

SEPARATIONS OF PAIRS OF LIGHT RARE-EARTH METAL IONS BY CHROMATOGRAPHY WITH POLYACRYLOYLACETONE CHELATING RESIN AS A STATIONARY PHASE

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The separations of pairs of light rare-earth metal ions [La(III), Ce(III), Pr(III), Nd(III), and Sm(III)] were achieved by chromatography using glass beads coated with polyacryloylacetone as the stationary phase. Favorable resolutions were obtained by stepwise decrease in pH of the eluent (HCl). Better resolution was attained with an increase in duration of the stepwise decrease in pH. Even with pairs of neighboring elements, a fairly good separation was achieved.

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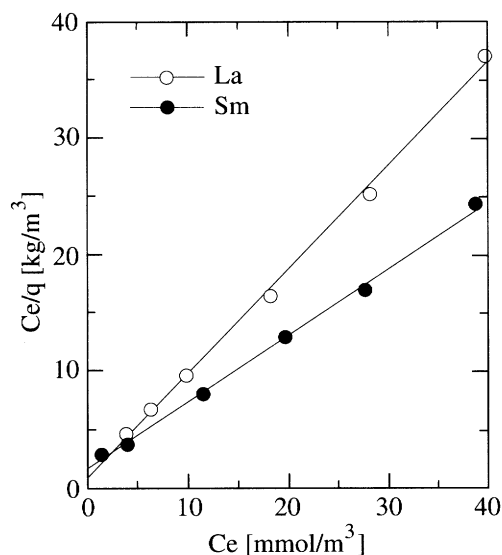


Fig. 1 Langmuir plots of adsorptions of La(III) and Sm(III) to PAA-coated glass beads

Introduction

Rare-earth metal ions have similar chemical properties, so their separations are difficult. But ion exchange chromatography seems one of the most useful methods for this purpose^{4, 5, 9}.

Recently, chromatography using chelating resin as a stationary phase was shown to be effective for separation of rare-earth metal ions^{3, 6}. As their separations by this method depend on the selectivity of the chelating resin, that is, differences in stability of the resin-metal complexes, a solution of a cheap inorganic acid such as HCl can be used as an eluent, and the metal ions can easily be recovered from the effluent. On these points, chromatography on chelating resin is preferable to conventional ion exchange chromatography, which requires expensive chelating reagents for the eluent.

Previously, we studied the adsorption properties of metal ions to the chelating resin polyacryloylacetone (PAA) which was prepared in our laboratory⁸. Results showed that PAA adsorbed divalent metal ions [Hg(II) and Cu(II)] selectively. PAA is also reported to form stable complexes with rare-earth metal ions¹. Therefore, we examined the possibility of using PAA-coated glass beads as a stationary phase for chromatographic separation of rare-earth metal ions⁷.

In the present work, the chromatographic separations of pairs of light rare-earth metal ions [La(III), Ce(III), Pr(III), Nd(III), and Sm(III)] were achieved by elution with stepwise decrease in pH. The relations between separation efficiency and the conditions of elution were studied.

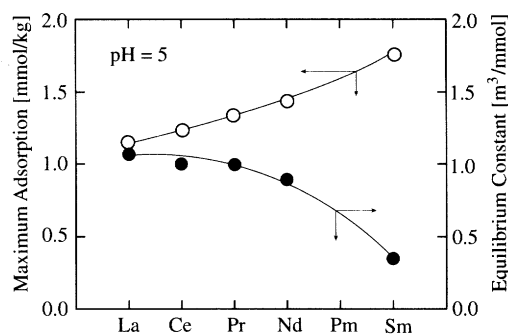


Fig. 2 Maximum adsorptions and equilibrium constants of Langmuir parameters for rare-earth metal ions

1. Experimental

1.1 PAA-chelating resin and chemicals

PAA was prepared in our laboratory as described previously⁸. It was dissolved in benzene and coated on porous glass beads (60 to 80 mesh) at 0.2 kg/kg of glass beads by a conventional method. All chemicals used were of analytical or special grade. Lanthanide chlorides and demineralized, distilled water were used.

1.2 Batch process for measuring maximum adsorption

The maximum adsorption of rare-earth metal ions onto PAA was determined by the batch procedure. Volumes of 10 μm^3 of solution with different initial concentrations of metal ions, adjusted to a given pH, were stirred with PAA (0.5 mg) in a water bath (30°C). After 24 hours, the concentrations of metal ions in the samples were determined from the absorbance at 650 nm with a UV-spectrophotometer. A solution of 2, 7-bis (2-arsenophenylazo)-1, 8-dihydroxynaphthalene-3, 6-disulfonic acid (Arsenazo III) was used as an indicator. The amounts of metal ions adsorbed to PAA were evaluated from the changes in their concentrations in solution.

1.3 Column operation

A column of 3.5 mm inside diameter, packed with PAA-coated beads to a height of 80 cm, was used for separation of metal ions. A mixture of two metal ions [0.05 μm^3 , 4 mmol/dm³ of each metal ion] 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. Then, for stepwise elution, the pH of the eluent was decreased stepwise at fixed intervals. The effluent from the column was mixed with a solution of Arsenazo III [0.02 mmol/dm³, 0.2 μm^3 /min] and the metal-Arsenazo III complexes formed were monitored at 650 nm with a spectrophotometer.

2. Results and Discussion

2.1 Maximum adsorption

Amount of adsorption was measured by the batch

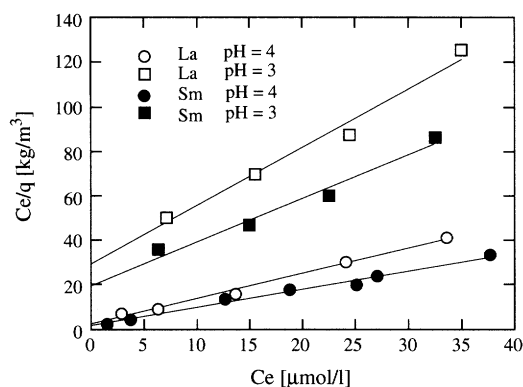


Fig. 3 Langmuir plots of adsorptions of La(III) and Sm(III) at pH = 3 and pH = 4

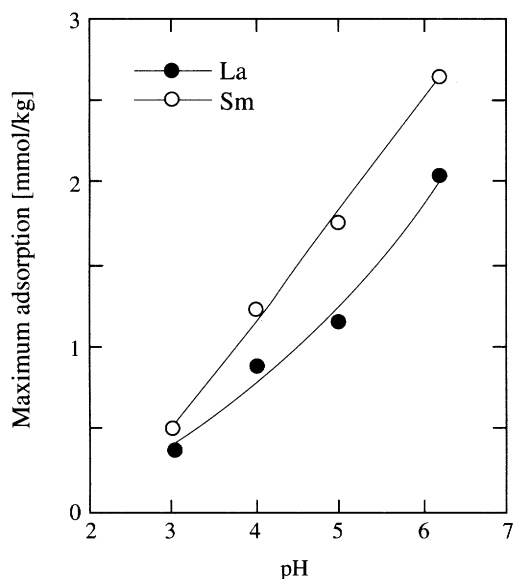


Fig. 4 Effects of pH of solutions on maximum adsorptions of La(III) and Sm(III)

method. The adsorption equilibrium relationship was found to conform to the Langmuir isotherm. Typical examples are shown in **Fig. 1**. The maximum adsorptions of rare-earth metal ions to PAA, q_0 and the equilibrium constants, K , were evaluated from the slopes and intercepts of conventional Langmuir plots based on the following equation:

$$\frac{Ce}{q} = \frac{1}{q_0 K} + \frac{Ce}{q_0} \quad (1)$$

where C_e and q are the equilibrium concentration of solution and the amount of adsorbed metal ion respectively.

The Langmuir parameters obtained are shown in **Fig. 2**. The maximum amounts of adsorption of rare earth metal ions to PAA-coated beads increased gradually with increase in atomic number, although the maximum adsorption was generally limited. The equilibrium constants, K , decreased as atomic number increased. The K value for every metal ion examined was very large and on the order of 0.5 to 1 m³/mmol at pH = 5.

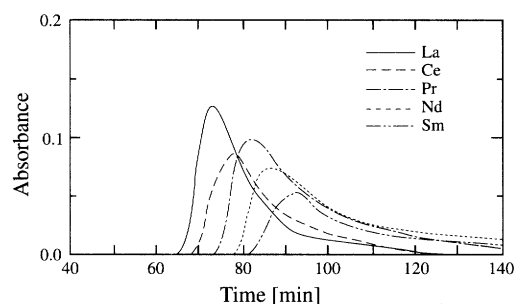


Fig. 5 Elution profiles of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) with HCl solution of pH 2.5. Sample, 4 mmol/dm³, 0.05 μm³; flow rate of eluent, 0.2 μm³/min

The adsorption isotherms of these metal ions to PAA were strongly influenced by the pH of the solution, as shown in **Fig. 3**. From the slopes and the intercepts of Langmuir plots, the values of K for La(III) and Sm(III) respectively were determined to be 0.38 m³/mmol and 0.40 m³/mmol at pH = 4, and 0.089 m³/mmol and 0.099 m³/mmol at pH = 3.

As shown in **Fig. 4**, the maximum amounts of adsorption of La(III) and Sm(III) increased with increase in pH of the solution. The amount of maximum adsorption of Sm(III) was slightly greater than that of La(III). However, neither of the metal ions adsorbed on PAA in highly acidic solution below pH 1. The adsorbed metal ions could be completely desorbed from PAA with 0.2 mol/dm³ hydrochloric acid.

2.2 Chromatographic separations

Figure 5 shows the elution profiles of rare-earth metal ions with eluents buffered at pH 2.5. All elution curves show pronounced tailing. However, there were slight differences between the elution curves. La (III) was eluted first, closely followed by Ce(III), Pr(III), Nd(III) and Sm(III). The retention time tended to increase slightly with increase in atomic number of the metal ions. This order was the same as that of the stability of PAA-metal ion complexes [La < Ce < Pr < Nd < Sm.], which was determined in preliminary studies by pH titration. This order of stability was the same as that for the complexes of elements with acetylacetone, which is a model compound of PAA²⁾.

First, we tried to separate La(III) and Sm(III) because their difference in retention times was the greatest among the rare-earth metal ions examined (**Fig. 5**). The retention time of Sm(III) was about 1.5 times that of La(III). However, both La(III) and Sm(III) were strongly retained and were not eluted easily by eluent buffered at pH > 4. In general, non-isocratic elution is successful for chromatographic separation using chelating resin as a stationary phase.

Figure 6 shows examples of the chromatograms of a pair of metals [La(III)/Sm(III)] obtained by stepwise decrease in pH of the eluent. A stepwise decrease of 0.25 pH units/60 minutes from an initial pH of 4 allowed La(III) to be separated completely from Sm(III). On elu-

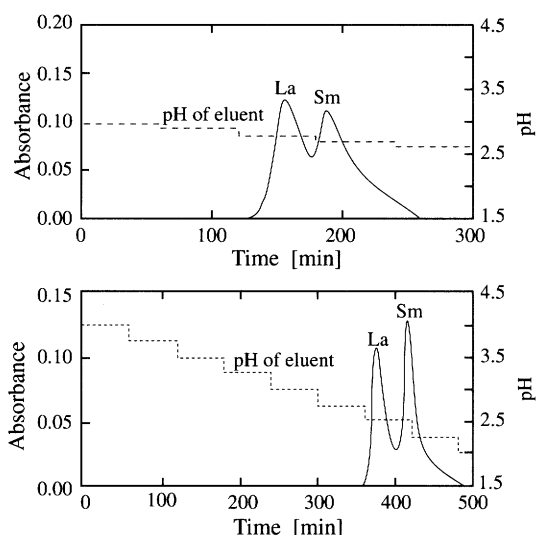


Fig. 6 Elution curves of La(III)/Sm(III) on stepwise decrease in pH. Samples, $0.05 \mu\text{m}^3$ [4 mmol/dm^3 La(III), 4 mmol/dm^3 Sm(III)]; flow rate of eluent, $0.2 \mu\text{m}^3/\text{min}$

tion with a decrease of 0.1 pH unit/60 minutes from an initial eluent of pH 2.75, the separation was not complete, but the elution time was much shorter.

Elution curves were influenced significantly by the pH of the eluent; that is, by the time intervals of the stepwise decrease in pH. As shown in **Fig. 7**, the increase in the time intervals of pH decrease lengthened the time intervals of elution of peaks, but also caused tailing of the elution curves.

Assuming Gaussian distribution of the elution curves, the resolution, R_s , was evaluated from the following equation:

$$R_s = \frac{2(t_{R2} - t_{R1})}{(t_{w1} + t_{w2})} \quad (2)$$

where t_R is the mean residence time of the peaks, and t_w is the peak width on the base line. Suffixes 1 and 2 refer to peaks for species 1 and 2 respectively.

In the separation of a mixture of La(III) and Sm(III), the relationship between the resolution and the time intervals of stepwise decrease in pH is shown in **Fig. 8**. The resolution increased with lengthening of the time interval for stepwise decrease of 0.25 pH units, but tended to level off at time intervals of about 70 minutes. This is understandable because the lengthening of the time interval between reductions in pH increased not only in the time interval between peaks but also the tailing of each elution curve which would counteract resolution. As seen from the figure, a resolution of more than unity could be achieved by stepwise elution with a relatively short time interval of 45 minutes between reductions of 0.25 pH units.

As shown in **Fig. 9**, in the separation of La(III) from other light rare-earth metal ions, favorable resolutions were also achieved by the same method of stepwise decrease of 0.25 pH units/60 min. Even in the separation

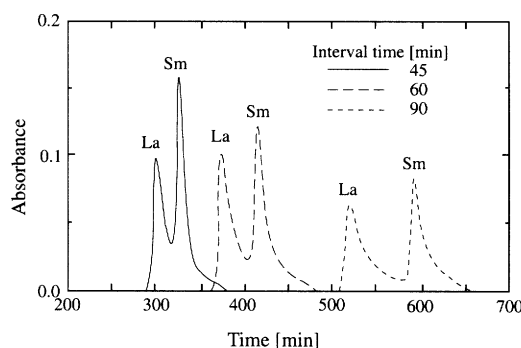


Fig. 7 Effect of time intervals in stepwise decrease of 0.25 pH units on elution curves. Elution conditions were the same as for Fig. 6.

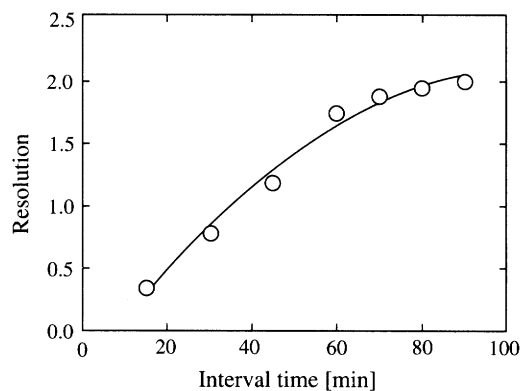


Fig. 8 Relationship between resolution and intervals in stepwise decrease by 0.25 pH units.

of a mixture of the neighboring elements La(III)/Ce(III) a relatively high resolution value of 0.9 was obtained. Similarly, the resolutions of the pairs of neighboring elements Ce(III)/Pr(III) and Pr(III)/Nd(III) were 0.8 and 0.75 respectively. These values were high enough to allow partial, although not complete, separations of these metal ions.

These results demonstrate that a PAA column is effective for separating rare-earth metal ions. In this study, although the size of the adsorbent used was relatively large (60 to 80 mesh), the separations of rare-earth metal ions were successful. Higher separations may be achieved by the use of PAA particles of smaller diameter as a stationary phase.

Conclusion

The chromatographic separations of pairs of light rare-earth metal ions [La(III), Ce(III), Pr(III), Nd(III), and Sm(III)] were achieved with glass beads coated with polyacryloylaceton chelating resin as a stationary phase and by using HCl solutions as eluents. The resolution increased with increase in the time intervals between stepwise reductions in pH. Even with pairs of neighboring elements, a fairly good separation was achieved by elution with stepwise decrease in pH.

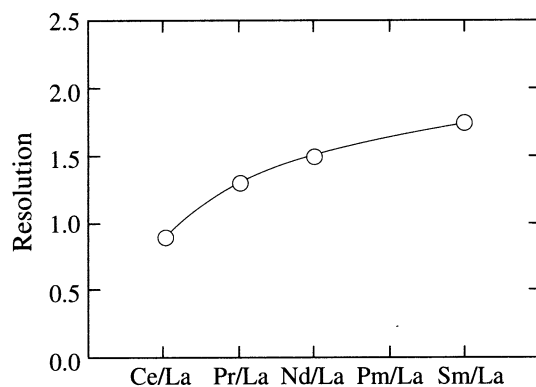


Fig. 9 Resolutions in binary systems.

Nomenclature

C_e	= equilibrium concentration	[mmol/m ³]
K	= equilibrium constant	[m ³ /mmol]
q	= amount of adsorption	[mmol/kg]
q_0	= maximum amount of adsorption	[mmol/kg]

R_s	= resolution defined by Equation (2)	[-]
t_R	= mean residence time of peak	[min]
t_w	= peak width on base line	[min]

<Subscripts>

1,2 = refer to species 1 and 2 respectively

Literature Cited

- 1) Hoeschele, G.K., J.B. Andelman, and H.P. Gregor: *J. Phys. Chem.*, **62**, 1239 (1958)
- 2) Izatt, R.M., W.C. Fernelius, C.G. Haas, Jr., and B.P. Block: *J. Phys. Chem.*, **59**, 170 (1955)
- 3) Kanesato, M., T. Yokoyama, and T.M. Suzuki: *Bull. Chem. Soc. Jpn.*, **62**, 3451 (1989)
- 4) Spedding, F.H., E.I. Fulmer, J.E. Powell, T.A. Butler, and I.S. Yaffe: *J. Am. Chem. Soc.*, **73**, 4840 (1951)
- 5) Spedding, F.H., J.E. Powell, and E. J. Wheelwright: *J. Am. Chem. Soc.*, **76**, 612 (1954)
- 6) Takeda, K., M. Akiyama, F. Kawakami, and M. Sasaki: *Bull. Chem. Soc. Jpn.*, **59**, 2225 (1986)
- 7) Tomida, T., K. Inagawa and S. Masuda: *Chem. Lett.*, 1253, 1991
- 8) Tomida, T., M. Tomida, Y. Nishihara, I. Nakabayashi, T. Okazaki, and S. Masuda: *Polymer*, **31**, 102 (1990)
- 9) Yamabe, T. and T. Hayashi: *J. Chromatography*, **76**, 213 (1973)