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Chromatographic Separation of Light Rare Earth Metal Ions on Polyacryloylacetone Chelating Resin

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The chromatographic separation of La(Ⅲ) from other light rare earth metal ions [Ce(Ⅲ), Pr(Ⅲ), Nd(Ⅲ), Sm(Ⅲ)] was achieved by using polyacryloylacetone as a stationary phase. High resolutions were obtained when pH of the eluent (HCl) was decreased stepwise.

Ion exchange chromatography is one of the most useful methods for separation of rare earth metal ions. In most cases, an aqueous solution of a chelating reagent is used as a mobile phase,1,2) and thus, the separation depends on the selectivity of the chelating reagents, that is, differences in stability of the metal-reagent complexes. However, this method has certain disadvantages such as the use of expensive chelating reagents, difficulties in recovering the metal ions from the stable complexes, and the problem of precipitations both the protonated reagents and the complexes in the column due to their low solubilities.3) On the other hand, chromatography using chelating resins as a stationary phase was shown to be effective for separation of rare earth metal ions and not to involve the problems mentioned above.4,5) However, so far only a few effective chelating resins are known.

Previously, we showed that polyacryloylacetone (PAA) adsorbed divalent metal ions selectively.6) PAA is also reported to form stable complexes with rare earth metal ions.7) Therefore, in this work, we have examined the possibility of using PAA as a stationary phase for chromatographic separation of rare earth metal ions.

PAA was prepared in this laboratory as described previously.6) PAA-coated glass beads (60-80 mesh) were prepared by a conventional method. The amount of PAA coated was 0.2 g/g of glass beads. All chemicals used were of analytical or special grade. Lanthanide chlorides were used. Demineralized, distilled water was used. A column of 3.5 mm inside diameter, packed with PAA-coated beads to a height of 80 cm, was used for the separation of metal ions. A mixture of the two metal ions [0.05 mℓ, each metal ion; 4 mM ($1\text{ M} = 1\text{ mol}\,\ell^{-1}$)] was injected into the stream of water at the top of the column. Thirty minutes later, the eluent was changed from water to HCl solution of the required pH. After that, pH of the eluent was decreased step by step at a fixed time interval. The effluent from the column was mixed with a solution of 2,7-Bis(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Arsenazo Ⅲ) [0.02 mM, 0.2 mℓ / min], and the metal-Arsenazo Ⅲ complexes formed were monitored at 650 nm.

Figure 1 shows an example of the chromatogram of a pair of metals [La(Ⅲ) / Sm (Ⅲ)] which was obtained by stepwise decrease in pH of the eluent. La(Ⅲ) could be completely separated from Sm(Ⅲ) by this method. As shown in Table 1, high resolutions were also achieved for the separation of La(Ⅲ) from other rare earth metal ions under the same conditions as in Fig.1. These results demonstrate that the system of a PAA column and a mineral acid such as HCl solution as eluent is effective for separating rare earth metal ions.

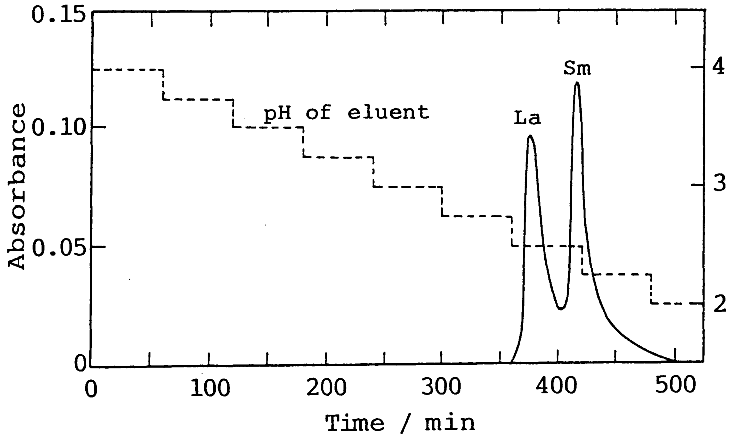

Fig.1. Elution curve for La(Ⅲ)/Sm(Ⅲ) obtained by stepwise decrease in pH (0.25 pH/hour) at 30 ℃. Sample;0.05 mℓ [4 mM La(Ⅲ), 4 mM Sm(Ⅲ)]. Flow rate of eluent; 0.2 mℓ /min.

Table 1. Resolution of chromatographic separation

System	Ce/La	Pr/La	Nd/La	Sm/La
Resolution	0.9	1.3	1.5	1.9

References

1) F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler, and I. S. Yaffe, J. Am. Chem. Soc., 73, 4840 (1951).
2) F. H. Spedding, J. E. Powell, and E. J. Wheelwright, J. Am. Chem. Soc., 76, 612 (1954).
3) J. K. Marsh, J. Chem. Soc., 1957, 978.
4) K. Takeda, M. Akiyama, F. Kawakami, and M. Sasaki, Bull. Chem. Soc. Jpn., 59, 2225 (1986).
5) M. Kanesato, T. Yokoyama, and T. M. Suzuki, Bull. Chem. Soc. Jpn., 62, 3451 (1989).
6) T. Tomida, M. Tomida, Y. Nishihara, I. Nakabayashi, T. Okazaki, and S. Masuda, Polymer, 31, 102 (1990).
7) G. K. Hoeschele, J. B. Andelman, and H. P. Gregor, J. Phys. Chem., 62, 1239 (1958).

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