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Chromatographic separation by a new chelating resin containing β-hydroxydithiocinnamic acid

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Summary. The distribution coefficients of Ag(I), Au(III), Cd(II), Cu(II), Fe(III), Hg(II), Ni(II), Pb(II), Pt(IV), and Zn(II) on a new chelating resin containing β-hydroxydithiocinnamic acid at various acidity were studied. In the strongly acidic region, the resin shows high affinity for Ag(I), Hg(II), Au(III) and Pt(IV) and high resistance against air oxidation. The effect of diverse foreign ligands on the sorption of metal ions and the possibility of application to speciation studies with this resin were also considered. Some quantitative separations of Cd-Cu-Pb, Cu-Au and Au-Pt with this resin column were described. Detection of the chromatography system was carried out via post column derivatisation of the column effluent with PAR at 520 nm or direct UV detection of the chloride complexes at 215 nm.

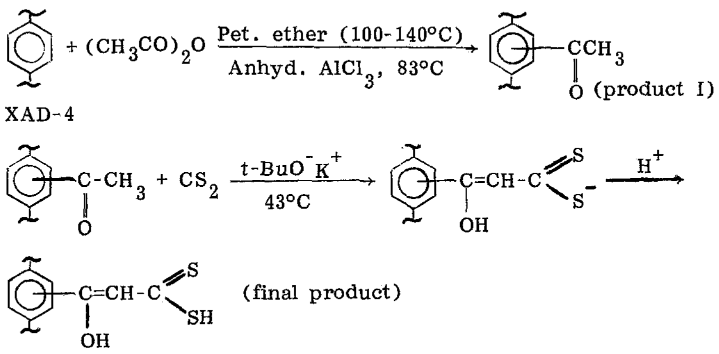
Introduction

Ion chromatography, since its introduction in 1975 [1], has gained extremely wide acceptance in inorganic analysis. Over the fourteen years, the practice of ion chromatography has witnessed continuing growth in both the seperator column and the detector. Instead of the normal conductivity or direct UV absorption detection, for the determination of transition and rare earth metals, a post column reactor using PAR or Arsenazo I, respectively, has been proposed [2]. Generally, two basic types of resins have been used in ion chromatography. Silica based resins are readily available but suffer the problem of limited pH range due to the degradation of silica. Polymer columns do not have such strict pH limitations and have gained a wider use than silica columns. A common type of polymer is a copolymer of styrene and divinylbenzene. Functional groups can be added to the benzene ring of the polymer to affect ion exchange. However, the functional groups of most of the seperator columns used in ion chromatography are those of the conventional ion exchangers. Increasing selectivity in ion chromatography often requires the use of a metal-complexing additive in the buffered eluent. In this investigation, we synthesized a novel ion exchanger containing the β-hydroxydithiocinnamic acid functional group used as stationary phase of ion chromatography. Because selectivity has been designed into the stationary phase, the pretreatment of the sample solution is generally not necessary and simpler mobile phases can be used. Based on the complexation study of β-hydroxydithiocinnamate resin in a previous paper [3], it was found that the synthesized resin was highly selective for noble metal ions. In this paper, the sorption of some metal ions from various acidic solution was reported and the possibility of speciation study using this resin was discussed, the synthesized chelating resin was also used as packing material in ion chromatography to separate µg amounts of mixtures of noble metal ions or noble metal ions with other transition metal ions.

Experimental

Apparatus. A Dionex Model 2000i ion chromatograph and a Dionex UV-VIS detector were used. A sample loop of 50 µl was employed, and a Chem Inert glass column (50 mm long and 6 mm I.D.) packed with 100–200 mesh of β-hydroxydithiocinnamate (β-HDTCA) resin was used in separation.

Preparation of the resin. The β-hydroxydithiocinnamate resin was synthesized in our laboratory. The reaction steps were the following:



The detailed procedure of the preparation and some of the properties of this resin have been described in previous paper [3].

Determination of the sorption properties in various acidic media. Air dried resin samples (0.3 g) were equilibrated by mechanically shaking with 25 ml 5×10^{-4} mol/l solutions of the individual metal salts at various pH (pH adjusted by

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Table 1. Distribution coefficients of metal ions on β-hydroxydithiocinnamate resin in various pH solution[a]

Metal ion	pH						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
Ag(I)	$> 7\times10^3$	$> 7\times10^3$	$> 7\times10^3$	$> 7\times10^3$	$> 7\times10^3$	–	–
Au(III)	$>10^5$	$>10^5$	$>10^5$	$>10^5$	–	–	–
Cd(II)	< 1	< 1	15	139	472	$>10^3$	$>10^5$
Cu(II)	< 2	8	28	155	$>10^3$	$>10^4$	$>10^5$
Fe(III)	< 2	150	$>10^3$	–	–	–	–
Hg(II)	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$	–	–
Ni(II)	< 0.5	< 2	34	184	$>10^3$	$>10^4$	$>10^5$
Pb(II)	< 2	228	540	$>10^3$	$>10^4$	$>10^5$	–
Pt(IV)	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$	–	–
Zn(II)	< 0.5	< 0.5	8	32	164	$>10^3$	$>10^5$

[a] Means of three determinations. Amount of resin: 0.3 g, amount of metal ion: 0.0125 mmol, volume of solution: 25 ml

Table 2. Distribution coefficients of metal ions on β-hydroxydithiocinnamate resin in perchloric acid media[a]

Metal ion	Acid concentration (mol/l)					
	0.1	0.5	1	2	3	5
Ag(I)	$> 7\times10^3$	$> 5\times10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Au(III)	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$
Cd(II)	< 1	–	< 0.5	–	< 0.5	–
Cu(II)	< 2	–	< 0.5	–	< 0.5	< 0.5
Fe(III)	< 2	–	< 0.5	–	< 0.5	–
Hg(II)	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$
Ni(II)	< 0.5	–	< 0.5	–	< 0.5	< 0.5
Pt(IV)	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$
Zn(II)	< 0.5	–	< 0.5	–	< 0.5	< 0.5

[a] Means of three determinations. Amount of resin: 0.3 g, amount of metal ion: 0.0125 mmol, volume of solution: 25 ml

sodium hydroxide or perchloric acid) or in strongly acidic medium (usually perchloric acid or hydrochloric acid). After a shaking time of 24 h at 25 ± 0.02°C, aliquots were taken from the aqueous solutions and analyzed spectrophotometrically. The distribution coefficients D were calculated in the usual way.

General chromatographic conditions. Chromatograms were generally run at ambient temperature of a flow rate of 1 ml min^{-1}. All mobile phases were degassed with nitrogen before use. Prior to sample injection, the column was equilibrated with the eluent for at least 0.5 h at 1 ml/min. The columns were considered to be equilibrated, when a stable baseline was obtained, and when two successive injections of sample yielded the same retention time.

The PAR flow rate was generally one half that of the mobile phase, 0.5 ml min^{-1}. The detector was set at 520 nm at usually 0.2 or 0.5 absorbance for full scale.

Results and discussion

Sorption of metal ions by batch operation. The sorption of metal ions on the synthesized resin at various acidity was investigated, and the results are shown in Tables 1 and 2. Most of the metal ions showed higher affinity to the resin as the pH of the solution increased (Table 1). The sorption behavior of Fe(III), Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) was the same and different from that of Ag(I), Au(III), Hg(II) and Pt(IV). The distribution coefficients of these metal ions on β-hydroxydithiocinnamate resin in various concentrations of perchloric acid media indicated that the distribution coefficients of Hg(II), Au(III) and Pt(IV) were larger than 10^5 even at 5 mol/l perchloric acid solution, those of Ag(I) were somewhat lower, while those of the other metal ions such as Cd(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) showed nearly no adsorption on this resin. Further, if hydrochloric acid was used instead of perchloric acid, the distribution coefficients (Table 3) showed a large decrease for Ag(I), Hg(II) and Pt(IV), while those of Au(III) nearly did not decrease even at 5 mol/l hydrochloric acid. The affinity of these metal ions toward the synthesized resin based on the distribution coefficients data decreases in the order Au(III) > Hg(II) > Pt(IV) > Ag(I) > Fe(III) > Pb(II) > Ni(II) > Cu(II) > Cd(II) > Zn(II). The distribution coefficients of the metal ions vary with the stability of the metal complexes formed with the chelating groups of the resin. Thus, in this investigation, the stability of the noble metal-resin complexes might be higher than that of the other metal-resin complexes. These results indicated that the synthesized resin was highly selective for noble metal ions, especially in strongly acidic solution and the competition of the chloride ion with the resin was more severe as the acid concentration increased, and the results also suggested that

Table 3. Distribution coefficients of metal ions on β-hydroxydithiocinnamate resin in hydrochloric acid media[a]

Metal ion	Acid concentration (mol/l)					
	0.1	0.5	1	2	3	5
Ag(I)	–	–	139	6	< 5	< 2
Au(III)	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$	$>10^5$
Cd(II)	< 0.5	–	< 0.5	–	< 0.5	< 0.5
Cu(II)	< 1	–	< 0.5	–	< 0.5	< 0.5
Fe(III)	< 1	–	< 0.5	–	< 0.5	< 0.5
Hg(II)	$>10^5$	$>10^3$	484	18	< 0.5	< 0.5
Ni(II)	< 0.5	–	< 0.5	–	< 0.5	< 0.5
Pb(II)	< 0.5	–	< 0.5	–	< 0.5	< 0.5
Pt(IV)	156	–	–	70	63	22
Zn(II)	< 0.5	–	< 0.5	–	< 0.5	< 0.5

[a] Means of three determinations. Amount of resin: 0.3 g, amount of metal ion: 0.0125 mmol, volume of solution: 25 ml

Table 4. Effects of foreign ligands on the sorption of metal ions on β-hydroxydithiocinnamate resin[a]

Ligand [mol/l]	Sorption of metal ion (%)				
	Ag(I)	Cd(II)	Cu(II)	Hg(II)	Pb(II)
Citric acid (10^{-2})	75.4	63.7	22.6	86.8	31.6
Citric acid (10^{-4})	92.7	89.5	92.0	92.4	99.0
EDTA (10^{-3})	82.1	~0	~0	74.5	13.2
EDTA (10^{-4})	93.1	46.9	55.7	88.2	60.0
Glycine (10^{-1})	78.5	77.0	27.3	–	57.1
Glycine (10^{-4})	99.1	96.2	94.5	–	97.4
Tartaric acid (10^{-1})	81.2	7.4	3.1	91.7	86.7
Thiourea (10^{-3})	84.5	64.2	82.3	90.7	85.7
Thiourea (10^{-4})	94.5	85.6	94.8	96.3	91.6

[a] Means of three determinations. Amount of resin: 0.3 g, amount of metal ion: 0.125 mmol, volume of solution: 25 ml

the resin could be used very advantageously for the separation of the noble metal ions from other transition metal ions.

Within the past decade, especially in the field of toxicology and the cycling of metals in the environment, the term "speciation" has become increasingly important [4–7]. In "speciation" studies with chelating resins, we can distinguish metal ions in natural water into two categories [8–9]. Metal ions of the first category (lowly complexed form) can be exchanged with the synthesized resin. Metal ions of the second category (highly complexed form) cannot be exchanged with the synthesized resin. Table 4 shows the retention of metal ions in the presence of some foreign ligands with β-hydroxydithiocinnamate resin. The ligands chosen may most probably compete with the functional groups of the resin. They are citric acid, ethylenediaminetetraacetic acid, glycine, tartaric acid and thiourea. Thiourea was chosen as the representative of the sulfur ligand. By variation of these ligands concentration, the results showed that if the ligand concentration was decreased, the retention percentage of metal ions was obviously increased. In the presence of 10^{-3} mol/l EDTA, copper and cadmium are nearly not adsorbed by the resin. Nevertheless, in the presence of 10^{-4} mol/l EDTA, it showed that a large increase of the retention for both copper and cadmium ion. The retention for copper is 55% and that for cadmium is 47%. However, silver and mercury are still strongly retained by the resin, even in the medium of 10^{-3} mol/l EDTA. In view of the mass action effect and by comparing the stability constant data shown in Table 5, the results except that of mercury are obviously reasonable. Since EDTA might be a mostly strong ligand in natural water and 10^{-7} mol/l EDTA might be a reasonable upper limit to the possible ligand concentration in nature [10], we can conclude that the use of the synthesized resin in speciation studies may be very useful. Further studies are now in progress. The results in Table 4 also show that higher concentration of EDTA can be used as eluent for the column study and that the resin might be useful for the concentration and recovery of metal ions from natural water which might contain various kinds of chelating substances.

Mixtures of several metal ions were separated on β-hydroxydithiocinnamate resin column. The β-HDTCA resin was found to be extremely stable, and no deterioration in its performance was observed even after two months of continuous use.

Separation of cadmium(II), copper(II) and lead(II). Cadmium, copper and lead were taken up by a column of the resin from pH 2.5 hydrochloric acid solutions. The method chosen for the separation of cadmium, copper and lead from each other was as follows: A sample containing cadmium, copper and lead was injected into an eluent stream of pH 2.5 hydrochloric acid. Under these conditions cadmium was eluted completely, copper and lead ions were retained. The

Table 5. Stability constants of metal complexes

Ligand	log K					Ref.
	Ag(I)	Cd(II)	Cu(II)	Hg(II)	Pb(II)	
β-Hydroxydithiocinnamate resin	–	1.10	2.44	–	–	[3]
Citric acid	–	3.75	5.90	10.9	4.44	[11]
EDTA	7.32	16.46	18.80	21.80	18.04	[11]
Glycine	3.2	4.22	8.15	3.42	5.47	[11]
Tartaric acid	–	1.70	3.39	7.0	3.12	[11]
Thiourea	7.11	1.33	–	21.3	0.17	[11]

copper ion was then eluted with 0.01 mol/l hydrochloric acid, and the lead ion was eluted with 0.1 mol/l hydrochloric acid. The separation is shown in Fig. 1.

Separation of copper(II) and gold(III). The β-HDTCA resin sorbed gold strongly from highly acidic solution. In 2 mol/l hydrochloric acid, copper passed through the column completely and auric ion was retained. The auric ion was then eluted with 4 mol/l hydrochloric acid. The separation is shown in Fig. 2.

Separation of gold(III) and platinum(IV). Column studies with 2 mol/l hydrochloric acid showed that gold was taken up strongly, but platinum was not retained. Hence, in 2 mol/l hydrochloric acid, platinum passed through to column and the auric ion was retained. By 4 mol/l hydrochloric acid, gold was eluted completely. The separation is shown in Fig. 3.

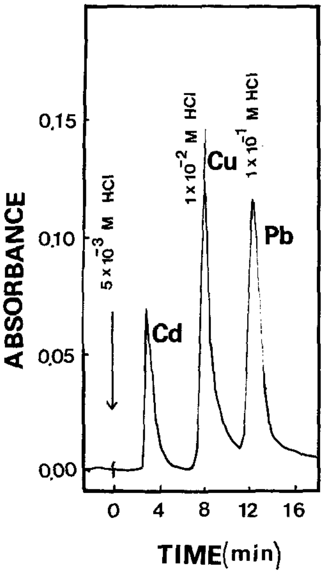
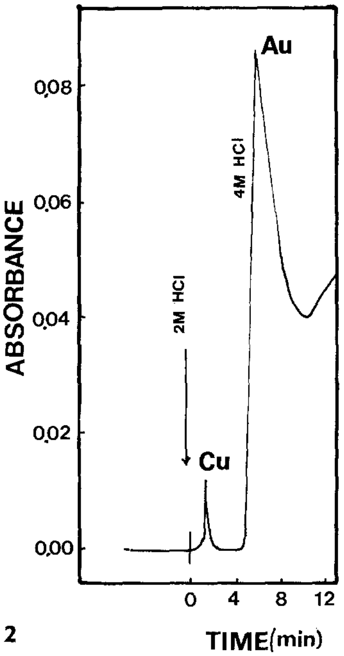


Fig. 1
Separation of metal ion mixtures. Sample: 50 μl 4.0 μg copper(II); 11.4 μg cadmium(II); and 15.2 μg lead(II). Detector: 0.5 AUFS, 520 nm; Eluent flow: 1 ml/min; Reagent flow: 0.5 ml/min, 0.4 mmol/l PAR



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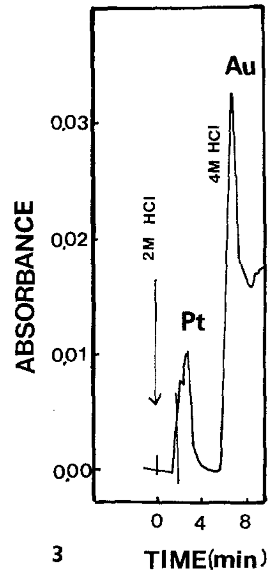

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Fig. 2. Separation of metal ion mixtures. Sample: 50 μl 4.3 μg copper(II) and 6.6 μg gold(III). Detector: 0.2 AUFS, 215 nm; Eluent flow: 1 ml/min

Fig. 3. Separation of metal ion mixtures. Sample: 50 μl 6.6 μg gold(III) and 6.4 μg platinum(IV). Detector: 0.1 AUFS, 215 nm. Eluent flow: 1 ml/min

Conclusion

Based on these results, it can be concluded that β-hydroxydithiocinnamate resin is an effective stationary phase in ion chromatography for efficient separation of noble metals from associated base and noble metals. Should the metal ion need to be recovered after elution from the column, only mineral acid conditions are present, so that purification is not difficult.

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