Supplementary Information for

Two-zone ligand-assisted displacement chromatography for producing high-purity praseodymium, neodymium, and dysprosium with high yield and high productivity from crude mixtures derived from waste magnets

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S1. Separation mechanism in Ligand-Assisted Displacement (LAD) chromatography

A schematic of the separation mechanism of ligand-assisted displacement chromatography for a binary mixture is shown in Fig. S1. The cation exchange resin is first pre-equilibrated with a presaturant (P), in this case, copper ions (Cu^{2+}). The presaturant should have a lower affinity to the sorbent but a higher affinity to the ligand than the REEs. When a mixture of REE ions (Nd^{3+} and Pr^{3+}) is fed into the column, the trivalent REE ions displace the divalent Cu^{2+}. Because the sorbent selectivities for the REE ions are quite small (<1.1), no separation occurs during the loading and a uniform REE mixture band forms near the inlet of the column.

When a solution of the EDTA ligand is fed into the column, EDTA competes with the sorbent to form a non-adsorbing ligand-REE (L-REE) complex. Each complex moves with the mobile phase down the column, resulting effectively in the displacement of the REEs by Na^{+}. Since EDTA has a higher selectivity for Nd^{3+} than for Pr^{3+}, the L-Nd complex will move ahead of the L-Pr complex, resulting in the separation of the Nd band from the Pr band. When the L-Nd reaches the boundary between the Nd band and the Cu band, the ligand releases Nd^{3+} to form a complex with Cu^{2+}, since Cu^{2+} has the highest affinity for EDTA. Then, the released Nd^{3+} ions re-adsorb onto the column. As more ligand is fed in the column, the L-Pr complex reaches the boundary between the Pr and Nd bands. Similarly, Pr^{3+} is released from the ligand and re-adsorbs onto the sorbent. As the adsorbed Nd ions desorb and form complexes with the ligand, the Nd band is displaced by the Pr band. If the column is sufficiently long, this displacement process will continue until two successive bands of Nd and Pr are formed, moving in the column with the same velocity. The separation of the two bands is driven by the EDTA as the apparent displacer. In ideal cases, with no mass transfer effects, this set of bands is called an “isotachic train”. In non-ideal cases, the overlapping regions between adjacent bands shrink as the bands continue to separate. Eventually, as each mass transfer zone reaches a constant length, the system reaches a “constant-pattern” state.

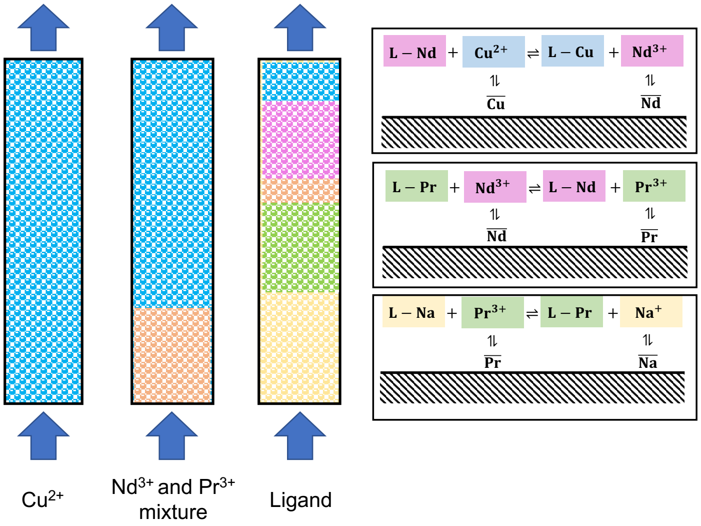

Figure S1. Schematic illustration of the separation mechanism of LAD for rare earth elements.

S2. Isotachic train, constant-pattern isotachic train, and general map

If the sorbent has selectivities $\alpha_{ij}^{sorbent}$, then the effective selectivity, α_{ij}^{e}, is equal to the ratio of $\alpha_{ij}^{sorbent}$ to the ligand selectivity α_{ij}^{ligand}, Eq. (S1).[1] When the sorbent selectivity is negligible, then the effective selectivity is equal to the inverse of the ligand selectivity.

$$\alpha_{ij}^{e} = \frac{\alpha_{ij}^{sorbent}}{\alpha_{ij}^{ligand}} \tag{S1}$$

For ideal systems (with no spreading due to mass transfer) the minimum column length to form an isotachic train in LAD was first derived by Helfferich using h-transformation theory.[2]

For nonideal systems, the constant-pattern mass transfer zone length ($L_{MTZ,CP}$) was derived by Choi et al.[3] as

$$\frac{L_{MTZ,CP}}{L_C} = L_f k_f^* \left(\frac{\alpha^e + 1}{\alpha^e - 1}\right) \ln\left(\frac{1-\theta}{\theta}\right) \tag{S2}$$

where L_C is the column length, L_f is the loading fraction, k_f^* is the dimensionless overall mass transfer coefficient, θ is the breakthrough cut.

The loading fraction (L_f) is defined as

$$L_f = \frac{L_{feed}}{L_C} = \frac{(c_F V_F / q_{max} A_c)}{L_c} = \frac{C_F V_F}{q_{max} A_c L_c} = \frac{C_F V_F}{q_{max} V_c} \tag{S3}$$

where c_F is the total feed concentration, V_F is the feed volume, q_{max} is the sorbent capacity based on column volume, and A_c is the cross-sectional area.

The dimensionless overall mass transfer coefficient (k_f^*) depends on three dimensionless variables.[1]

$$\frac{1}{k_f^*} = \frac{1}{N_f} + \frac{1}{Pe_b} + \frac{1}{15 N_D} \tag{S4}$$

where N_f is the ratio of film mass transfer rate to the convection rate

$$N_f = \frac{3L_C}{R_p} \frac{(1-\varepsilon_b) k_f}{\varepsilon_b u_0} \tag{S5}$$

Pe_b is the Peclet number, which is the ratio of the axial convection rate to the axial dispersion rate. When the Reynolds number is smaller than 1, the axial dispersion coefficient is simplified to $E_b = 10\varepsilon_b R_p u_0$

$$Pe_b = \frac{L_c u_0}{E_b} = \frac{L_c u_0}{10\varepsilon_b R_p u_0} = \frac{L_c}{10\varepsilon_b R_p} \tag{S6}$$

N_D is the ratio of intraparticle diffusion rate to the convection rate.

$$N_D = \frac{K_{se}(1-\varepsilon_b)\varepsilon_p D_p L_C}{\varepsilon_b u_0 R_p^2} \tag{S7}$$

where R_p is the particle radius, ε_b is the bed void fraction, ε_b is the particle porosity, k_f is the film mass transfer coefficient, u_0 is the linear velocity, K_{se} is the size exclusion factor, D_p is the intraparticle diffusivity.

The length of the constant-pattern mass transfer zone $L_{MTZ,CP}$ is:

$$L_{MTZ,CP} = u_d t_{MTZ,CP} \tag{S8}$$

where $t_{MTZ,CP}$ is the elution time of the constant-pattern mass transfer zone, and u_d is the velocity of the displacer,

$$u_d = \frac{u_0}{1+K_d} \tag{S9}$$

The nonlinear distribution coefficient K_d is

$$K_d = P\varepsilon_p + \frac{\Delta q}{\varepsilon_b \Delta c} = P\varepsilon_p + \frac{q_d}{\varepsilon_b c_d} \tag{S10}$$

where the phase ratio P is defined as $P = \frac{1-\varepsilon_b}{\varepsilon_b}$, ε_b is the bed void fraction, ε_p is the particle porosity, Δq is the change in the stationary phase concentration, Δc is the change in mobile phase concentration, q_d is the adsorbed concentration of displacer and c_d is the displacer concentration in the mobile phase. K_d is usually larger than 1.

The minimum column length required to form a constant-pattern isotachic train $L_{iso-nid}$ was correlated to several key dimensionless groups.[1] Rate model simulations were used to find $L_{iso-nid}$ values. A dimensionless column length, ϕ, is the ratio of the column length in a non-ideal system to the minimum column length needed to form an isotachic train in an ideal system. If the column length is fixed, ϕ is the ratio of ideal loading fraction to the non-ideal loading fraction.

A combination of the key dimensionless groups was used to reduce the multi-dimensional design parameter space to two dimensions, ϕ as a function of X, where X is the product of the key dimensionless groups that control the mass transfer zone length.

$$X = L_f k_f^* \left(\frac{\alpha^e - 1}{\alpha^e + 1}\right) \tag{S11}$$

where L_f is the loading fraction, k_f^* is the dimensionless overall mass transfer coefficient, α^e is the effective selectivity. The minimum dimensionless column length ϕ_{min} that is required to reach a constant-pattern state is related to X with a general correlation, which divides the two-dimensional space into two distinct regions, a constant-pattern region and a transient pattern region. Operating in the first region can result in high product concentrations and high yields of high purity products.

Choi et al.[1,3] used a constant separation factor isotherm to simulate the LAD process:

$$q_i = \frac{q_{max} \alpha_{i,ref}^e C_{p,i}}{\sum_{j=1}^{N} \alpha_{j,ref}^e C_{p,j}} \tag{S12}$$

where q_i is the sorbent phase concentration of component “i”, q_{max} is the sorbent capacity, and this capacity is the same for all REEs in LAD systems, $\alpha_{i,ref}^e$ is the effective selectivity between component “i” and the reference component, $C_{p,i}$ is the concentration of component “i” in the mobile phase.

In the rate model simulations based on constant separation factors, it was assumed that the sorbent has significant selectivities for REEs during loading. This assumption was inaccurate for feed solutions with no chelating agent. Because most sorbents have negligible selectivities for the REEs, no partial separation will occur during the loading before the ligand is introduced into the column. New rate model simulations were done to improve the accuracy of the general correlation.

The multi-component Langmuir isotherm, Eq. ($S13$) is equivalent to the constant separation factor isotherm, and is expressed as:

$$q_i = \frac{a_i C_{p,i}}{1 + \sum_{j=1}^{N} b_j C_{p,j}} \tag{S13}$$

If the sorbent capacity for each component is the same and the $b_j C_{p,j}$ terms are much larger than 1, Eq. (S13) is simplified to

$$q_i = \frac{a_i c_{P,i}}{\sum b_j c_{P,j}} \tag{S14}$$

and

$$q_{max} = \frac{a_i}{b_i} \tag{S15}$$

This simplified isotherm is equivalent to the constant separation factor isotherm Eq. (S12) where the selectivity is defined as

$$\alpha_{i,ref}^{e} = \frac{a_i}{a_{ref}} \tag{S16}$$

To simulate the process in which the separation factors change after a ligand is introduced, a modulated Langmuir isotherm is used:

$$q_i = \frac{a_{0,i} e^{-S_{a_i} c_m} c_{P,i}}{1 + \sum b_{0,j} e^{-S_{b_j} c_m} c_{P,j}} \tag{S17}$$

In this equation the values of the effective Langmuir “a” and “b” parameters vary with the modulator concentration c_m by the exponential terms, $e^{-S_{a_i}c_m}$ and $e^{-S_{b_j}c_m}$.

When the $b_j C_{p,j}$ terms are much larger than 1, the isotherm can be simplified to

$$q_i = \frac{a_{0,i} e^{-S_{a_i}c_m} c_{P,i}}{\sum b_{0,j} e^{-S_{b_j}c_m} c_{P,j}} \tag{S18}$$

where $a_{0,i}$ and $b_{0,i}$ are the effective Langmuir “a” and “b” values at an initial modulator concentration. In LAD systems, the capacity of all components is the same. Then, the ratio between the overall Langmuir “a” and “b” values is the same. During loading, the modulator concentration c_m is set to 0.Then the isotherm is simplified to:

$$q_i = \frac{a_{0,i} c_{P,i}}{\sum b_{0,j} c_{P,j}} \tag{S19}$$

The sorbent capacity is:

$$q_{max} = \frac{a_{0,i}}{b_{0,i}} \, (i = 1,2, \dots, N) \tag{S20}$$

The effective selectivity is

$$\alpha_{i,j}^{e} = \frac{a_{0,i}}{a_{0,j}} \tag{S21}$$

If there is no selectivity between the two components during loading, then $a_{0,i} = a_{0,j}$. The effective selectivity between the presaturant Cu^{2+} and the fastest eluting REE (the one with the highest affinity for the ligand) was approximated as 5 in the simulations. Such a high selectivity is sufficient for predicting the sharp wave between the two species.

The separation begins after the ligand is introduced into the column. Because each REE has a different affinity for the ligand, the modulator concentration c_m in the exponential term changes to 1 when the ligand is fed into the column, resulting in a substantial selectivity.

$$q_i = \frac{a_{0,i} e^{-S_{a_i}} c_{P,i}}{\sum b_{0,j} e^{-S_{b_j}} c_{P,j}} \tag{S22}$$

Since the capacity remains the same, the ratio between the overall Langmuir “a” and “b” values should be the same.

$$q_{max} = \frac{a_{0,i}}{b_{0,i}} = \frac{a_{0,i} e^{-S_{a_i}}}{b_{0,i} e^{-S_{b_i}}} \tag{S23}$$

Therefore, $S_{a_i} = S_{b_i}$.

Thus, the selectivity can be expressed as

$$\alpha_{i,j}^{e} = \frac{a_{0,i} e^{-S_{a_i}}}{a_{0,j} e^{-S_{a_j}}} = \frac{a_{0,i}}{a_{0,j}} e^{S_{a_j} - S_{ai}} \tag{S24}$$

If the REEs have no selectivity during loading, then $a_{0,i} = a_{0,j}$. Therefore, $\alpha_{i,j}^{e} = e^{S_{aj} - S_{ai}}$, The values of S_a are chosen so that $S_{aj} - S_{ai} = \ln \alpha_{i,j}^{e}$, and the selectivity is activated after the modulator concentration is changed from 0 to 1.

The simulations based on the new isotherms were used to find the minimum column length to reach a constant pattern in non-ideal binary systems. In each case, two REEs (REE1 and REE2) were separated using LAD. The sorbent had a negligible selectivity for these elements. REE1 had a higher affinity to the ligand, resulting in a lower effective sorbent selectivity, and is eluted ahead of REE2. Various virtual binary systems with a 2-meter long column were simulated. A range of

X values (from 8 to 41) was obtained by varying the flow rate and the effective selectivity between the two REEs.

The value of α^e was varied from 1.5 to 10. The effective selectivity between REE1 and the presaturant was set to 5, and the effective selectivity between the ligand (EDTA-Na) and REE2 was also set to 5 to simulate the sharp displacement waves. The effective capacity, the ratio between a_0 and b_0, in these systems was 1.45 meq/ml bed volume. The isotherm parameters for the virtue binary systems are given in S5, Table S1.

The minimum column length to reach the constant-pattern mass transfer zone length for each binary system was identified from the column profiles, Fig. S2, when the simulated mass transfer zone length remained fixed with increasing column length. The minimum column lengths were then divided by the ideal column length to form an isotachic train in corresponding ideal systems. The dimensionless column length ϕ was plotted against the different X values (Fig. S3). A best-fitting curve for the data points was found and plotted in Fig. S3. This figure is a general map for predicting whether a non-ideal system is in the constant-pattern region. In the non-linear regression to fit the exponential expression for the curve, the constant term was fixed at 1, because as the X value approaches infinity, the system approaches an ideal system, and the minimum column length approaches that for an ideal system.

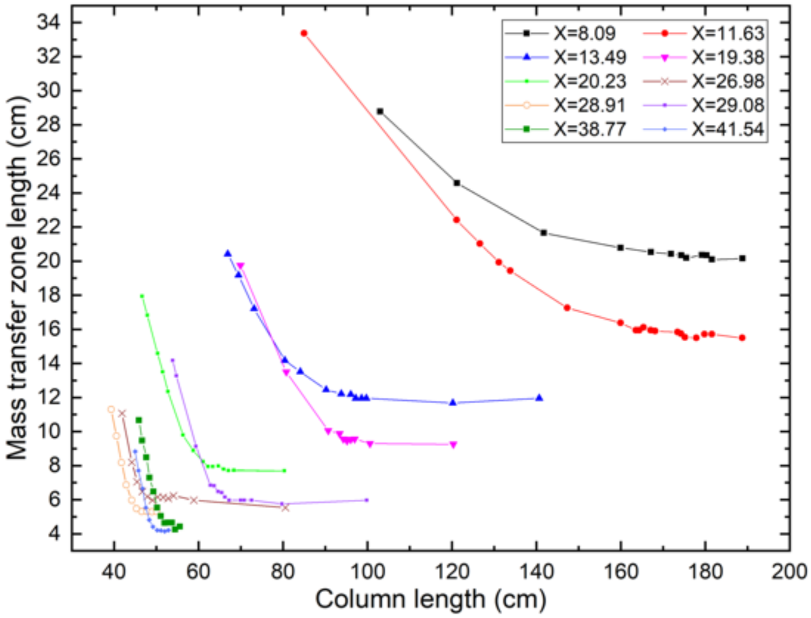

Figure S2. Mass transfer zone length for a given system first decreases with increasing column length, and then no longer decreases after the column length reaches the minimum column length to form a constant pattern.

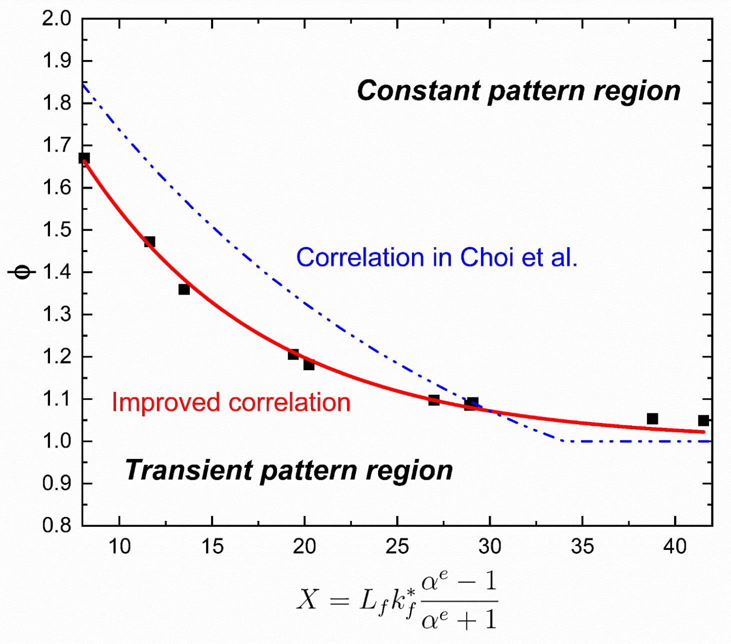

Figure S3. The constant-pattern general map.

The new correlation of ϕ_{min} as a function of X is given below.

$$\phi_{min} = 1 + 1.5e^{-\frac{X}{9.8}} \tag{S25}$$

S3. Yield and productivity in constant-pattern design method for multi-component mixtures

A dimensionless yield equation was derived by Choi et al.[3]:

$$Y_i = 1 - \frac{\beta}{2x_i L_f k_f^*}\left(\frac{\alpha_{i,i-1}^e + 1}{\alpha_{i,i-1}^e - 1} + \frac{\alpha_{i+1,\,i}^e + 1}{\alpha_{i+1,\,i}^e - 1}\right) = 1 - \frac{\beta}{2\gamma_i L_f k_f^*} \tag{S26}$$

where x_i is the molar fraction of component "i" in the feed mixture, $\beta = \ln(\frac{1-\theta}{\theta})$ and θ is the breakthrough cut,[1,3] and γ_i is selectivity weighted composition factor, which is defined as:

$$\gamma_i = \frac{x_i}{\dfrac{\alpha_{i,i-1}^e + 1}{\alpha_{i,i-1}^e - 1} + \dfrac{\alpha_{i+1,\,i}^e + 1}{\alpha_{i+1,\,i}^e - 1}} \tag{S27}$$

The sorbent productivity $P_{R,i}$ for component i in a LAD system (the amount of REEs produced per unit sorbent volume per unit time) was derived previously.[3]

$$P_{R,i} = \frac{\varepsilon_b c_d u_0 x_i L_f}{L_c}\left(1 - \frac{\beta}{2\gamma_i L_f k_f^*}\right) \tag{S28}$$

To maximize the productivity in a given system, one can scan a range of linear velocities (u_0). For each u_0, the overall dimensionless mass transfer coefficient k_f^* is calculated using Eq. (*S*4). $L_{f,id}$ is calculated using the h-transformation theory.[2] For a constant-pattern design with the minimum column length, the ratio between $L_{f,id}$ and the L_f is equal to ϕ_{min}. The loading fraction is then found from the ϕ_{min} value, Eq.(*S*25). The productivity for each linear velocity (u_0) is then calculated. An algorithm flowchart is shown in Fig. S4.

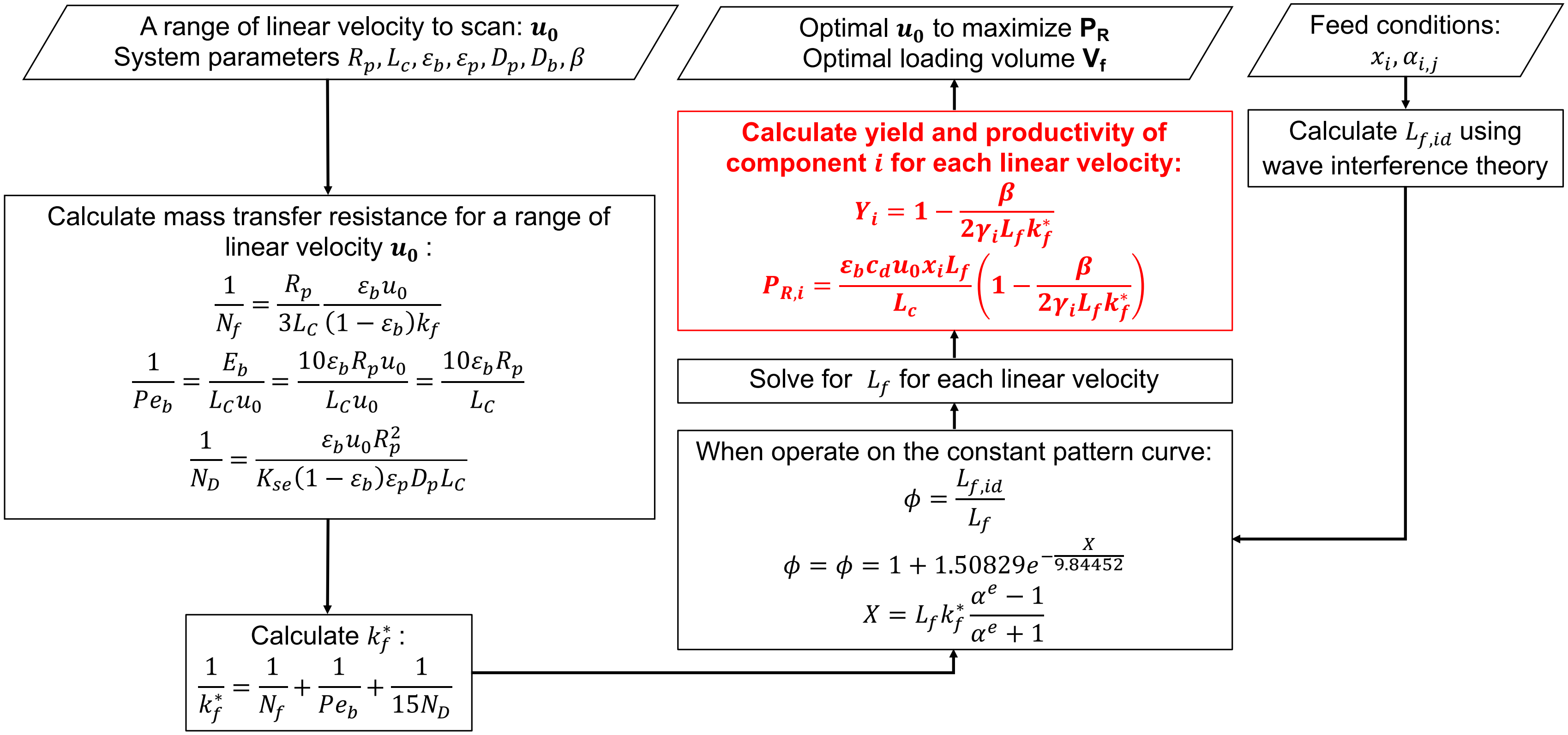

Figure S4. Flowchart of productivity optimization in the constant-pattern design.

For a ternary mixture of Dy, Nd and Pr with molar fractions 0.05, 0.83, and 0.12, respectively,[4] the design results for yield and productivity as a function of the linear velocity are shown in Fig. S5. The highest productivity, 120 kg Nd/m^3 sorbent/day was found from Fig. S5 at a yield of 77.5%.

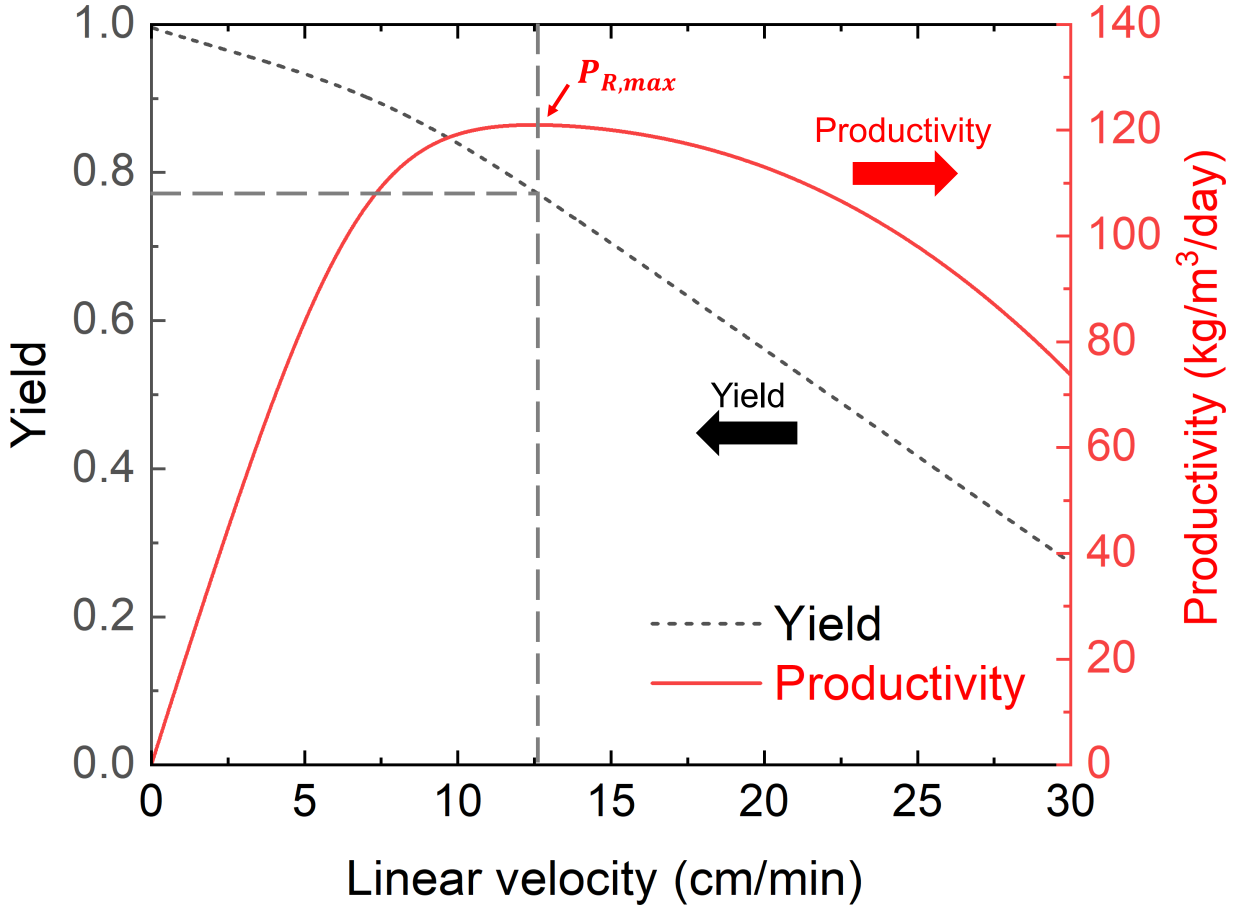

Figure S5. Calculated yield (black dashed curve) and productivity (red solid curve) of Nd versus linear velocity u_0 for a fixed column length for separating the ternary REE mixture.

S4. Relation between yield, purity, and breakthrough cut θ in the constant-pattern design

In collecting products from a column effluent, a breakthrough cut θ, which controls the width of a product band, is defined as the ratio of the lowest concentration c_{bot} to the maximum band concentration c_d (Fig. S6). The cut controls the yield of the product component as it determines the amount in the collected product relative to the total amount of this component in the feed. It also controls the purity of the product because it determines the amount of the impurities from the adjacent bands (shown in red circle in Fig. S6).

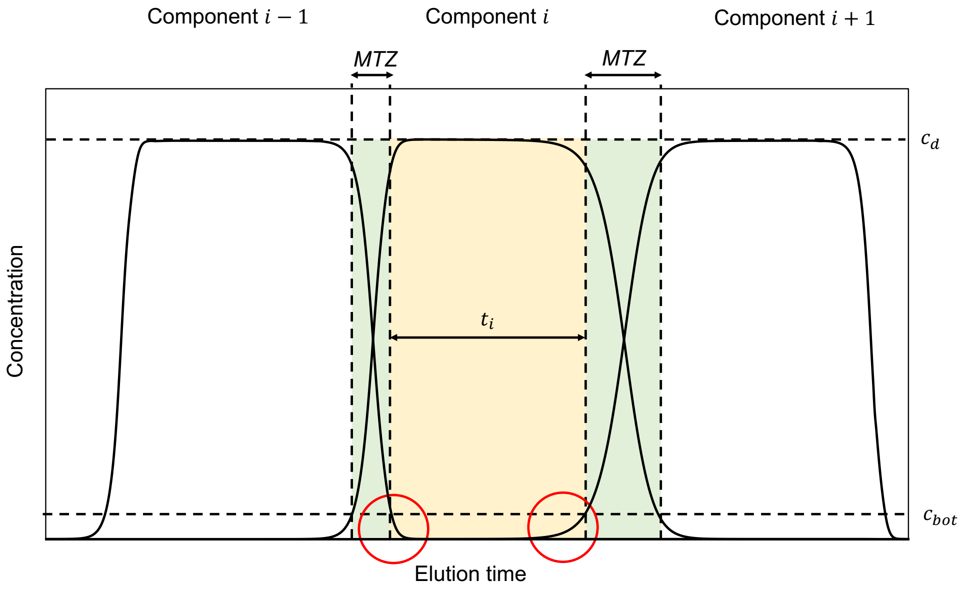

Figure S6. The breakthrough cut θ for collecting products from the column effluent in LAD.

The product collected is the band region between the two mass transfer zones (yellow region in Fig. S6). From the elution profile, the yield of component i is calculated as

$$Y_i = \frac{c_d t_i Q_f}{c_{f,i} V_f} \tag{S29}$$

where c_d is the band concentration t_i is the time for collecting the product band, Q_f is the flow rate, $c_{f,i}$ is the concentration of component i in the feed, and V_f is the total feed volume.

To calculate the purity of the product, the amount of the impurities from the two adjacent bands is calculated first. The impurities from the adjacent band on the right-hand-side is enlarged and shown in Fig. S7. It is difficult to find an analytical function that can describe the change in concentration over time, but the elution time corresponding to mass transfer zone length, $t_{MTZ,CP}$, is related to θ, through the analytical solution, Eq. (S2) and Eq. (S8).

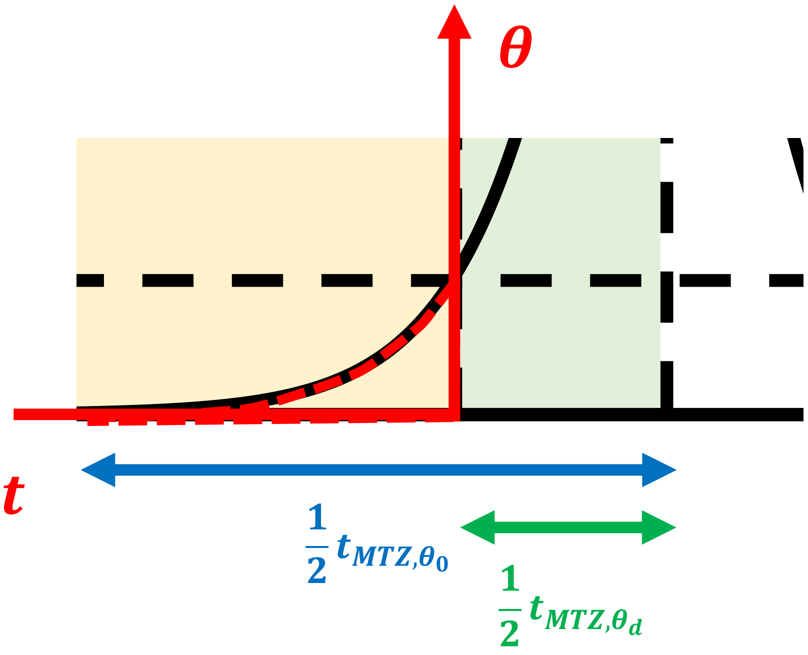

Figure S7. The impurities from the adjacent component

Combining Eq. (S2) and Eq. (S8) gives:

$$t_{MTZ,CP} = \frac{L_{MTZ,CP}}{u_d} = \frac{L_c L_f k_f^*}{u_d}\left(\frac{\alpha^e+1}{\alpha^e-1}\right)\ln\left(\frac{1-\theta}{\theta}\right) \tag{S30}$$

The elution time as a function of θ is expressed as:

$$t(\theta) = \frac{1}{2}t_{MTZ,\,\theta} - \frac{1}{2}t_{MTZ,\,\theta_d} \tag{S31}$$

The area within the red curve region in Fig. S7 is found from

$$S = c_d \int_{\theta_0}^{\theta_d} t(\theta)d\theta \tag{S32}$$

where θ_0 is a very small breakthrough cut (almost 0), and θ_d is the breakthrough cut in the design. Combining Eq. (S30) and Eq. (S31), $t(\theta)$ is:

$$t(\theta) = \frac{1}{2}\frac{L_c}{u_0}\frac{K_d}{k_f^*}\left(\frac{\alpha^e + 1}{\alpha^e - 1}\right)\left(ln\left|\frac{1-\theta}{\theta}\right| - ln\left|\frac{1-\theta_d}{\theta_d}\right|\right) \tag{S33}$$

Then the area is expressed as

$$S = c_d Q_f \int_{\theta_0}^{\theta_d} t(\theta)d\theta = \frac{c_d Q_f}{2}\frac{L_c}{u_0}\frac{K_d}{k_f^*}\left(\frac{\alpha^e + 1}{\alpha^e - 1}\right)\int_{\theta_0}^{\theta_d}\left(ln\left|\frac{1-\theta}{\theta}\right| - ln\left|\frac{1-\theta_d}{\theta_d}\right|\right)d\theta \tag{S34}$$

We define the term *k* as

$$k \equiv \frac{c_d Q_f}{2}\frac{L_c}{u_0}\frac{K_d}{k_f^*}\left(\frac{\alpha^e + 1}{\alpha^e - 1}\right) \tag{S35}$$

and β_d is defined as

$$\beta_d \equiv ln\left|\frac{1-\theta_d}{\theta_d}\right| \tag{S36}$$

Then

$$\begin{aligned} S &= k\int_{\theta_0}^{\theta_d}\left(ln\left|\frac{1-\theta}{\theta}\right| - \beta_d\right)d\theta = k[\theta\cdot ln\frac{1-\theta}{\theta} - \beta_d\theta - ln(1-\theta)]|_{\theta_0}^{\theta_d} \\ &= k\left[ln\frac{1-\theta_0}{1-\theta_d} + \beta_d\theta_0 - \theta_0\cdot ln\frac{1-\theta_0}{\theta_0}\right] \end{aligned} \tag{S37}$$

In the limit of $\theta_0 \to 0$

$$S = k\left[ln\frac{1-\theta_0}{1-\theta_d} + \beta_d\theta_0 - \theta_0\cdot ln\frac{1-\theta_0}{\theta_0}\right] = -k\,ln(1-\theta_d) \tag{S38}$$

The amounts of the impurities from the two adjacent bands S_{left} and S_{right} are calculated using Eq. (S38). The purity Pu_i is calculated from the two areas and the total area of the collected product:

$$Pu_i = \frac{c_d t_i Q_f - S_{left} - S_{right}}{c_d t_i Q_f} = 1 + \frac{ln(1-\theta_d)}{c_d t_i Q_f}(k_{left} + k_{right}) \tag{S39}$$

To link the yield with the purity and the cut, the k term is simplified first by substituting the Q_f and the K_d:

$$k = \frac{c_d Q_f}{2} \frac{L_c}{u_0} \frac{K_d}{k_f^*} \left(\frac{\alpha^e + 1}{\alpha^e - 1} \right) = \frac{c_d u_0 \varepsilon_b A_c}{2} \frac{L_c}{u_0} \frac{\frac{q_d}{\varepsilon_b c_d}}{k_f^*} \left(\frac{\alpha^e + 1}{\alpha^e - 1} \right) = \frac{L_c A_c q_d}{2k_f^*} \left(\frac{\alpha^e + 1}{\alpha^e - 1} \right) \qquad \text{(S40)}$$

where A_c is the cross-sectional area of the column.

The loading fraction L_f is

$$L_f = \frac{c_f V_f}{L_c A_c q_d} \qquad \text{(S41)}$$

where c_f is the total feed concentration.

The purity is related to yield and the breakthrough cut θ_d by combining Eqs. (S29), (S40), and (S41):

$$Pu_i = 1 + \left(\frac{1}{Y_i} - 1 \right) \frac{ln(1 - \theta_d)}{\beta_d} \qquad \text{(S42)}$$

This equation indicates that for a single column design, only two out of the three variables (purity, yield, and breakthrough cut θ) can be independently specified.

S5. System and simulation parameter tables

Table S1. Simulation parameters for generating a binary LAD system for Fig. S2, α values varied between 1.5 to 10.

Component		a_0	b_0	S_a	S_b	$\alpha_{i,2}$
1	Modulator	0	0	0	0	
2	Presaturant	1,450	1,000	0	0	1
3	REE1	7,250	5,000	0	0	5
4	REE2	7,250	5,000	$-\ln(\alpha)$	$-\ln(\alpha)$	5α
5	Ligand	7,250	5,000	$-\ln(5\alpha)$	$-\ln(5\alpha)$	25α

Table S2. Experimental conditions and simulation parameters for the verification of the improved general map

L (cm)	ID (cm)	R (μm)	ε_b	ε_p	$C_{f,i}$ (N)	Experiment #	X value	Feed volume (ml)	Q_f (mL/min)
38	1.16	63	0.4	0.28	0.3	1	8.40	24.3	1.73
						2	10.52	26.7	1.47
						3	14.04	29.3	1.19
						4	20.98	33.9	0.88
						5	32.15	37.7	0.60

Isotherm parameters (Modulated Langmuir isotherm)

Component		a	b	Sa	Sb
1	Modulator	0	0	0	0
2	Cu	1380	1000	0	0
3	Nd	6900	5000	0	0
4	Pr	6900	5000	-0.58779	-0.58779
5	EDTA-Na	6900	5000	-2.19722	-2.19722

Mass transfer parameters

Component	Brownian diffusivity, D_b (cm^2/min)	Pore diffusivity, D_p (cm^2/min)	Axial dispersion coefficient, E_b (cm^2/min)	Film mass transfer coefficient, k_f (cm/min)
All species	4×10^{-4}	9×10^{-5}	Chung and Wen (1968)	Wilson and Geankoplis (1966)

Numerical parameters (unit: N)

Axial element	Step size (L/u_0)	Collocation points		Tolerance	
		Axial	Particle	Absolute	Relative
151	0.01	4	2	$1\text{x}10^{-4}$	$1\text{x}10^{-3}$

Table S3. Experimental conditions for the separation of Zone I

Ligand	L (cm)	ID (cm)	R (μm)	ε_b	ε_p	Feed volume (ml)	Flow rate (ml/min)	Feed concentration (N)
0.09 M pH=9	127	1.16	63	0.40	0.28	56	5.3	Dy: 0.05
								Nd: 0.83
								Pr: 0.12

Isotherm parameters (Modulated Langmuir isotherm)

Component		a	b	Sa	Sb	Selectivity $\alpha_{i,i-1}$
1	Modulator	0	0	0	0	-
2	Cu	1360	1000	0	0	1
3	Dy	6800	5000	0	0	5
4	Nd	6800	5000	-1.60944	-1.60944	5
5	Pr	6800	5000	-2.19723	-2.19723	1.8
6	EDTA-Na	6800	5000	-3.80666	-3.80666	5

Mass transfer parameters

Component	Brownian diffusivity, D_b (cm^2/min)	Pore diffusivity, D_p (cm^2/min)	Axial dispersion coefficient, E_b (cm^2/min)	Film mass transfer coefficient, k_f (cm/min)
All species	4×10^{-4}	9×10^{-5}	Chung and Wen (1968)	Wilson and Geankoplis (1966)

Numerical parameters (unit: N)

Axial element	Step size (L/u_0)	Collocation points		Tolerance	
		Axial	Particle	Absolute	Relative
151	0.01	4	2	5×10^{-6}	10^{-3}

Table S4. Experimental conditions for the separation of Zone II Column A

Ligand	L (cm)	ID (cm)	R (μm)	ε_b	ε_p	Feed volume (ml)	Flow rate (ml/min)	Feed concentration (N)
0.09 M pH=9	89	1.16	63	0.40	0.28	451.5	5.40	Dy: 0.043
								Nd: 0.053

Isotherm parameters (Constant Separation Factor Isotherm)

q_{max} (eq./L)		1.35
Component		Selectivity α
1	Cu	1
2	Dy	5
3	Nd	25
4	EDTA-Na	125

Mass transfer parameters

Component	Brownian diffusivity, D_b (cm^2/min)	Pore diffusivity, D_p (cm^2/min)	Axial dispersion coefficient, E_b (cm^2/min)	Film mass transfer coefficient, k_f (cm/min)
All species	4×10^{-4}	9×10^{-5}	Chung and Wen (1968)	Wilson and Geankoplis (1966)

Numerical parameters (unit: N)

Axial element	Step size (L/u_0)	Collocation points		Tolerance	
		Axial	Particle	Absolute	Relative
151	0.01	4	2	5×10^{-6}	10^{-3}

Table S5. Experimental conditions for the separation of Zone II Column B

<table>
<tr><td>Ligand</td><td>L (cm)</td><td>ID (cm)</td><td>R (μm)</td><td>ε_b</td><td>ε_p</td><td>Feed volume (ml)</td><td>Flow rate (ml/min)</td><td>Feed concentration (N)</td></tr>
<tr><td rowspan="2">0.09 M
pH=9</td><td rowspan="2">89</td><td rowspan="2">1.16</td><td rowspan="2">63</td><td rowspan="2">0.40</td><td rowspan="2">0.28</td><td rowspan="2">137.4</td><td rowspan="2">1.36</td><td>Nd: 0.086</td></tr>
<tr><td>Pr: 0.074</td></tr>
<tr><td colspan="9">Isotherm parameters (Constant Separation Factor Isotherm)</td></tr>
<tr><td colspan="5">q_{max} (eq./L)</td><td colspan="4">0.95</td></tr>
<tr><td colspan="5">Component</td><td colspan="4">Selectivity α</td></tr>
<tr><td>1</td><td colspan="4">Cu</td><td colspan="4">1</td></tr>
<tr><td>2</td><td colspan="4">Nd</td><td colspan="4">5</td></tr>
<tr><td>3</td><td colspan="4">Pr</td><td colspan="4">9</td></tr>
<tr><td>4</td><td colspan="4">EDTA-Na</td><td colspan="4">45</td></tr>
<tr><td colspan="9">Mass transfer parameters</td></tr>
<tr><td>Component</td><td colspan="2">Brownian diffusivity, D_b (cm^2/min)</td><td colspan="2">Pore diffusivity, D_p (cm^2/min)</td><td colspan="2">Axial dispersion coefficient, E_b (cm^2/min)</td><td colspan="2">Film mass transfer coefficient, k_f (cm/min)</td></tr>
<tr><td>All species</td><td colspan="2">4×10^{-4}</td><td colspan="2">9×10^{-5}</td><td colspan="2">Chung and Wen (1968)</td><td colspan="2">Wilson and Geankoplis (1966)</td></tr>
<tr><td colspan="9">Numerical parameters (unit: N)</td></tr>
<tr><td rowspan="2">Axial element</td><td rowspan="2">Step size (L/u_0)</td><td colspan="3">Collocation points</td><td colspan="4">Tolerance</td></tr>
<tr><td colspan="2">Axial</td><td>Particle</td><td colspan="3">Absolute</td><td>Relative</td></tr>
<tr><td>151</td><td>0.01</td><td colspan="2">4</td><td>2</td><td colspan="3">5×10^{-6}</td><td>10^{-3}</td></tr>
</table>

Table S6. Simulation parameters for the Moore's chromatogram

System parameters							
L (cm)	ID (cm)	R (μm)	ε_b	ε_p	Feed volume (L)	Feed concentration for all component (mN)	Flow rate (ml/min)
40	2.2	112.5	0.35	0.45	1	33	3.8

Isotherm parameters (Modulated Langmuir isotherm)						
Component		a	b	Sa	Sb	Selectivity $\alpha_{i-1,i}$
1	Modulator	0	0	0	0	-
2	Er	1920	1000	0	0	1
3	Ho	2112	1100	-0.66783	-0.66783	1.95
4	Dy	2112	1100	-1.36098	-1.36098	2
5	Tb	2112	1100	-2.35423	-2.35423	2.7
6	Gd	2112	1100	-3.60699	-3.60699	3.5
7	Eu	2112	1100	-3.94346	-3.94346	1.4
8	Sm	2112	1100	-4.47409	-4.47409	1.7
9	EDTA-Na	2112	1100	-6.08353	-6.08353	5

Mass transfer parameters				
Component	Brownian diffusivity, D_b (cm^2/min)	Pore diffusivity, D_p (cm^2/min)	Axial dispersion coefficient, E_b (cm^2/min)	Film mass transfer coefficient, k_f (cm/min)
All species	4×10^{-4}	5×10^{-5}	Chung and Wen (1968)	Wilson and Geankoplis (1966)

Numerical parameters (unit: N)					
Axial element	Step size (L/u_0)	Collocation points		Tolerance	
		Axial	Particle	Absolute	Relative
151	0.01	4	2	10^{-3}	10^{-3}

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