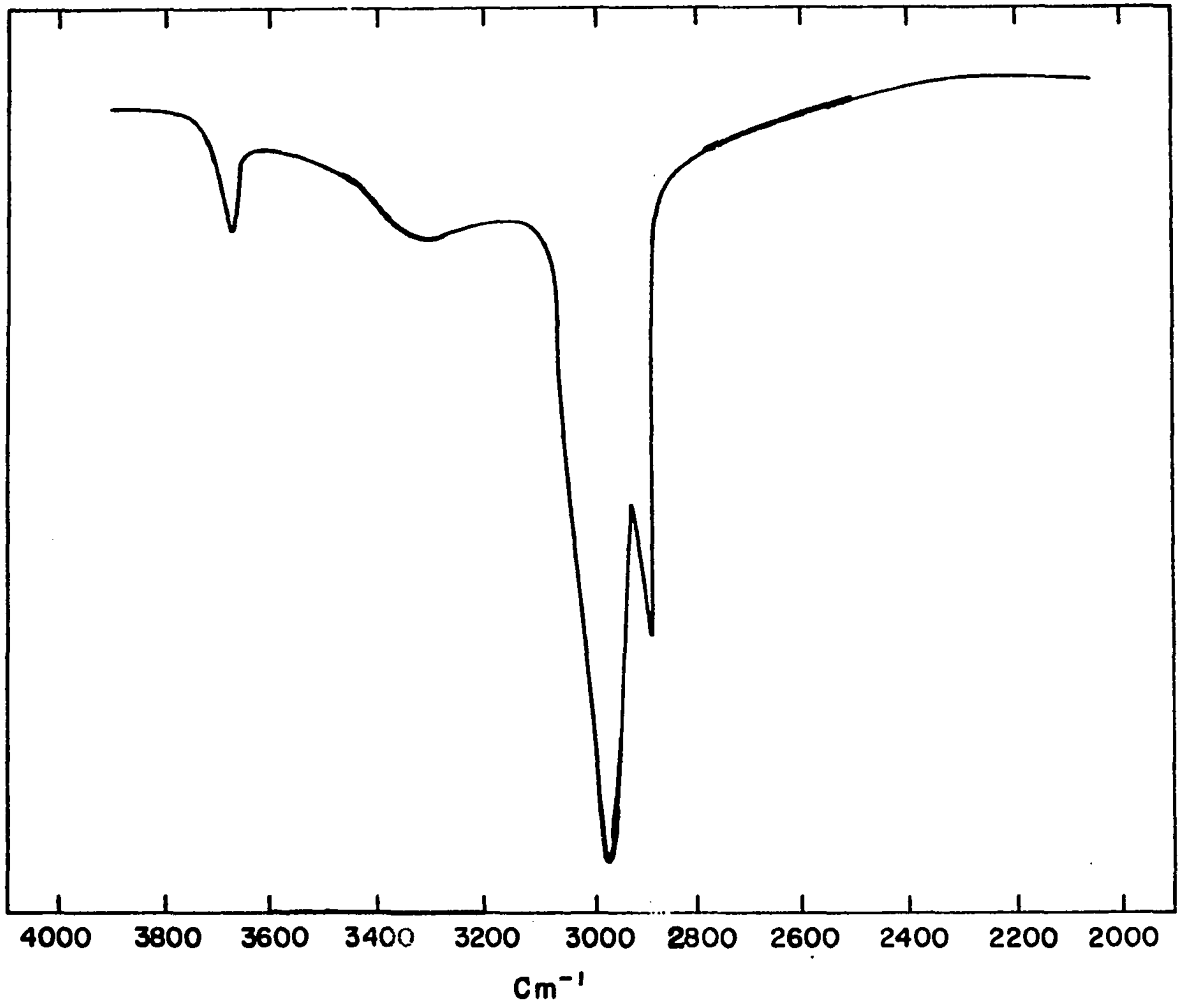


Figure 19. The infrared spectrum of the $(DHDO)_2Cu$ complex

and DHDO (0.64 and 0.54 mmoles respectively). All metals investigated, except copper(II), were eluted with 20 ml or less of the acetate eluent (pH 5) and required 4 to 5 minutes for the elution. Copper(II) was then stripped from the column with 30 ml of 6 M hydrochloric acid at the same flow rate. This required about 7 minutes for the elution.

Still faster elutions appear feasible. In the copper-vanadium separation, the effluent was passed through a 1 cm flow-through cell in a spectrophotometer. The elution curves were recorded as each metal was removed from the column (Figure 20). Using a flow rate of approximately 20 ml per minute, the entire separation was completed within 2 minutes. The use of finer mesh resin and pressure would probably reduce the tailing of the copper and allow still faster separations.

In the palladium-copper separation, the resin bed was equilibrated with 0.1 M sulfuric acid instead of the above acetate eluent. The copper was eluted first with the 0.1 M sulfuric acid while the palladium was retained by the oxime substrate. A 6 M hydrochloric acid eluent was used to remove the palladium as the yellow chloride complex. Gold and molybdenum were also retained by the oxime when using 0.1 M sulfuric acid as the eluent.

Data for individual separations on the DHDO column are given in Table 4. The average recovery was 99.9% for copper and 99.6% for the other metal ions. The separations on the

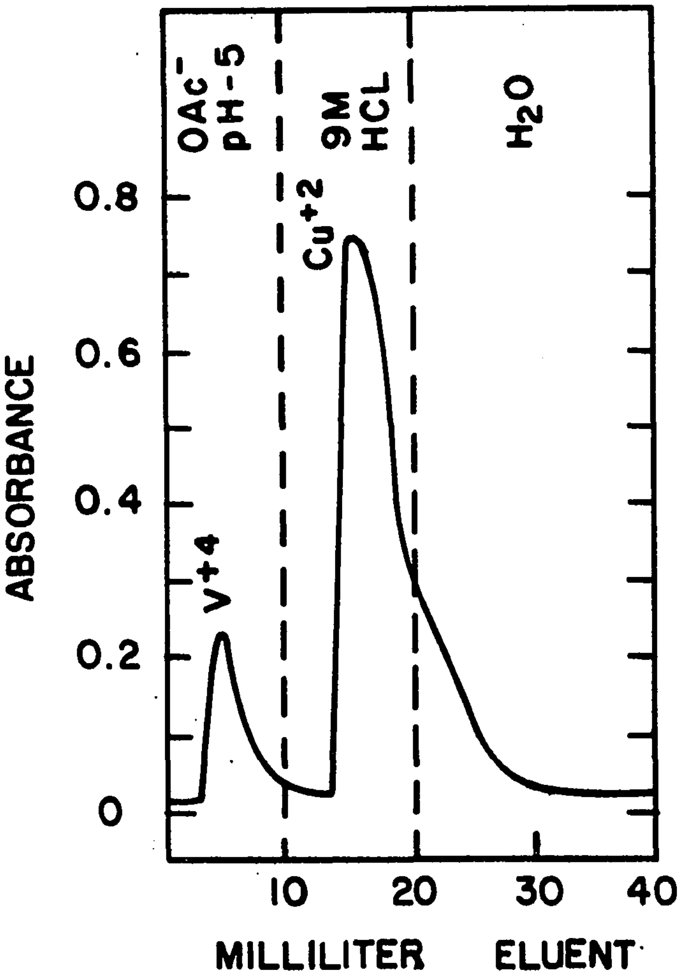


Figure 20. Elution curves for 0.025 mmoles of V(IV) and Cu(II) from a 9 x 62 mm column containing DHDO impregnated on Amberlite XAD-2 (flow rate = 20 ml/min)

Table 4. Separation of copper from aqueous solutions of metals using a 9 x 62 mm column of 20% DHDO on Amberlite XAD-2 support (eluents = acetate solution pH 5 for ion A and 6 M hydrochloric acid for copper)

Separation			ml to complete elution	mmoles taken	Activity taken CPM	Percent recovery
I	a.	Co(II)	15	0.0225		100.3
	b.	Cu(II)	30	0.0265		100.3
II	a.	Ni(II)	15	0.0362		99.6
	b.	Cu(II)	30	0.0265		100.0
III	a.	Cr(III)	9		2795	99.8
	b.	Cu(II)	30	0.0265		100.0
IV	a.	Fe(III)	18	0.0284		99.6
	b.	Cu(II)	30	0.0265		100.3
V	a.	Zn(II)	15	0.0222		100.0
	b.	Cu(II)	30	0.0265		99.4
VI	a.	Cd(II)	18	0.0325		100.0
	b.	Cu(II)	30	0.0284		99.7
VII	a.	Sn(IV)	12		5766	98.6
	b.	Cu(II)	30	0.0265		99.6
VIII	a.	Mo(VI)	24	0.0286		98.9
	b.	Cu(II)	30	0.0248		99.2
IX	a.	Pd(II)	30	0.0278		99.7
	b.	Cu(II)	30	0.0246		100.0
X	a.	Pb(II)	15	0.0375		100.2
	b.	Cu(II)	30	0.0265		99.8

Table 4. (Continued)

Separation			ml to complete elution	mmoles taken	Activity taken CPM	Percent recovery
XI	a.	Bi(III)	24	0.0184		98.6
	b.	Cu(II)	30	0.0226		99.6
XII	a.	Th(IV)	24	0.0272		99.2
	b.	Cu(II)	30	0.0265		99.6
XIII	a.	Hg(II)	24	0.0286		100.0
	b.	Cu(II)	30	0.0265		100.8
XIV	a.	V(IV)	12	0.0387		101.7
	b.	Cu(II)	30	0.0265		99.2
XV	a.	Ti(IV)	20	0.0200		50.8
	b.	Cu(II)	30	0.0265		150.5
XVI	a.	Sb(III)	12		53530	97.5
	b.	Cu(II)	30	0.0265		99.6
XVII	a.	U(VI)	15		770206	100.3
	b.	Cu(II)	30	0.0265		100.0
XVIII	a.	W(VI)	12		51207	99.6
	b.	Cu(II)	30	0.0265		100.7

HEO column are listed in Table 5. The average recovery was 99.9% for copper and 99.7% for the other metal ions. Copper was successfully separated from titanium when using HEO but not with DHDO.

This column method was applicable to samples containing extremely low concentrations of copper(II). Distilled water was adulterated with 31 ppb of ^{64}Cu(II) and adjusted to a pH of 5.0 with acetate buffer. The solution (200 ml) was passed through a 0.9 x 6.2 cm column containing 0.96 mmole of DHDO in toluene. The copper was retained by the column, removed with 6 M hydrochloric acid and determined radiometrically. The average recovery from duplicate experiments was 100.1%.

Capacity of DHDO column

A copper solution was introduced onto a column containing 0.8935 mmole of DHDO pretreated with acetate solution (pH 5) until copper appeared in the effluent. The column retained 0.3950 mmole of copper. This corresponds to a capacity of 0.44 moles copper per mole of DHDO. The capacity of HEO was determined to be 0.34 moles copper per mole HEO.

Analysis of National Bureau of Standard samples

Sample no. 124-d, a high copper (83.60%), low tin (4.56%) alloy was dissolved in aqua regia. Tartrate solution, (approx. 0.06 M) was added to prevent the interference of tin. Sodium hydroxide (1 M) was added until the solution turned dark blue (pH 5.2). An aliquot was placed on a column of 20% (w/w) DHDO where the copper was separated from iron(III), nickel(II),

Table 5. Separation of copper from aqueous solutions of metals using a 9 x 62 mm column of 20% HEO on Amberlite XAD-2 support (eluents + acetate solution pH 5 for ion A and 6 M hydrochloric acid for copper)

Separation			ml to complete elution	mmoles taken	Activity taken CPM	Percent recovery
I	a.	Co(II)	15	0.0225		99.5
	b.	Cu(II)	30	0.0265		99.7
II	a.	Ni(II)	15	0.0362		100.1
	b.	Cu(II)	30	0.0265		99.8
III	a.	Cr(III)	9		2883	100.2
	b.	Cu(II)	30	0.0265		99.5
IV	a.	Fe(III)	18	0.0284		100.2
	b.	Cu(II)	30	0.0265		99.5
V	a.	Zn(II)	15	0.0222		100.1
	b.	Cu(II)	30	0.0265		100.0
VI	a.	Cd(II)	18	0.0325		99.7
	b.	Cu(II)	30	0.0284		99.9
VII	a.	Sn(IV)	12		5689	98.6
	b.	Cu(II)	30	0.0265		99.6
VIII	a.	Mo(VI)	24	0.0286		100.3
	b.	Cu(II)	30	0.0265		99.2
IX	a.	Pd(II)	30	0.0273		99.4
	b.	Cu(II)	30	0.0265		100.2
X	a.	Pb(II)	15	0.0375		99.4
	b.	Cu(II)	30	0.0265		100.0

Table 5. (Continued)

Separation			ml to complete elution	mmoles taken	Activity taken CPM	Percent recovery
XI	a.	Bi(III)	24	0.0184		101.0
	b.	Cu(II)	30	0.0265		101.0
XII	a.	Th(IV)	24	0.0272		101.0
	b.	Cu(II)	30	0.0265		100.0
XIII	a.	Hg(II)	24	0.0286		100.0
	b.	Cu(II)	30	0.0265		100.4
XIV	a.	V(IV)	12	0.0387		98.9
	b.	Cu(II)	30	0.0265		99.9
XV	a.	Ti(IV)	20	0.0200		101.2
	b.	Cu(II)	30	0.0265		99.9
XVI	a.	Sb(III)	12		53750	98.5
	b.	Cu(II)	30	0.0265		99.6
XVII	a.	U(VI)	15		770206	99.0
	b.	Cu(II)	30	0.0265		100.0
XVIII	a.	W(VI)	12		50986	99.4
	b.	Cu(II)	30	0.0265		100.7

lead(II), zinc(II), tin(IV) and antimony(V) by the method described previously.

Sample no. 54-d, a high tin (88.57%), low copper (3.62%) alloy was treated as above except that 10 to 20 drops hydrofluoric acid was added to effect a solution and prevent the interference of tin. Tartrate solutions did not prevent the interference of tin at this high concentration. The major elements in these samples and the recoveries of copper are listed in Table 6. The average recovery of copper from these experiments was 99.7%.

Table 6. Analysis of National Bureau of Standard samples

Sample no.	Major elements	% reported	% found
124d	Cu	83.60	83.58*
	Pb	5.20	
	Zn	5.06	
	Sn	4.56	
54d	Sn	88.57	
	Sb	7.04	
	Cu	3.62	3.60**

*Average of two determinations.

**Average of four determinations.

Development of Thiolactic Acid Method for the Determination of Molybdenum

Will and Yoe (95) and Hamence (41) have described a method to determine molybdenum by measuring the absorbance of the yellow complex formed with thioglycollic acid. Numerous ions were reported to interfere with this method. Pribil and Adams (73) eliminated many of these interferences by extracting the complex into a 5% Alamine 336-S solution and measuring the absorbance at 370 nm. Bismuth(III), mercury(II), tungsten(VI), chloride, fluoride and nitrate ions interfered.

Busev, Nacu and Redzit (12) used thiolactic acid (TLA) and its anilides to extract molybdenum into an organic solvent. This required a 30 minute extraction process to obtain quantitative results. The above method was modified to provide one more selective than the thioglycollic method (95) and eliminate the time consuming extraction procedures (73).

Reagents

Thiolactic acid (TLA) was obtained from Evans Chemetics, Inc. and used as received. The assay was reported as 99.4%.

Molybdenum(VI) solutions were prepared by dissolving molybdenum(VI) oxide in 7 M ammonium hydroxide. The 0.05 M solutions of other metal ions were made by dissolving the appropriate salts in distilled water, slightly acidified. Tartaric acid (approx. 0.05 mmoles/ml) was added to antimony(V), tungsten(VI), tin(IV) and titanium(IV) to prevent hydrolysis.

Absorption spectra

Spectra of thiolactic acid and the TLA-molybdenum complex at pH 1.0 are shown in Figure 21. The shoulder on the TLA-Mo spectrum is useful for the determination of molybdenum. A wavelength of 365 nm was found to be the most free from foreign ion interferences.

Effect of variables

Effect of pH: Figure 22 shows the effect of pH on the absorbance of the TLA-Mo complex at a concentration of 2×10^{-4} M. The chemistry of molybdenum is complex due to the formation of isopolymeric and heteropolymeric compounds in acidic solutions. Therefore, no attempt was made to determine the cause for the deviation between pH 1.6 and 2.6. This phenomenon occurred in three experiments using perchloric, hydrochloric and sulfuric acids respectively. The final method is based on the pH range of 1.0-1.6. The absorbance is less dependent on small changes in acidity within this range and there are fewer interferences than at higher pH values.

Effect of TLA concentration: If an excess of molybdenum was present in the final solution, a green to blue color was formed due to a partial reduction of Mo(VI) to Mo(V) and the formation of a molybdenum blue complex of mixed oxidation states. However, if an excess of TLA was present, the yellow TLA-Mo complex was formed without problems.

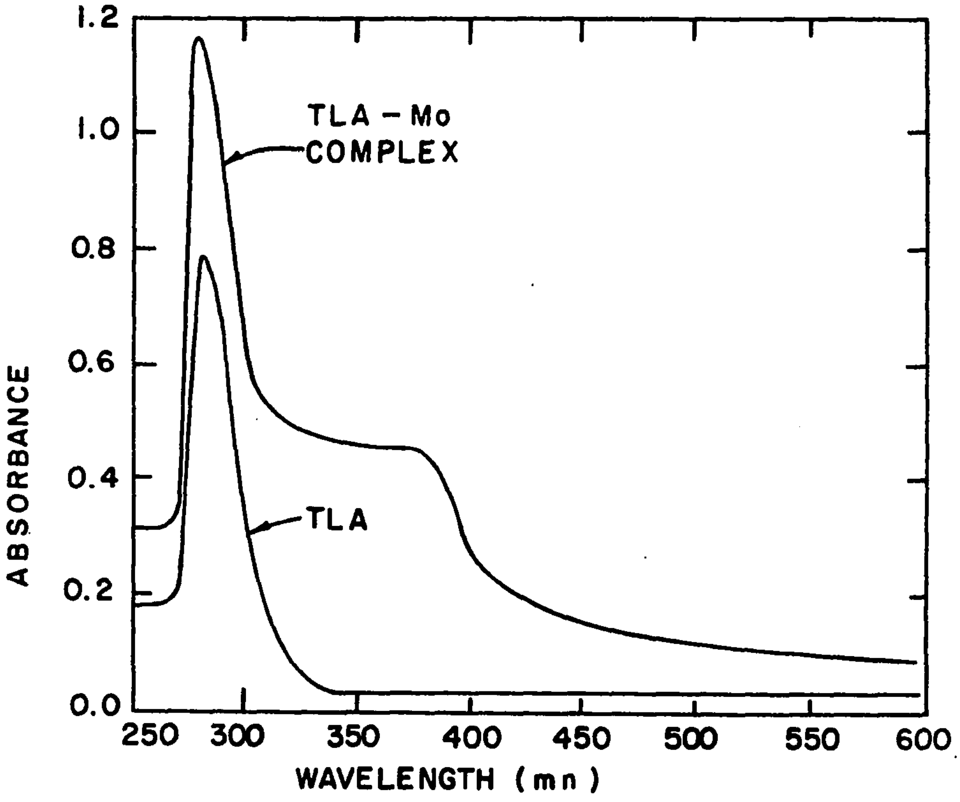


Figure 21. The absorption spectra of thiolactic acid (TLA) and the TLA-Mo complex in perchloric acid solution (Mo = 2×10^{-4} M)

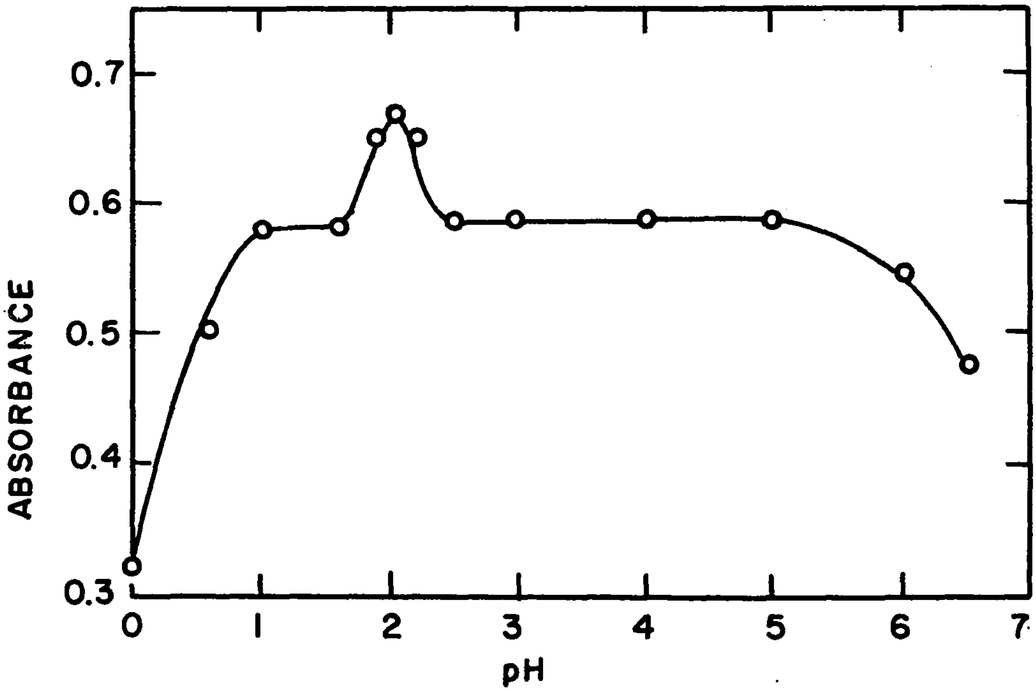


Figure 22. The effect of pH on the absorbance of the TLA-Mo complex (Mo = 2 x 10^{-4} $\underline{M}$)

Effect of acids: Sulfuric, hydrochloric and perchloric acids were used to adjust the pH of the analytical solutions. None of these interfered with the determination of molybdenum except in the presence of antimony, tin and uranium. The chloride forms of these ions caused high results.

Effect of foreign ions: The absorbance of solutions containing 5 μmole of molybdenum and 500 times as much (2.5 mmole) of a foreign metal ion was measured. The following ions caused no interference: Na(I), Al(III), K(I), Ca(II), Cr(III), Ni(II), Zn(II), Ga(III), Sr(II), Y(III), Zr(IV), Cd(II), La(III), Yb(III), Hf(IV), Hg(II), Pb(II) and Th(IV). In sulfuric acid solution 2.5 mmole of tin(IV), antimony(V) or uranium(VI) caused no interference, but did interfere seriously in hydrochloric acid solution. Vanadium(V) and chromium(VI) were reduced to vanadium(IV) and chromium(III) respectively. These did not interfere with the determination of molybdenum if sufficient TLA was added to compensate for the amount consumed in the reduction.

Copper(II) and iron(III) caused some error in the molybdenum determination unless a suitable masking agent was added. Phosphoric acid effectively masked iron(III), and thiourea masked copper(II) if the absorbance of the latter was read within 10 minutes (Table 7). Tungsten(VI) caused no error if tartrate was added and bismuth did not interfere if EDTA was present. Of the metals studied, only gold(III), platinum(IV) and silver(I) interfered with the molybdenum determination.

The effect of several anions was investigated. Sulfate, perchlorate, phosphate or chloride (5.0 mmole), EDTA (2.5 mmole), and acetate, nitrate, tartrate and citrate (1.0 mmole) caused no error. Fluoride caused low results.

Table 7. Masking agents used in reducing interference in the absorption of the TLA-Mo complex

Ion	mmoles added	Masking agent	mmoles added
Cu	0.25	thiourea	2.4
Fe	0.25	H_3PO_4	1.5
Bi	0.25	EDTA	2.5
W	0.25	tartrate	1.0

Stability of complex

The use of thioglycollic acid according to the method of Will and Yoe (95) yielded a slightly turbid solution. The addition of potassium chlorate suggested by these researchers did not eliminate this interference. This turbidity did not form when using TLA. The TLA-Mo complex was found to be stable for 24 hours.

Beer's Law

The complex obeys Beer's Law for molybdenum concentrations between 2.5×10^{-5} and 4×10^{-4} $\underline{M}$ (Figure 23). The molar absorptivity was 2800 l. moles^{-1} cm^{-1} at 365 nm and a pH of 1.0-1.6.

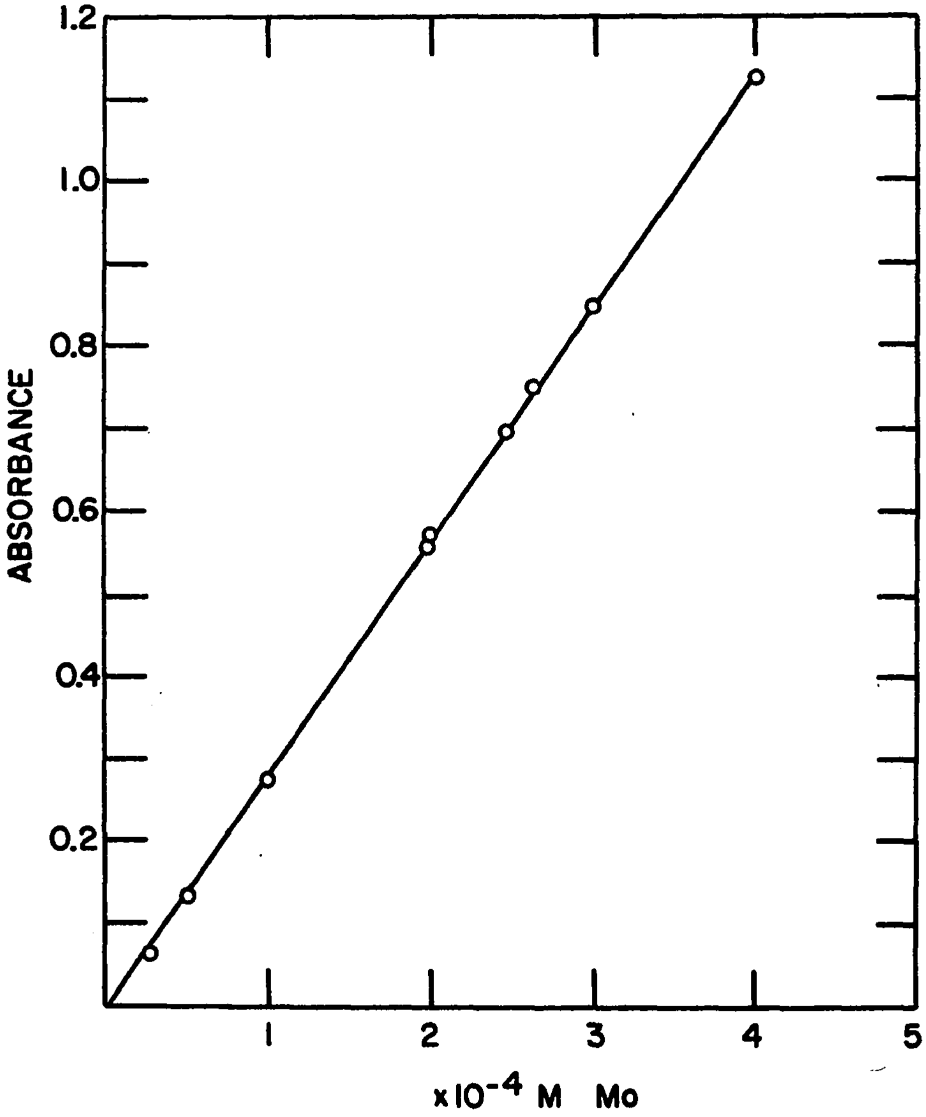


Figure 23. Conformance of the TLA-Mo complex with Beer's Law at 365 nm

Procedure

Take a sample containing 1.25 to 20 µmoles (120 to 1915 µg) of molybdenum and dilute to 35 ml. Add a masking agent if required (see Table 7). Adjust the pH to 1.0-1.6 with sulfuric acid, perchloric acid or sodium hydroxide. Transfer to a 50 ml volumetric flask, add 0.5 ml of TLA and dilute to volume with water. Measure the absorbance at 365 nm vs. a blank prepared the same as the sample. This absorbance must be measured within 10 minutes if copper(II) is present.

Investigation of Molybdenum(VI)

Batch distribution ratio

The results of the paper chromatographic study discussed previously, suggest that molybdenum can be removed from acidic solutions by toluene solutions of HEO or DHDO. The effect of oxime and hydrogen ion concentration on the efficiency of the extraction was determined by a series of batch extractions according to the general procedure described previously.

A 0.0061 M solution of molybdenum in either 0.01 N hydrochloric or sulfuric acid was extracted with oxime solutions of various concentrations. Table 8 presents the variation of the D values with the oxime concentration. The distribution ratio increases with increasing oxime concentration. The straight chain HEO is a better extractant than the branch chain DHDO. Lower results are obtained from hydrochloric than from sulfuric acid solutions since the chloride ion can form MoO_2Cl_2 (18) and compete with the oxime for the MoO_2^{++} ion.

Table 8. Distribution ratios of molybdenum(VI) between acid solutions and toluene solutions of HEO and DHDO as a function of the oxime concentration (Mo = 0.0061 M)

Acid	M oxime	Distribution ratio	
		HEO	DHDO
0.01 N HCl	0.25	163	118
	0.12	47	34
	0.10	35	24
	0.05	12	8
0.01 N H_2SO_4	0.20	591	204
	0.10	160	60
	0.05	31	20
	0.02	3	2

The relationship of the distribution ratio and the pH of the aqueous phase is presented in Table 9 and graphically in Figure 24. The D increases to a maximum with increasing proton concentration and then decreases sharply. Taylor and Austin (87) obtained better extractions of molybdenum with benzoinoxime at hydrogen ion concentrations of 0.9 M than at either 0.01 or 2.8 M. Weiss and Lai (93) reported the same trend in their study of recovering ultra-micro amounts of molybdenum from sulfuric acid solutions by precipitation with benzoinoxime. The recovery reached a maximum between pH 1.8 and 3.0 and decreased sharply to 55% at pH 0. The data in Table 9 show the same trend although the maximum is shifted to a lower pH value.

Figure 24. The distribution ratio of molybdenum(VI) between 0.01 N sulfuric acid and toluene solutions of HEO as a function of the hydrogen ion concentration (Mo = 0.0061 M)

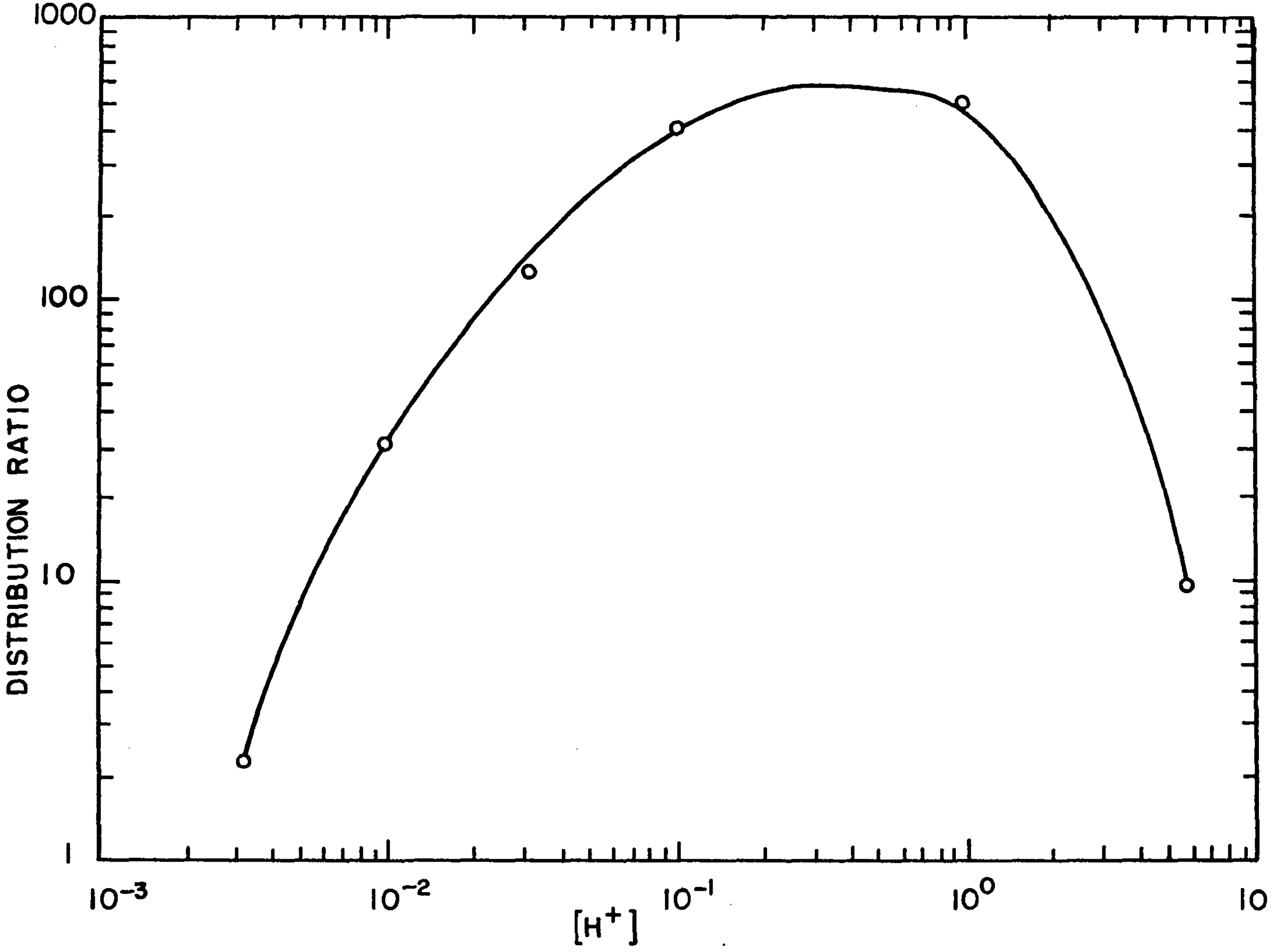

DISTRIBUTION RATIO
1000
100
10
1
10^{-3}
10^{-2}
10^{-1}
10^{0}
10
$[H^+]$

Table 9. Distribution ratios of molybdenum(VI) between acid solutions and toluene solutions of HEO as a function of the hydrogen ion concentration (HEO = 0.10 M)

Hydrogen ion concentration	pH	Distribution ratio
6.0×10^{0}	-0.8	10
1.0×10^{0}	0.0	500
1.0×10^{-1}	1.0	351
3.2×10^{-2}	1.5	122
1.0×10^{-2}	2.0	34
3.2×10^{-3}	2.5	3

The chemistry of molybdenum is complex. It can form isopolymeric and heteropolymeric ions in acidic solutions (13, 21, 63). The nature of these ions and the relationship between their formation and the acidity of the solution is not fully understood.

Characterization of the Mo-HEO complex

The MoO_2^{++} ion is one species that has been reported to be formed in acid solutions (54, 91). Hoenes and Stone (45) suggest that the α-benzoinoxime complex was formed with this ion. They reported that the molybdenum concentration of the α-benzoinoxime complex was 16.45% compared to the theoretical 16.51% for the MoO_2(α-benzoinoxime)$_2$ complex postulated by these researchers.

Factors which affect the relationship between the hydrogen ion concentration and the distribution ratio are first, the consumption of hydrogen ions to break up the isopolymeric molybdenum species, and second, the ionization of the oxime to form the ionic species necessary for a neutral complex. If the molybdenum species in the sample solution is the $Mo_7O_{24}^{-6}$ ion (13, 50) and if the MoO_2^{++} ion is utilized in forming the oxime complex (11, 91), the following combination of reactions could take place.

$$20\ H^+ + Mo_7O_{24}^{-6} \text{ ---------> } 7\ MoO_2^{++} + 10\ H_2O$$

and

$$7\ MoO_2^{++} + 14\ H_2Ox \text{ -----> } 7\ MoO_2(HOx)_2 + 14\ H^+$$

The net effect is the consumption of 0.86 protons per molybdenum.

This value will change with the equilibrium mixture of polymeric species and account for the consumption of hydrogen ions at the higher pH values. Figure 24 indicates that hydrogen ions are consumed at varying rates during the formation of the complex.

Consider the oxime to ionize as follows:

$$H_2Ox \text{ ----> } HOx^- + H^+ \quad \text{then} \quad K_a = \frac{[H^+]\,[HOx^-]}{[H_2Ox]}$$

A continual increase of the hydrogen ion concentration will suppress this ionization. Therefore, the formation of the HOx^- ion needed to form the neutral complex will decrease, followed by a decrease in the distribution ratio. This can explain the sharp decrease of D values below pH 0 and the trend reported by Weiss and Lai (93) when using α-benzoinoxime. The total effect of pH is a combination of the above reactions.

The data from Table 8 is presented graphically in Figure 25. The slope of the best straight lines through these points indicates that two oxime molecules are associated with each metal ion. Parallel slopes were obtained from hydrochloric acid solutions. A treatment of similar data was presented previously for the formation of the Cu-oxime complex.

The Mo-HEO complex was extracted from an aqueous solution of ammonium paramolybdate where the hydrogen ion concentration was 1.5×10^{-2} $\underline{M}$. According to the NMR spectrum (Figure 26), the hydroxyl hydrogen at δ 3.9 was removed from the ligand during the formation of the complex while the oxime hydrogen at δ 4.3 remained on the ligand.

If the complex contains the MoO_2^{++} ion as suggested by Hoenes and Stone (45) and Tourky and El Shany (91), the infrared spectrum should show evidence of a Mo=O stretching frequency.

The infrared spectrum (Figure 27) contained three absorption bands in the 870-950 cm^{-1} region that were not assigned to the parent ligand. It was reported that M=O double bonds gave absorption bands between 850 and 1000 cm^{-1} (5, 66, 68). The frequency varied with the amount of double bond character. Barraclough and Nyholm (5) and Nakamoto (68) stated that any absorption in this region was strong evidence for a metal-oxygen double bond providing that an atom of similar mass (e.g. nitrogen) was not bonded to the metal in a like manner. This spectrum suggests that the complex is $MoO_2(HEO)_2$.

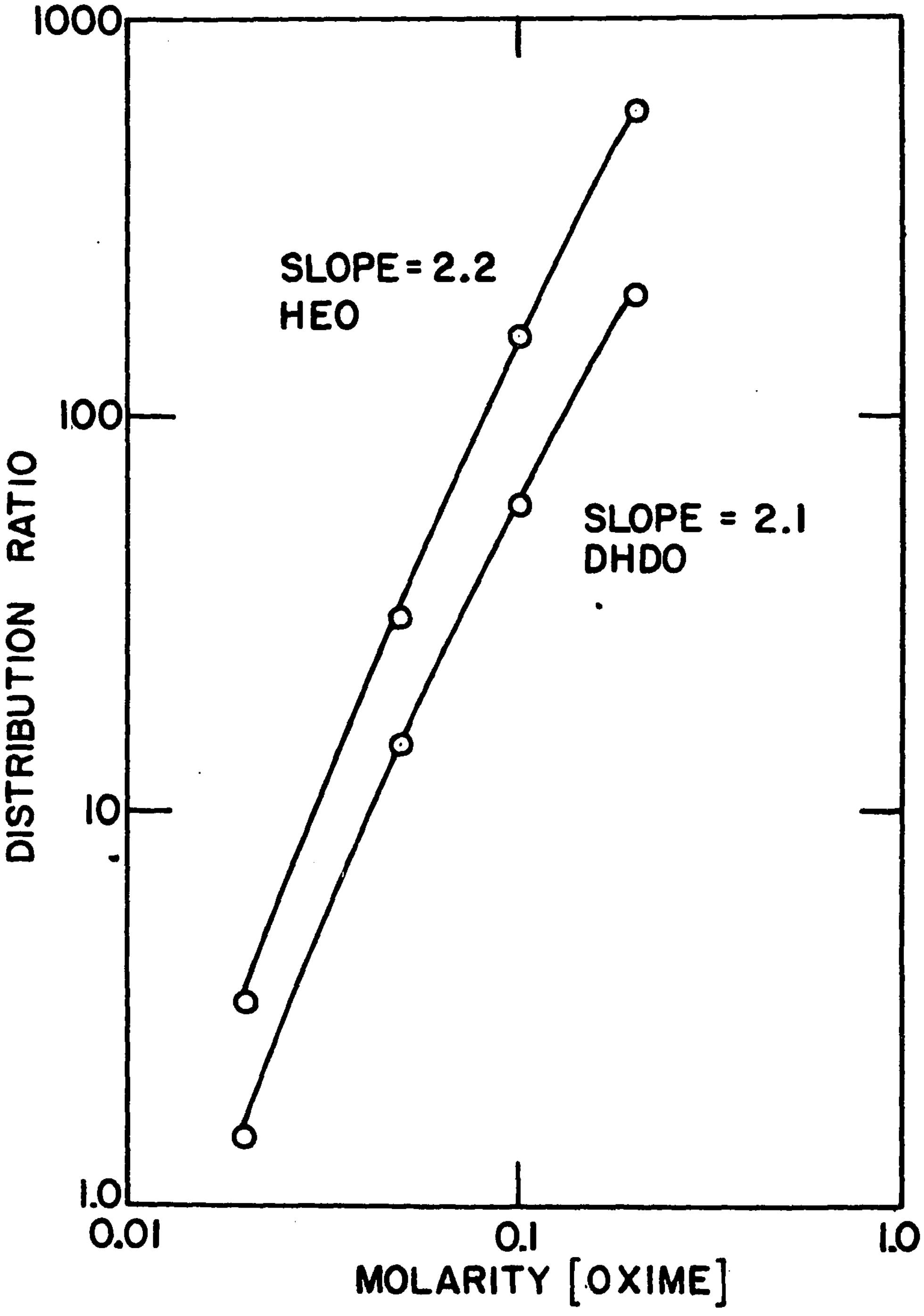


Figure 25. The distribution ratio of molybdenum(VI) between 0.01 N sulfuric acid and oxime solutions as a function of the oxime concentration (Mo = 0.0061 M)

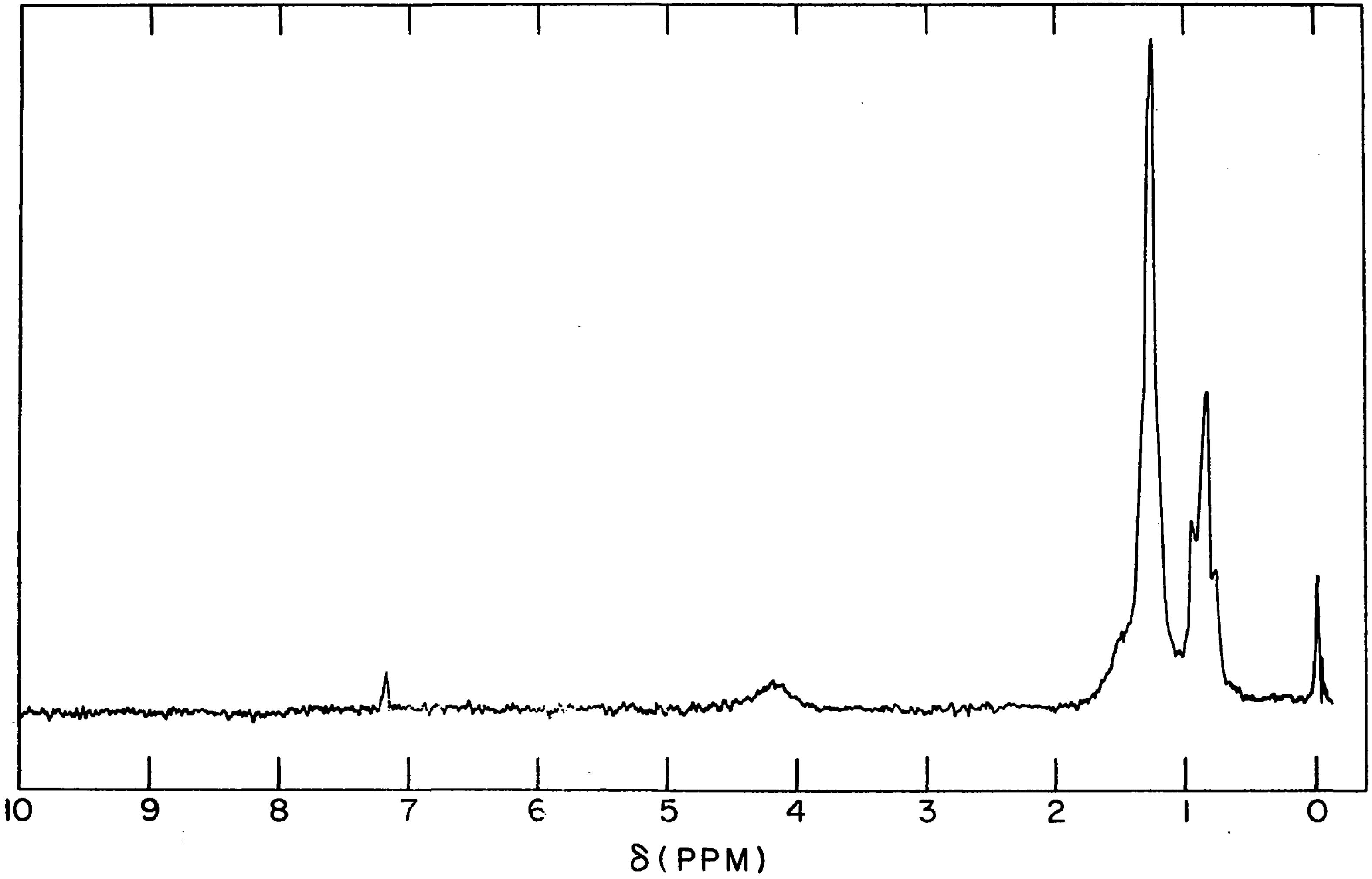


Figure 26. The NMR spectrum of the $(HEO)_2MoO_2$ complex

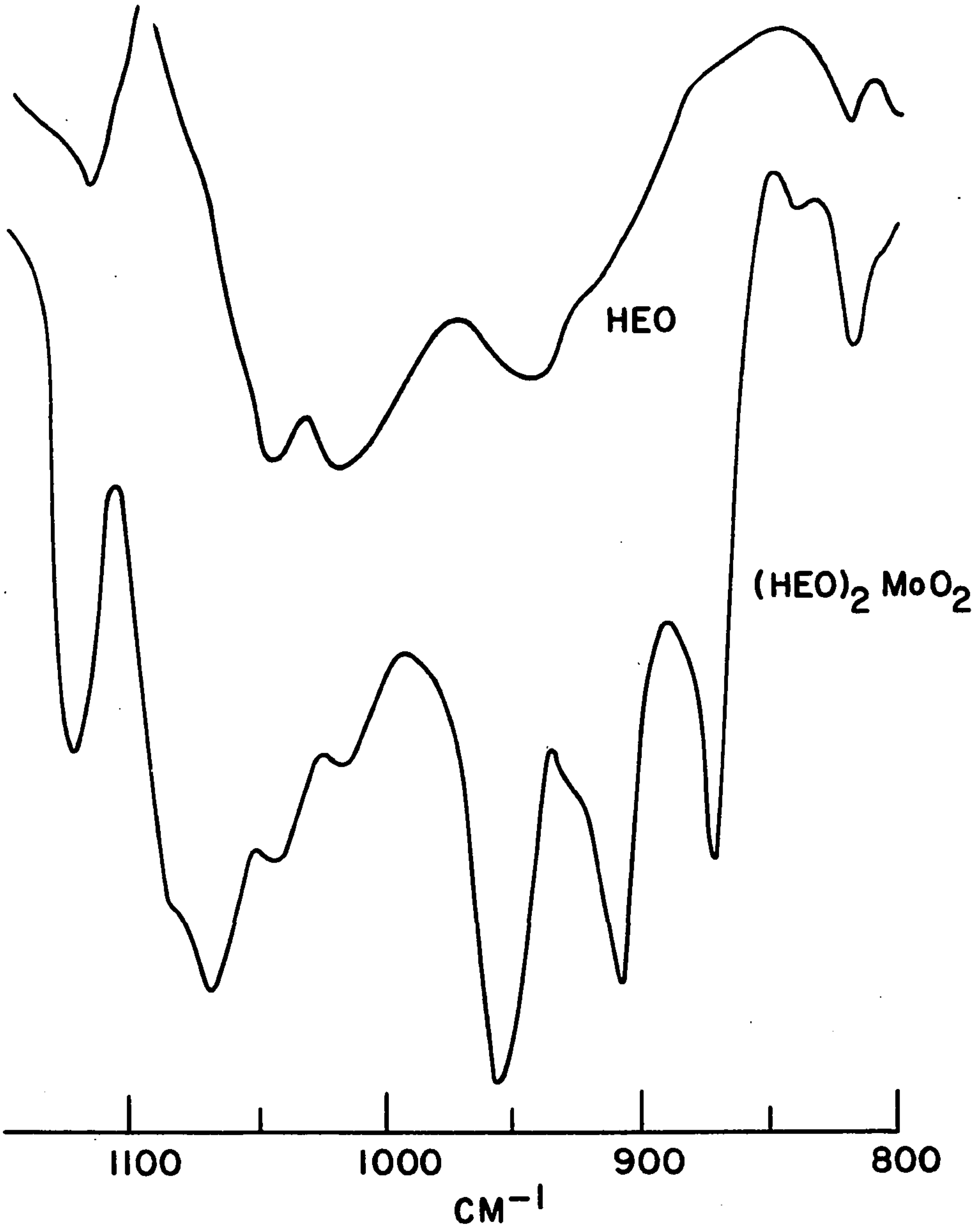
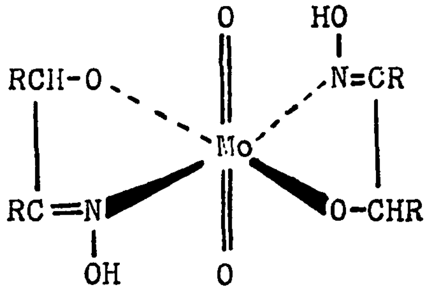
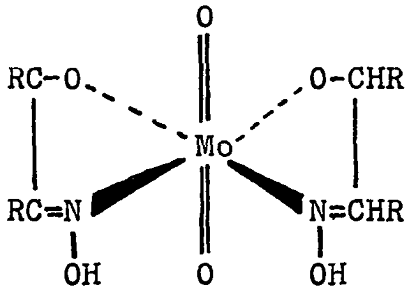


Figure 27. The infrared spectra of HEO and (HEO)$_2$MoO$_2$ complex

Two structures that are compatible with the above findings are shown below.





The symbol R represents the C_9H_{19} group.

It is not the purpose of this study to make assignments for the spectral bands or to exhaustively study the isomerism of the complex. These structures are mentioned as possibilities and left for a later investigation.

Column separations

The procedure for separating molybdenum from other metal ions was the same as for copper except as noted below. The column of 20% HEO or DHDO was preconditioned with 0.1 N sulfuric acid. All metals, except molybdenum, were eluted with 0.01 N sulfuric acid although 0.01 N hydrochloric acid was also satisfactory. The molybdenum was eluted with either a solution of sodium carbonate (pH 12) or ammonium hydroxide (pH 12). The solution of sodium carbonate was preceded by a portion of distilled water to reduce the acid in the column and minimize the formation of carbon dioxide. However, some gas was still formed and caused disruption of the resin bed.

The ammonium hydroxide solution was used in most of the separations. The molybdenum content of the effluent was determined by the absorbance of the thiolactic acid complex as described previously.

Molybdenum was separated from each of 10 other metals. When using a column of 20% HEO, the average recovery of molybdenum from these separations was 99.4% while the average recovery of the other metals was 99.8%. These separations are listed in Table 10.

When a column of DHDO was used, the average recovery of molybdenum decreased to 68.6%. The column packing turned blue, indicating a reduction of some molybdenum(VI) to molybdenum(V) to form a molybdenum blue type compound of mixed oxidation states. This phenomenon was not noticed when using HEO. It was prevented by adding 10-15 drops of bromine water to the metal solution before introducing it onto the column. The separation of molybdenum(VI) from other metals on a column of DHDO was then successful with an average recovery of 99.1% for molybdenum and 100.2% for the other ions. This compares favorably with the data in Table 10 using HEO. A small amount of tartrate was added to the metal solutions containing iron and tungsten. This did not affect the efficiency of the separation. A typical elution curve is shown in Figure 28.

The kinetics involved in retaining the molybdenum on the column appeared to be somewhat slow. When the effluent flow

Table 10. Separation of molybdenum from aqueous solutions of metal ions using a 9 x 62 mm column of 20% HEO on Amberlite XAD-2 support (eluents = 0.01 N sulfuric acid for ion A and ammonium hydroxide pH 12 for molybdenum)

Separation			ml to complete elution	mmoles taken	Activity taken CPM	Percent recovery
I	a.	Fe(III)	15	0.0273		99.6
	b.	Mo(VI)	24	0.0248		99.7
II	a.	Ni(II)	15	0.0318		101.2
	b.	Mo(VI)	24	0.0248		98.2
III	a.	Co(II)	15	0.0337		99.6
	b.	Mo(VI)	24	0.0248		99.6
IV	a.	Zn(II)	15	0.0472		99.5
	b.	Mo(VI)	24	0.0248		98.9
V	a.	Cu(II)	15	0.0286		100.7
	b.	Mo(VI)	24	0.0248		99.2
VI	a.	Sn(IV)	15		12,310	98.9
	b.	Mo(VI)	24	0.0248		100.3
VII	a.	W(VI)	15		83,548	99.1
	b.	Mo(VI)	24	0.0248		100.1
VIII	a.	Cd(II)	15	0.0362		100.3
	b.	Mo(VI)	24	0.0248		99.2
IX	a.	Hg(II)	12	0.0362		100.0
	b.	Mo(VI)	24	0.0128		100.0
X	a.	Th(IV)	12	0.0365		100.0
	b.	Mo(VI)	24	0.0128		100.2

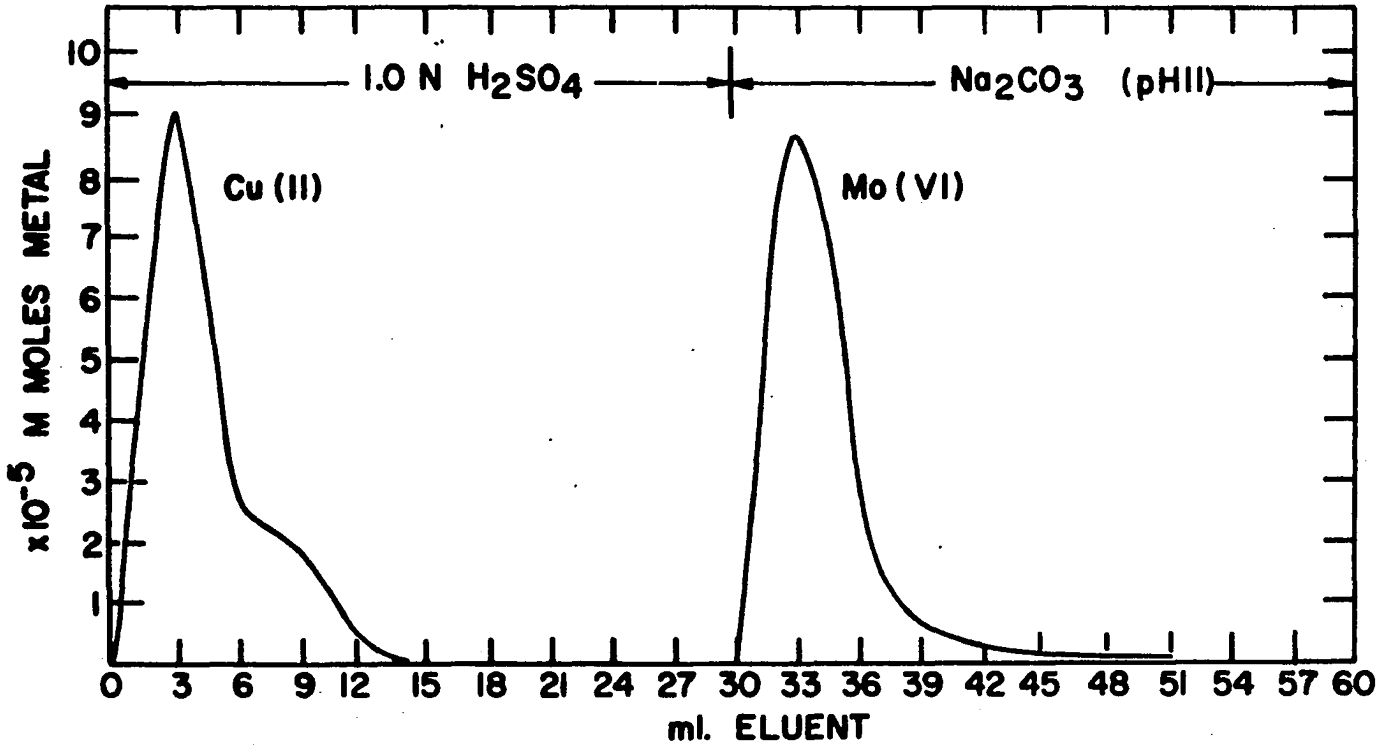


Figure 28. Elution curves for 0.0134 mmoles copper(II) and 0.0123 mmoles molybdenum(VI) from a 9 x 62 mm column containing Amberlite XAD-2 (flow rate approximately 5 ml/min) impregnated with DHDO

was increased from 4 ml per minute to 10 ml per minute, the molybdenum bled through with the elution of the other metals.

Column capacity

The capacity of HEO and DHDO for molybdenum was found by saturating the columns with the molybdenum(VI) ion and determining its breakthrough point. The capacity was 0.24 moles Mo/mole HEO and 0.20 moles Mo/mole DHDO. This corresponds to an oxime:Mo ratio of 4.16 and 5.0 for HEO and DHDO respectively. Taylor and Austin (87) reported that when extracting molybdenum with α-benzoinoxime, the concentration of the oxime must be 4-6 times the concentration of molybdenum to obtain quantitative extraction. The capacity of the HEO and DHDO show that this is true when using the aliphatic α-hydroxyoximes also.

Analysis of National Bureau of Standard samples

National Bureau of Standard samples no. 160 and 168, high nickel and cobalt, low carbon and silicon, were dissolved in 6 M hydrochloric acid while adding just enough concentrated nitric acid to effect a solution. The solution was heated to boil off the excess nitrogen oxides and filtered to remove the carbon and silicon dioxide. The residue was washed with a 0.1 M solution of hydrochloric acid. After diluting and adjusting the pH to 1.0, 5-10 drops of aqueous bromine were added to prevent the reduction of molybdenum(VI). The sample was passed through a prepared 20% (w/w) HEO column where the molybdenum was separated from the other metals by the procedure described previously. Tartrate was added to sample no. 168 to prevent problems with tungsten. The necessity of adding the tartrate was not determined. Its use was a precautionary procedure.

Sample no. 107, a high carbon, high silicon alloy, was treated the same as above except that 6 M sulfuric acid was used in place of hydrochloric acid and the insoluble residue was washed 4 times with 0.1 N sulfuric acid.

The major elements reported in these samples and the recovery of molybdenum are listed in Table 11. The average recovery of molybdenum from the heat resistant, chrome-nickel alloys, nos. 160 and 168, was 99.1%. The recovery was lower (96.2%) in the high carbon and silicon steel sample no. 107. It is possible that the molybdenum was not completely washed from the heavy residue remaining from the initial treatment.

Table 11. Analysis of molybdenum(VI) in National Bureau of Standard samples (triplicate analysis)

Sample number	Major elements	Percent reported	Percent found
107	C	2.57	
	Si	2.34	
	Mo	.687	.661
160	Cr	19.12	
	Ni	8.91	
	Mo	2.59	2.57
	Si	1.13	
168	Co	41.20	
	Cr	20.33	
	Ni	20.35	
	Mo	3.95	3.90
	W	3.95	
	Nb	2.95	

Investigation of Silver(I)

Batch distribution ratio

The paper chromatographic study (Figure 8) suggests that silver can be extracted from aqueous solutions by a toluene solution of DHDO. A series of batch extractions were made at varying concentrations of DHDO and hydrogen ions according to the general procedure described previously. These results are tabulated in Table 12 and presented graphically in Figures 29 and 30.

Table 12. Distribution ratios of silver(I) between acetate solutions and toluene solutions of DHDO at varying concentrations of DHDO and hydrogen ions (Ag = 0.0063 M)

pH	Molarity DHDO	Distribution Ratio
3.0	0.031	0.12
3.0	0.063	0.28
3.0	0.125	0.63
3.0	0.472	2.3
4.0	0.031	0.13
4.0	0.063	0.37
4.0	0.125	1.1
4.0	0.472	9.7
4.6	0.031	0.14
4.6	0.063	0.43
4.6	0.125	1.6
4.6	0.472	17.5
4.9	0.472	21.5
6.0	0.031	0.12
6.0	0.063	0.43
6.0	0.125	1.6
6.0	0.472	23.8

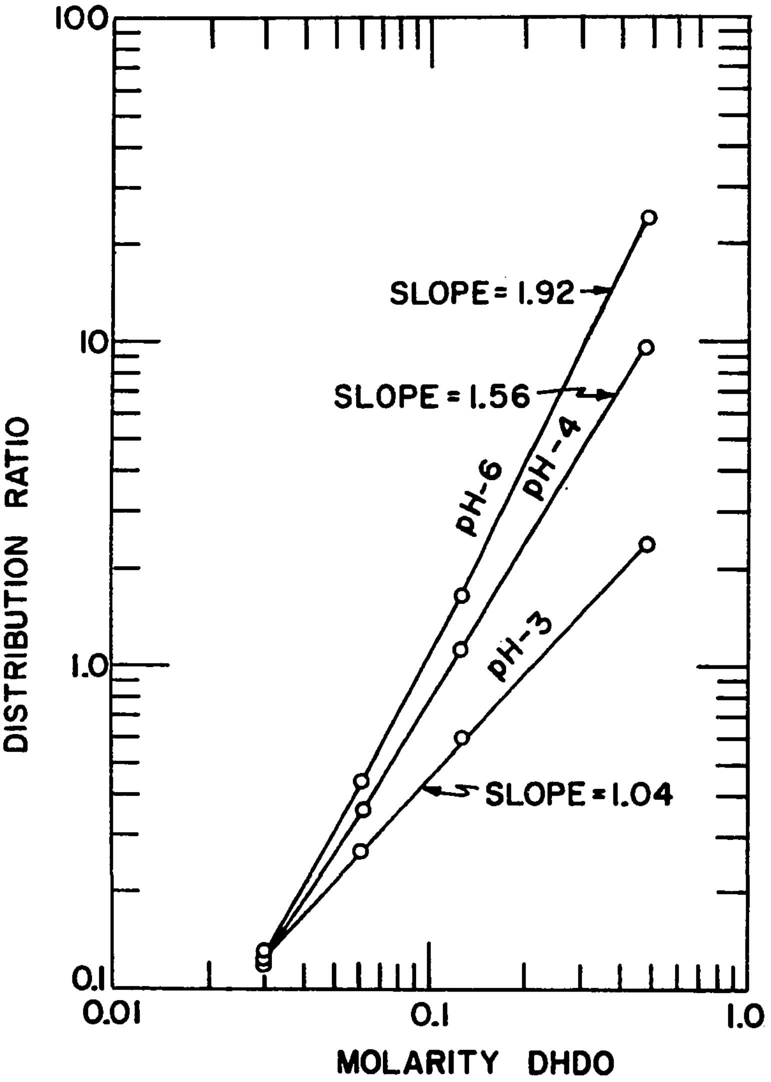


Figure 29. The distribution ratio of silver(I) between acetate and DHDO solutions as a function of the DHDO concentration at various pH values (Ag = 0.0061 M)

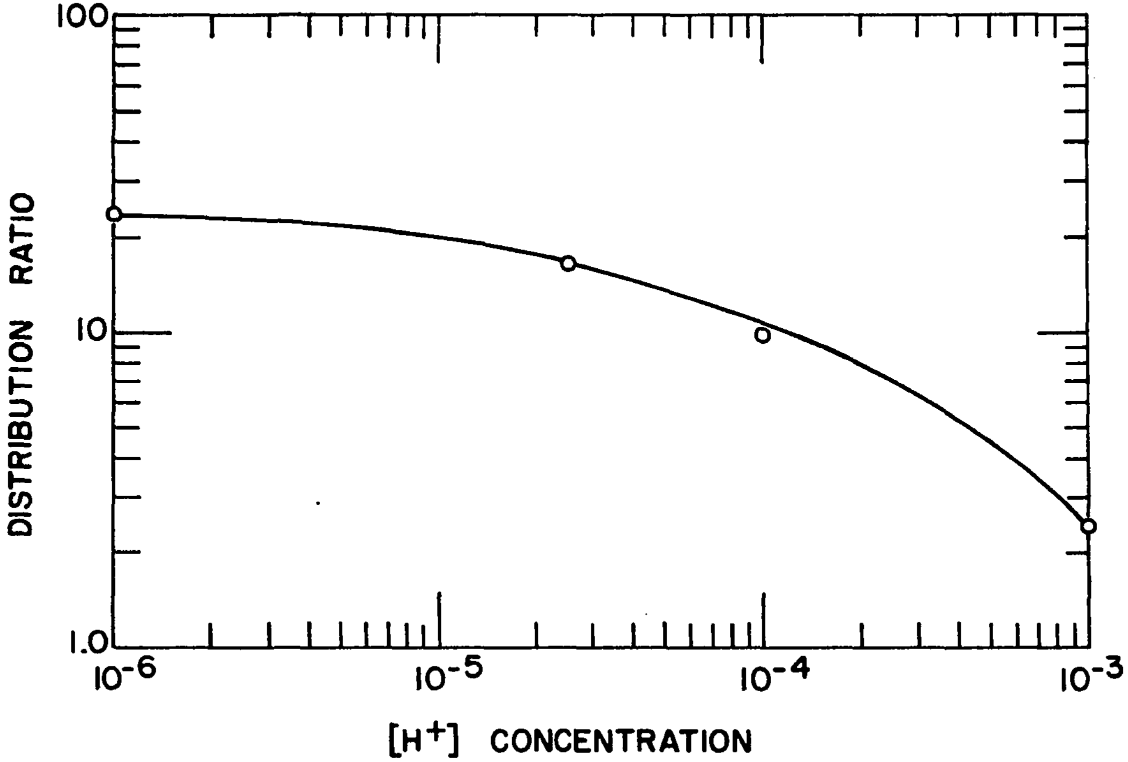


Figure 30. Dependence of the distribution ratio on the hydrogen ion concentration for the extraction of 0.006 M silver by 0.472 M DHDO

The slopes of the lines in Figure 29 indicate that the complex formed at pH 3 had one oxime associated with each silver ion while the one formed at pH 5-6 had two oximes in the coordination sphere of the silver ion. The complex formed at pH 4 appears to be a mixture of these. The data for pH 4.6 was not plotted since it was almost congruent with that for pH 6.

In a 1:1 complex, each oxime must lose one hydrogen to obtain charge neutralization. In a 2:1 complex, the loss of hydrogen should be 0.5 hydrogen per oxime to form a neutral complex. Figure 30 suggests that the number of hydrogens lost during the formation of the silver complex changes with the pH. The slope of the best straight line between pH 3 and 5 was computed to be 0.52. The formation of a $Ag(DHDO)_2$ complex at pH 5 is, therefore, a reasonable assumption.

The above discussion is not intended to be conclusive evidence for the type of complex formed but is mentioned as an initial interpretation of the data. A more complete interpretation of the Ag-DHDO complex including its structure is reserved for a later investigation.

Column separations

The procedure for separating silver(I) from other metal ions was the same as for copper except that a 35% (w/w) solution of the DHDO (0.96 mmole) was used as the substrate on the XAD-2 resin. The column was preconditioned with acetate buffer of pH 5. All metals investigated, except silver, were eluted with acetate buffer (pH 5) while silver was retained on the column. Silver was later eluted with 9 M hydrochloric acid. A 6 M solution of the acid was used in one experiment and caused severe tailing of the silver band.

Silver was successfully separated from ten other metals with an average recovery of 99.9% for silver and 100.0% for the other metals. The results of these separations are listed in Table 13. A separation of copper from silver was attempted by using an acetate buffer of pH 3. It was believed that at this pH, copper would pass through the column while silver would be retained. The separation was not successful since copper tailed severely into the elution of the silver. Lengthening the column from 7.0 cm to 14 cm did not resolve these metals. A typical elution curve for the Ni-Ag separation is shown in Figure 31.

Capacity of DHDO

The capacity of the DHDO for silver was determined by saturating the column with a solution of radioactive silver and locating the initial appearance of the activity in the eluent. The capacity was low at 0.12 moles silver per mole of DHDO. This low capacity necessitated the use of higher loading of DHDO for column separations than used for copper or molybdenum. It also limits the use of DHDO in separating large amounts of silver from other metals. However, separations were possible and the interference of silver with the separation of copper from other metals was indicated.

Table 13. Separation of silver from aqueous solutions of metals using a 9 x 62 mm column of 30% DHDC on Amberlite XAD-2 support and acetate solution (pH 5) as an eluent for ion A and 9 *M* hydrochloric acid for silver

Separation			ml to complete elution	mmoles taken	Activity taken CPM	Percent recovery
I	a.	Ni	15	0.0332		99.6
	b.	Ag	21		94,832	99.9
II	a.	Pb	15	0.0371		100.3
	b.	Ag	21		94,371	99.8
III	a.	Co	9	0.0256		99.6
	b.	Ag	21		94,832	99.8
IV	a.	Fe	15	0.0371		99.7
	b.	Ag	21		94,371	99.8
V	a.	Cd	15	0.0411		99.5
	b.	Ag	21		101,756	99.7
VI	a.	Zn	9	0.0272		100.4
	b.	Ag	21		36,910	99.9
VII	a.	Th	15	0.0470		100.0
	b.	Ag	21		35,217	99.9
VIII	a.	Pt	9	0.0392		100.0
	b.	Ag	21		31,927	99.9
IX	a.	Hg	15	0.0371		100.5
	b.	Ag	21		31,729	100.0
X	a.	Bi	15	0.0472		100.2
	b.	Ag	21		31,876	99.9

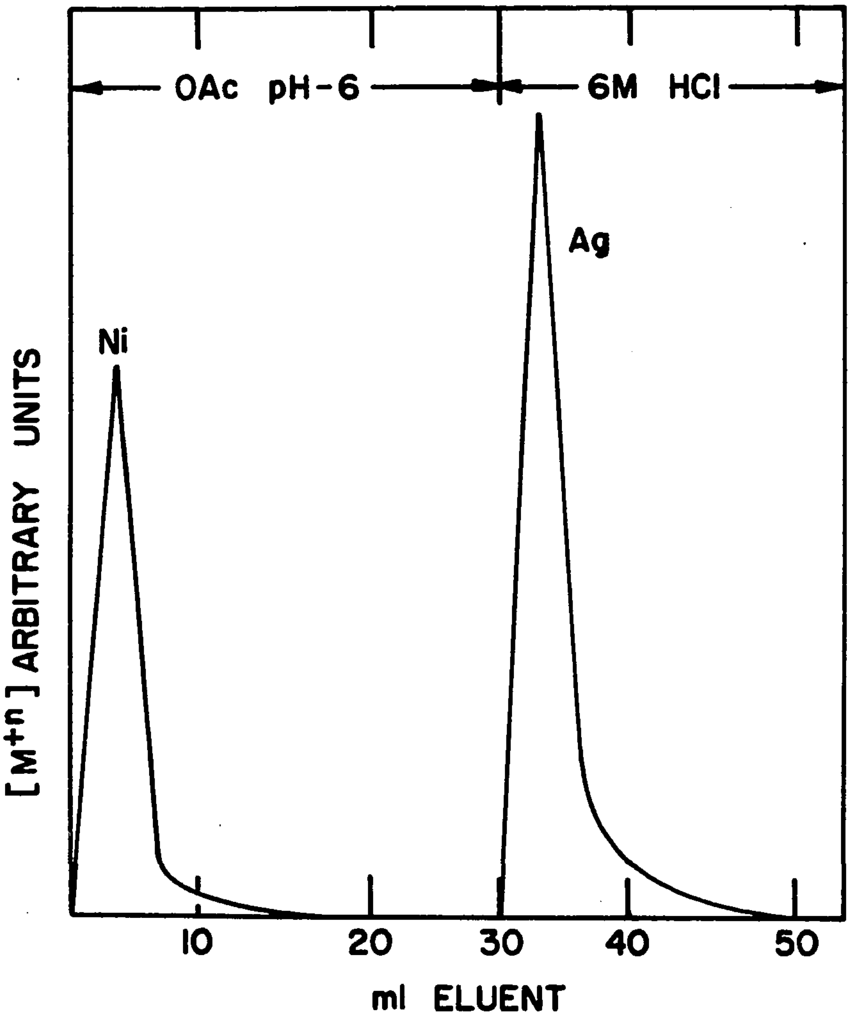


Figure 31. Elution curves for equal concentrations of Ni(II) and silver(I) from a 9 x 70 mm column containing XAD-2 resin impregnated with DHDO

Investigation of Other Metals

The data from Figures 6 and 8 suggest that palladium and gold would be retained by a column of HEO or DHDO. The action of these metals on a column were of minor interest in this investigation. Their retention would indicate an interference with the separation of copper, molybdenum and silver from other metals; therefore, a brief discussion of these metals is included in this presentation.

Palladium

Palladium is associated with sperrylite ($PtAs_2$) in the copper-nickel ores of Sudbury, Ontario. Other minerals associated with platinum and palladium are chromite ($FeCr_2O_4$) and various iron-magnesium minerals such as olivene and pyroxine (8, 20). Palladium was separated from seven other metals including those associated with it in nature. Palladium was retained by the 20% DHDO column when using an acetate buffer (pH 5) to elute the other metal. These separations are tabulated in Table 14. The effluent from the separations was tested with sulfide ion to determine the presence or absence of the metals.

Table 14. Separation of palladium(II) from other metal ions on a 9 x 62 mm column of 35% DHDO on Amberlite XAD-2 support and using acetate solution (pH 5) as an eluent for ion A and 9 M hydrochloric acid for palladium

Metal	mmoles taken	ml to complete elution
Ni(II)	0.0238	9
Pd(II)	0.0248	24
Co(II)	0.0369	9
Pd(II)	0.0248	24
Cu(II)*	0.0246	9
Pd(II)	0.0248	24
Pt(II)	0.0120	8
Pd(II)	0.0248	24
Zn(II)	0.0362	12
Pd(II)	0.0248	24
Fe(III)	0.0321	15
Pd(II)	0.0248	24
Cd(II)	0.0492	15
Pd(II)	0.0248	24

*Acetate buffer pH 3 used to elute copper.

Gold

A gold solution was placed on columns of 20% DHDO and HEO equilibrated with acetate buffer (pH 5). The gold was retained on each column. Solutions of 6 M and 9 M perchloric or hydrochloric acid were unsuccessful in removing all of the gold from the column. That remaining on the resin was reduced to the violet color of colloidal gold. This should be soluble in aqua regia or potassium cyanide. Aqua regia was not used because of the possibility of changing the characteristics of the substrate by nitration and cyanide solution was not used because of its potential safety hazard. Acetone removed the gold from the column along with the oxime substrate. Recharging the column with a new oxime solution was necessary before proceeding with the next separation. The above discussion exemplifies the interference of gold in the separation of copper, molybdenum and silver from aqueous solutions as described previously.

Fritz and Millen (38) have developed a method to remove gold from 1 M hydrochloric acid solution. The gold was sorbed onto a column of Amberlite XAD-7, a porous polyacrylate resin made by Rohm and Haas Inc. Acetone was used to elute the gold from the short column. The use of acyloin oximes appeared to have no advantage over the method of Fritz and Millen. Therefore the above study was not pursued further.

SUMMARY

A straight chain and a branch chain α-hydroxyoxime, 10-hydroxyeicosan-9-oxime (HEO) and 5,8-diethyl-7-dodecanone-oxime (DHDO) respectively, were investigated to determine their usefulness in the quantitative separations of metal ions in aqueous solutions. Paper chromatography was used to rapidly determine interactions between metal ions and the oxime substrates and point out possible separation systems.

The distribution coefficients of metals having strong interactions with the oximes were determined at various oxime and proton concentrations. Graphical interpretation of these data, supported by NMR and infrared spectra of the metal-oxime complexes gave some insight into the structure of the complexes. Structures for the copper and molybdenum complexes were suggested.

These aliphatic α-hydroxyoximes demonstrate greater selectivity than their aromatic counterpart, α-benzoinoxime. By proper choice of substrates and eluents, copper(II), molybdenum(VI), silver(I) and palladium(II) were separated from a number of metal ions using chromatographic columns of Amberlite XAD-2 impregnated with HEO or DHDO. These separations were rapidly made using short columns, with the above metals being retained on the resin in tight bands. Gold(III) was also removed from aqueous solutions but it was not completely recovered from the resin. Finally, to measure the usefulness of HEO and DHDO in analytical separations, a series

of National Bureau of Standard samples were successfully analyzed for copper or molybdenum.

The main emphasis of this work was to study the interaction of the oximes with copper and molybdenum. The short studies with silver and palladium were interesting by-products of the original purpose of this work. The specificity of these α-hydroxyoximes and their adaptability as substrates in reversed-phase chromatography make them useful as agents in the analytical separation of metal ions.

SUGGESTIONS FOR FUTURE WORK

A study of the extraction of vanadium(V), bismuth(III), chromium(VI) and titanium(V) by HEO or DHDO may add to the versatility of these reagents in analytical chemistry. Different experimental conditions may show that these metals can be extracted.

The use of unsaturated or unsymmetrical acyloin oximes as separation agents for metal ions could be investigated. Their reaction to gold and tungsten may be of interest.

A more complete structural study of the copper, molybdenum and silver complexes should be of interest to structural chemists. The neutral species filling the coordination sphere of these complexes was not determined in this investigation. An assignment of the absorption bands between 850 and 1050 cm^{-1} for the molybdenum complex may yield information about the isomerism of the complex.

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