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Poly(acrylamidoxime) Chelate Resin의 성질과 응용

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Properties and Application of Poly (acrylamidoxime) Chelate Resin

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요약 : Divinylbenzene으로 Crosslink한 Poly(acrylamidoxime)수지의 Li, B, La (Ⅲ), Ce (Ⅳ), Nd (Ⅲ)에 대한 complexation property를 ICP-AES를 사용하여 연구하였다. 이 수지는 La (Ⅲ), Ce (Ⅳ) 및 Nd (Ⅲ)과는 complex 화합물을 효과적으로 생성하나 Li과 B와는 complex화합물을 생성하지 않았다.

수지에 흡착한 미량의 금속은 1 : 1-HNO_3—물의 혼합물에 의하여 추출 회수되었다. 이 수지의 응용으로서 거의 순수한 알미늄 시료중에 함유되어있는 불순물을 column법에 의하여 정량하였다.

ABSTRACT : Complexation properties of a divinylbenzene crosslinked poly (acrylamidoxime) resin for Li, B, La (Ⅲ), Ce (Ⅳ) and Nd (Ⅲ) were investigated by inductively coupled plasma-atomic emission spectroscopy. The resin was found to be effective for the sequestering of La (Ⅲ), Ce (Ⅳ) and Nd (Ⅲ) from aqueous solutions. The resin exhibited no affinity for Li and B cations. Recovery of trace levels of metals sequestered on the resin was achieved by elution with either 1 : 1 nitric acid-water or 1 : 1 hydrochloric acid-water. The application of trace concentation levels of impurities in high purity aluminum was examined.

1. INTRODUCTION

Recently the knowledge of the detrimental effects of trace amounts of metals in water, food and the other environment has greatly increased. In order to solve the effect, these

trace levels of metals are having on the environment, accurate and reliable methods must be developed for their determinations. Many kinds of instruments for their determinations exist and have exellent sensitivities for most metals.

Occationally, the amounts of the metals are ultra trace, so that the species of interest must be determined at or below the minimum detection limit of the instrumental method. Suitable methods for the preconcentration and isolation of the trace metals from the related samples must be developed for the solution of the problem.

Metal chelating resins are very selective to metal uptake and have been extensively used for these fields. Many metal chelate resins have been used for the concentration and isolation of trace metals.

Dingman[1] studied with complexation of trace metal cations with polyamine-polyurea resin. Barnes and Genna[2] investigated a method of simultaneous multielement analysis of trace elements of interest from biological matrices with poly (dithiocarbamate) resin.

Miyazaki and Barnes[3] worked with complexation of some transition metals, rare earth elements and thorium using a poly (dithiocarbamate) resin, and with differential determinatin of chromium(Ⅳ)-chromium(Ⅲ) with poly (dithiocarbamate) resin[4]. Manolov and Motekov[5] demonstrated determination method of trace cobalt-manganese with 2,4-dimethylbenzamido xime.

In addition to polymeric chelating resins several chemically modified silicas have been used as selective ion-exchangers.

Leyden[6,7] has developed several of these substrates for the collection of trace metals from natural waters. Hercules has used ESCA to quantitate trace metals collected on dithiocarbamate modified glass fibers[8]

The purpose of this study is in demonstrating the complexation properties of 5 metals with the resin and in applying their resin to real sample using inductively coupled plasma-atomic emission spectrometry.

2. EXPERIMENTAL

2-1. Apparatus

The ICP-AES instruments and their operating conditions are given in Table Ⅰ and Ⅱ. Infrared spectra were obtained with a Perkin Elmer 137 infrared spectrophotometer. Agitation of sample solutions was conducted with a New Brunwick Scientific Company mechanical shaker. Resin columns were made with disposable Pasteur pipette, and sample reservoirs were 1L, 500ml and 250ml separatory funnels that had been modified by sealing a 1-inch piece of 7mm o.d. tubing to the funnel outlets.

2-2. Reagents

Lithium standard solution was prepared by dissolving Li_2CO_3 (Aldrich) in a minimum volume of (1+1) HCl. Boron standard solution was prepared by dissolving H_3BO_3 (Aldrich) in DDW and stored in a polyethylene bottle. Lan-

Table Ⅰ. ICP-AES INSTRUMENTS

ICP Source	Plasma-Therm Model HFS-5000D
Monochromator	Minuteman Model 310-SMP
Nebulizer	Crossflow Type
Optics	Quartz Lens, 2in. Diameter, 200 mm Focal Length
Recorder	Heath EH-20B
Amperemeter	414S-Picoammeter (Keithley Instrument)
Local Coil	3-Turn copper tubing, 1/3 in. o.d.

Table Ⅱ. ICP Operating Conditions

	Li	B	La (Ⅲ)	Ce (Ⅳ)	Nd (Ⅲ)
Power, Kw	0.8	0.9	0.8	0.8	0.7
Observation Height, mm	14	14	14	14	14
Coolent Flow, l/min	15.86	16.23	16.75	16.75	15.78
Nebulizer Flow, l/min	0.76	0.98	0.55	0.55	0.48
Nebulizer Back Pressure, psig	28	30	34.5	34.5	34.5
Sample Uptake, ml/min	1.6	1.6	1.6	1.6	1.6
Entrance Slit Height, mm	5	5	4	4	5
Entrance Slit Width, μm	100	30	30	30	50
Exit Slit Width μm	100	30	30	30	50
Wavelength, nm	670.784	249.678	394.910	434.8	401.225

thanium (Ⅲ) standard solution was prepared by La $(NO_3)_3$ $6H_2O$ (Aldrich) in dilute nitric acid.

Cerium (Ⅳ) standard solution was prepared by dissolving Ce $(SO_4)_2$ $2(NH_4)_2SO_4 2H_2O$(Alfa) in dilute nitric acid. Neodymium (Ⅲ) standard solution was prepared by dissolving Nd_2O_3 (Aldrich) in a minimum volume of HCl.

The reagents for the synthesis of poly (acrylamidoxime) resin included divinylbenzene(Pfaltz and Bauer), acrylonitrile (Aldrich), potassium metabisulfite (Mallinckrodth), potassium persulfate and anhydrous sulfate (Aldrich), hydroxylamine hydrochloride and phenolphthalein (Eastman), barium chloride, n-butyl alcohol and ethyl ether (Aldrich).

ACS reagent grade chemicals and distilled, deionized water were used in this study.

2-3. Resin Synthesis

The divinylbenzene-acrylonitrile copolymer was prepared by a redox polymerization[9,10], 1.5g $K_2S_2O_8$, 1.5g $K_2S_2O_5$ and 100g Na_2SO_4 were added to 1L of DDW in a 2L, 3-neck round bottom flask equipped with a water cooled condensor and overhead stirrer. The solution was heated to 60°C, and a 20 : 1 mixture of acrylonitrile (150ml) and divinylbenzene (15g) was slowly added. Polymerization was carried out for 3h after addition of the reactants. The resin was then filtered and washed with hot DDW until the washings did not include sulfate, that is, no precipitate was produced upon the addition of approximately 5ml of 0.1 n-$BaCl_2$ solution to the washings.

The resin was first air dried for 72h, then dried at 100°C for 1h, ground, and sieved. A solution of free hydroxylamine in a n-butanol was prepared as repored by Hurd and Brownstein[11] : 12.0 to 12.5g Na was added to 170ml of n-butanol and heated with stirring until the Na was completely dissolved. The solution was added dropwise to a separate flask containing 34.8g $NH_2OH \cdot HCl$, 0.1g phenolphthalein and 40ml n-butanol. After addition of the sodium butylate solution, the NaCl was filtered and washed with 30ml n-butanol and 10ml ethyl ether. To the combined filtrates was added 22g of 60/80 mesh divinylbenzene-acrylonitrile copolymer. The reaction mixture was heated at 60°C, with stirring for 24h. The resin was then suction-filtered and washed with three 500ml volumes of ethanol and 500ml of DDW. The resin, pale yellow in color, turns white in acidic solutions and bright yellow in basic solutions. The resin was air dried overnight,

ground, sieved, and stored in a vacuum desiccator over P_2O_5.

2-4. Infrared Spectra

Infrared spectra were obtained from KBr pellets of both the divinylbenzene-acrylonitrile copolymer and the poly(acrylamidoxime) resin.

2-5. pH Dependence of Metal Ion Uptake

Stock metal ion solutions containing 250ppm of the various test elements were prepared over a range of pH. 25.0ml aliquots of the metal ion solutions were equilibrated with 50mg samples of 60/80 mesh resin in 60ml Nalgene polyethylene bottles for 24 hours on a mechanical shaker.

Subsequently, the amount of metal present still in solution was determined using ICP-AES. Samples were run with excess metal ion concentration.

2-6. Determination of Resin Capacity

The capacity of the poly (acrylamidoxime) resin was determined for a variety of metals using a batch equilibration technique. The resin capacity for La (Ⅲ) and Nd (Ⅲ) were determined at pH 5, except the Ce (Ⅳ) solution, which was determined at pH 4. 50mg of 60/80 mesh resin samples were equilibrated with 250 ml of stock metal ion solutions for 24h. After equilibration, the amount of excess metal ion remaining still in solution was determined by ICP-AES. Concentration of all sample solutions was 250ppm.

2-7. pH Dependence of Trace Metal Ion Uptake

The procedure was the same as that described for the determination of pH dependence of metal ion uptake by a batch equilibration technique. In this study, the resin was in exess of metal ion concentration.

The conditions of this study were as follows: 50mg of 60/80 mesh resin samples were equilibrated with 25.0ml of 10ppm stock solutions of La (Ⅲ), Ce (Ⅳ) and Nd (Ⅲ).

2-8. Recovery of Trace Metals

The ability of the poly(acrylamidoxime) resin to concentrate solutions containing trace metals was demonstrated using laboratory prepared samples by a column method. Columns of the resin were prepared from the 8.5cm long by 0.5cm o.d. disposable Pasteur pipettes with silanized (with trimethylchlorosilane) glass wool plugs in the tips.

Pasteur pipette columns were packed with 60/80 mesh resin and 2ml of metal ion solution passed through the column with the effluent from the column being collected. The La (Ⅲ) test solution was used at an initial concentration of 20.0ppm at pH 5 with 100mg resin.

The 50.0ppm Ce (Ⅳ) and Nd (Ⅲ) test solutions were employed at pH 5 with 300mg resin. The columns were then eluted with 5.0ml of either 1 : 1 HNO_3/DDW, 1 : 1 HCl/DDW or a 1M sodium thiosulfate solution.

Both the effluent and eluent from the column were analyzed to determine the recovery of the sequestered metals using ICP-AES.

2—9. Analysis of Cd in high purity aluminum sample

The concentration procedure with the resin was extended to real sample. Sveral examinations were run in advance for the determination of cadmium in high purity aluminum sample. The first examination was pH dependence of cadmium uptake in aluminum solution. The process was performed according to that described for pH dependence of metal ion uptake by a batch equilibration technique. The conditions under

which this study was run were as follows: 50 mg of 60/80 mesh resin samples were equilibrated with 25.0ml of metal stock solution which included both cadmium and aluminum at the same concentration of 30ppm.

In the other hand, 50mg of 60/80 mesh resin samples were equilibrated with 25.0ml of metal stock solution containing 30ppm cadmium only.

The second examination was aluminum concentration dependence of the uptake of cadmium. The process was the same as above.

This examination was performed at pH 7 under varying aluminum concentration(50, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000ppm) and resin amount (50, 100, 200and 300mg). In the end, analysis of real sample was run by column methed. A Pasteur pipette column was packed with 100mg of 60/80 mesh resin and 1000ml of a 0.005% (50ppm) aluminum sample solution at pH 7 passed throungh the column. The column was rinsed with 10.0ml of DDW and then eluted with 3.0ml of 1 : 1 HCl/DDW mixture. Cadmium in the eluent was determined by ICP-AES.

3. BESULTS AND DISCUSSION

3—1. IR Spectra

In the IR spectrum of the divinylbenzene-acrylonitrile copolymer (Fig.1), the characteristic nitrile absorption is at 4.45μ, absorption in the 10-14μ exhibits the existence of the aromatic rings in the copolymer[12]. Fig.2 indicates the IR spectra of the poly(acrylamidoxime) resin. Comparing these spectra with that of the divinylbenzene-acrylonitrile copolymer, a lot of changes are found: the amine absorption at 3.0μ, the-OH absorption at 3.18μ, the C=N of the oxime group at 6.04μ, and the broad absorption of the N-O of the oxime at 10.94μ,[13,14] Absorption at 4.45μ exhibits the unreacted nitrile groups through the resin.

3—2. pH Dependence of Metal Ion Uptake

The study was carried out as a process to determine which metals would produce complexes with poly(acrylamidoxime) resin. According to this study, lithium and boron exhibited no affinity for the resin over the pH range 1-8. Fig.3 shows the results of the tests, i.e., the pH of the metal ion solutions was found to have a considerable effect on the uptake of the metal ions by the resin. Ideally pH range for metal uptaking should be as broad as possible to rend sample pH modification unnecessary, which in turn reduces the possibility of metal contamination. Uptake of La (Ⅲ), Ce (Ⅳ) and Nd (Ⅲ) are favorable from pH 3 and greater. The pH range makes them ideally suited for concentration by the resin.

Uptake for Ce (Ⅳ) showed the maximum at

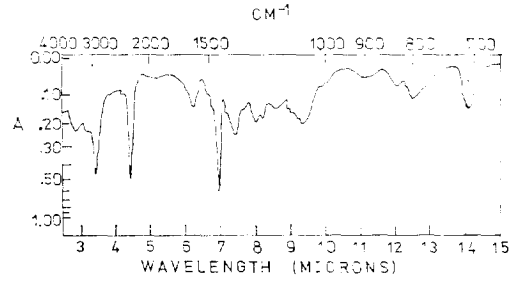

Fig. 1. IR spectrum of DVB-Acrylonitrile copolymer

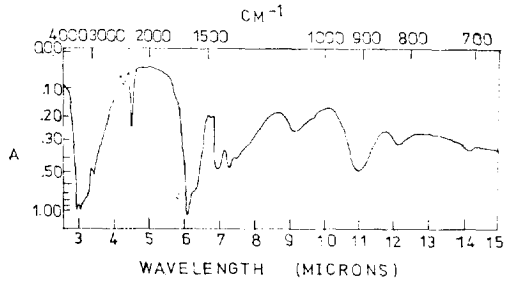

Fig. 2. IR spectrum of poly (acrylamidoxime)

pH 3 and 4 and decreased gradually with increasing pH above 5. Uptake of Ce(Ⅳ) on poly (dithiocarbamate) resin described by Miyazaki and Barnes[15] was somewhat lower as compared with poly (acrylamidoxime) resin and showed maximum at pH 5.

3—3. Determination of Resin Capacity

How large a quantity of resin will be needed for quantitative elimination of a specific metal ion from sample solution is one of the important factors for the quality of the resin. It has been of primary importance to synthesize resins of high metal capacity in order that a trace analytical method of practical value could be developed. Conventional ion-exchangers generally have capacities greater than chelating ion exchangers. This lack of capacity is compensated for in the increased selectivity that they possess for specific classes of elements. It was found that the resin capacity varied considerably from metal to metal. The capacity of the resin for each metal is summarized in Table Ⅲ

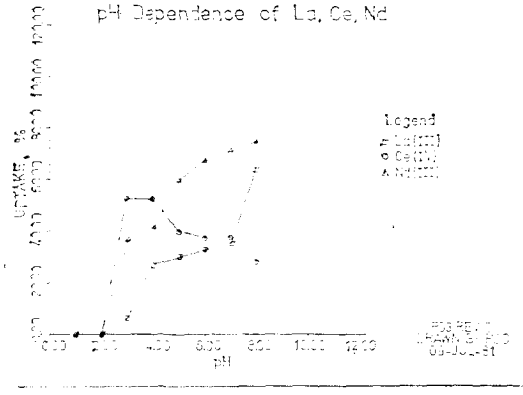

Fig. 3. pH Dependence of Metal Ion Uptake

Table Ⅲ. Metal Capacity of Poly(acrylamidoxime) resin at pH 4

Metal	Capacity (mg M^{n+}/g resin)
La (Ⅲ)	33.8
Ce (Ⅳ)	66.7
Nd (Ⅲ)	53.2

Poly(acrylamidoxime) resin has greater capacity as compared to poly (dithiocarbamate) resin studied for these metals by Miyazaki and Barnes.[15]

3—4. pH Dependence of Trace Metal Ion Uptake

This study was carried out to determine if the uptake of trace amounts of metals is possible at pH values other than the optimum pH for chelation. In this case the resin is in excess of the metal ion concentration. Fig. 4 indicates the results tested here. According to the data, pH showed little the effect on the uptake of the trace metal amounts.

La (Ⅲ), Ce(Ⅳ) and Nd(Ⅲ) were at the level of 80-100% uptaked at pH 3 and above. In the result, this data shows that they can be removed quantitatively even Ce (Ⅳ) over the broad pH range except pH 1 and 2 at which are not complexed like pH dependence of metal ion above.

3—5. Recovery of Trace Metal

Concentration and separation of metals from sample solution containing trace or ultratrace quantities of metals can only be performed when the volume of the eluent is small com-

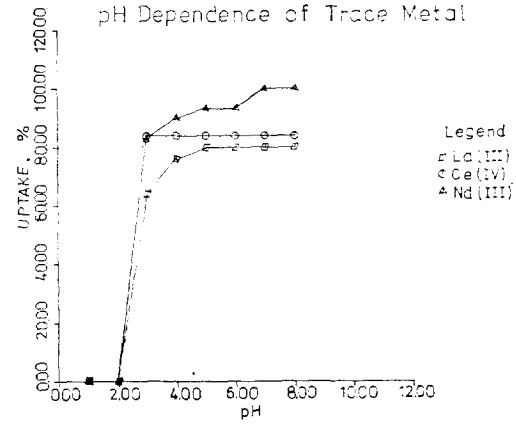

Fig. 4. pH Dependence of trace metal ion uptake

pared to the initial sample volume.

In this recovery study the uptake of trace metals was 90% and above for the metals tested here, and the recovery percentage of the trace metals was obtained from the amount of metal uptaked. A 1 : 1 HCl/DDW mixture was used as the first eluent. The recovery of uptaked metals with the eluent was 100% for La (Ⅲ) and≥ 92% for Ce (Ⅳ) and Nd (Ⅲ). A 1 : 1 HNO_3/ DDW mixture was employed as the second eluent. This eluent was more effective than 1 : 1 HCl/DDW mixture for the recovery of the metals studied here, i.e., La (Ⅲ) was also at the level of 100% recovered and Ce (Ⅳ) and Nd (Ⅲ) were 95.1% and 94.5% recovered, respectively.

Lastly 1M-sodium thiosulfate solution was tested for the recovery of sequestered La(Ⅲ), Ce(Ⅳ) and Nd(Ⅲ) from the resin matrix but this eluent had no affinity for the metals. Colella, Siggia and Barnes reported that the use of thiosulfate as an eluent effected the quantitative removal of sequestered Ag(Ⅰ) from the resin matrix[16].

A summary of the recovery of the trace metals with various eluents from the resin matrix is present in Table Ⅳ

3—6. Analysis of Cd in high purity aluminum sample

Several preliminary studies were carried out to determine the trace amount of cadmium in aluminum sample. They were pH dependence of the uptake of cadmium in aluminum solution and concentration dependence of aluminum on the upatke of cadmium. As illustrated in Fig. 5, although the uptake of Cd in Al solution was somewhat lower as compared to laboratory prepared Cd solution which did not include Al, the interference at the the level of 30ppm Al is so small to be negligible. The uptake of Cd ion increases gradually with increasing pH and rapidly at pH 6.

Occasionally the presence of a metal ion of high concentration in sample solution has greater interference on the uptake of a trace metal ion which will be determined. Fig. 6 exhibits that the uptake of Cd decreases with increasing Al concentration, i.e., the higher the concentration of Al the greater the interference on the uptake of Cd. Cd was above 90% removed below the concentration of 50ppm at pH 7 and above. According to Fig. 6, the uptake of Cd in Al solution increased with increasing the amount of the resin, but the difference was so small not to be considered in this conditions.

Finally, it was found that the amount of Cd in Al solution could be determined in dilute solution at the level of below 50ppm using the resin concentration procedure. Analysis of the real sample wes conducted with appropriate conditions referring to the above results tested here. The content of Cd in this sample Switzerland Alusuisse (No. 124) was 0.014±0.003%.

Table Ⅳ. Recovery of Trace Metal

	1 : 1HCl	1 : 1HNO_3	1 : 1$Na_2S_2O_3$	Replicates
La(Ⅲ)	100±2	100±3	0	3
Ce(Ⅳ)	83.6±4	95.1±1	0	3
Nd(Ⅲ)	92.6±3	94.5±4	0	3

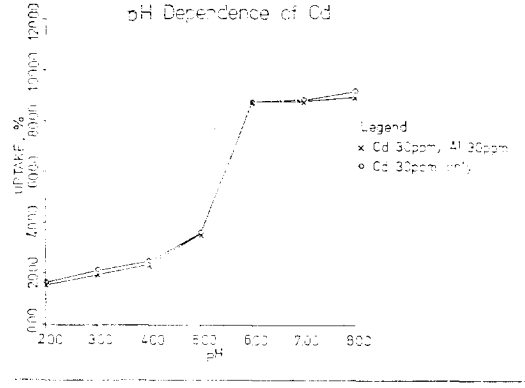

Fig. 5. pH Dependence of Cd in Al

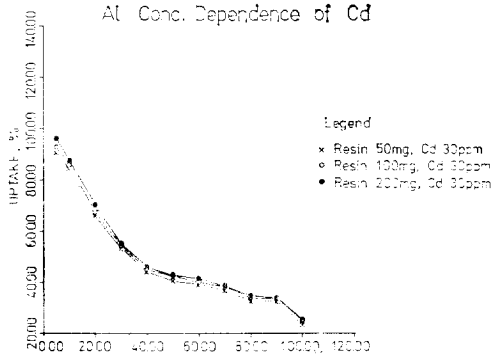

Fig. 6. Al-concention depenence of Cd uptake

CONCLUSIONS

Poly (acrylamidoxime) resin indicated strong potential for the complexation of metals from aqueous solutions. La(Ⅲ), Ce(Ⅳ) and Nd(Ⅲ) were complexed, whereas Li and B were not.

Trace metals were found to be 80% and above uptaked for most metals over the pH range 3-8 which would be encountered in our environment. In the application of the resin, this resin was found to be capable of cocentrating low level of Cd present in high purity Al and of separating this element from Al matrix. Solution and pH adjustment are simple treatment of Al sample prior to sequestering the trace element with the resin.

The technique developed can be applied to other elements known to chelate with the resin.

References

1. Dingman, J., Siggia, S., Barnes, R.M. and Hiscock, J.B., *Anal. Chem.*, **44**, 1351—1356(1972).
2. Barnes, R.M., Genna, J.S., *Anal. Chem.*, **51**, 1065(1979).
3. Miyazaki, A. and Barnes, R.M., *Anal. Chem.*, **53**, 299(1981).
4. Miyazaki, A. and Barnes, R.M., *Anal. Chem.*, **53**, 364(1981).
5. Manolov, K. and Motekov, N., *Mikrochimica Acta* (Wien), 231(1974).
6. Leyden, D.E. and Luttrel, G.H. and Patterson, T.A., *Anal. Letteer*, 8, 51 (1975).
7. Leyden, D.E. and Luttrel, G.H., *Anal. Chem.*, **47**, 1612 (1975).
8. Hercules, D.M., Cox, L.E., Onisick, S., Nichols, G.D. and Carver, J.C., *Anal. Chem.*, **45**, 1973, (1973).
9. Schouteden, F.L.M., *Makromol. Chem.*, **24**, 25(1975).
10. Colelia, M.B., Siggia, S. and Barnes, R.M., 52, 967(1980).
11. Hurd, C.D. and Brownstein, H.J., *J. Am. Chem. Soc.*, **47**, 67(1925).
12. Schouteden, F.L.M., *Macromol. Chem.*, **24**. 25(1957).
13. Palm, A. and Werbin, H., *Can. J. Chem.*, **32**, 858(1954).
14. Colella, M.B., Siggia, S. and Barnes, R.M., Anal. Chem., **52**, 969(1980).
15. Miyazaki, A. and Barnes, R.M., *Anal. Chem.*, **53**, 301(1981).
16. Colella, M.B., Siggia, S. and Barnes, R.M., *Anal. Chem.*, **52**, 2347(1980).