

## PREPARATION AND ANALYTICAL PROPERTIES OF A CHELATING RESIN CONTAINING CYSTEINE GROUPS

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### SUMMARY

A macroporous, cross-linked polyacrylonitrile copolymer was synthesized, the nitrile groups were converted to carboxylic acid by hydrolysis, and these carboxylic acid groups were treated with L-cysteine and 1,6-hexanediol (binding agent). Studies of the basic characteristics of this resin showed that it was highly selective for silver(I), mercury(II), gold(III) and platinum(IV) in aqueous acidic solution, the maximum capacities being 0.97, 0.65, 1.22 and 0.39 mmol g<sup>-1</sup> of dry resin, respectively. These four metal ions can be separated from each other, or concentrated from very dilute solutions, on a short column of the resin. The effects of different acids and of various common metal ions are reported.

The chemical behavior of an ion-exchange resin is determined by the nature of the functional groups attached to the hydrocarbon skeleton. Highly selective chelating resins can be synthesized by attaching appropriate ligand groups to the resin matrix. Cysteine, with three coordination sites, is an interesting ligand: at low pH values, only the sulfhydryl group is used in complex formation [1]. Studies have shown that sulfur-containing ligands exhibit better selectivity for the noble and heavy metals than their oxygen and nitrogen analogs [2]. Although many complexes of cysteine and its alkyl esters, both in solution and in the solid state with a variety of metals have been described [3–10], less information is available about the complexes of noble metals with cysteine [11, 12]. No information on resins containing cysteine groups seems to have been reported. This paper describes the synthesis and basic characteristics of a resin with cysteine ligands and its analytical application in the chromatography of silver and some noble metals.

### EXPERIMENTAL

#### *Instrumentation and reagents*

A Radiometer pH meter was used with saturated calomel (Type K401) and glass (Type G202B) electrodes, which were calibrated against Beckman standard buffer solutions of pH 4.00 and 7.00. A Hitachi model 624 digital spectrophotometer connected to a Hitachi model QD<sub>15</sub> recorder and 10-mm

quartz cells was used for all absorbance measurements. Infrared spectra were recorded on a Perkin-Elmer model 580 spectrophotometer.

Analytical-grade chemicals were used throughout. Stock solutions of silver and platinum ions were standardized by classical titrimetric and gravimetric method. The stock solutions of all other metal ions were standardized by EDTA titration.

#### *Synthesis of the chelating cysteine-containing resin*

A macroporous, cross-linked copolymer was prepared by the reaction of acrylonitrile and divinylbenzene as described by Vernon and Eccles [13]. The copolymer was air-dried, ground and sieved. The 60–100 mesh fraction was used for the further synthesis after being washed with 12 M HCl, water and acetone. The copolymer (200 g) was stirred at 80°C with 1 l of 37% (w/v) sodium hydroxide solution until ammonia evolution ceased. The hydrolyzed polymer was cooled to room temperature, collected by filtration under suction and washed with 12 M HCl, water and acetone.

For the first esterification, the carboxylic acid resin (200 g) was mixed with 600 g of molten 1,6-hexanediol (m.p. 41°C) containing 50 ml of 18 M sulfuric acid as catalyst. The mixture was kept at 70°C for 30 h for esterification. The product was collected from the hot solution by filtration under suction, and washed with boiling methanol. For the second esterification, a mixture of 55 g of this product and 300 g of L-cysteine was added to 500 ml of dioxane containing 20 ml of 18 M sulfuric acid. The mixture was heated at 90°C for 30 h. The final product was collected by filtration under suction and washed sequentially with water, 12 M HCl, water and acetone.

#### *Characterization of resin*

In order to verify the presence of cysteine groups in the synthesized resin, the infrared spectrum of the resin was obtained with KBr pellets after each step in the synthesis. The i.r. spectrum of the polyacrylonitrile–divinylbenzene copolymer showed bands at 2260–2240  $\text{cm}^{-1}$  ( $-\text{C}\equiv\text{N}$ ), whereas the spectrum of the hydrolyzed product exhibited bands at 3500–2500, 1720, and 920  $\text{cm}^{-1}$  ( $-\text{COOH}$ ). The spectrum of the diol ester intermediate (Fig. 1a) exhibited bands at 3450 ( $-\text{OH}$ ), 1735, 1163, and 1064  $\text{cm}^{-1}$  ( $-\text{COOR}$ ). The spectrum of the final product (Fig. 1b) showed bands at 2545 ( $-\text{SH}$ ), 2960, 1610, and 1513 ( $-\text{NH}_3^+$ ), and 1735, 1163 and 1064  $\text{cm}^{-1}$  ( $-\text{COOR}$ ).

The nitrogen and sulfur contents, the hydrogen ion capacity, the capacities for Ag(I), Hg(II), Au(III) and Pt(IV) at pH 1, and the acid ionization constants, were determined with the results shown in Table 1.

The distribution coefficients of the metal ions, defined by the equation  $D = (\text{mmol of metal/g of dry resin})/(\text{mmol of metal/ml of solution})$ , were determined by using the batch equilibrium method. For each equilibrium experiment, 25 ml of a mixture consisting of various amounts of acid and 0.3 mmol of the metal ion in question was treated with 0.2 g of fresh resin and the solution was stirred for 8 h at room temperature (25°C). The solution

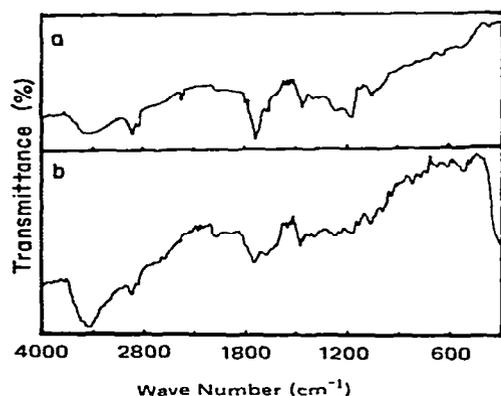


Fig. 1. Infrared spectra: (a)  $\text{RCOO}(\text{CH}_2)_4\text{OH}$  intermediate; (b) resin with cysteine group.

was filtered to remove the resin and the metal ion content of the filtrate was determined by conventional spectrophotometric procedures. The results are shown in Tables 2 and 3.

On the basis of these experiments, the order of selectivity of the resin was  $\text{Au} > \text{Ag} > \text{Hg} > \text{Pt} > \text{Mo}$ . The results also show that the resin readily retains  $\text{Au}(\text{III})$ ,  $\text{Ag}(\text{I})$ ,  $\text{Hg}(\text{II})$  and  $\text{Pt}(\text{IV})$  from either 0.1 M  $\text{HClO}_4$  or 0.1 M  $\text{HCl}$ . Molybdenum is also retained by the resin from 0.1 M  $\text{HCl}$ . Negligible adsorption was shown by the alkali metals, alkaline earths, iron(III), cobalt(II), nickel(II), zinc(II), cadmium(II), and lead(II) in 0.1 M acid. This suggested that column chromatographic separation and concentration of metal ions ( $\text{Pt}(\text{IV})$ ,  $\text{Hg}(\text{II})$ ,  $\text{Ag}(\text{I})$ ,  $\text{Au}(\text{III})$ ) should be possible with this resin.

#### Chromatographic application

The resin column (6 mm i.d., 55 mm long) was conditioned with 30 ml of 0.1 M  $\text{HCl}$  at  $0.5 \text{ ml min}^{-1}$ . A sample that contained 0.4–1.5  $\mu\text{mol}$  each of  $\text{Ag}(\text{I})$ ,  $\text{Hg}(\text{II})$ ,  $\text{Au}(\text{III})$  and  $\text{Pt}(\text{IV})$  in 0.1 M acid was added to the column and the liquid level was allowed to drop to the top of the resin bed. The wall of the reservoir was rinsed with 0.1 M hydrochloric acid and then 10 ml of 0.1 M hydrochloric acid was used to elute any other metal ions from the column while the above metals were retained. The retained

TABLE 1

Physical and chemical characterization of the cysteine-containing resin (60–100 mesh)

Percent cross-linking	5.8%	Gold capacity <sup>b</sup>	1.22 mmol g <sup>-1</sup>
Nitrogen content <sup>a</sup>	1.16 mmol g <sup>-1</sup>	Mercury capacity <sup>b</sup>	0.65 mmol g <sup>-1</sup>
Sulfur content	1.15 mmol g <sup>-1</sup>	Silver capacity <sup>b</sup>	0.97 mmol g <sup>-1</sup>
Hydrogen ion capacity	2.85 mmol g <sup>-1</sup>	Platinum capacity <sup>b</sup>	0.39 mmol g <sup>-1</sup>
$\text{p}K_a$ ( $-\text{COOH}$ , $-\text{NH}_3^+$ , $-\text{SH}$ )	5.65, 6.59, 7.16	Molybdenum capacity <sup>b</sup>	0.22 mmol g <sup>-1</sup>

<sup>a</sup>The nitrogen content of the original copolymer was 25.0% (17.9 mmol g<sup>-1</sup>). All weights refer to dry resin. <sup>b</sup>At pH 1.0.

TABLE 2

Distribution coefficients in perchloric, hydrochloric or hydrobromic acid of varied molarity

Final acidity (M)									
Ion	0.1	0.5	1.0	2.0	3.0	5.0	6.0	7.0	8.0
<i>Perchloric acid</i>									
Ag	95	102	104	104	117	96	—	—	—
Au	1360	2430	13300	18000	24300	28300	20600	2800	1150
Hg	54	43	40	38	22	21	21	17	13
Pt	39	46	55	75	68	50	34	34	—
<i>Hydrochloric acid</i>									
Au	220	315	337	442	473	473	537	—	—
Hg	58	22	20	16	0	0	—	—	—
Pt	17	6	9	14	9	4	—	—	—
Mo	16	28	1	3	27	12	16	26	—
<i>Hydrobromic acid</i>									
Au	112	195	165	282	374	326	195	—	—

Pt(IV), Hg(II), and Ag(I) were eluted sequentially with 0.5 M HCl, and with a 6 M HCl—2 M HClO<sub>4</sub> solution. The metals were determined spectrophotometrically as their chloride complexes at 262, 229 and 213 nm, respectively. The gold(III) retained by the resin was eluted with 0.1% thiourea in 0.1 M HCl and determined spectrophotometrically at 269 nm as the thiourea complex. A separation curve for the 4-component mixture is shown in Fig. 2.

The effects of other metal ions on the recoveries of Pt, Hg, Ag and Au are listed in Table 4. Samples containing gold and various other metal ions were separated on the column by elution with 6 M HCl; good recoveries of gold were obtained in all cases (Table 5).

TABLE 3

Distribution coefficients in mixtures of hydrochloric acid and perchloric acid

Ion	Final concentration (M)						
	HClO <sub>4</sub>	1.5	2.0	2.5	3.0	3.5	4.0
	HCl	7.0	6.0	5.0	4.0	3.0	2.0
Au		498	548	577	578	578	676
Hg		10	0	12	12	12	12
Pt		25	26	25	25	19	19

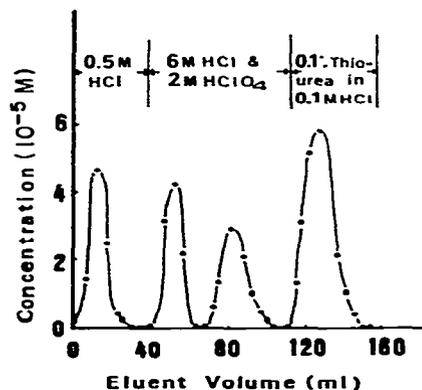


Fig. 2. Separation of Pt(IV), Hg(II), Ag(I) and Au(III) with the resin column. Column  $55 \times 6$  mm i.d.; flow rate  $0.5 \text{ ml min}^{-1}$ ;  $0.45 \mu\text{mol}$  each of Ag, Hg and Pt;  $1.50 \mu\text{mol}$  of Au.

#### Concentration procedure

The resin column (6 mm i.d., 25 mm long) was conditioned with 0.1 M HCl; then 500 ml of a very dilute solution of the metal ion tested was passed through the column at a flow rate of  $0.5 \text{ ml min}^{-1}$ . The sorbed metal ions were eluted and determined spectrophotometrically. The results are shown in Table 6.

#### DISCUSSION

The infrared frequencies for the cysteine-containing resin are in good agreement with those for the cysteine monomer [5]. A potentiometric titration curve obtained when the synthesized resin in the acid form was titrated with 0.1 M KOH at ionic strength 0.1 showed three breaks, only the first of which was quite distinct, corresponding to pK values of 5.65, 6.59 and 7.16 which are assignable to the residual carboxylic acid, amino and the sulfhydryl

TABLE 4

Effect of  $5.0 \mu\text{mol}$  of various metal ions on the recovery of  $0.45 \mu\text{mol}$  of Pt(IV), Hg(II) and Ag(I) and  $1.50 \mu\text{mol}$  of Au(III)

Metal ion	Recovery (%)			
	Pt	Hg	Ag	Au
Cu	97	100	100	100
Fe	99	101	101	100
Pb	97	99	99	100
Zn	100	101	100	100
Ni	100	100	100	100

TABLE 5

Separation of 1.50  $\mu\text{mol}$  of gold from 15  $\mu\text{mol}$  of another metal ion

Metal ion	Ca(II)	Cd(II)	Co(II)	Cu(II)	Hg(II)	Mg(II)	Mn(II)	Ni(II)	Fe(III)	Pb(II)
Au found ( $\mu\text{mol}$ )	1.48	1.40	1.45	1.47	1.40	1.51	1.46	1.45	1.58	1.64
Error ( $\mu\text{mol}$ )	-0.02	-0.10	-0.05	-0.03	-0.10	+0.01	-0.04	-0.05	+0.08	+0.14

group, respectively. Accordingly, the resin capacities were measured at pH 1.0, which was sufficiently acidic to avoid any interaction of the metal ions with other coordinated groups in the synthesized resin, and ensured that only the sulfhydryl group was involved in complexation.

The maximum capacity of the resin, determined by the batch method in perchloric acid medium, was 1.10 mmol  $\text{g}^{-1}$  for silver, 0.65 mmol  $\text{g}^{-1}$  for mercury, 1.34 mmol  $\text{g}^{-1}$  for gold and 0.59 mmol  $\text{g}^{-1}$  for platinum (Fig. 3A). The sulfur content of this resin is 1.15 mmol  $\text{g}^{-1}$ , so that 1:1 complexes are indicated for the resin functional group with silver and gold while 2:1 complexes are indicated for mercury and platinum. Several workers have similarly reported that cysteine binds silver and gold at a 1:1 ligand-to-metal ratio [14, 15], but mercury and platinum at a 2:1 ratio [12, 16]. The formation of the 1:1 complex with gold suggests that gold(III) was reduced to gold(I) by the resin [15]. The higher than theoretical capacity for gold on the basis of 1:1 complex formation in perchloric acid medium may be due to some reduction of gold to the metal. In hydrochloric acid medium, the maximum capacity was 1.16 mmol  $\text{g}^{-1}$  for gold, 0.48 mmol  $\text{g}^{-1}$  for mercury and 0.14 mmol  $\text{g}^{-1}$  for platinum (Fig. 3B). The formation of a 1:1 complex of gold with the resin functional group is indicated. The reduction potential of the metal ions is clearly decreased by the formation of stable chloro complexes in the hydrochloric acid medium compared with in perchloric acid medium.

TABLE 6

Collection of metal ions from dilute solutions

Metal ion	Amount added <sup>a</sup> ( $\mu\text{mol}$ )	Eluent	Recovery (%)
Ag	0.45	6 M HCl-2 M HClO <sub>4</sub>	100.2
	0.23	6 M HCl-2 M HClO <sub>4</sub>	98.1
Au	1.50	0.1% thiourea in 0.1 M HCl	99.5
	1.50	10 <sup>-3</sup> M thiourea in 10 <sup>-3</sup> M HCl	90.3
	0.45	0.1% thiourea in 0.1 M HCl	78.4
Hg	0.45	6 M HCl-2 M HClO <sub>4</sub>	101.2
	0.23	6 M HCl-2 M HClO <sub>4</sub>	91.1
Pt	0.45	0.5 M HCl	99.6
	0.23	0.5 M HCl	65.7

<sup>a</sup>In 500 ml of 0.1 M HCl.

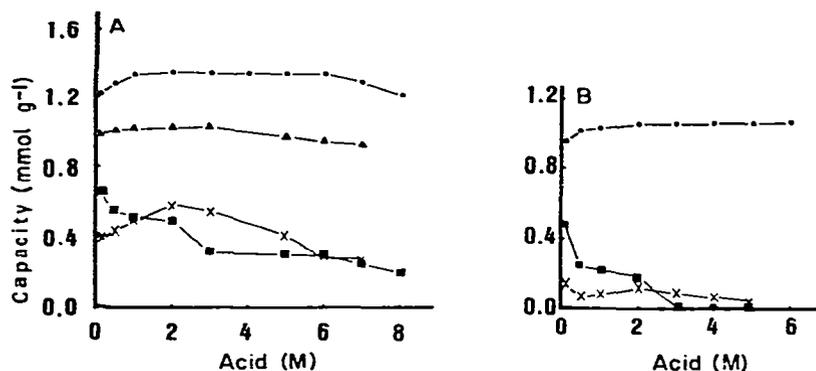


Fig. 3. Total capacity of the cysteine-containing resin for metal ions versus molarity of (A) perchloric acid and (B) hydrochloric acid: (●) Au(III); (▲) Ag(I); (■) Hg(II); (×) Pt(IV).

The lower capacities for mercury and platinum in hydrochloric acid than in perchloric acid at the same hydrogen concentration can be ascribed to competition of the chloride ion with the resin ligand.

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