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Retention and Peak Width in Field-Flow Fractionation with Wall Effects

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Abstract

Retention and peak width are calculated in field-flow fractionation with boundary absorption. Results obtained by other authors are covered as particular cases of our more general treatment.

INTRODUCTION

Field-flow fractionation is a method in which particles are separated in a nonuniform flow under the influence of a field perpendicular to the flow (*1–9*). In most cases, the flow has a parabolic velocity profile. The field can be produced by gravitational or centrifugal force, by a thermal or electrical gradient. Under the influence of this field, different types of particles will move to regions of the flow with different flow velocity, leading to different peaks in the chromatographic experiment. Apart from calculating theoretically the positions of these peaks in terms of the characteristics of the particles (e.g., mobility, radius, charge, etc.), it is also important to evaluate the peak widths. This allows one to discuss the separating power of the set-up. The explanation for the width of the peaks is to be found in the stochastic nature of the particles' motion: particles, even though perfectly identical, will not follow the same trajectory. Although the resulting dispersion is a nuisance to the chromatographic experiment *per se,* it reflects properties of the stochastic motion of the particle and can therefore be used, in combination with appropriate theoretical results, to measure dynamic properties of this motion (e.g., diffusion constant, reaction rates, etc.). In this context, we mention the work of Westhaver (*10*), Taylor (*11*), Aris (*12*), Giddings (*13–15*), and Mysels (*16*).

In many cases the suspended particles can undergo adsorption in a thin retentive layer at the boundaries of the tube through which the carrier fluid is flowing. Results were obtained for this case by Golay (*17*) in the absence of a field and for infinitely fast equilibration. Surface transport and finite equilibration times were considered in Refs. *18* and *19–21,* respectively; see also Ref. *22.*

The purpose of this paper is to calculate the retention and peak width in the presence of both boundary adsorption (with finite equilibration times) and an external field. All the above cited results are covered as particular cases.

GENERAL RESULT FOR RETENTION AND PEAK WIDTH

The general results, which we will apply to more specific cases in the next section, can be obtained as a limit of a discrete model which was discussed by one of the authors (*23*). In this model (see Fig. 1) one considers a system of N layers or channels. The layers are planar and parallel to the x–z plane. In each layer i, $i = 1, 2, \ldots, N$, fluid is flowing in the x direction with velocity u_i. Particles suspended in the fluid are carried along with the local fluid velocity. The transition rates for going from layer i to layer $i + 1$ and $i - 1$ are denoted by k_i^+ and k_i^-, respectively (see Fig. 1). We consider here reflecting boundary conditions, so that $k_1^- = k_N^+ = 0$. Moreover, all other $k_i^\pm$'s are assumed to be nonzero, i.e., the random walk is irreducible.

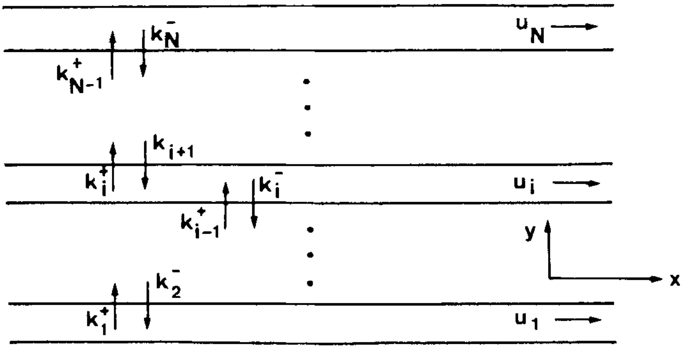

FIG. 1. Kinetic model of field-flow fractionation system.

The steady-state distribution p_i^* of particles undergoing the above described random walk over the layers i, $i = 1, \ldots, N$, is determined by the detailed balance conditions $k_i^+ p_i^* = K_{i+1}^- p_{i+1}^*$, leading to

$$p_i^* = N k_1^+ \ldots k_{i-1}^+ k_{i+1}^- \ldots k_N^- \tag{1}$$

with N a normalization constant.

It can be shown (*23*) that the distribution of the particles (i.e., the concentration or probability profile) along the flow direction x is asymptotic for $t \to \infty$, a Gaussian distribution with average position of its peak $\langle x(t) \rangle$ and peak width $\langle \delta x^2(t) \rangle$ (or dispersion) given as

$$\lim_{t \to +\infty} \frac{\langle x(t) \rangle}{t} = \bar{u}^* \tag{2}$$

$$\lim_{t \to \infty} \frac{\langle [x(t) - \langle x(t) \rangle]^2 \rangle}{2t} = K^* \tag{3}$$

with

$$\bar{u}^* = \sum_{i=1}^{N} u_i p_i^* \tag{4}$$

and

$$K^* = \sum_{i=1}^{N-1} \frac{\left[\sum_{j=1}^{i} (u_j - \bar{u}^*) p_j^* \right]^2}{k_i^+ p_i^*} \tag{5}$$

K^* is sometimes called the effective longitudinal diffusion coefficient.

We will now take the limit in which the discrete parameter i goes over into a continuous parameter $y \in [0,L]$ except for one or two discrete states $i = 1$ and $i = N$, which are to model the retentive boundary layers. The details of this limit are given in the Appendix.

Let us first consider the case in which only the lower state $i = 1$ is kept as a discrete state. The flow profile then consists of a continuum $u = u(y)$ and the velocity $u_1 = 0$ in the boundary layer. The particles occupy a position y in the continuum with a probability density $p^*(y)$ while the probability for sitting in the retentive boundary layer will be denoted by P_{abs}. Obviously, one has

$$\int_0^L p^*(y) dy + P_{\text{abs}} = 1 \tag{6}$$

The random walk over the states $i = 2, \ldots, N$ becomes a diffusive process (possibly with drift) with diffusion coefficient $D(y)$.

By splitting off the term $i = 1$ in the summations appearing in Eqs. (4) and (5) and taking the continuum limit for the remaining layers, we obtain

$$\bar{u}^* = \int_0^L u(y)p^*(y)dy \tag{7}$$

$$K^* = \int_0^L dy \frac{\left\{\int_0^y dy'[u(y') - \bar{u}^*]p^*(y') - \bar{u}^* p_1^*\right\}^2}{D(y)p^*(y)} + \frac{(\bar{u}^*)^2 p_1^*}{k_{\text{des}}} \tag{8}$$

where we have written k_{des} for k_1^+ (k_{des} is the desorption rate, i.e., k_{des}^{-1} is the average time spent in the retentive layer per visit).

We will now express $\bar{u}^*$ and K^* in terms of the stationary probability profile $p(y)$ *in the absence of a retentive layer* in order to make the effect of these layers more apparent. This is possible because *the form* of the steady-state probability profile is not modified by the presence of this layer, i.e., $p^*(y)$ is proportional to $p(y)$. Let us call k the ratio of the sample in the retentive layer to the sample in the mobile continuum phase:

$$k = \frac{p_1^*}{\int_0^L p^*(y)dy} \tag{9}$$

Since

$$\int_0^L p(y)dy = 1 \tag{10}$$

we obtain by combining Eqs. (6), (9), and (10):

$$p_1^* = p_{\text{abs}} = \frac{k}{k+1} \tag{11}$$

and

$$p^*(y) = \frac{p(y)}{1+k} \tag{12}$$

Inserting these results in Eqs. (7) and (8), we obtain

$$\bar{u}^* = \frac{\int_0^L u(y)p(y)dy}{1 + k} = \frac{\bar{u}}{1 + k} \tag{13}$$

$$K^* = \int_0^L dy \frac{\left\{\int_0^y dy'[u(y')(1 + k) - \bar{u}]p(y') - k\bar{u}\right\}^2}{D(y)p(y)(1 + k)^3} + \frac{k\bar{u}^2}{k_{\text{des}}(1 + k)^3} \tag{14}$$

Proceeding in the same way for the case where both the upper and lower states $i = 1$ and $i = N$ play the role of retentive layers (with identical properties $k_1^+ = k_N^- = k_{\text{des}}$ and $k_2^- = k_{N-1}^+ = k_{\text{abs}}$), we obtain

$$\bar{u}^* = \frac{\bar{u}}{1 + k} \tag{15}$$

$$K^* = \int_0^L dy \frac{\left\{\int_0^y dy'[u(y')(1 + k) - \bar{u}]p(y') - \frac{k\bar{u}}{2}\right\}^2}{D(y)p(y)(1 + k)^3} + \frac{k\bar{u}^2}{k_{\text{des}}(1 + k)^3} \tag{16}$$

Equations (13)–(16) are the basic results of this paper. The peak velocity and peak width can thus be obtained by filling in the flow profile $u(y)$ and the steady-state probability profile $p(y)$ in the absence of boundary absorption. Clearly, the effect of a retentive layer on the average peak velocity is merely a reduction of its speed by a factor $(1 + k)$. The effect on the peak width is much more intricate. As can be seen from Eqs. (14) and (16), K^* consists of two terms. The first term is of the form

$$K \frac{1 + Bk + Ck^2}{(1 + k)^3} \tag{17}$$

where K stands for the effective longitudinal diffusion coefficient in the absence of boundary effects ($k = 0$). Not much can be said in general about the correction factor (except that it is nonnegative), without specifying the flow and probability profile.

The second term in Eqs. (14) and (16) is a correction term in the case of a finite equilibration speed of the absorption–desorption mechanism, i.e., finite k_{des}. This additional contribution to the dispersion is the consequence of the dispersion on the residence time at each visit of the retentive layer.

It is instructive to compare the above results with the case where temporary trapping of the particles can take place at any place in the system. This situation has been considered in Ref. *22* (see Eqs. IV.16, IV.19, and IV.20 with the notation $k = k^+/k^-$ and $k_{\text{des}} = k_-$). One then has

$$\bar{u}^* = \frac{\bar{u}}{1 + k} \tag{18}$$

and

$$K^* = \frac{K}{1 + k} + \frac{k\bar{u}^2}{k_{\text{des}}(1 + k)^3} \tag{19}$$

Note that the first term in Eq. (19) corresponds to the values $B = 2$ and $C = 1$ in Eq. (17) and this, independent of flow and probability profile, while the second term is identical with the one obtained for boundary retentive layers.

RETENTION AND PEAK WIDTH FOR THE CASE OF A CONSTANT FIELD

As an application of the general result given by Eqs. (15) and (16), we consider particles suspended in a parabolic flow $u(y)$, $y \in [0,L]$ between two plane parallel layers at a distance L:

$$u(y) = 6u_s \frac{y}{L}\left(1 - \frac{y}{L}\right) \tag{20}$$

u_s is the average solvent velocity. A constant (gravitational, electrical, or centrifugal) field is acting on the particles, inducing an average setting (or sedimentation) speed V_S. The probability (or concentration) profile attained under the influence of this force is given by a barometric distribution:

$$p(y) = \frac{\alpha e^{\alpha}}{L(e^{\alpha} - 1)} e^{-\alpha(y/L)}, \quad y \in [0,L] \tag{21}$$

where α is the so-called Peclet number:

$$\alpha = V_S L/D \tag{22}$$

It describes the relative importance of sedimentation versus diffusion (D is the diffusion coefficient of the suspended particles) for the given (vertical) dimension L of the system. In chromatography, one often uses the basic retention parameter λ instead of α (see, e.g., Ref. 7, Eq. 10):

$$\lambda = \alpha^{-1} \tag{23}$$

Suppose now that the upper and lower plate are coated such as to form retentive layers for the suspended particles. The peak velocity and peak width can now be calculated on the basis of Eqs. (15) and (16) by inserting for $u(y)$ and $p(y)$ the expression given by Eqs. (20) and (21) (moreover, $D(y) = D$ is a constant).

After extremely lengthy but straightforward calculation, we obtain the following results:

$$\bar{u}^* = \frac{\bar{u}}{1 + k} \tag{24}$$

with

$$\bar{u} = \frac{6}{\alpha}\left(\coth\frac{\alpha}{2} - \frac{2}{\alpha}\right)u_s \tag{25}$$

and

$$K^* = \frac{\bar{u}^2 L^2}{210D}\,\frac{A(\alpha) + B(\alpha)k + C(\alpha)k^2}{(1 + k)^3} + \frac{k\bar{u}^2}{k_{\mathrm{des}}(1 + k)^3} \tag{26}$$

with

$$\begin{aligned} A(\alpha) = {} & \frac{5040}{(e^\alpha - 1)^3\alpha^6}\,[(3\alpha^2 - 30\alpha + 84)e^{3\alpha} + (\alpha^4 - 6\alpha^3 - 21\alpha^2 + 30\alpha \\ & - 252)e^{2\alpha} + (-\alpha^4 - 6\alpha^3 + 21\alpha^2 + 30\alpha + 252)e^\alpha + (-3\alpha^2 \\ & - 30\alpha - 84)] \end{aligned} \tag{27}$$

$$\begin{aligned} B(\alpha) = {} & \frac{1260}{(e^\alpha - 1)^2\alpha^6}\,[(-\alpha^4 + 8\alpha^3 + 12\alpha^2 - 288\alpha + 768)e^{2\alpha} \\ & + (6\alpha^4 - 216\alpha^2 - 1536)e^\alpha + (-\alpha^4 - 8\alpha^3 + 12\alpha^2 \\ & + 288\alpha + 768)] \end{aligned} \tag{28}$$

$$C(\alpha) = \frac{210}{\alpha^6 e^\alpha (e^\alpha - 1)} [(9\alpha^2 - 36\alpha + 36)e^{3\alpha} + (-6\alpha^4 + 12\alpha^3 + 225\alpha^2 - 1404\alpha + 2772)e^{2\alpha} + (6\alpha^4 + 12\alpha^3 - 225\alpha^2 - 1404\alpha - 2772)e^\alpha - (9\alpha^2 + 36\alpha + 36)] \tag{29}$$

Note that, for α small, one has

$$A(\alpha) = 1 + \frac{7}{60}\alpha^2 - \frac{89}{7920}\alpha^4 \tag{30}$$

$$B(\alpha) = 9 - \frac{29}{30}\alpha^2 + \frac{113}{2640}\alpha^4 \tag{31}$$

$$C(\alpha) = \frac{51}{2} + \frac{79}{24}\alpha^2 + \frac{125}{3168}\alpha^4 \tag{32}$$

Note also that A, B, and C are even functions of α, as was to be expected on the basis of the $y \rightarrow -y$ symmetry of the system.

From Eqs. (24) and (25), one immediately obtains the familiar result for the so-called retention ratio R:

$$R = \frac{\bar{u}^*}{u_S} = \frac{6\lambda(\coth \frac{1}{2\lambda} - 2\lambda)}{1 + k} \tag{33}$$

The peak dispersion is usually expressed in terms of the so-called plate height H (see, e.g., Ref. *24*):

$$H = \frac{2K^*}{\bar{u}^*} = \frac{2k\bar{u}}{k_{\text{des}}(1 + k)^2} + \frac{u_S L^2}{D}\chi(\lambda) \tag{34}$$

with

$$\chi(\lambda) = \frac{6\lambda(\coth \frac{1}{2\lambda} - 2\lambda)}{105(1 + k)^2}\left[A\left(\frac{1}{\lambda}\right) + B\left(\frac{1}{\lambda}\right)k + C\left(\frac{1}{\lambda}\right)k^2\right] \tag{35}$$

For the particular case $\lambda \rightarrow \infty$ (or $\alpha \rightarrow 0$), one recovers, in view of Eqs. (30)–(32), the result of Golay (*17*):

$$\chi(\infty) = \frac{1 + 9k + \frac{51}{2}k^2}{105(1 + k)^2} \tag{36}$$

For $k = 0$, Eq. (35) reduces to the result first obtained by Giddings et al. (*6*); see also Ref. *23* (note, however, the missprint in Eq. 3.14 of the sign of $21\alpha^2 e^{2\alpha}$).

Note that numerical results for $\chi(\lambda)$ were obtained for several values of λ in Refs. *18* and *2*. Note also that the result for $\lambda \rightarrow \infty$ and $k \rightarrow 0$:

$$H = \frac{u_s L^2}{105 D}$$

was given by Westhaver in 1947 (see Eqs. 12 and 32 in Ref. *10* with the notation $V_a = u_s$ and $W = L/2$).

RETENTION AND PEAK WIDTH IN A CYLINDRICAL TUBE

As a second application we consider the case of particles suspended in a fluid in Poiseuille flow streaming through a cylindrical tube of radius R. The flow profile is then

$$u(r) = 2u_S\left[1 - \left(\frac{r}{R}\right)^2\right] \tag{37}$$

We will only consider the simple case in which no external field is acting on the particles. The probability profile is then

$$P(r) = 2r/R^2, \qquad r \in [0,R] \tag{38}$$

The peak velocity and peak width for the case in which the particles can be temporarily adsorbed at the tubes surface is obtained from Eqs. (13) and (14) by inserting the above given expressions for the flow and probability profile (with $D(r) = D$, a constant). One obtains:

$$\bar{u}^* = \frac{\bar{u}}{1 + k} = \frac{u_S}{1 + k} \tag{39}$$

and

$$K^* = \frac{\bar{u}^2 R^2}{48D} \frac{1 + 6k + 11k^2}{(1 + k)^3} + \frac{k\bar{u}^2}{k_{\mathrm{des}}(1 + k)^3} \tag{40}$$

These results are in agreement with the results given in Refs. *17–21*.

APPENDIX

We denote by $P(x,i,t)dx$ the probability that a particle is observed in the ith layer between x and $x + dx$ at time t. These probabilities obey the following set of conservation equations:

$$\partial_t P(x,i,t) = -\frac{\partial}{\partial x} u_i P(x,i,t) + k_{i-1}^{+} P(x,i-1,t) + k_{i+1}^{-} P(x,i+1,t)$$

$$-(k_i^{+} + k_i^{-}) P(x,i,t) \qquad i = 2, \ldots, N-1 \tag{A1a}$$

$$\partial_t P(x,N,t) = -\frac{\partial}{\partial x} u_N P(x,N,t) + k_{N-1}^{+} P(x,N-1,t) - k_N^{-} P(x,N,t) \tag{A1b}$$

$$\partial_t P(x,1,t) = -\frac{\partial}{\partial x} u_1 P(x,1,t) + k_2^{-} P(x,2,t) - k_1^{+} P(x,1,t) \tag{A1c}$$

The layers $i = 2, \ldots, N$ are now given a thickness η, and we introduce the coordinate

$$y = (i-2)\eta \tag{A2}$$

We define:

$$P(x,y,t) = \frac{P(x,(i-2),t)}{\eta} \tag{A3}$$

and

$$\begin{aligned} k_i^{\pm} &= k_i \pm \varepsilon_i \qquad i = 3, \ldots, N-1 \\ k_N^{-} &= k_N - \varepsilon_N \\ k_2^{+} &= k_2 + \varepsilon_2 \end{aligned} \tag{A4}$$

We then take the limit $\eta \to 0$, $N \to \infty$, $k_i \to \infty$, and $\varepsilon_i \to \infty$, $i = 2, \ldots, N$ and $k_2^{-} \to \infty$ such that the products

$$\begin{aligned} k_i \eta^2 &= D(y) \\ \varepsilon_i \eta &= W(y) \end{aligned} \tag{A5}$$

$$k_2^- \eta = k_{\mathrm{abs}}$$

$$(N - 1)\eta = L$$

remain constant. We also write $k_1^+ = k_{\mathrm{des}}$, $P(x,1,t) = P_{\mathrm{abs}}(x,t)$, and set $u_1 = 0$. In this limit the set of Eqs. (A1) goes over into a diffusive equation for the continuum:

$$\partial_t P(x,y,t) = \left[-\frac{\partial}{\partial x} u(y) - \frac{\partial}{\partial y} V(y) + \frac{\partial}{\partial y} D(y) \frac{\partial}{\partial y} \right] P(x,y,t) \quad \text{(A6)}$$

with

$$V(y) = 2W(y) - \frac{dD(y)}{dy} \quad \text{(A7)}$$

and in an absorption-desorption rate equation for the retentive layer:

$$\partial_t P_{\mathrm{abs}}(x,t) = k_{\mathrm{abs}} P(x,y = 0,t) - k_{\mathrm{des}} P_{\mathrm{abs}}(x,t) \quad \text{(A8)}$$

We have a reflecting boundary condition at $y = L$:

$$\left[-V(y) + D(y) \frac{\partial}{\partial y} \right] P(x,y,t) \,|_{y=L} = 0 \quad \text{(A9)}$$

while at $y = 0$ the probability flux of particles leaving the continuum is equal to the influx of probability in the retentive layer:

$$\left[-V(y) + D(y) \frac{\partial}{\partial y} \right] P(x,y,t) \,|_{y=0} = k_{\mathrm{abs}} P(x,0,t) - k_{\mathrm{des}} P_{\mathrm{abs}}(x,t) \quad \text{(A10)}$$

These two boundary conditions ensure that probability is preserved. Performing the above described limit on the results of Eqs. (4) and (5) leads us to Eqs. (7) and (8). The derivation of Eqs. (15) and (16) proceeds along similar lines.

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Note Added in Proof

An extension of the results obtained by Golay (*17*) was given by R. Aris, *Proc. R. Soc. London*, A252, 538 (1959), while results for strong retention ($k \to +\infty$) were given earlier by J.W. Westhaver, *Ind. Eng. Chem.*, 34, 126 (1942).