

Supplementary Material: The chromatographic separation of particles using optical electric fields

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Small decay length model

We now consider a channel of finite length L_E in the limit $d_L/H \ll 1$, i.e., when the decay length is small compared to the channel height. In this limit, the concentration in Eq. (9) rapidly decays to the value k outside of a boundary layer near the wall. The sharp definition of the boundary layer suggests that a first approximation to the transport problem may be obtained by dividing the column into a convective phase and a stagnant phase similar to the analysis of SEC columns. The convective phase contains the molecules outside of the boundary layer while the stagnant phase contains the molecules inside the boundary layer. At a given axial position z , the relative number of molecules in the two compartments are assumed to be given by Eq. (9). In the convective phase the number of molecules (per unit column length and column width) is given to a first approximation as

$$n_1 = \int_{x=-H}^H k dx W = 2HWk \quad (\text{S.1})$$

The corresponding number of molecules in the stagnant phase is then

$$n_2 = \int_{x=-H}^H [c(x) - k] dx W = H \int_{y=0}^{\infty} [c(x') - k] dx' W. \quad (\text{S.2})$$

Here $x' = 1 + x/H$ and the range on x' has been extended to infinity. Due to the sharp definition of the boundary layer this has a negligible effect on the value of the integral. For the profile in Eq. (9), the integrand in Eq. (S.2) may be expanded in a Taylor series to obtain

$$c(x') - k = k \sum_{n=1}^{\infty} \frac{(-\Phi)^n}{n!} \exp\left(-\frac{2nx'}{d_L/H}\right) \quad (\text{S.3})$$

The integral in S.2 is simply evaluated to obtain

$$n_2 = kHW \sum_{n=1}^{\infty} \frac{(-\Phi)^n}{n!} \frac{d_L/H}{2n}. \quad (\text{S.4})$$

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Now if we define the partition coefficient K as

$$n_2 = Kn_1, \quad (\text{S.5})$$

then

$$K = \frac{d_L}{4H} F(\Phi), \quad (\text{S.6})$$

where we have defined the function

$$F(\Phi) = \sum_{n=1}^{\infty} \frac{(-\Phi)^n}{n!n}. \quad (\text{S.7})$$

While the present treatment is concerned with $\Phi < 0$ (attraction) the expression above may be used also for $\Phi > 0$ (depletion). The latter situation corresponds to a SEC column. Note that the value of k does not enter in the value of K . This allows the derivation of a model for a column of finite length in which the concentration is equilibrated at all axial positions. This is possible because the potential Φ is essentially zero outside of the boundary layer. Therefore Eq. 1 reduces to the advection-diffusion equation outside of the boundary layer. Hence the transport of solute molecules in this phase may be described by the Taylor-Aris dispersion model. In particular, molecules n_1 are advected in the axial direction on average with a mean flow velocity and dispersed with an effective dispersion coefficient

$$D_T = D \left(1 + \frac{2}{105} \text{Pe}^2\right). \quad (\text{S.8})$$

A mass balance on a cross-section of the column therefore gives

$$\frac{\partial n_1}{\partial t} + \frac{\partial n_2}{\partial t} + v \frac{\partial n_1}{\partial z} - D_T \frac{\partial^2 n_1}{\partial z^2} = 0, \quad (\text{S.9})$$

where n_2 may be eliminated by Eq S.5. This results in the dimensionless unsteady second order equation

$$\tau_p \frac{\partial n_1}{\partial t} + \frac{\partial n_1}{\partial \bar{z}} - \frac{1}{\text{Pe}_L} \frac{\partial^2 n_1}{\partial \bar{z}^2} = 0, \quad (\text{S.10})$$

where

$$\tau_p = \tau_f(1 + K), \quad (\text{S.11})$$

and the axial Peclet number is defined as

$$\text{Pe}_L = \frac{U_f L_E}{D_T} = \frac{\text{Pe}}{1 + \frac{2}{105} \text{Pe}^2} \frac{L_E}{H}. \quad (\text{S.12})$$

The Laplace transformation of Eq. S.10 for a column that is empty at $t = 0$ yields in Laplace space

$$N_1(s, 1) = N_1(s, 0) \exp\left(\frac{\text{Pe}_L - \sqrt{\text{Pe}_L(\text{Pe}_L + 4\tau_p s)}}{2}\right), \quad (\text{S.13})$$

where $N_1(s, \bar{z})$ is the Laplace transformation of $n_1(t, \bar{z})$. Given a unit pulse input ($N_1(s, \bar{z}) = 1$), we arrive at

$$n_1(z = 1) = \frac{1}{2\tau_p} \left(\frac{\text{Pe}\tau_p^3}{\pi t^3}\right)^{\frac{1}{2}} \exp\left(\frac{\text{Pe}}{4} \left(2 - \frac{t}{\tau_p} - \frac{\tau_p}{t}\right)\right) \quad (\text{S.14})$$

For large values of Pe_L , the time signal becomes symmetric and centered around $t = \tau_p$. We may therefore expand in $t - \tau_p$ to find the normal distribution given by

$$n_1(z = 1) \approx \frac{1}{2\tau_p} \left(\frac{\text{Pe}_L}{\pi}\right)^{1/2} \exp\left(-\frac{\text{Pe}_L(t - \tau_p)^2}{4\tau_p^2}\right) \quad (\text{S.15})$$

$$n_1(z = 1) \approx \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} \exp\left(-\frac{1}{2} \frac{(t - \tau_p)^2}{\sigma^2}\right). \quad (\text{S.16})$$

From which it is clear that τ_p is the retention time and $\sigma^2 = 2\tau_p^2/\text{Pe}_L$ is the variance of the signal.

It follows that the resolution for the small decay length model is given by

$$R_{SDLM} = \frac{1}{2\sqrt{2}} \left(\frac{\text{Pe}}{1 + \frac{2}{105}\text{Pe}^2}\right)^{\frac{1}{2}} \left(\frac{L_E}{H}\right)^{1/2} \frac{|\tau_2 - \tau_1|}{\tau_2 + \tau_1}, \quad (\text{S.17})$$

where

$$\frac{|\tau_2 - \tau_1|}{\tau_2 + \tau_1} = \frac{\frac{d_L}{4H} |F(-\Phi_2) - F(-\Phi_1)|}{2 + \frac{d_L}{4H} (F(-\Phi_2) + F(-\Phi_1))}. \quad (\text{S.18})$$

Note that there exists an optimum resolution corresponding to $\text{Pe} = \sqrt{105}/2 \approx 7.2$.

Numerical Methods

Infinite Series of Fields

For an infinite series of optical fields, a steady state calculation for $c(x, z)$ is performed in COMSOL. The retention ratio, χ_f , is determined by numerically integrating the numerator and denominator of Eq. 7 using the steady state concentration profile. The specifics of the COMSOL model used in the infinite series analysis are as follows. The *Transport of Diluted Species* module with the *Migration in Electric Field* option was used to carry out all simulations. Both *Streamline diffusion* and *crosswind diffusion* stabilization options were turned

off. Periodic conditions were prescribed at the left and right boundaries given by,

$$c(z = 0) = c(z = d_s), \quad (\text{S.19})$$

and a no flux condition prescribed at the top and bottom boundaries. The constants used for these calculations are given in Table 2.

Discrete Number of Fields

For calculations concerning a discrete number of defects, one domain of size L_T is specified in a rectangular geometry. The region before the electric field accounts for dispersion in the solute concentration before entering the region where the radial and axial particle concentrations are affected by the polarization potential. U_p is determined by the time required t_f for the mean of the concentration distribution to pass through the length L_E , i.e.,

$$U_p = \frac{L_E}{t_f}. \quad (\text{S.20})$$

The region after the electric fields is where the resulting concentration distributions of different sized particles/molecules are assessed in order to calculate the resolution of separation using Eq. 8. The specifics of the COMSOL model used in this analysis are as follows. The *Transport of Diluted Species* module with the *Migration in Electric Field* option was used to carry out all simulations. Both *Streamline diffusion* and *crosswind diffusion* stabilization options were turned off. A Gaussian distribution was assumed for the initial condition given by

$$c(t = 0, x, z) = c_0 \exp\left(\frac{-(z - Z_{c,0})^2}{2\sigma_c^2}\right), \quad (\text{S.21})$$

where $Z_{c,0}$ is the initial z position of the concentration profile and σ_c^2 is the initial variance of the solute concentration distribution and a no flux boundary condition is specified on both the top and bottom walls. Constants used in all COMSOL simulations are specified in Table 1.

Meshing

A custom free triangular mesh was specified with max element size less than $0.18 \mu\text{m}$ and refinement around a secondary boundary that began $10 \mu\text{m}$ before the first electric field and ended $10 \mu\text{m}$ after, with a max element size less than $0.05 \mu\text{m}$. The *Generalized alpha* time stepping method was used with a time step $\leq L/(600U_f)$.