Separations in Conventional, Hyperlayer, and Steric Field-Flow Fractionation

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Separation in field-flow fractionation is caused by the interaction of a longitudinal flow in a narrow channel with a transverse flow or flux (Giddings, 1985). The transverse flux is due to an imposed field—electrical, magnetic, or gravitational—acting on the particles or molecules to be separated. A transverse flow may be caused by a wall permeable to the solvent but impermeable to the particles to be separated. For conventional field-flow fractionation, the flux downward is counteracted by diffusion upward, giving rise to exponential distributions of the different species over the cross section of the channel formed between two closely spaced parallel surfaces, Figure 1. The longitudinal flow, which increases with distance from the confining walls, convects the components at different longitudinal rates, thus causing separation of solute bands. The process called steric field-flow fractionation separates particles of different diameter whose closest approach to the wall is their radius (Giddings and Myers, 1978).

In hyperlayer field-flow fractionation (Giddings, 1983), particles are focused at a layer parallel to the boundary surfaces by, for example, a transverse density gradient. Giddings showed that Brownian motion about this layer induces a Gaussian concentration profile transversely across the channel, Figure 1. The layer is convected longitudinally at the rate of the velocity profile at that position, and separation of different layers can occur.

Applications and fundamental ideas of field-flow fractionation were reviewed recently by Giddings (1985). Experimental studies by Schallinger et al. (1984) suggest that sedimentation field-flow fractionation is a rapid and quantitative method mild enough for bioproducts, such as DNA. Schunk et al. (1984) investigated magnetic field-flow fractionation of metal oxide particles. Peterson et al. (1984) applied steric field-flow fractionation to spherical particles up to 100 μm in diameter. The commercialization of a field-flow fractionation instrument for separation of ultrafine particles and macromolecules has recently been announced (Blaine, 1986).

As with chromatography, field-flow fractionation is a nonequilibrium separation process influenced by interacting transport phenomena. An early nonequilibrium treatment of field-flow fractionation (Giddings, 1968), showed that the dispersion coefficient, and thus the height equivalent to a theoretical plate, could be expressed in terms of spatial averages of concentration and velocity. These essential ideas were implemented by Giddings et al. (1975) for parallel wall columns. Gajdos and Brenner (1978) extended the theory of field-flow fractionation to nonspherical particles and general power-series velocity profiles. Jayaraj and Subramanian (1978) discussed relaxation phenomena in field-flow fractionation. Lightfoot et al. (1981) provided a critical review of the foundations of the subject.

The present study applies a temporal moment analysis to reveal the similarities among processes with different transverse concentration profiles, for example, conventional, steric, and hyperlayer field-flow fractionation. The hypothesis that longitudinal dispersion in field-flow fractionation is not substantially different from dispersion in the absence of the external field simplifies the algebraic computations of the band spreading. Nonideal or secondary processes, however, can disturb the system and aggravate the band-spreading beyond the usual dispersion in a zero-field channel. For example,

a. The velocity profile can be disturbed by wall roughness or by solute particles
b. Solute particles or molecules may adhere to the walls
c. Natural convection can occur due to nonuniform temperature (or density), or
d. Particles can associate

The present analysis, intending to address more fundamental aspects, does not treat these secondary effects. Dispersion, due to longitudinal diffusion and to the interaction of transverse diffusion with the longitudinal velocity, ideally would be relatively independent of the concentration profile across the channel (under the assumption that the diffusion coefficients are independent of concentration). This condition was quantitatively inves-

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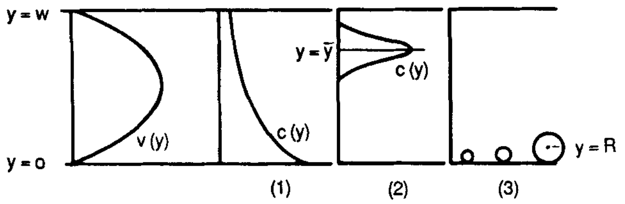

Figure 1. Velocity profile $v(y)$ and concentration profiles $c(y)$.

(1) Conventional, (2) hyperlayer field-flow fractionation
(3) Steric field-flow fractionation, spherical particles positioned at their radius, R, from wall

tigated by Reis et al. (1978) and by Lightfoot et al. (1981) in their mathematical investigation of convective mass transfer in the presence of polarizing fields. For the planar channel of interest in field-flow fractionation, Reis et al. calculated that an increase in the transverse field causes a decrease in dispersion coefficient. A very large increase in the field may be impractical due to consequent large increases in retention time (Giddings et al., 1983). Nonideal processes, as noted above, would augment the dispersion. In the present work we assume that the longitudinal dispersion is given by a modification of the Taylor theory, and is independent of field strength. Thus a new treatment of band-spreading in field-flow fractionation, and its extension to resolution of peaks, is proposed in the present study.

The concept of resolution, easily defined in terms of the temporal moments for a chromatographic process, can be utilized for field-flow fractionation, as suggested previously by Yau and Kirkland (1981). This concept can be applied to the optimization of chromatographic separations (McCoy, 1986). The present work shows the effects of operating and design parameters such as flow rate, applied transverse force or flux, and channel height, on resolution of two species in field-flow fractionation.

Velocity and Concentration Profiles

We consider a duct of rectangular cross section with breadth w very much greater than height. The longitudinal flow, Figure 1, is laminar with average velocity $\langle v\rangle$, and $v(y)$ represents the parabolic profile as a function of height y above the lower wall,

$$v(y) = 6\langle v\rangle(y/w)(1 - y/w) \qquad (1)$$

The velocity is assumed to be uniform across the breadth of the channel. The interaction of species in the transverse concentration profile, Figure 1, with the velocity gradient causes longitudinal migration at different rates. The assumption is made that the transverse concentration profile has either already formed before flow begins, or is established on a time scale very short (essentially instantaneous) compared to the time for longitudinal migration. The y dependence of concentration can be expressed as

$$c(y, z, t) = c_o(z, t)f(y) \qquad (2)$$

The form of $f(y)$ depends upon the physics of the separation mechanism.

For conventional field-flow fractionation, the transverse force acts in the negative y direction, causing a flux, uc, counterbalanced by backdiffusion under the quasi steady-state condition,

$$uc = -Ddc/dy \qquad (3)$$

which integrates to Eq. 2 with

$$f(y) = \exp(-y/\ell) \qquad (4)$$

$$\ell = D/u \qquad (5)$$

We have the functional dependence, $c(y, z, t)$, and since the only y dependence of c is in the exponential of Eq. 4, we therefore have $c_o(z, t)$, as the concentration at the lower wall.

The result, Eq. 4, is the basis for all other models of conventional field-flow fractionation, for example, the models of Berg and Purcell (1967), Giddings (1968), and Gajdos and Brenner (1978). Jayaraj and Subramanian (1978) showed that the relaxation time for the exponential profile to be established can be very small. The ratio of the characteristic times for transverse drift and diffusion is simply the parameter

$$\lambda = D/uw = (w/u)/(w^2/D) \qquad (6)$$

For satisfactory separation, λ must be substantially less than one, indicating from Eq. 6 that the relaxation due to the applied force is faster than the relaxation of diffusion. This is consistent with the rapid formation of the exponential concentration profile. Therefore, we ignore this initial relaxation period, as well as the very short entry distance, required for the transverse concentration distribution to be established. For systems that may relax slowly—for example, very small particles in a weak field—an initial waiting period may be necessary before flow begins to establish the concentration profile.

In hyperlayer field-flow fractionation, as Giddings (1983) has explained, diffusion counteracts the focusing effect of the density gradient to impart a Gaussian concentration profile in the transverse direction. The concentration profile (Giddings, 1983) is given by Eq. 2 with

$$f(y) = \exp -(y - \bar{y})^2/\sigma^2 \qquad (7)$$

in terms of the mean position layer, y. In Eq. 2, $c_o(z, t)$ is the concentration at layer $\bar{y}$. The variance σ^2 is related to the particle volume V, the acceleration g, and the density gradient $d\rho/dy$ by

$$\sigma^2 = KT/Vg(d\rho/dy) \qquad (8)$$

For steric field-flow fractionation the particles are positioned at a distance equal to their radius, R, from the wall, and the distribution is the delta function

$$f(y) = \delta(y - R) \qquad (9)$$

Moment Expressions

As in chromatography, temporal moments are useful for characterizing the concentration histories of chemical species as they proceed along the channel. To quantify the separation properties for a given system, it is necessary to have temporal moments at the channel exit. Unlike standard forms of chromatography, in field-flow fractionation a gradient of concentration exists across the channel cross section, that is, in the y direction. Whereas moments are usually defined for the uniform concentration at any cross section, in field-flow fractionation we can define moments for each fluid streamline:

$$m_n(y, z) = \int_0^\infty t^n c(y, z, t)\, dt \qquad (10)$$

in terms of longitudinal distance z from the entrance of the channel. These moments are assumed invariant across the breadth of the channel. Such moments can be averaged in an appropriate manner over y to determine the value that is measured over the entire cross section, for example, at the exit detector. Separation occurs as different components migrate to form distributions that are a function of distance from the wall, and are convected downstream at different rates due to the velocity profile. The separation can be quantified by use of magnitudes of moments. The temporal moments, defined by $\mu_n' = m_n/m_o$, have simple expressions for the open channel (Suzuki and Smith, 1975). The first moment is written as

$$\mu_1' = \mu_1'(z = 0) + z/v \qquad (11)$$

and the second central moment as

$$\mu_2 = \mu_2' - (\mu_1')^2 = \mu_2(z = 0) + 2zD_a/v^3 \qquad (12)$$

in terms of the longitudinal dispersion coefficient D_a. For an impulse input, we can set $\mu_1'(z = 0) = \mu_2(z = 0) = 0$.

Since the moments are defined as time integrals of the concentration $c(y, z, t)$, the y dependence of the nth moment is given by $f(y)$, and the cross-sectional average is in general

$$\begin{aligned}\langle m_n(z)\rangle &= (1/w) \int_0^w dy \int_0^\infty dt\, t^n c(z, t, y)\\ &= m_n(z, y = 0) I_0 \qquad (13)\end{aligned}$$

where we have substituted Eq. 2 to obtain

$$m_n(z, y = 0) = \int_0^\infty c_o(z, t) t^n\, dt \qquad (14)$$

and for any concentration profile

$$I_0 = (1/w) \int_0^w f(y)\, dy \qquad (15)$$

The average peak position is determined by averaging over z, which is taken from Eq. 11 and is weighted by the concentration fraction in that layer,

$$\langle z\rangle = (1/w) \int_0^w \frac{m_0(z, y)}{\langle m_0(z)\rangle} z\, dy = 6\langle v\rangle \langle \mu_1'(z)\rangle I_1/I_0 \qquad (16)$$

The last equality is obtained after substitution of $m_1(z)$ from Eqs. 13 and 14. The quantity $m_0(z, y)/w\langle m_0(z)\rangle$ represents the concentration fraction at the layer y. The integral I_1 is defined as

$$I_1 = (1/w) \int_0^w dy\, f(y)(y/w)(1 - y/w) \qquad (17)$$

This gives the relation for the cross section-averaged first moment,

$$\langle \mu_1'(z)\rangle = \langle m_1(z)\rangle/\langle m_0(z)\rangle = \langle z\rangle I_0/6\langle v\rangle I_1 \qquad (18)$$

For all forms of field-flow fractionation the retention ratio can be defined as the ratio of the fluid retention time to the particle retention time, or

$$r = \langle z\rangle/\langle v\rangle\langle \mu_1'(z)\rangle = 6I_1/I_0 \qquad (19)$$

and the second equality is obtained when Eq. 18 is substituted.

Band-spreading is characterized by the second central moment, which by substituting for z from Eq. 12 indicates the following expression for the average peak position,

$$\langle z\rangle = (1/w) \int_0^w z \frac{m_0(z, y)}{\langle m_0(z)\rangle} z\, dy = \langle \mu_2(z)\rangle I_a/I_0 \qquad (20)$$

in terms of the integral

$$I_a = (1/w) \int_0^w dy\, f(y) v(y)^3/2D_a(y) \qquad (21)$$

Equation 20 provides an expression for the second central moment

$$\langle \mu_2(z)\rangle = \langle z\rangle I_0/I_a \qquad (22)$$

which is essential to understanding separation efficiency.

Here, the longitudinal dispersion coefficient is considered to be related to the Taylor expression, which neglects the contribution of longitudinal diffusion (Dullien, 1979). Because we require the dispersion coefficient at the plane y, we assume

$$D_a(y) = av(y)^2/D \qquad (23)$$

in terms of the molecular or Brownian diffusion coefficient D. The coefficient a depends, in part, on the geometry. In the absence of transverse force or flux, $I_0 = 1$, and the expression for the average distance, $\langle z\rangle$, must yield the well-known Taylor longitudinal dispersion for the slit (Dullien, 1979)

$$D_a = w^2\langle v\rangle^2/210D \qquad (24)$$

which requires setting $a = w^2/210$ in Eq. 23. This treatment of longitudinal dispersion is approximate, in that it ignores the effect of the transverse concentration profile on dispersion. But as mentioned earlier, other secondary effects in field-flow fractionation are in fact liable to dominate the dispersion process. Development of better expressions for $D_a(y)$ should take these secondary effects into consideration.

When Eq. 23 for $D_a(y)$ is substituted into Eq. 21, the expression for I_a, one obtains

$$I_a = 630D\langle v\rangle I_1/w^2 \qquad (25)$$

which, as we shall see, allows substantial simplification of results for field-flow fractionation.

A standard quantity representing separation efficiency is the height equivalent to a theoretical plate (HETP), defined in our notation as

$$H = \langle \mu_2(z) \rangle \langle z \rangle / \langle \mu_1'(z) \rangle^2 = 36 \langle v \rangle^2 I_1^2 / I_0 I_a \tag{26}$$

and the last equality derives from substitution of Eqs. 18 and 22. When I_a in the form of Eq. 25 is substituted, we find

$$H = 6w^2 \langle v \rangle I_1 / 105 D I_0 \tag{27}$$

Giddings et al. (1975) defined the coefficients Ψ and χ in terms of H,

$$H = \Psi \ell^2 v_p / D = \chi w^2 \langle v \rangle / D \tag{28}$$

where the pulse velocity v_p is given by

$$v_p = \langle z \rangle / \langle \mu_1'(z) \rangle \tag{29}$$

It is not difficult to show, using Eqs. 19 and 28, that

$$\chi / \Psi = \lambda^2 r \tag{30}$$

a relationship also presented by Giddings et al.

The separation resolution for two species A and B is defined, in terms of moments, as

$$R_s = \frac{\mu_{1A}' - \mu_{1B}'}{\mu_{2A}^{1/2} + \mu_{2B}^{1/2}} \tag{31}$$

If the expressions for first and second moments, Eqs. 18 and 22, are substituted, Eq. 31 becomes

$$R_s = [\langle z \rangle^{1/2} / 6 \langle v \rangle] \frac{[(I_0/I_1)_A - (I_0/I_1)_B]}{[(I_0/I_a)_A^{1/2} + (I_0/I_a)_B^{1/2}]} \tag{32}$$

Further, allowing for the expression for I_a, Eq. 25, yields

$$R_s = (105 D \langle z \rangle / 6 \langle v \rangle w^2)^{1/2} [(I_0/I_1)_A^{1/2} - (I_0/I_1)_B^{1/2}] \tag{33}$$

In this section we have presented expressions valid for any form of the concentration profile $f(y)$. Next we reduce this general approach to the special cases of interest.

Steric Field-Flow Fractionation

When $f(y) = \delta(y - R)$ the integrals I_0 and I_1 are given, in terms of $y^* = y/w$, by

$$I_0 = \int_0^1 \delta(y^* - R/w)\, dy^* = 1 \tag{34}$$

and

$$I_1 = \int_0^1 \delta(y^* - R/w) y^* (1 - y^*)\, dy^* = (1 - R/w) R/w \tag{35}$$

The retention ratio, Eq. 19, is immediately expressed as

$$r = 6(1 - R/w) R/w \tag{36}$$

The range of r according to Eq. 36 is $0 \leq r \leq 3/2$. For $R \ll w$, we obtain $r \sim 6R/w$, the ideal case discussed by Peterson et al. (1984), who also considered the complex factors contributing to deviations from this idealization.

Conventional Field-Flow Fractionation

When the concentration profile is exponential in y, Eq. 4, it is possible to show that

$$I_0 = \lambda[1 - \exp(-1/\lambda)] \tag{37}$$

and

$$I_1 = \lambda^2 \{-2\lambda[1 - \exp(-1/\lambda)] + [1 + \exp(-1/\lambda)]\} = \lambda[\coth(1/2\lambda) - 2\lambda] I_0 \tag{38}$$

The retention ratio is, therefore, given by

$$r = 6\lambda[\coth(1/2\lambda) - 2\lambda] \tag{39}$$

which is the same expression found by Giddings (1985). Inserting Eqs. 37 and 38 into Eqs. 27 and 28 then provides

$$\chi = r/105 \quad \text{and} \quad \Psi = 1/(105\lambda^2) \tag{40}$$

The quantity χ, from Eq. 40, is plotted in Figure 2 to compare the present results with those of other investigators. The present approximate treatment underestimates the dispersion in comparison to other theories. Secondary effects, however, can cause substantial deviations from the values displayed in Figure 2.

Hyperlayer Field-Flow Fractionation

For hyperlayer field-flow fractionation the Gaussian profile, Eq. 7, applies. The interval of integration for y extends not from 0 to w, but from $\bar{y} - m\sigma$ to $\bar{y} + m\sigma$, where $m = 2$ ensures that almost all of the Gaussian profile is included in the integration.

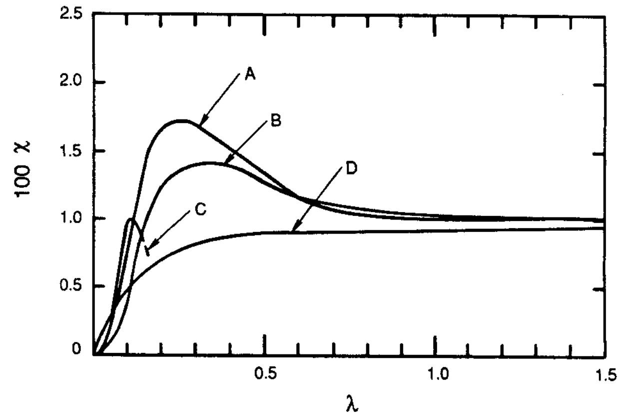

Figure 2. Plot of χ, defined in terms of HETP by Eq. 28, vs. field strength parameter λ.

A, Giddings et al (1975); B, Gajdos and Brenner (1978); C, Reis et al. (1978); D, present work

The expression for I_0 is

$$I_0 = \frac{1}{2m\sigma} \int_{\bar{y}-m\sigma}^{\bar{y}+m\sigma} dy \exp\left[-(y-\bar{y})^2/\sigma^2\right]$$

$$= \frac{\sqrt{\pi}}{2m} \operatorname{erf}(m) \simeq \sqrt{\pi}/2m \quad (41)$$

and for I_1

$$I_1 = \frac{1}{2m\sigma} \int_{\bar{y}-m\sigma}^{\bar{y}+m\sigma} dy \exp\left[-(y-\bar{y})^2/\sigma^2\right](y/w)(1-y/w)$$

$$\simeq \left[(\bar{y}/w)(1-\bar{y}/w) - (\sigma/w)^2/2\right] \sqrt{\pi}/2m \quad (42)$$

which is readily obtained with the integration variable $\hat{y} = (y - y)/\sigma$. Replacing the limit of integration $\hat{y} = m$ with ∞ is equivalent to recognizing that erf (2) ~ 1, and this simplifies the integration. The ratio of integrals is

$$I_1/I_0 = [\bar{y}/w - (\bar{y}/w)^2] - (\sigma/w)^2/2 \quad (43)$$

The maximum value of the term in square brackets of Eq. 43 is given at the center plane, that is, where the position of the species layer is $\bar{y} = 0.5w$. Furthermore, since $\bar{y}$ is bounded, $m\sigma \leq \bar{y} \leq w - m\sigma$, and we have

$$I_1/I_0 \geq (\sigma/w)(2 - 9\sigma/2w) \quad (44)$$

The permissible region for I_1/I_0, based on Eqs. 43 and 45, is sketched in Figure 3. From the definition of retention ratio, Eq. 19, we see that the maximum value is found at the center plane, where $r = 1.5$, the value established by Giddings (1983) in the absence of transverse spreading. The present treatment allows that result to be extended to include the transverse spreading due to Brownian diffusion. Figure 4 is another plot showing the permissible region for the ratio of integrals, I_1/I_0.

Based on the general expression for HETP in field-flow fractionation, Eq. 27, we may utilize Figure 3 or 4 to determine the bounds of H.

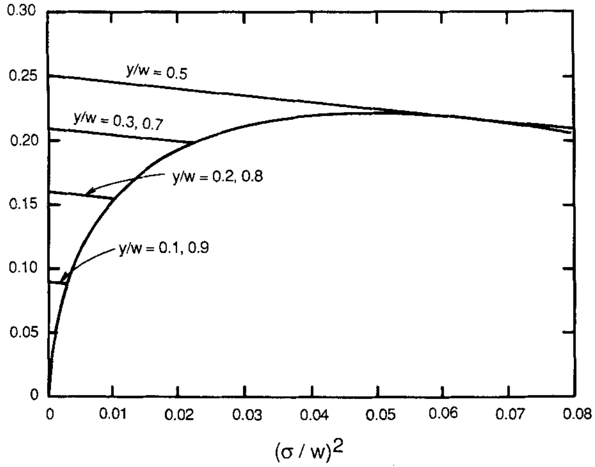

Figure 3. Ratio of integrals, I_0/I_1, vs. dimensionless variance for hyperlayer field-flow fractionation.

Curve, as indicated by Eq. 44, is $I_1/I_0 = 2(\sigma/w) - (9/2)(\sigma/w)^2$
Point x, (1/16, 7/32), is intersection of the curve with the line $y/w = 0.5$

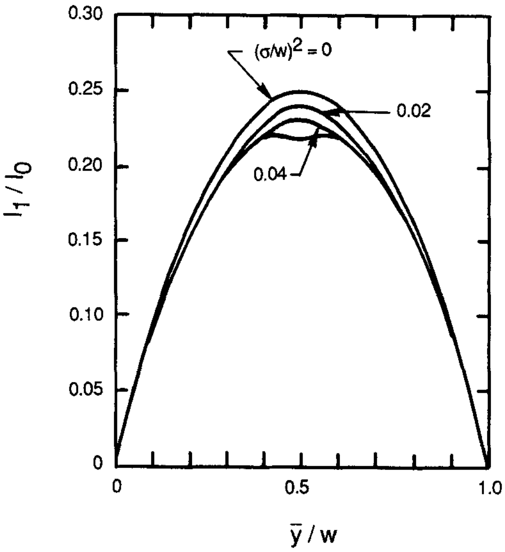

Figure 4. Relation between ratio of integrals, I_1/I_0, and dimensionless mean position, $\bar{y}/w$, of concentration profile in hyperlayer field-flow fractionation.

Allowable values are between top and bottom curves

Notation

a = coefficient, Eq. 23
c = concentration, mol/m^3
$c(y, z, t)$ = concentration as a function of y, z, t, mol/m^3
$c_o(z, t)$ = concentration at basic position of y, mol/m^3
D = molecular or Brownian diffusion coefficient, m^2/s
D_a = longitudinal dispersion coefficient, m^2/s
$f(y)$ = distribution function for transverse concentration profile
g = acceleration, m/s^2
H = height equivalent to a theoretical plate, m
I_0 = integral, Eq. 15
I_1 = integral, Eq. 17
I_a = integral, Eq. 21
k = Boltzmann constant, joule/mol · deg
l = characteristic length, Eq. 5, m
m = integer
$m_n(y, z)$ = nth moment at y, z, Eq. 10, mol/m^3 · s^n
R = radius of particle, m
R_s = separation resolution, Eq. 31
r = retention time ratio, Eq. 19
T = absolute temperature, K
t = time, s
u = transverse particle velocity (in y direction), m/s
V = particle volume, m^3
$v(y)$ = fluid velocity in z direction at y layer, m/s
v_p = pulse velocity, Eq. 29, m/s
$\langle v \rangle$ = average velocity (z direction), m/s
w = channel width, m
y = transverse coordinate, m
$\bar{y}$ = height above the lower wall, m
y^* = dimensionless distance, = y/w
z = longitudinal coordinate, m

Greek letters

$\delta(y)$ = Dirac delta function
λ = parameter, Eq. 6

μ_2 = second central moment, Eq. 12, s^2
μ_n' = nth temporal moment, s^n
ρ = particle density, g/m^3
σ = transverse concentration profile width in hyperlayer field-flow fractionation
χ = parameter, Eq. 28
Ψ = parameter, Eq. 28

Subscripts

A, B = components to be separated
$\langle\ \rangle$ = average value over cross section

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