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Note

Rare-earth separations by mixed ion-exchange columns

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Two recent articles by Yamabe and Hayashi[1] and Yamabe[2] introduce the technique of rare-earth element separations by elution chromatography on mixed beds of cation- and anion-exchange resins. These authors conclude that the most favorable conditions for separation may be attained by changing the mixing ratio (γ) of the cation- and anion-exchange resins or by changing the pH value of the eluent. Although their development of the theory of mixed beds as represented by distribution coefficients is certainly proper, no evaluation of the technique comparative to existing methods was evident. If one accepts the elution peak volume ratios of two species (corrected for column void volume) as a measure of effectiveness of separation, then it will be shown that the mixed resin technique offers no advantage over use of either one or the other resins individually, depending on the chemistry.

In column chromatography the ratio of peak volumes for lanthanide $Ln^{3+}{}_{(2)}$ to lanthanide $Ln^{3+}{}_{(1)}$ is given in general by the separation factor S (S' of ref. 1)

$$S = K_{d2}/K_{d1}$$

where K_{d2} and K_{d1} are the total distribution coefficients ($\bar{K}$ in refs. 1 and 2) of $Ln^{3+}{}_{(2)}$ and $Ln^{3+}{}_{(1)}$, respectively, between the exchange resin and the complex-forming mobile phase. In particular

$$S^{+} = K_{d2}{}^{+}/K_{d1}{}^{+}$$

$$S^{-} = K_{d2}{}^{-}/K_{d1}{}^{-}$$

$$S^{M} = K_{d2}{}^{M}/K_{d1}{}^{M}$$

where the superscripts $^{+}$, $^{-}$ and ^{M} refer to cation, anion, and mixed cation–anion-exchange resin systems. If the mixing ratio $\gamma = V_R{}^{+}/V_R{}^{-}$, where $V_R{}^{+}$ and $V_R{}^{-}$ are the volumes of cation and anion resins, respectively, in the composite of total volume V_R, then,

$$K_{d1}{}^{M} = \frac{V_R{}^{+}K_{d1}{}^{+} + V_R{}^{-}K_{d1}{}^{-}}{V_R} \quad \text{etc.}$$

A straightforward substitution shows that

$$S^M = S^- \left(\gamma \frac{K_{d2}^+}{K_{d2}^-} + 1\right) \Big/ \left(\gamma \frac{K_{d1}^+}{K_{d1}^-} + 1\right) = S^+ \left(\gamma + \frac{K_{d2}^-}{K_{d2}^+}\right) \Big/ \left(\gamma + \frac{K_{d1}^-}{K_{d1}^+}\right)$$

For mixed-bed columns to give improved separations relative to single-bed columns either

$$\frac{S^M}{S^-} > 1 \text{ or } \frac{S^M}{S^+} > 1$$

These two inequalities require that either $S^+ > S^-$ or $S^- > S^+$, respectively. The relative improvement in separability as measured by $S^M/S^- \geqslant 1$ or $S^M/S^+ \geqslant 1$ is a function of mixing ratio γ $(0 \leqslant \gamma \leqslant 1)$, being confined to the limits*

$$1 \leqslant \frac{S^M}{S^-} \leqslant \frac{\left(\frac{S^+}{S^-}\right)\left(\frac{K_{d1}^+}{K_{d1}^-}\right) + 1}{\left(\frac{K_{d1}^+}{K_{d1}^-}\right) + 1} \quad (\text{for } S^+ \geqslant S^-)$$

and

$$\frac{1 + \left(\frac{S^-}{S^+}\right)\left(\frac{K_{d1}^-}{K_{d1}^+}\right)}{1 + \left(\frac{K_{d1}^-}{K_{d1}^+}\right)} \leqslant \frac{S^M}{S^+} \leqslant \frac{S^-}{S^+} \quad (\text{for } S^- \geqslant S^+)$$

Maximum improvement is therefore achieved with $\gamma = 1$ (100% cation resin) for comparison to an anion-exchange bed when $S^+ > S^-$ and with $\gamma = 0$ (100% anion resin) for comparison with a cation-exchange bed when $S^- > S^+$. Mixed resins provide either less than maximum improvement or actual deterioration of separation.

Put in simpler terms, the above argument shows that maximum separability is attained on either a cation-exchange resin alone or an anion-exchange resin alone as $S^+ > S^-$ or $S^- > S^+$, respectively. A mixed resin provides only an intermediate degree of separability always less than that obtained from the appropriately selected single resin.

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REFERENCES

1 T. Yamabe and T. Hayashi, *J. Chromatogr.*, 76 (1973) 213.
2 T. Yamabe, *J. Chromatogr.*, 83 (1973) 59.

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* Limits other than those specified exist but pertain only to systems where $S^M/S^\pm < 1$ and are hence not of interest to this discussion.