

A Study on the Desorption Behaviors of Some Heavy Metals on Duolite GT-73 Chelating Resin

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Abstract : Effect of stripping solutions on the Duolite GT-73 chelating resin for ten elements, Ag(I), Al(III), Ca(II), Cd(II), Cu(II), Fe(II), Hg(II), Mn(II), Pb(II), and Zn(II), was investigated. Relation between affinities of the metal ions and solubility products of metal sulfides was studied. The smaller the solubility product of metal sulfide is, the larger the affinity with the ions. The ions which have the solubility products larger than 10^{-23} could be effectively desorbed with nitric acid. Complexation with chloride ion enhanced the desorption efficiencies of the ions having moderately strong affinity with the resin. The ions which have very strong affinity by the chelating resin can be desorbed by complexation with thiourea and hydrochloric acid.

Key words : Duolite GT-73 chelating resin, desorption of heavy metals, solubility product of metal sulfides

1. Introduction

Separation and preconcentration are inevitable steps in ultra-trace analysis, and the chelating ion exchange method¹ affords simple and rapid separation techniques. Conforming with the hard and soft acids theory, the functional group containing S donor atoms interacts strongly with the soft acid like heavy metals. Among these groups, extensive attention has been given to chelating resin bearing thiol(-SH)²⁻⁶ for selective separation of heavy metals.

Duolite GT-73 is a macro porous resin based on a cross linked polystyrene-divinylbenzene matrix. The functionality of the resin is mainly provided by the thiol group [-SH], with minor quantities of sulfonic acid

group. It has a high affinity with Hg(II), Ag(I), Cu(II), Pb(II) and Cd(II), since the solubility products of metal sulfides are very low. These ions are completely adsorbed in acidic and neutral pH. On the other hand, the ions having relatively high solubility products of metal sulfide have high affinity at neutral pH. Recently, relationships between the affinity for Duolite GT-73 chelating resin and the solubility products of metal sulfides have been reported by several groups.⁷⁻⁹

Since some ions including Hg(II), Ag(I), Cu(II) have strong affinity with chelating resin and they can be adsorbed from strongly acidic solution, the desorption of the ions from the resin is rather difficult. Recently, Iglesia⁸ studied the desorption of Pd(II) and Au(III) on Duolite GT-73 with several stripping solutions. However, only 13 and 1% were desorbed with 3.2 M of hydrochloric acid. Antico et al.⁹ also investigated the desorption of Pd(II) on Spheron Thiol-1000 chelating resin with several stripping solutions including thiourea.

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They reported that thiourea enhanced the desorption of Pd(II), but the desorption percents were only 59%.

In the present paper, we have studied the desorption of some heavy metals on Duolite GT-73 with several stripping solutions. Ten elements [Ag(I), Al(III), Ca(II), Cd(II), Cu(II), Fe(II), Hg(II), Mn(II), Pb(II), and Zn(II)] were chosen, and the effect of stripping solutions on the desorption efficiencies was investigated. Among the above ions, Hg(II) and Ag(I) have very strong affinity with chelating resin and the solubility products with metal sulfides are smaller than 10^{-50} . Cu(II), Pb(II) and Cd(II) have moderately strong affinity, and the solubility products ranges $10^{-26} \sim 10^{-36}$. The other ions have relatively weak affinities, and the solubility products are larger than 10^{-23} . Nitric acid, hydrochloric acid, perchloric acid, sulfuric acid, thiourea, and sodium cyanide were employed as stripping solutions.

2. Experimentals

2.1 Instrumentation and reagents.

Inductively coupled plasma-atomic emission spectrometer(ICP-AES) from Baird ICP 2070(Bedford, MA, U.S.A.) was used for determination of the elements. Operating conditions and spectral lines are shown in Table 1. Water of 18 M Ω was used throughout the experiment. It was prepared by distillation followed by further purification using mixed bed ion exchange resin and activated carbon columns. All single element stock solutions [1000 ppm of Ag(I), Al(III), Ca(II), Cd(II), Cu(II), Fe(II), Hg(II), Mn(II), Pb(II), Zn(II)] were purchased from Junsei Chemical Co.(Tokyo, Japan), and the pH of the eluent for adsorption was adjusted to 6 by HNO₃ and NaOH.

2.2. Procedure

Duolite GT-73 chelating resin in 16~50 mesh, which was purchased from Sigma Chem, Co.(St. Louis, MO, U.S.A.), has ground to 100 mesh. The original resin had capacity of 1.4 meq/mL(3.9 meq/g). Solution of 50 mL of 1 ppm was loaded at flow rate of 0.36 mL/min into a 150 mm(*l*) x 7 mm(*i.d.*) column containing 100 mg of

resin, and pH was adjusted to 6 by 0.2 M of acetic acid and sodium acetate buffer. For desorption studies, 50 mL of stripping solution was eluted with the flow rate of 0.20 mL/min.

3. Results and Discussion

3.1. Adsorption Behaviors of Metal Ions on Duolite GT-73 Chelating Resin

Adsorption conditions were the same as the previous work.⁷ Table 2 shows K_{sp} values¹⁰ of metal sulfides, and adsorption percents when 50 mL of 1 ppm ions was eluted with flow rates of 0.36 mL/min on 100 mg resin. Hg(II), Ag(I), Cu(II) and Pb(II) which have small solubility products of metal sulfides($<10^{-27}$) were completely adsorbed at pH 4~7. The ions which have large solubility products of metal sulfides showed lower adsorption at pH 3~5, but more than 90% of the ions were adsorbed at pH 6 except Ca(II). Some ions

Table 1. Specifications and operating conditions of ICP-AES

Spectrometer	750 mm focal length 1800 grooves/mm 0.2 nm/mm(2nd order)
RF generator	40.68 MHz
RF power	800 W
Flow rate(L/min)	Carrier 0.64 Coolant 8.5 Auxiliary 1.0
Nebulizer	Concentric type
Observation height	10 mm above induction coil
Spectral line(nm)	Ag(I) 328.068 Al(III) 396.152 Ca(II) 393.366 Cd(II) 214.438 Cu(II) 324.700 Fe(II) 259.740 Hg(II) 194.227 Mn(II) 257.610 Pb(II) 220.053 Zn(II) 213.856

Table 2. K_{sp} values of metal sulfides and adsorption percents of metal ions at several pH

Element	pK_{sp}	Adsorption percent at pH				
		3	4	5	6	7
Hg(II)	52.4	98	100	100	100	100
Ag(I)	50.1	98	100	100	100	100
Cu(II)	35.2	97	100	100	100	100
Pb(II)	27.9	97	100	100	100	100
Cd(II)	26.1	91	94	97	100	100
Zn(II)	21.6	60	69	84	95	97
Fe(II)	17.2	61	70	82	94	-
Mn(II)	12.6	50	58	69	96	-
Al(III)	6.7	63	70	84	92	-
Ca(II)	5.0	45	51	63	71	-

were partly precipitated as metal hydroxides above pH 7. Therefore, subsequent adsorption experiments were carried out at pH 6.

3.2. Desorption with inorganic acids

Table 3 shows desorption percents with 50 mL of inorganic acids at flow rate of 0.20 mL/min. The desorption percents were obtained by differences with the amounts adsorbed (50 μ g for 100% adsorption) and desorbed. For all ions, nitric acid and hydrochloric acid appeared to be better stripping solutions than perchloric acid and sulfuric acid. For each metal ion investigated, the ions which have relatively larger solubility products ($> 10^{22}$) showed high desorption percents with 2 M of nitric acid and hydrochloric acid. Zn(II), Fe(II), Mn(II) and Al(III) were desorbed completely with 2 M of nitric acid. On the other hand, desorption percents were 12~90% with 2 M of perchloric acid and sulfuric acid.

3.3. Effect of complexation with chloride ion

Hg(II), Ag(I), Pb(II) and Cd(II), which have low solubility products, were not completely desorbed with nitric acid, and the desorption percents of Hg(II) and Ag(I) were only 8 and 17 % with 3 M of nitric acid, respectively. On the other hand, desorption percents by hydrochloric acid for Ag(I), Cu(II), Pb(II) and Cd(II) were much higher than those by nitric acid. More than

95% of Pb(II) and Cd(II) were desorbed with 3 M hydrochloric acid, and the ions could be completely desorbed with another 50 mL of 3 M hydrochloric acid (total 100 mL). It can be explained that the complexation of metals with chloride ion enhances the desorption of metal ions.

The fraction of metal ions complexed in stripping solution is dependent on the stepwise formation constants¹⁰ with chloride ions, and concentration of chloride ion.

Table 3. Desorption percents of metals with 50 mL of inorganic acids

Element	Desorption percent						
	1M HNO ₃	2M HNO ₃	3M HNO ₃	2M HCl	3M HCl	2M HClO ₄	1M H ₂ SO ₄
Hg(II)	<2	2	8	<2	5	<2	<2
Ag(I)	6	13	17	42	76		
Cu(II)	48	54	59	80	88	79	11
Pb(II)	56	75	77	83	98	72	12
Cd(II)	25	73	79	90	96	76	15
Zn(II)	88	100	100	94	100	85	25
Fe(II)	86	95	100	95	100	86	20
Mn(II)	89	100	100	96	100	89	30
Al(III)	85	100	100	94	100	90	20
Ca(II)	91	100	100	100	100	90	43

Cumulative formation constants for Pb(II) and Cd(II) with chloride ion are $10^{7.36}$ and $10^{9.85}$, since the stepwise formation constants for Pb(II) are $K_1=10^{1.62}$, $K_2=10^{2.44}$, $K_3=10^{1.70}$ and $K_4=10^{1.60}$, and those for Cd(II) are $K_1=10^{1.95}$, $K_2=10^{2.50}$, $K_3=10^{2.60}$ and $K_4=10^{2.80}$. Therefore, the fractions of free metal ions in the stripping solution for Pb(II) and Cd(II) are $10^{-9.3}$ and $10^{-11.8}$, respectively, when the concentration of the chloride ion is 3 M. It is expected that complete complex formation of Pb(II) and Cd(II) with chloride ion enhances the desorption equilibrium. The stepwise formation constants for Cu(II) are small ($K_1=10^{0.1}$, $K_2=10^{0.6}$), but Cu(II) forms various complexes ($CuCl_4^{2-}$, $CuCl_5^{3-}$, $Cu_2Cl_6^{3-}$ and $Cu_2Cl_8^{4-}$) with chloride ion¹¹. Therefore, complexation of Cu(II) with chloride ion also plays role for desorption efficiency.

Cu(II) was completely desorbed with 100 mL of 3 M chloride ion.

3.4. Effect of complexation with thiourea

Although Hg(II) and Ag(I) form stable complexes with chloride ion, they were not completely desorbed with 3 M chloride ion since the solubility products of mercury and silver sulfides are so small. Therefore, the desorption of Hg(II), Ag(I), and Cu(II) with several stripping solutions which form more stable complexes than the chloride ion were investigated.

The ions having strong affinities with chelating resin containing thiol group also have strong affinities with the compound containing S donor ligands, and thiourea is the one of the commonly available S donor ligand. Thiourea has large stepwise formation constants with Hg(II) and Ag(I). Cumulative formation constants of thiourea with Hg(II) and Ag(I) are $10^{73.6}$ and $10^{20.5}$, and the values are much higher than those of the chloride ion. Therefore, the effects of thiourea on desorption efficiencies were investigated.

Desorption percents of Hg(II), Ag(I) and Cu(II) with several stripping solutions containing thiourea are shown in Table 4. Marked increase in desorption percents were observed with the addition of thiourea in chloride ion. Ag(I) and Cu(II) were completely desorbed with 50 mL of 1.0 M thiourea in 3.0 M chloride ion. 54 % of Hg(II) was desorbed with 1.5 M of thiourea in 0.1 M chloride ion, and the desorption percent was much higher than that with 3 M chloride ion. 87 % of Hg(II) was desorbed with 50 mL of 2.0 M thiourea in 3.0 M chloride ion, and Hg(II) could be completely desorbed with another 50 mL of stripping solution (total 100 mL). Therefore, it is expected that the metal ions which have high affinities with Duolite GT-73 chelating resin can be effectively desorbed with thiourea containing S donor ligand.

Desorption by batch method is less effective than the column one. 45 % of Hg(II) was desorbed with 25 mL of 2.0 M thiourea in 3.0 M chloride ion for 24 hours stirring. On the other hand, increase of chloride ion concentrations from 0.1 M to 3.0 M in 1.5 M thiourea

increased the desorption percent of Hg(II) from 54% to 70%. It indicates that complexation with thiourea plays more important role than chloride ion for desorption of Hg(II). Ag(I) and Cu(II) showed similar desorption behaviors with Hg(II).

3.5. Effect of complexation with cyanide ion

Cyanide ion also forms stable complex with Hg(II). The ion forms $\text{Hg}(\text{CN})_4^{2-}$ with Hg(II), and the formation constant (K_4) is as large as $10^{41.4}$. However, addition of 0.2 M of NaCN in 3 M chloride ion did not enhance the desorption percent, and 6 % of Hg(II) was desorbed with the stripping solution. Desorption studies at higher NaCN concentration were not studied since NaCN is toxic, and the increase of NaCN concentration up to 0.5 M caused plasma unstable. Increase of NaCN concentration also increased ionization interference in ICP spectrometry. On the other hand, addition of thiourea in stripping solution did not affect plasma stability, and the resin could be regenerated for further use by stripping with 2.0 M thiourea in 3.0 M chloride ion.

Table 4. Desorption percents of Hg(II), Ag(I) and Cu(II) with 50 mL stripping solutions

Composition of stripping solution	Desorption percent		
	Hg(II)	Ag(I)	Cu(II)
1.0 M thiourea + 3.0 M HCl	29	100	100
1.5 M thiourea + 3.0 M HCl	71, 84 ^a	100	100
2.0 M thiourea + 3.0 M HCl	87, 100 ^a , 45 ^b	100	100
1.5 M thiourea + 1.0 M HCl	70	64	89
1.5 M thiourea + 0.1 M HCl	54	60	65

a : 100 mL of stripping solution.

b : batch experiment (stirred 24 hours with 25 mL of stripping solution).

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