121- 128

121

Acetohydroxamate Resin as Column Packing for Ion Chromatography

Min-Jane Chen (陳明娟), Jia-Der Fang (方嘉德) and Chuen-Ying Liu* (劉春櫻)
Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

A chelating resin with acetohydroxamate functional groups was synthesized and used as the stationary phase in ion chromatography for the determination of copper. As the reaction mechanism was mainly complexation, the coordination behavior of the synthesized resin toward Cu(II) was studied by means of EPR, IR and electronic spectrometry and potentiometry. The kinetic study shows that the resin is suitable for use in ion chromatography. We employed a resin column 250 mm long by 3 mm I.D. in conjunction with a mixture of hydrochloric acid and acetone as mobile phase for the determination of Cu(II). Detection of the chromatography system was carried out via post-column derivatisation of the column effluent with PAR at 520 nm. The detection limit is 0.22 ppm, and the relationship was linear in the range 0.25-1.20 ppm. We investigated the effect of other metal ions, As(V), Cd(II), Cr(III), Hg(II), Ni(II), Pb(II) and Zn(II), or foreign ligands, EDTA, ascorbic acid, humic acid or sodium chloride on the determination of Cu(II) ion. A concentration column packed with acetohydroxamate resin combined with the above separation system was also used to determine of copper ion; the dynamic range is 2-15 ppb and the detection limit is 0.70 ppb. The proposed system was applied to the analysis of Cu(II) in sea water.

INTRODUCTION

For the past twenty years, trace metals in a marine environment have been investigated extensively because of their biological and geochemical importance.[1] Their direct determination is possible by means of only a few techniques; a preconcentration step is generally needed. Solvent extraction has, until recently, been a popular method of separation for the preconcentration of metal ions before their determination; because the process is a batch method, it is unsuitable for the concentration of traces of ions in large samples. Most work on the determination of trace metals was devoted to ion-exchange techniques. Although ion-exchange separation of metal ions has been used in several important applications,[2] there remain problems associated with this approach, especially for a sample containing electrolyte in large concentration, such as sea water or a biological sample. Too great an ionic strength causes a temporary great change in column capacity of high-performance liquid chromatography, so preventing the separation. Incorporation of chelating agents in various supports as column-packing materials for the concentration and separation of metal ions has gained popularity because of their high concentrating ability and simple operation in the determination of trace metals in concentrated electrolytes. Chelating resins are well known in classical column chromatography, in which they were used principally for matrix isolation. However, there are few publications that describe separations of metal ions on high-performance liquid chromatographic (HPLC) grade or near HPLC-grade chelating stationary phases. We investigated the feasibility of applying a resin containing hydroxamic acid as the stationary phase of an ion chromatograph to separate and determine copper ion. Although the reaction mechanism in this system may involve ion exchange, adsorption and complexation, the predominant feature is complexation. Hence the coordination behavior of Cu(II) for the synthesized resin was also studied by means of EPR, IR and electronic spectrophotometry and potentiometry.

EXPERIMENTAL SECTION

Apparatus

IR spectra of the synthesized resin and its metal complexes in KBr, in the range 4000-200 cm^{-1}, were recorded on an infrared spectrophotometer (Perkin-Elmer 983). The electronic spectra were recorded on a spectrophotometer (Hitachi U-3200). The EPR spectra of the metal-resin complexes in the solid state at room temperature were recorded on an EPR spectrophotometer (Bruker ESP 300).

An ion chromatograph (Dionex Model 2000i) and a variable-wavelength detector (Dionex UV-VIS) were used. The system had a post-column derivatisation pump and a computing integrator (Hitachi Chromato Integrator D-2500) or a recorder (Dionex). A sample loop of volume 50 μL was employed, and a chemically inert glass column packed with acetohydroxamate resin was used in separation and concentration.

Reagents

The chemicals used in this investigation were all of reagent grade.

We prepared a copper(II) stock solution (10^{-2} M) by *dissolving pure copper* (>99.999%) (Fluka, Switzerland) in nitric acid, and prepared working solutions by diluting the stock solution just before use.

PAR Solution

A solution (4×10^{-4} mol L^{-1}) was prepared by dissolving 4-(2-pyridylazo)resorcinol monohydrate (102.08 mg) in ammonia-ammonium acetate buffer solution (1 L, pH 10-11).

Synthesis of the Acetohydroxamate Resin[3]

Separate solutions of hydroxylamine hydrochloride (140 g) in methanol (720 mL), and of potassium hydroxide (112 g) in methanol (280 mL), were prepared at the boiling point of the solvent. Both were cooled to 30-40 °C and potassium hydroxide solution was added, with shaking, to the hydroxylamine solution; excessive increase of temperature during the addition was prevented by cooling in an ice bath. After all alkali had been added, the mixture was allowed to stand in an ice bath for 5 min to ensure complete precipitation of potassium chloride. These hydroxylamine solutions were used to prepare the chelating resin.

A macroporous cross-linked copolymer was prepared by the reaction of acrylonitrile and divinylbenzene according to ref. 4. The hydrolyzed product of polyacrylonitrile-divinylbenzene copolymer was prepared.[4] The carboxylic acid resin was then converted to acetohydroxamate resin by *heating a mixture* (at pH 8-9) of the resin and hydroxylamine prepared as above at 70 °C in methanol for 30 h. The final product was collected by *filtration under* suction and washed sequentially with water, sulfuric acid (0.25 M), water and acetone.

Determination of Resin-Metal Complexation as a Function of pH

The metal complexation behavior as a function of pH *were studied in two ways*. We used a large excess of metal ion relative to the amount of resin to observe maxima in the metal uptake as a function of pH. We used limited amounts of metal ion so that the pH ranges for quantitative metal uptake could be determined.

In both procedures, samples (0.30 g) of resin (60/100 mesh) were weighed into polyethylene bottles (100 mL). Metal ion solution of varied pH was prepared by addition of the required amount of metal ion solution to a beaker (100 mL) with sodium acetate (1 M, 5 mL) and enough dis-tilled, deionized water to make a total volume about 30 mL. The pH of the samples was adjusted with perchloric acid and/or sodium hydroxide to the desired value; then the sample was quantitatively transferred into a volumetric flask (50 mL). The pH of the resulting solution was then measured.

Duplicate resin samples at each pH were equilibrated with each particular metal ion solution (50 mL). Following equilibration during two days, the samples were filtered to remove the suspended particles of resin. The amount of metal ion remaining in solution was then determined, after appropriate dilution, by spectrophotometry. The pH of the solution was also determined.

Effect of Shaking Period on the Sorption and Desorption of Metal Ions

The sorption of metal ion from aqueous solution was studied by a batch method, using acetic acid-sodium acetate buffer solution (0.1 M, 50 mL, pH 5) which contained metal ion (0.01 mmol), equilibrated with acetohydroxamate resin (0.25 g), after various periods.

The retained metal ions in the metal-resin complex were eluted with the mixture (25 mL) of HCl (0.03 M) and acetone (1% by volume). After each period of shaking, the samples were filtered to remove the suspended particles of resin, and the amount of metal ion in solution was determined.

Potentiometric Titrations
Acid dissociation constant

As this system is heterogeneous, equilibrium cannot be obtained as rapidly as in a homogeneous system. Hence the potentiometric titration could not be done continuously in a single vessel, but rather in batches. We weighed accurately at least fourteen samples (0.2 g) of the resin and placed each respectively into a PE bottle (100 mL). Aqueous solutions containing various amounts of sodium hydroxide (0.1 M) were brought to ionic strength 0.5 M with potassium chloride and then to the total volume of 50 mL. The solutions were added to the PE bottle containing the resin. The mixture was stirred for 4 h at 25 ± 0.1 °C. After equilibration, the pH was monitored by a meter (Radiometer pH M 61) and a combined electrode (GK 2401 C). Electrodes were standardized immediately before measurement with buffer solutions (pH 4.01 and 6.86).

Stability constant

The apparatus and procedures of these experiments were identical to those described above except that in each case metal salt at a ratio either three to one or one to one of

Acetohydroxamate Resin as Column Packing

J. Chin. Chem. Soc., Vol. 39, No. 2, 1992 **123**

metal to ligand was added to the resin solution. The total volume was 50 mL.

General Chromatographic Conditions

Chromatograms were generally run at ambient temperature at a flow rate 1 mL min^{-1}. All mobile phases were degassed ultrasonically before use. Prior to sample injection, the column was equilibrated with the eluent for at least 0.5 h at 1 mL min^{-1}. The columns were considered to be equilibrated when the acidity of the effluent matched that of the entering mobile phase within ± 0.02 pH units, when a stable baseline was obtained, and when two successive injections of sample yielded the same retention periods. The rate of flow of PAR was generally half that of the mobile phase, 0.5 mL min^{-1}. The detector was set at 520 nm.

RESULTS AND DISCUSSION

The synthesized resin was characterized by elementary analysis, infrared spectra, water regain, hydrogen capacity and metal capacity. The detailed procedures were done according to ref. 5. The amount of functional groups incorporated into the resin was determined by acid-base titration. Analytical and physical data of the synthesized resin are listed in Table 1.

Copper(II) displays diverse coordination geometries in its many salts and complexes; its common coordination numbers are four, five and six. Hydroxamic acids are important analytical reagents. Hydroxamic acids and their metal complexes also play an important role in living systems.[6] Despite the great interest in hydroxamic acid and metal hydroxamates, studies of hydroxamate resin are few. Reports of the coordination behavior of metal-hydroxamate resin complexes are even fewer. We investigated the coordination behavior of the synthesized resin by means of EPR, IR and electronic spectrometry and potentiometry. The interpretation of the EPR spectrum of

an isolated transition metal ion yields values of parameters of two types, the spectral splitting parameters (g values) and the hyperfine coupling parameters (A). Values of these parameters depend on the presence of ligands around the central metal ion. The EPR spectra of acetohydroxamate resin as a function of pH in either highly loaded or slightly loaded metal ion were measured at room temperature. When these spectra were recorded at 77 K they showed no better resolution than those at room temperature. The $g_\perp$, and $g_{||}$ values, calculated from the spectral data, are given in Tables 2-3. The results showed that $g_{||} > g_\perp$, characteristic of tetragonal or square-planar geometry;[7] that g exceeds 2.3 indicates the ionic character of the metal-ligand bond.[8] In a medium with pH < 3, most copper-resin complexes studied showed $g_{||}$ components in their EPR spectra. These facts indicate the motion of copper ion to be slow in these cases. In contrast, for pH > 3 few or no $g_{||}$ component shows. According to this com-

Table 2. Parameters of the EPR Spectra of Cu(II)-acetohydroxamate Resin Complexes (Highly Loaded Resin)

pH	Capacity/mmol g^{-1}	$g_\perp$	$g_{||}$	ΔHpp(G)
2.01	0.31	2.066	-	100
3.11	0.82	2.085	-	183
3.94	1.83	2.100	-	260
5.01	2.57	2.102	-	267

Table 3. Parameters of the EPR Spectra of Cu(II)-acetohydroxamate Resin (Lightly Loaded Resin)

pH	log D	$g_\perp$	$g_{||}$	A(G)	ΔHpp(G)
2.65	1.44	2.069	2.302	135	80
2.80	1.66	2.072	2.302	141	79
2.93	1.83	2.077	2.314	123	142
3.07	2.02	2.076	2.302	135	156
3.22	2.15	2.075	-	-	173
3.39	2.28	2.074	-	-	184
3.59	2.42	2.074	-	-	184
3.80	2.55	2.073	-	-	182
4.01	2.71	2.072	-	-	182
4.22	2.89	2.074	-	-	188

Table 1. Characteristics of Acetohydroxamate Resin

Cross linkage/%		5-12	
Particle size/mesh	100(batch)		230-300(column)
Elemental C		54.87	
analysis/% H		6.43	
N		5.97	
Functionality/mmol g^{-1}		2.48	
Water regain/g g^{-1}	2.74/5%*	1.97/8%*	1.14/12%*
Hydrogen capacity/mmol g^{-1}		6.72	
Copper capacity/mmol g^{-1}		2.57	

*Degree of cross-linkage

124   *J. Chin. Chem. Soc., Vol. 39, No. 2, 1992*

Chen et al.

parison, the mobility of copper ions decreases with decrease of pH as the resin ligand is excess in these conditions. Comparison of the EPR spectrum of copper ion on hydroxamate resin with those of copper ion on Dowex A-1 and Unicellex UR-50 indicates that the g and A values are consistent among them.[9,10] We conclude that the CuO_4 model is useful to explain the complexing behavior of the synthesized resin.

The color and the absorption maxima of the electronic spectrum of the resin-copper complex and some reference compounds are presented in Table 4. The electronic spectrum of this resin complex involves two intense bands and one shoulder; in this respect it resembles the reported spectra of Cu(BHA) and Cu(MAHA)$_2$ with square planar geometry,[11] BHA being benzohydroxamic acid and MAHA being N-methylhydroxamic acid. The peak at greater wavenumber is assigned to a charge-transfer state and the peaks with smaller wavenumber and the shoulder are assigned as the d-d transition in the copper-resin complex. The 10 Dq value is slightly smaller than that of monomeric hydroxamate complexes.

Positions and assignments of peaks in the IR spectra of acetohydroxamate resin and its copper complex are given in Table 5. For the resin, peaks centered at 3188 cm^{-1} (-NHOH), 1687 cm-1 (-C=O of -CONH), 1453, 941 cm^{-1} (amide II band), 1403 cm^{-1} (amide III band), 618 cm^{-1} (-N-C=O bending) indicate the presence of the hydroxamate group. Peaks at 1736 cm^{-1} (-C=O of -COOH) and 1188 cm^{-1} are assigned to unreacted carboxylate groups. In the metal-resin complex, vibrational evidence for oxygen-coordination of the hydroxamate groups concerning the ν(C-O) and ν(N-O) is obvious; coordination causes these peaks to move to greater wavenumber (Table 5). The broad ν(OH) peak (3660-3080 cm^{-1}) is attributed to hydrogen bonding between the coordinated water molecule and the oxygen atom of the hydroxamate group. If any hydroxamate groups remained free, a medium intensity band would have been observed at the positions appropriate for free hydroxamate groups. Therefore, assignments for the metal-resin complex may be complicated by the presence

Table 5. Principal IR Absorption Bands/cm^{-1} of Acetohydroxamate Resin and its Metal Complexes

	Resin(R)	R-Cu
-NHOH	3188	3188
$\overset{O}{\overset{\|}{-C}}$-OH	1736	1722
$\overset{O}{\overset{\|}{-C}}$-NH	1687	
Amide II band		
-COO-asym.str.,		1599
NH def.	1452	1452
	941	943
Amide III band		
-COO-sym.str.	1403	1409
	1352	
-C-O str.	1188	1213
N-C=O bending	618	609

of bound and free hydroxamate groups.

Investigation of the stability of the copper chelate of this resin makes possible comparison with chelation tendencies of the corresponding monomeric hydroxamic acid. The titration curves of acetohydroxamate resin and its copper complexes are shown in Fig. 1. The acid dissociation constant of the resin and stability constants of the copper-resin complexes were calculated according to a modified Bjerrum's method.[12] The 3:1 metal-chelate titration curve was used for the calculation of stability constants. The results are shown in Table 6. By comparison with data of the corresponding monomer, acetohydroxamic acid,[13] both the acid dissociation constant and the stability constants are reasonable. Although the stability constants of metal-resin complexes exceed those of the corresponding monomer, they reflect the general trend for a normal system and follow the Irving-Williams sequence,[14] viz. Fe > Cu > Pb > Zn > Ni > Co > Cd > Mn.

Analytical Application of the Synthesized Resin

The recovery of metal ions with acetohydroxamate resin from aqueous solution was examined by the batch method at various values of pH for metal ion solution (25 mL 4 x 10^{-4} M) and of acetohydroxamate resin (0.3 g). The

Table 4. Electronic Spectra of Cu(II) in Hydroxamate Resin and some Reference Compounds

Complex	Color	Observed Absorption Bands v/cm^{-1}			Dq /cm^{-1}
Cu-resin	green	24390	15197	14084	1408
Cu(BHA)*	blue green	25000	15900	12700	1270
Cu(MAHA)$_2$*	deep blue	25970(23200)(19230)(17200)16070(14920)			

*see ref. 11

BHA: Benzohydroxamic acid

MAHA: N-methylhydroxamic acid

Acetohydroxamate Resin as Column Packing

J. Chin. Chem. Soc., Vol. 39, No. 2, 1992 **125**

Table 6. Equilibrium Constants

Metal Complex	Equilibrium	log k_f
Resin (R)	[HL]/[H][L]	9.95
R-Cu	[ML]/[M][L]	8.90
	[ML$_2$]/[ML][L]	8.50
Acetohydroxamic acid (AHA)*	[HL]/[H][L]	9.36
AHA-Cu*	[ML]/[M][L]	7.90

I = 0.5 M KCl, Temp = 25 ± 0.1 °C
* Ref. 13

results are illustrated in Fig. 2. At pH 1.5, the recovery of metal ions was less than 30%, whereas at pH > 4 the recovery of each metal ion nearly approached completeness.

The sorption rate of various metal ions on acetohydroxamate resin is shown in Fig. 3. The results indicate that the periods for half saturation, $t_{1/2}$, were in the order Fe(III) > Co(II) > Zn(II) - Cd(II) - Pb(II) - Cu(II). For each metal ion, the sorption rate decreased with increasing degree of cross linkage of the synthesized resin within the tested range, 5% to 12%. However, if the resin were swollen before use, resins of all three types achieved complete sorption within 15 s for the metal ions tested, except for Fe(III) ion. The desorption of metal ions from the synthesized resin was also examined by the batch method. The results showed that when acetohydroxamate resin (0.25 g) was shaken with the mixture (25 mL) of HCl (0.03 M) and acetone (1%), the desorption was also rapid enough and was achieved within five min for all metal ions tested.

The rapid sorption and desorption of metal ions from the synthesized resin indicates that such a resin can be utilized as a stationary phase for column-chromatographic separation and concentration of metal ions from aqueous
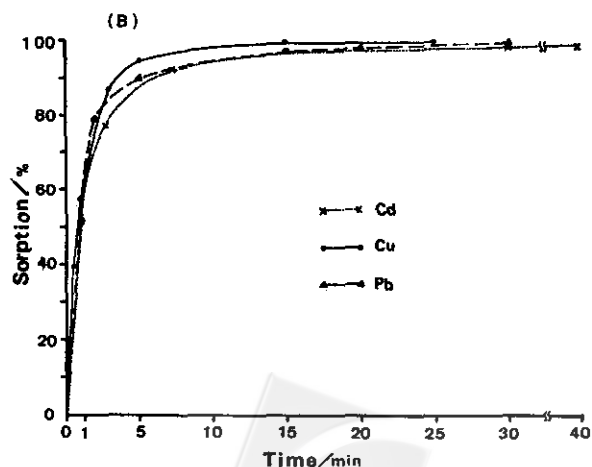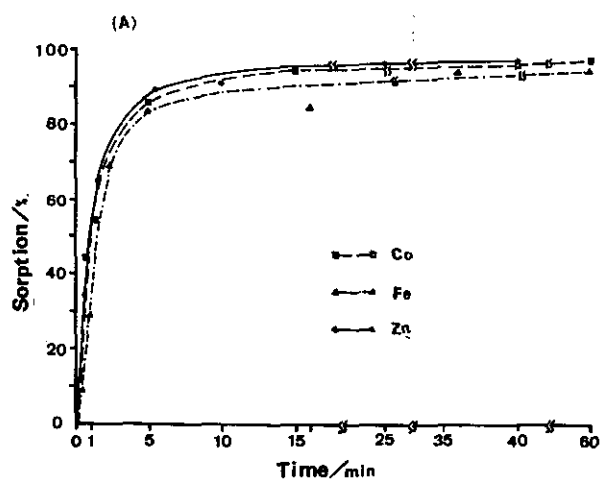
Fig. 1. Titration curves of acetohydroxamate resin and its metal complexes. Volume of solution: 25 mL; Amount of resin: 0.2 g; Ionic strength: 0.5 M; Temp.: 25 ± 0.1 °C; [NaOH]: 0.1 M.

Fig. 3. The sorption rate of various metal ions on acetohydroxamate resin.
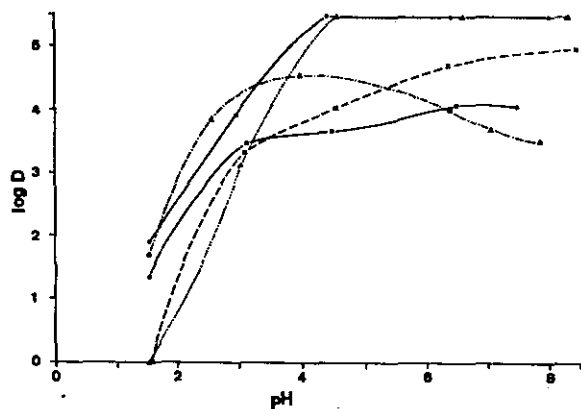
Fig. 2. Distribution ratio of metal ions on acetohydroxamate resin as a function of pH.

solutions.

Several reagents, HCl (0.1 M - 0.001 M), or the mixture of HCl (0.006 M - 0.01 M) and NaCl (0.03 M - 0.1 M) were used as mobile phases for the elution of metal ions in the column. The addition of different modifiers to the mobile phase, such as oxalic acid and tartaric acid, or methanol, ethanol and acetone was also investigated. We found that the mixture of hydrochloric acid and acetone was the best for elution and separation of metal ions absorbed on the column.
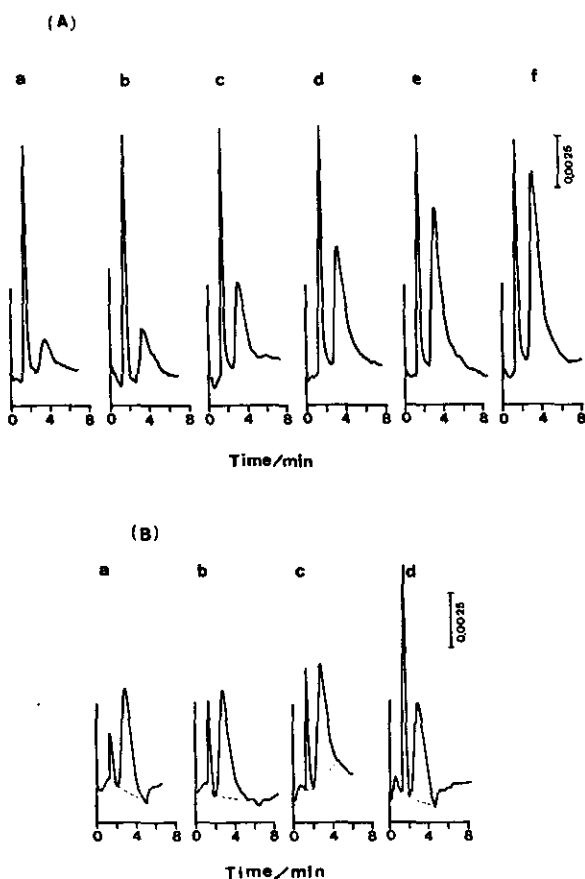
Figs. 4-6 are the chromatograms obtained with

Fig. 4. Chromatogram obtained for the determination of metal ion in binary mixture. (A) For Cu(II) at $[Zn(II)] = 0.2$ ppm a. $[Cu(II)]/[Zn(II)] = 6/5$, b. $[Cu(II)]/[Zn(II)] = 2$, c. $[Cu(II)]/[Zn(II)] = 3$, d. $[Cu(II)]/[Zn(II)] = 4$, e. $[Cu(II)]/[Zn(II)] = 5$, f. $[Cu(II)]/[Zn(II)] = 6$. (B) For Zn(II) at $[Cu(II)] = 0.8$ ppm a. $[Cu(II)]/[Zn(II)] = 1/20$, b. $[Cu(II)]/[Zn(II)] = 1/10$, c. $[Cu(II)]/[Zn(II)] = 3/20$, d. $[Cu(II)]/[Zn(II)] = 1/4$. Column: Acetohydroxamate resin; 250 x 3 mm I.D. (120 psi). Mobile phase: 0.05 M HCl-1% acetone. Volume of sample loop: 50 μl. Flow rate: 1.0 mL min^{-1}. Detection: Post-column reagent: 4 x 10^{-4} M PAR, $\lambda = 500$ nm; AUFS = 0.05.

acetohydroxamate resin stationary phase and the UV-visible detector. Fig. 4 shows the peaks obtained for the determination of copper and zinc in a binary mixture. The parameters, flow rate, column pressure and the concentration of mobile phase, the resolution and detection limits of the chromatographic system were varied within ranges and indicated in Table 7. The influence of other metal ions and various matrices (salt, ascorbic acid, EDTA and humic acid) on the reproducibility of the results was investigated. Fig. 5 shows the determination of copper in the presence of other metal ions, and Fig. 6 shows the determination of copper in the presence of other metal ions and complexing agents. We employed acetohydroxamate resin of length 250 mm and 3 mm internal diameter in conjunction with a mixture of hydrochloric acid and acetone as mobile phase, to determine copper ion; the detection limit is 0.22 ppm. In the presence of As(V), Cd(II), Cr(III), Hg(II), Ni(II), Pb(II) and Zn(II) or sodium chloride, ascorbic acid, humic acid and EDTA, copper was also determined with relative error in the range of 1.5-15.9% (Table 8). However, the relative error for the determination of copper decreased to the range 0.4-6.4%, when the concentration of lead in the sample was decreased to 1 ppm. The results are shown in Table 9.
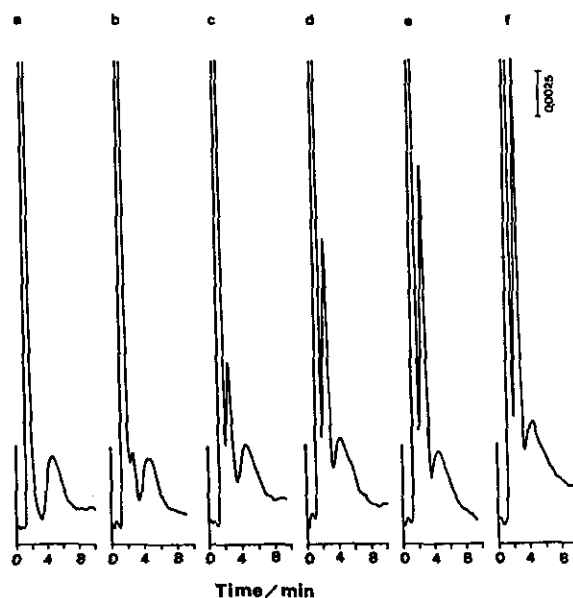

Fig. 5. The determination of copper in the presence of other metal ions. $[As(V)] = [Cd(II)] = [Cr(III)] = [Cu(II)] = [Hg(II)] = [Ni(II)] = [Zn(II)] = 1$ ppm; a. without Pb, b. $[Pb] = 1$ ppm, c. $[Pb] = 2$ ppm, d. $[Pb] = 3$ ppm, e. $[Pb] = 4$ ppm, f. $[Pb] = 5$ ppm. Details of the chromatographic conditions were as in Fig. 4, except that column pressure: 370 psi, Mobile phase: 0.03 M HCl-1% acetone.

Acetohydroxamate Resin as Column Packing

J. Chin. Chem. Soc., Vol. 39, No. 2, 1992 127

Table 7. Summary of Characteristics of the HPIC Method for the Determination of Copper and Zinc Ion Mixture

Pressure	120 psi	120 psi	260 psi
Mobile phase	0.05 M HCl-1% acetone	0.03 M HCl-1% acetone	0.03 M HCl-1% acetone
Flow rate/mL min⁻¹	1.0	1.0	0.5
Retention time/min			
Zn(II)	1.4	1.4	2.4
Cu(II)	2.8	3.2	5.8
Resolution	1.1	1.4	1.7
Detection limit/ppm			
Zn(II)	0.006		
Cu(II)	0.14	0.22	0.22

*Column: 250 x 3 mm I.D.

Sample volume: 50 μL

Detection: Post-column reagent: 4×10^{-4} M PAR; λ = 500 nm

Selective Column Concentration of Metal Ions

On-line preconcentration and determination of trace copper(II) were done using a short (30 mm x 4.6 mm I.D.) concentrator, also packed with acetohydroxamate resin, combined with the above separation system. The linear range is 2-15 ppb, and the detection limit is 0.70 ppb (Table 10).
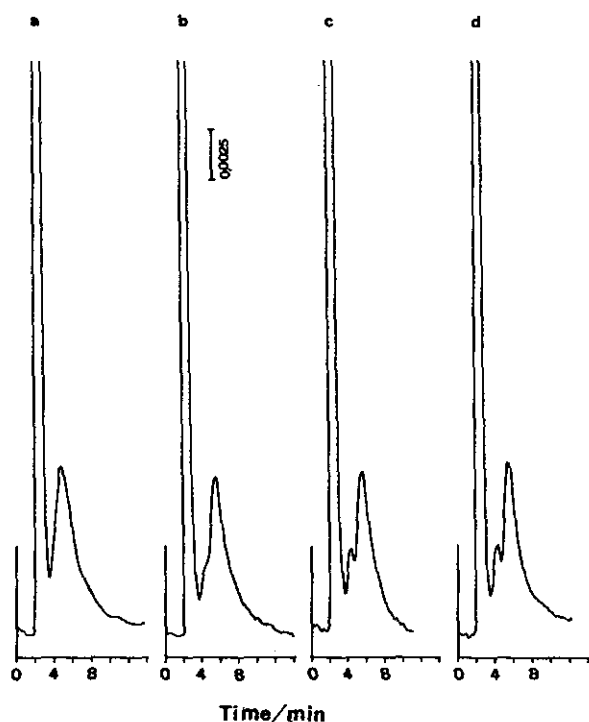

Fig. 6. The determination of copper in the presence of other metal ions and complexing agent. [As(V)] = [Cd(II)] = [Cr(III)] = [Cu(II)] = [Hg(II)] = [Ni(II)] = [Pb(II)] = [Zn(II)] = 1 ppm a. in 0.1 M NaCl, b. in 10^{-5} M EDTA, c. in 10^{-3} M Ascorbic acid, d. in 10 ppm Humic acid. Details of the chromatographic conditions were as in Fig. 5.

Table 8. The Determination of Copper in the Presence of Other Metal Ions and Complexing Agents

Complexing Agent	Metal Ions	Cu(II)/ppm		Relative
		Added	Found**	Error/%
NaCl (0.1 M)	*	1.000	0.960(±0.125)	-4.0
EDTA (10^{-5} M)	*	1.000	0.841(±0.010)	-15.9
Ascorbic acid (10^{-3} M)	*	1.000	0.985(±0.040)	-1.5
Humic acid (10 ppm)	*	1.000	0.975(±0.023)	-2.5

*[As(V)] = [Cd(II)] = [Cr(III)] = [Cu(II)] = [Hg(II)] = [Ni(II)] = [Zn(II)] = 1 ppm, [Pb(II)] = 5 ppm

**95% confidence limit

Application of the Proposed Method

The major advantage of the proposed method is its high sensitivity and high selectivity for the separation and determination of metal ions in highly concentrated
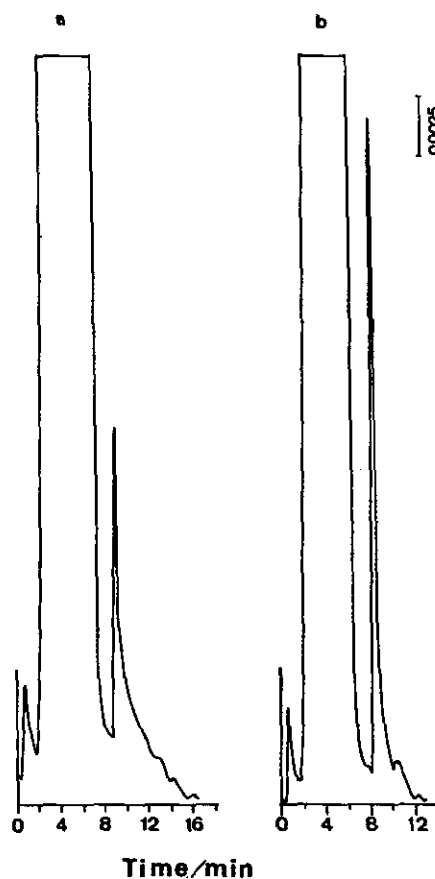

Fig. 7. The determination of copper in sea water. a. Sea water, b. Sea water spiked with 6 ppb of Cu(II). Concentration column: Acetohydroxamate resin; 30 x 4.6 mm I.D. Loading rate: 0.5 mL min⁻¹; Loading time: 10 min. Analytical column: Acetohydroxamate resin; 250 x 3 mm I.D. Mobile phase: 0.03 M HCl-1% acetone. Flow rate: 0.6 mL min⁻¹. Detection: Post-column reagent: 4×10^{-4} M PAR. λ = 500 nm; AUFS = 0.05.

Table 9.   The Determination of Copper in the Presence of Other Metal Ions and Complexing Agents

Complexing Agent	Metal Ions	Cu(II)/ppm		Relative
		Added	Found**	Error/%
NaCl (0.1 M)	*	1.000	0.982(±0.014)	-1.8
EDTA (10^{-5} M)	*	1.000	0.936(±0.008)	-6.4
Ascorbic acid (10^{-3} M)	*	1.000	0.988(±0.004)	-1.2
Humic acid (10 ppm)	*	1.000	0.996(±0.032)	-0.4

*[As(V)] = [Cd(II)] = [Cr(III)] = [Cu(II)] = [Hg(II)] = [Ni(II)] = [Pb(II)] = [Zn(II)] = 1 ppm
**95% confidence limit

Table 10.   Summary of Characteristics of the HPIC Systems for the Concentration and Determination of Copper

Concentration column	30 x 4.6 mm I.D.
Condition	pH 5.0
Loading rate/mL min^{-1}	0.5
Loading time/min	10
Analytical column	250 x 3 mm I.D. (260 psi)
Mobile phase	0.03 M HCl - 1% acetone
Flow rate/mL min^{-1}	0.6
Dynamic range/ppb	2-15
Detection limit/ppb	0.70

electrolyte samples. The present method was employed for the determination of copper ion in sea water. Results for this sample and a sample with added copper ion (6 ppb) are given (Fig. 7). The selectivity of the proposed method is evident when we consider the similarity between the standard and the sea water sample. The recovery was 97.3% in three trials.

ACKNOWLEDGMENT

REFERENCES

1. Maccarthy, P.; Klusman, R. W. *Anal. Chem.* 1989, *61*, 269R.
2. Nickless, G. *J. Chromatogr.* 1985, *313*, 129.
3. Liu, C. Y.; Sun, P. J. *Fresenius Z. Anal. Chem.* 1986, *325*, 553.
4. Liu, C. Y.; Sun, P. J. *Anal. Chim. Acta* 1981, *132*, 187.
5. Liu, C. Y.; Chang, H. T.; Hu, C. C. *Inorg. Chim. Acta* 1990, *172*, 151.
6. Eichhorn, G. L. *Inorganic Biochemistry*; Elsevier: New York, 1977; Vol. 1.
7. Baul Hausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962; p 134.
8. Kivelson, D.; Neiman, R. *J. Chem. Phys.* 1961, *35*, 149.
9. Umezawa, K.; Yamabe, T. *Bull. Chem. Soc. Jpn.* 1972, *45*, 56.
10. Heitner-Wirguin, C.; Cohen, R. *Inorg. Chim. Acta* 1969, *3;4*, 647.
11. Brown, D. A.; Mckeith, D.; Glass, W. K. *Inorg. Chim. Acta* 1979, *35*, 5.
12. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*; P. Haase and Son; Copenhagen, 1941.
13. Martell, A. E.; Smith, R. M. *Critical Stability Constants*, Plenum Press; New York, 1974; Vol. 1.
14. Martell, A. E.; Calvin, M. *Chemistry of the Metal Chelate Compounds*; Prentice-Hall: Englewood Cliffs, New Jersey, 1952.