Analytic Solution for Chromatography with Nonuniform Sorbent Particles

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Mathematical modeling of chromatographic operations has received considerable attention in the past. For systems where equilibrium and mass transfer processes are represented by linear relationships, analytic solutions of the models are possible in general. A comprehensive review of such solutions is given by Ruthven (1984).

Solutions for the calculation of breakthrough curves have been obtained by taking into account external film mass transfer resistance (Anzelius, 1926), axial dispersion and intraparticle diffusion (Lapidus and Amundson, 1952; Rosen, 1952, 1954), and combinations of axial dispersion with external film resistance and macropore/micropore diffusion within the sorbent particles (Kawazoe and Takeuchi, 1974; Rasmuson and Neretnieks, 1980; Rasmuson, 1982). These solutions often require the numerical evaluation of infinite integrals, for which special algorithms have been devised (Rasmuson and Neretnieks, 1981; Rasmuson, 1985). Chen and Hsu (1987) have recently introduced an algorithm based on the Fast-Fourier-Transform which simplifies and speeds up such integrations.

The effects of particle-size distribution on chromatography have been addressed by several authors. Dougharty (1972) and Moharir et al. (1981) have treated linear chromatographic pulses with moment analyses, and Rasmuson (1985) has provided an analytic solution which permits the calculation of breakthrough curves with nonuniform particles from the numerical evaluation of an infinite integral. Rasmuson's solution includes the effects of particle shape, intraparticle diffusion, sorption kinetics, and external resistance.

Recently, Carta (1988) has introduced an explicit analytic solution for chromatography with a time-periodic input concentration. This solution allows the direct computation of breakthrough curves and chromatographic peaks, and can be integrated to obtain the time-average effluent concentration in any desired "product cut." In this note we provide a generalization of this solution which is valid for an arbitrary particle-size distribution. Unlike previous treatments by other authors, the solution provided does not require the numerical evaluation of infinite integrals and is valid both for pulse and step changes in the feed concentration. Finally, the solution permits the prediction of the cyclic performance of periodic operations.

Problem Statement

Considering a homogeneously packed bed, we define an arbitrary, normalized particle-size distribution function, $f(R)$, in such a way that $f(R)dR$ is the volume fraction of particles with radius between R and $R + dR$. Pore diffusion is assumed to occur in these particles with an effective diffusion coefficient, D_e.

Axial dispersion and film mass transfer resistance are recognized as dependent on the particle-size distribution (Dougharty, 1972). Yet, this dependence is generally not available in terms of explicit relationships and is best handled with empirical coefficients. Intraparticle diffusion, on the other hand, is dependent strongly on particle size and can be explicitly related to the particle-size distribution of a nonuniform sample. As a consequence, in our treatment we assume nondisperse plug flow with intraparticle diffusion control. This assumption is not greatly restrictive as many practically important liquid and gas chromatography systems involving transport of slowly diffusing species in porous sorbents are governed almost entirely by intraparticle diffusional limitations.

Material balances for the bed and the sorbet particles yield the following equations

$$\epsilon \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} + 3(1 - \epsilon) \int_0^\infty D_e \left(\frac{\partial c}{\partial \rho}\right)_{\rho = R} \frac{f(R)}{R} dR = 0 \quad (1)$$

$$[\epsilon_p + (1 - \epsilon_p)K] \frac{\partial c}{\partial t} = \frac{D_e}{\rho^2} \frac{\partial}{\partial \rho}\left(\rho^2 \frac{\partial c}{\partial \rho}\right) \quad (2)$$

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$$\frac{\partial c}{\partial \rho}(0,z,t) = 0, \quad c(R,z,t) = C(z,t) \tag{3}$$

Equation 2 assumes that the concentrations in the pore fluid and in the micropores of the sorbent are related by a linear isotherm $q = Kc$. At the column entrance, the solute concentration is assumed to vary in a periodic, square-wave fashion and is given by

$$C(0,t) = C_F \quad \text{for} \quad (j-1)(t_F + t_E) < t < j(t_F + t_E) - t_E$$

$$C(0,t) = 0 \quad \text{for} \quad j(t_F + t_E) - t_E < t < j(t_F + t_E)$$

$$\text{with} \quad j = 1, 2, 3 \ldots \tag{4}$$

t_F is the time during a period when the feed is injected to the column, while t_E is the time during which elution takes place. Initial conditions are not needed for this problem if one is simply interested in the asymptotic periodic state, which is approximated after a sufficient number of feed-elution cycles. Such periodic solution can be used to compute the response to a single pulse with an initially clean bed if t_E is chosen to be sufficiently large to bring the effluent concentration to zero at the end of a period. Breakthrough curves with an initially clean bed can be computed from the same solution taking both t_F and t_E large enough that the effluent concentration first approaches the feed concentration and then is reduced to zero at the end of the period.

Analytic Solution

A solution of Eqs. 1–4 in the Laplace domain is given by

$$\frac{\tilde{C}}{C_F} = \frac{1 - \exp(-\pi r_F s)}{s[1 - \exp(-2\pi r s)]} \cdot \exp\left\{-\frac{\epsilon z s}{u} - \frac{\beta z}{u}\int_0^\infty \left[\sqrt{\frac{s}{\alpha}}\coth\left(R\sqrt{\frac{s}{\alpha}}\right) - \frac{1}{R}\right]\frac{f(R)}{R}\,dR\right\} \tag{5}$$

where

$$\pi r_F = t_F, \qquad 2\pi r = t_F + t_E \tag{6}$$

$$\alpha = \frac{D_e}{\epsilon_p + (1-\epsilon_p)K}, \qquad \beta = 3(1-\epsilon)D_e \tag{7}$$

The time domain solution is found by applying the residue theorem to the inversion integral, as shown for example by Carta (1988). For the sake of simplicity, the solution is given here for an arbitrary but discrete distribution of particles sizes, such as might be obtained from sieve fractions or a particle-size analyzer. In this case

$$f(R) = \sum_{j=1}^{M} f_j\,\delta(R - R_j) \tag{8}$$

and the time-domain solution is

$$\frac{C}{C_F} = \frac{r_F}{2r} + \frac{2}{\pi}\sum_{k=1}^{\infty}\left\{\frac{1}{k}\prod_{j=1}^{M}\left\{\exp\left[-\frac{\beta z}{u}\frac{f_j}{R_j}\left(\sqrt{\frac{k}{2r\alpha}}\frac{\gamma_{k,j}}{\lambda_{k,j}} - \frac{1}{R_j}\right)\right]\right\} \cdot \sin\left(\frac{k\pi r_F}{2r}\right) \cdot \cos\left[\frac{kt}{r} - \frac{k\epsilon z}{ur} - \frac{k\pi r_F}{2r} - \frac{\beta z}{u}\sum_{j=1}^{M}\left(\sqrt{\frac{k}{2r\alpha}}\frac{\eta_{k,j}}{\lambda_{k,j}}\frac{f_j}{R_j}\right)\right]\right\} \tag{9}$$

where M is the number of sieve fractions and

$$\gamma_{k,j} = \sinh\left(R_j\sqrt{\frac{2k}{r\alpha}}\right) + \sin\left(R_j\sqrt{\frac{2k}{r\alpha}}\right) \tag{10}$$

$$\eta_{k,j} = \sinh\left(R_j\sqrt{\frac{2k}{r\alpha}}\right) - \sin\left(R_j\sqrt{\frac{2k}{r\alpha}}\right) \tag{11}$$

$$\lambda_{k,j} = \cosh\left(R_j\sqrt{\frac{2k}{r\alpha}}\right) - \cos\left(R_j\sqrt{\frac{2k}{r\alpha}}\right) \tag{12}$$

Equation 9 can be integrated term by term to yield the time average effluent concentration between any two times t_1 and t_2, yielding

$$\frac{\bar{C}}{C_F} = \frac{1}{t_2 - t_1}\int_{t_1}^{t_2} C(Z,t)/C_F\,dt = \frac{r_F}{2r} + \frac{4r}{\pi(t_2 - t_1)} \sum_{k=1}^{\infty} \cdot \left\{\frac{1}{k^2}\prod_{j=1}^{M}\left\{\exp\left[-\frac{\beta Z}{u}\frac{f_i}{R_j}\left(\sqrt{\frac{k}{2r\alpha}}\frac{\gamma_{k,j}}{\lambda_{k,j}} - \frac{1}{R_j}\right)\right]\right\} \cdot \sin\left(\frac{k\pi r_F}{2r}\right)\sin\left[\frac{k(t_2 - t_1)}{2r}\right] \cdot \cos\left[\frac{k(t_1 + t_2)}{2r} - \frac{k\epsilon Z}{ur} - \frac{k\pi r_F}{2r} - \frac{\beta Z}{u}\sum_{j=1}^{M}\left(\sqrt{\frac{k}{2r\alpha}}\frac{\eta_{k,j}}{\lambda_{k,j}}\frac{f_j}{R_j}\right)\right]\right\} \tag{13}$$

Note that because of the $1/k^2$ term in Eq. 13, this series is more rapidly convergent than Eq. 9 and may be conveniently used to determine the product purity of any desired product cut taken between times t_1 and t_2.

Examples and Discussion

Calculation examples of breakthrough curves and chromatographic peaks were carried out using the parameters given in Table 1 which had previously been used as an example by Carta (1988). The number of additive terms used for calculations with Eq. 9 or 13 depends upon the accuracy desired and the simulated conditions. Typically, however, for conditions where sig-

Table 1. Simulated Operating Conditions

Parameter	Value	Units
$\epsilon_p + (1-\epsilon_p)K$	0.66	—
D_e	2.8×10^{-8}	cm^2/s
ϵ	0.39	—
u	0.031	cm/s
Z	60	cm

nificant mass transfer resistance is present, 5–10 terms provide three digits of accuracy. Increasing the number of terms, of course, increases the accuracy.

Three particle-size distributions were used as given in Figure 1. For sample *A*, we assume that the bed is composed of a mixture of small particles (R_1 = 0.002 cm) which comprise 80% of the volume and of large particles (R_2 = 0.02 cm) which comprise the remaining 20%. The volume-average radius is thus 0.0056 cm. A calculated breakthrough curve for this sample is shown in Figure 2a (curve 1) in comparison with calculations using the average particle radius (curve 2) and the radius of the small particles (curve 3). It is apparent that, for these conditions, use of the average radius leads to significant error in estimating both the initial slope of the breakthrough curve, as well as its uppermost saturation portion. The 0.002-cm particles, present in the sample, delay the onset of breakthrough which is predicted to occur about 20% later than those by using the average radius. Note that the initial slope of the curve is actually quite close to that obtained with 0.002-cm particles alone. The later part of the breakthrough curve, on the other hand, is much more shallow than predicted using the average radius. This portion of the curve corresponds to the slow saturation of the large, 0.02-cm particles present in the sample. Similar effects are shown by the calculated chromatographic peaks shown in Figure 2b. The leading edges of the profiles calculated using the actual particle-size distribution (curve 1) and the radius of the small particles (curve 3) are quite similar, as this part of the peak is most strongly affected by the smallest particles. The trailing edge, on the other hand, is much more shallow for the mixture of particles than is predicted using the smallest radius and it is closer to the peak computed using the average particle radius. Using the average radius, however, provides a peak height which is less than 50% of the peak height computed for the actual distribution.

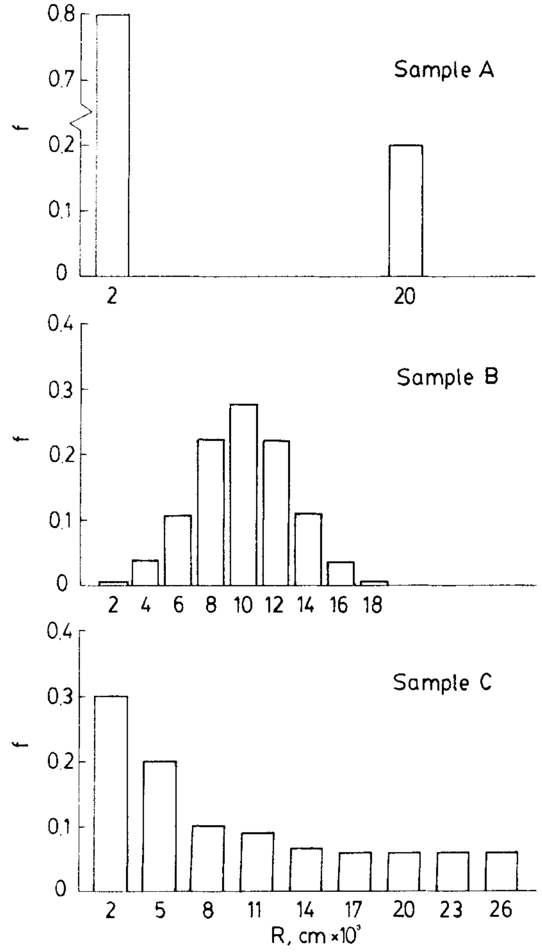

Figure 1. Particle-size distributions for samples A, B, and C.

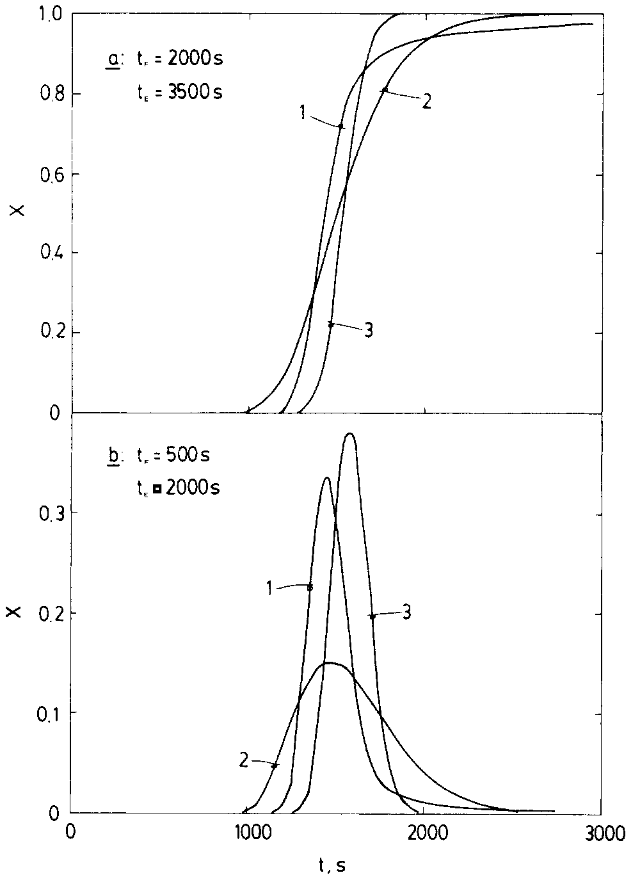

Figure 2. Comparison of breakthrough curves (a) and chromatographic peaks (b) obtained for: sample A (curve 1); uniform particles with *R* = 0.0056 cm (curve 2); uniform particles with *R* = 0.002 cm (curve 3).

Figure 3a shows a comparison of calculated breakthrough curves for a chromatographic bed consisting of particles with the size distributions of samples B and C shown in Figure 1. Both samples have a mean radius of 0.01 cm. However, sample B has a symmetrical distribution, while sample C has a skewed distribution with a median of about 0.0065 cm. As is seen in Figure 3a, the symmetrical distribution (curve 1) provides results which are very close to those obtained using the mean radius (curve 3). The skewed distribution (curve 2), on the other hand, exhibits an initial sharp rise due to the presence of a large fraction of small particles, followed by a much more gradual increase toward the feed concentration during the later part of

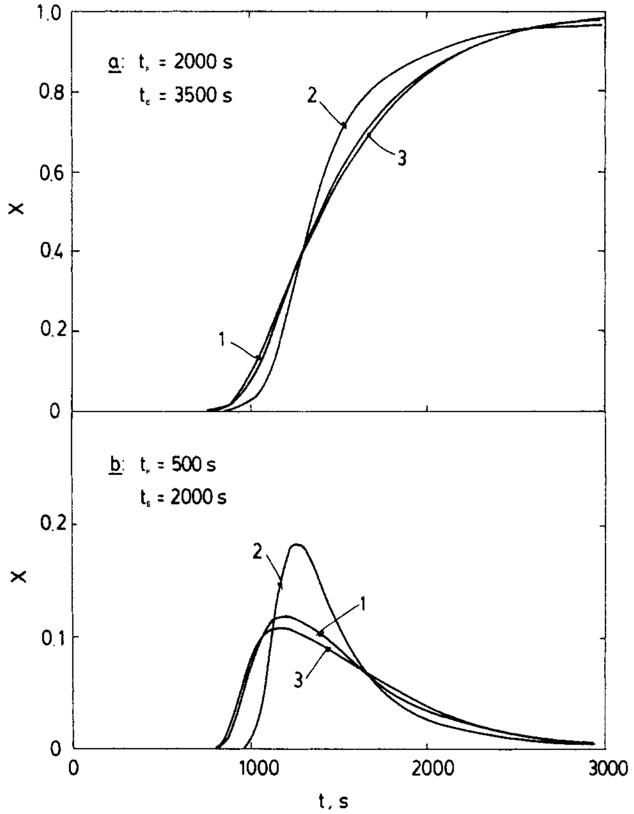

Figure 3. Comparison of breakthrough curves (a) and chromatographic peaks (b) obtained for: sample B (curve 1); sample C (curve 2); uniform particles with R = 0.01 cm (curve 3).

the curve. This later part corresponds to the saturation of the larger particles.

Figure 3b shows these effects on a chromatographic peak. The skewed distribution (curve 2) provides a peak height which is about 1.6 times higher than that computed with the mean radius (curve 3). The latter curve is, however, very close to that obtained with the symmetrical distribution of sample B (curve 1).

Conclusion

As was shown previously by other investigators, the particle-size distribution may significantly affect the shape of intraparticle diffusion-controlled chromatographic peaks and breakthrough curves. The analytic solution provided in this note allows a straightforward and rapid numerical evaluation of these effects. Further generalizations of this solution to include external mass transfer resistance and other nonuniform particle-dependent properties are possible with little effort following the same procedure.

Notation

c = macropore solute concentration, gmol/cm^3
C = fluid solute concentration, gmol/cm^3
D_e = effective diffusivity, cm^2/s
$f(R)$ = particle radius distribution function, 1/cm
f_j = volume fraction of particles of radius, R_j
K = linear equilibrium parameter
M = number of particle fractions
q = sorbent solute concentration, gmol/cm^3
r = defined by Eq. 6, s
r_F = defined by Eq. 6, s
R = particle radius, cm
s = Laplace transform variable, 1/s
t = time, s
u = fluid superficial velocity, cm/s
X = dimensionless concentration, C/C_F
z = bed axial coordinate, cm
Z = bed length, cm

Greek letters

α = defined by Eq. 7, cm^2/s
β = defined by Eq. 7, cm^2/s
δ = delta function
$\gamma_{k,j}$ = defined by Eq. 10
ϵ = bed void fraction
ϵ_p = particle void fraction
$\eta_{k,j}$ = defined by Eq. 11
$\lambda_{k,j}$ = defined by Eq. 12
ρ = particle radial coordinate, cm

Subscripts

E = elution period
F = feed injection period

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