Chemical Modification of Anion-Exchange Resin with Chrome Azurol S

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In order to prepare the chelate resin, the gel-type anion exchange resin was modified by the adsorption of Chrome Azurol S as a chelate agent. For the determination of trace metal ions by use of the graphite furnace atomic absorption spectrometry (GFAAS), this modified resin was applied to the separation and enrichment of metal ions in the aqueous solution. In a batchwise operation, the 2 ml of modified resin was simply stirred with the sample solution contained metal ions and pH buffer in a flask for 5 hours at room temperature. The resin which adsorbed metal ions was introduced in a 10 ml of 0.5 mol l^{-1} HCl solution and shaken for 5 minutes. The concentrations of desorbed metal ions in HCl solution were determined by use of GFAAS. When beryllium was determined, boric acid was added to the HCl solution. The optimum results were obtained for the copper(II) and beryllium ions. These ions were separated from another ion by controlling the pH of sample solution. Enrichment of copper ion by a factor of about 400 was possible. The interference with foreign metal ions was little. By use of enrichment, the trace copper in salt rock could be determined.

Keywords Anion Exchange Resin, Modification, Chrome Azurol S, Chelate Resin, Separation of Metal Ions.

1. INTRODUCTION

A remarkable improvement in the sensitivity and accuracy of analytical instrument has required the development of convenient pretreatment methods for determining a trace component. Ion exchange resins are widely used in various fields as an adsorbant of ions in aqueous solution. Chelate resins are also used as an adsorbant of metal ions. For separating the sought metal ions from the saline matrix, the use of cation exchange resin is not suitable, but a chelate resin is more convenient for the *in situ* dealing with sample for the analysis of natural and seawater sample.[1-3] Commercially available chelate resins, however, have generally no selectivity about the adsorbance of metal ions. Therefore, modifications of anion exchange resin by adsorption of organic ligand have been attempted.[4,5] The selectivity of modified resin as an adsorbant of metal ions may be depend on the selectivity of organic ligand reaction with metal ions.

In this paper, in order to prepare the chelate resin, modification of the gel-type resin by the adsorption of Chrome Azurol S (2,6-dichloro-4'-hydroxy-3',3"-dimethyl-2-sulfofuchsone-5',5"-dicarboxylic acid) as a chelate agent was attempted. Chrome Asurol S (CAS) was used as a chelating agent for the determination of copper[6] and beryllium[7] by use of spectrophotometry. For the determination of copper and beryllium by use of the graphite furnace atomic absorption spectrometry (GFAAS), this modified resin was applied to separation and enrichment of these metal ions in the aqueous solution.

2. EXPERIMENTAL

2.1 Reagents and apparatus

Gel-type anion exchange resin, Amberlite IRA-400 (Organo Co., Ltd.) in the chloride form ($0.40\sim0.53$ mm) and Chrome Azurol S (Nacalai Tequ, Inc) were used. Commercially available metal standard solutions for atomic absorption spectrometry were diluted with deionized-distilled water to a working solution. All other reagents used were of analytical grade.

A Hitachi Model 180-30 atomic-absorption spectrometer was used with a Hitachi Model GA-2B graphite-furnace atomizer. A tube type graphite cell was used in an argon atmosphere. The signal was recorded with a Hitachi Model D-2500 chromato-integrator. Hitachi hollow-cathode lamps were used as radiation sources. A deuterium-arc background correction was used throughout. Samples were deposited using a Hitachi autosampler.

2.2 Modification of anion exchange resin with CAS

A 10 ml portion of the anion exchange resin in the chloride form was introduced into a 200 ml round-bottomed flask and a 100 ml of 0.05 mol l^{-1} $Na_2B_2O_7$ (pH 9.2) and 1000 mg l^{-1} CAS solution was added. The mixture was stirred for 5 hours at room temperature. After that, the resin was filtered and washed with pure water. The modified resin was kept wet.

2.3 Adsorption and desorption of metal ions

A 2 ml portion of the modified resin in the chloride form was introduced into a 300 ml Erlenmeyer flask and sample solution containing metal ion and buffer solution were added. The mixture was shaken for 5 hours at room temperature. After that, the resin was filtered and washed with pure water. When beryllium ion was adsorbed, shaking time of 3 hours was used.

The resin which adsorbed metal ions was introduced into a 50 ml Erlenmeyer flask and a 10 ml of 0.5 mol l^{-1} HCl solution was added. After shaking the mixture for 5 minutes, the concentration of metal ion in the solution was determined by the use of GFAAS. When beryllium was desorbed, the mixture of 0.5 mol l^{-1} HCl and 0.01 mol l^{-1} B(OH)$_3$ was used, and when aluminum, gallium and indium were desorbed, the mixture of 0.5 mol l^{-1} HCl and 0.01 mol l^{-1} Ni(NO$_3$)$_2$ was used.

3. RESULTS AND DISCUSSION

3.1 Modification with CAS

The resin was modified by use of various initial concentration of CAS. After stirring the mixture of the resin and CAS, the residual concentration of CAS in a solution was determined by use of spectrometry. When the initial concentration of CAS was beyond 1000 mg l^{-1}, the residual CAS was observed. Therefore, the modification condition described above was used throughout this study. This adsorbed CAS could not be easily exchanged with other anions. When the modified resin was dried, the resin was broken. Therefore, the modified resin was kept wet.
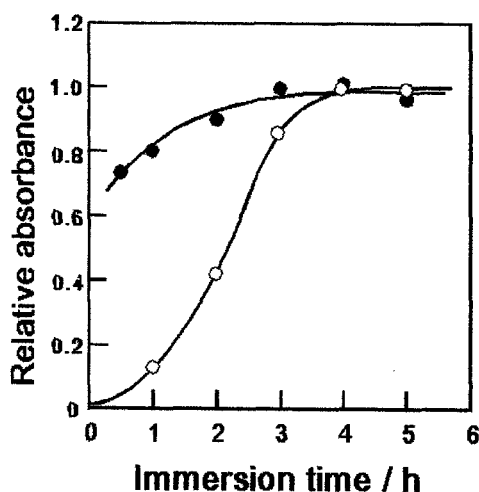

Fig. 1 Effect of immersion times on the adsorption of (○)copper and (●)beryllium on the modified resin. Resin, 2 ml; sample volume, 500 ml (Cu) and 100 ml (Be); initial concentration, 8 µg l^{-1} (Cu) and 1 µg l^{-1}(Be); pH, 9.2 (Cu) and 8.3 (Be).
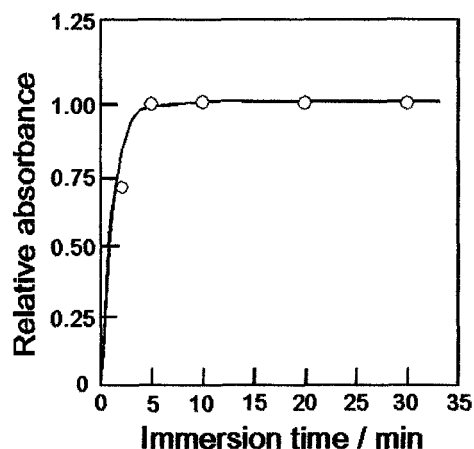

Fig. 2 Effect of immersion time on the desportion of copper from the modified resin. Resin, 2 ml; Cu, 2 µg.

3.2 Adsorption of metal ions on the resin

The effect of immersion time on the adsorbed amount of metal ion on the modified resin was investigated. The results for copper(II) and beryllium are shown in Fig.1. After shaking for 4 hours, the copper(II) ion was completely adsorbed. For beryllium ion, 3 hours shaking was required. Therefore, the immersion time of 3 hours for beryllium and 5 hours for another metal ions were used.

3.3 Desorption of metal ions from the resin

The HCl solution was used as an eluent. The effect of immersion time on the desorption of metal ion from the modified resin was investigated. The result for copper(II) is shown in Fig.2. After shaking for 5 minutes, the copper(II) ion was completely desorbed. The effect of HCl concentration was also investigated. The concentration of HCl required for copper and beryllium were above 0.1 and 0.4 mol l^{-1}, respectively. Therefore, the adsorption and desorption conditions described above was used throughout this study.

When the aluminum, gallium and indium are determined by GFAAS, the addition of matrix modifier to the sample solution is necessary.[8,9] When the beryllium was determined, as shown in Fig.3, the addition of 0.01 mol l^{-1} B(OH)$_3$ as a matrix modifier was most suitable. Therefore, as descried above, B(OH)$_3$ or Ni(NO$_3$)$_2$ were added as the modifier in HCl solution.

3.4 Effect of pH on the adsorption

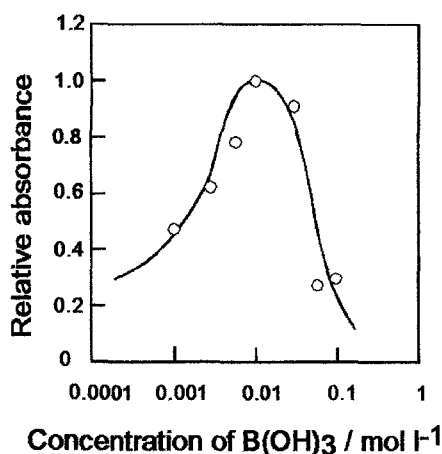The adsorption of metal ion on the modified resin

Fig. 3   Effect of B(OH)₃ on the determination of beryllium by use of GFAAS with pyrocoated tube.
Be, 20 μg l⁻¹; HCl, 0.5 mol l⁻¹.

may be largely affected by pH of sample solution and metal ion may be separated by the difference of pH. The effects of pH of the sample solution on the adsorption of various metal ions were investigated. The pH was adjusted with buffer solution of CH_3COOH-CH_3COONa or $B(OH)_3$-KCl-NaOH. The results for copper(II), chromium(III), nickel(II), cobalt(II) and manganese(II) are shown in Fig.3, and those for beryllium(II), aluminum(III) and gallium(III) are in Fig.4. The adsorption of indium on the resin could not be observed. These results show that this modified resin is excellent for the adsorption of copper and beryllium ions. In particular, the effective pH range for copper is wide (pH 8 to 12), therefore, copper ion may be easily separated from another ions by the use of this modified resin.
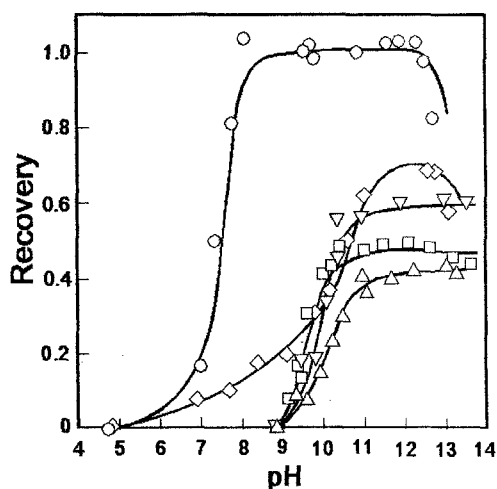

Fig. 4   Effect of pH on the adsorption of copper(○, 20 μg l⁻¹), chromium(III) (◇, 5.8 μg l⁻¹), nickel(▽, 25 μg l⁻¹), cobalt(□, 25 μg l⁻¹) and manganese(△, 25 μg l⁻¹). Resin, 2 ml; sample volume, 100 ml.
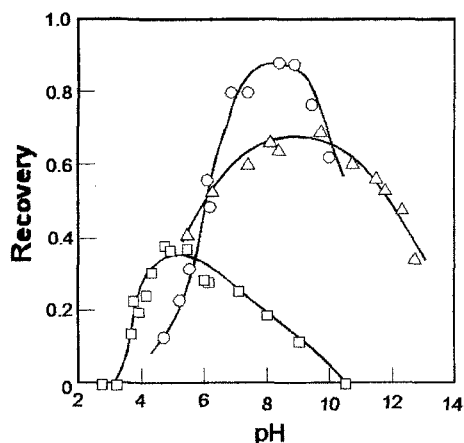
Fig. 5   Effect of pH on the adsorption of beryllium(○, 1.0 μg l⁻¹), aluminum(△, 25 μg l⁻¹) and gallium(□, 1.0 μg l⁻¹). Resin, 2 ml; sample volume, 100 ml.

3.5 Effect of sample volume

Under the conditions described above, the calibration graphs were liner over the ranges 20 – 200 ng copper and 2 – 20 ng beryllium. The concentration ratios of copper and beryllium were measured by varying these sample solution volumes. The pH was adjusted to 9.2 for copper and to 8.3 for beryllium. The results are presented in Table 1. Enrichment of copper by a factor of 400 and that of beryllium by a factor of 50 were possible. These possibilities of enrichment may be useful and practical.

3.6 Effect of foreign metal ions

The interference with foreign metal ions on the adsorption of copper and beryllium on the resin were investigated. The pH was adjusted to 9.2 or 8.5 for

Table I   Effects of sample volume on the recovery of copper and beryllium.

Sample volume / ml	Concentration ratio		Recovery	
	Cu	Be	Cu	Be
50	10		1.00	
100	20	10	1.00	1.02
200	40		1.00	
250	50		1.00	
500	100	50	1.01	0.93
1000	200	100	1.00	0.75
2000	400		1.01	

Resin, 2 ml.
Cu : Amount, 3.15×10^{-8} mol; pH, 9.2; Eluent, 5ml.
Be : Amount, 1.11×10^{-8} mol; pH, 8.3; Eluent, 10ml.

Table II   Effects of another cations on the recovery of copper and beryllium.

Cation	Relative concentration		Recovery	
	Cu	Be	Cu	Be
Mn(II)	20	20	0.89	1.02
	50	50	0.71	1.02
	50*	100	0.96	1.04
Co(II)	20	20	1.00	1.05
	50	50	0.77	1.00
	50*	100	1.00	0.99
Ni(II)	20	20	0.98	1.02
	50	50	0.78	1.09
	50*	100	1.00	1.02
Zn(II)	20	20	0.98	1.06
	50	50	0.74	1.06
	50*	100	1.04	1.06
Cu(II)	-	20	-	1.01
	-	50	-	1.02
	-	100	-	1.09
Al(III)	-	20	-	1.06
	-	50	-	1.04
	-	100	-	1.15
Na(I)	500	500	1.00	1.02
	1000	1000	0.98	1.00
K(I)	500	500	0.99	1.03
	1000	1000	0.87	1.01
Mg(II)	500	500	0.98	1.08
	1000	1000	0.94	1.08

Resin, 2 ml.

Cu : Amount, 3.15×10^{-8} mol; pH, 9.2(*8.5); Eluent, 5ml.

Be : Amount, 1.11×10^{-8} mol; pH, 8.3; Eluent, 10ml.

copper and to 8.3 for beryllium. The results are presented in Table 2. Up to presence of 50 times quantity to analyte, heavy metal ions can not interfere. This selectivity may be due to the selectivity by GFAAS determination. As the interference with

foreign metal ions are little in the determination by GFAAS, if the total amount of metal ions are smaller than ion exchange capacity of this modified resin, the interference with these metal ions may not be observed. Interferences with alkaline and alkaline earth metal ions are not observed. These phenomena may be due to that these cations can not react with CAS.

3.7 Determination of trace copper in salt rocks

This enrichment by modified resin with CAS was applied to the pretreatment for the determination of trace copper in the salt rocks by GFAAS, because, when this modified resin was used to enrich the copper ion, interference with alkaline and alkaline earth metal ions were not observed. The salt rocks were dissolved in 0.1 mol l^{-1} HCl. After filtration, the solution was diluted to 500 ml with 0.1 mol l^{-1} HCl. An aliquot of sample solution containing 0.5 ~ 2.0 μg of copper was treated by use of the method described above. As presented in Table 3, good results are obtained. These results show that this modified resin is the suitable absorbent of copper ion in the aqueous solution.

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Table III   Determination of trace copper in the rock salt.

Sample	Sample taken / g	Cu added / μg	Cu found / μg	Cu in the sample / μgKg^{-1}	Recovery
India	17.5	-	0.49	28.0	-
	17.5	0.25	0.74	-	0.997
Mexico	17.5	-	0.52	30.0 ± 0.8*	-

* n = 3