Effect of Adsorbent Particle-Size Distribution in Gas-Solid Chromatography

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It is known in chromatography that nonuniformity of column-packing particle size degrades column performance (Purnell, 1962). Accordingly, column packing is customarily size-classified, with only a relatively narrow range of sizes being used in the preparation of a column. The necessity and adequacy of this are not often subjected to test. It can be expected that the interaction of particle-size distribution with the numerous other factors affecting performance will be complex and that the conclusions of experimental studies of its importance cannot be extrapolated with confidence in the absence of direction from theory. Moment-analysis methods recently applied to the study of various rate and transport parameters for beds of porous solids (Schneider and Smith, 1968; Padberg and Smith, 1968; Adrian and Smith, 1970) can be adapted to this end.

For spherical packing particles, uniformity over the cross section of the column, and linear adsorption/desorption rates, one has for a packed column

$$\epsilon_b \frac{\partial c_e}{\partial t} = -\epsilon_b v \frac{\partial c_e}{\partial z} + D_A \frac{\partial^2 c_e}{\partial z^2} - (1-\epsilon_b) \int_0^{\epsilon} \frac{3}{R} k_m \left(c_e - c_i|_{r=R}\right) f(R)\, dR \quad (1)$$

$$\epsilon_p \frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} - \rho_p \frac{\partial c_a}{\partial t} \quad (2)$$

$$\frac{\partial c_a}{\partial t} = k_a \left(c_i - c_a/K_a\right). \quad (3)$$

The particle-size distribution appears in Equation (1) as part of a locally space-averaged rate of mass transfer from the extraparticle volume to the intraparticle volume.

Upon applying initial and boundary conditions corresponding to injection of a rectangular pulse

$c_a = 0$ at $t = 0$ for all z and r
$c_i = 0$ at $t = 0$ for all z and r
$c_i =$ finite at $r = 0$ for all t
$c_e = 0$ at $t = 0$ for all z
$c_e = c_0$ at $z = 0$ for $0 < t \leqq t_0$
$c_e = 0$ at $z = 0$ for $t > t_0$
$c_e =$ finite at $z \to \infty$ for all t,

the Laplace transformation permits one to obtain

$$\phi_e(z, s) = (c_0/s)\left(1 - e^{-st_0}\right) e^{\lambda z}. \quad (4)$$

This transform can be directly related (Schneider and Smith, 1968) to the moments of the chromatographic output $c_e(t)$ measured at a given z to yield

$$\mu_1' = \frac{t_0}{2} + \left(\frac{z}{v}\right)\left[1 + \frac{1-\epsilon_b}{\epsilon_b}\left(\epsilon_p + \rho_p K_a\right)\right] \quad (5)$$

and

$$\mu_2 = \frac{t_0^2}{12} + 2\left(\frac{z}{v}\right)\left(\frac{1-\epsilon_b}{\epsilon_b}\right)\left(\frac{\rho_p K_a^2}{k_a}\right) + 2\left(\frac{z}{v}\right)\left(\frac{D_A}{\epsilon_b v^2}\right)\left[1 + \frac{1-\epsilon_b}{\epsilon_b}\left(\epsilon_p + \rho_p K_a\right)\right]^2 + 2\left(\frac{z}{v}\right)\left(\frac{1-\epsilon_b}{\epsilon_b}\right)\frac{\left(\epsilon_p + \rho_p K_a\right)^2}{15 D_i}\int_0^\infty \left(R^2 + 5 D_i R/k_m\right) f(R)\, dR. \quad (6)$$

It is seen that the distribution of particle sizes does not affect the first moment, or retention time, of the pulse for a given ϵ_b. However, the second moment, and thus the peak width, *is* affected through the last term in Equation (6) explicitly and perhaps also through the third term via D_A. For uniform particles, one can readily verify that this relation for the second moment reduces to that given previously (Kubin, 1965).

Axial dispersion is recognized as depending on packing size, although the dependence on size distribution is not known. Dispersion also depends importantly on bed uniformity, and particle-size distribution undoubtedly affects the ease with which uniform columns can be prepared. Nevertheless, axial dispersion is not uniquely related to particle-size distribution but depends on other factors at least partially under the control of the experimenter. Consequently, in what follows the effect of particle-size distribution on D_A is neglected, although it should be understood that the effect on μ_2 of differences in D_A can be greater than that considered below.

The remaining effect, appearing in the last term of Equation (6), arises from intraparticle diffusion (R^2) and mass transfer from the fluid to the external particle surface ($5D_i R/k_m$). The resulting increment $\delta\mu_2$ to the second moment above that for uniform particles of radius $\overline{R}$ as a ratio to the contribution $\Delta\mu_2$ of this last term of Equation (6) is given by

$$\frac{\delta\mu_2}{\Delta\mu_2} = \frac{\int_0^\infty \left[R^2 - (\overline{R})^2 + 5D_i\left(\frac{R}{k_m(R)} - \frac{\overline{R}}{k_m(\overline{R})}\right)\right] f(R)\, dR}{\int_0^\infty \left[R^2 + 5D_i R/k_m(R)\right] f(R)\, dR} \quad (7)$$

For a given system and conditions, $\Delta\mu_2$ may account for any fraction of μ_2 from zero to unity.

Further consideration of the effect of particle-size distribution requires a knowledge of the dependence of k_m on R. Empirical correlations are available for the dependence of average mass-transfer coefficients on particle size for beds of uniform particles and on average particle size for beds of nonuniform particles. Neither is strictly applicable to the needs of Equation (7), which requires the average mass-transfer coefficient over the total particle surface for a *single* particle in the mixture. Nevertheless, one may reasonably hope to estimate the magnitude of the effects to be expected by considering two special cases: 1. that $k_m(R)$ is uniform at the value $k_m(\overline{R})$ given by correlations for a bed of particles of mean radius $\overline{R}$, and 2. that $k_m(R)$ as a function of R has the values $k_m(\overline{R})$ given by the correlations for $\overline{R} = R$. Wakao et al. (1958) give the correlation for mass transfer in packed beds at low Reynolds numbers

$$N_{Sh} = 2\overline{R}\ k_m/\mathcal{D} = 2.0 + 1.45\ N_{Re}{}^{1/2}\ N_{Sc}{}^{1/3} \qquad (8)$$

in which the dependence of k_m on $\overline{R}$ ranges from $k_m \propto 1/\overline{R}$ at very low Reynolds numbers to $k_m \propto 1/\sqrt{\overline{R}}$ as the Reynolds number becomes large.

Taking the case of a uniform $k_m(R) = k_m(\overline{R})$, one obtains

$$\frac{\delta\mu_2}{\Delta\mu_2} = [(\overline{R^2}) - (\overline{R})^2]/[(\overline{R^2}) + 5D_i\,\overline{R}/k_m(\overline{R})]$$

$$\leq [(\overline{R^2}) - (\overline{R})^2]/(\overline{R^2}) \qquad (9)$$

For Case 2, at low and high velocities, respectively, one has

$$\left(\frac{\delta\mu_2}{\Delta\mu_2}\right)_{N_{Re}\to 0} = [(\overline{R^2}) - (\overline{R})^2]/(\overline{R^2}) \qquad (10)$$

and

$$\left(\frac{\delta\mu_2}{\Delta\mu_2}\right)_{N_{Re}\to\infty} = \frac{[(\overline{R^2}) - (\overline{R})^2] + 5D_i\,(2\sqrt{\overline{R}}/\mathcal{D}N_{Sh})_{N_{Re}\to\infty}\,[(\overline{R^{3/2}}) - (R)^{3/2}]}{(\overline{R^2}) + 5D_i\,(2\sqrt{\overline{R}}/\mathcal{D}N_{Sh})_{N_{Re}\to\infty}\,(\overline{R^{3/2}})}$$

$$\leq [(\overline{R^2}) - (\overline{R})^2]/(\overline{R^2})\,. \qquad (11)$$

According to Equation (8), $(2\sqrt{\overline{R}}/\mathcal{D}N_{Sh})_{N_{Re}\to\infty}$ is a constant independent of $\overline{R}$. Noting the inequalities and also that $\Delta\mu_2 \leq \mu_2$, one arrives at the general result

$$\frac{\delta\mu_2}{\mu_2} \leq [(\overline{R^2}) - (\overline{R})^2]/(\overline{R^2}) \qquad (12)$$

as an upper bound on the fractional contribution of intraparticle diffusion and fluid-to-particle-surface mass transfer to the second moment.

Quantitative evaluation of the effect of particle-size distribution requires the introduction of a relation for $f(R)$. Since size classification is usually performed by screening between two sieve sizes, a reasonable distribution for examination is described by

$$f(R) = \begin{cases} 0 \text{ for } R < (1-\kappa)\overline{R} \\ \tfrac{1}{2}\kappa\overline{R} \text{ for } (1-\kappa)\overline{R} \leq R \leq (1+\kappa)\overline{R} \\ 0 \text{ for } R > (1+\kappa)\overline{R} \end{cases}$$

where $0 < \kappa \leq 1$. For this distribution one finds

$$\frac{\delta\mu_2}{\mu_2} \leq \frac{\kappa^2/3}{1 + \kappa^2/3}. \qquad (13)$$

Thus, for a particle-size distribution with tolerances of ± 10% about the mean, the maximum effect of intraparticle diffusion and fluid-to-particle-surface mass transport is calculated to be only 0.3%; and for tolerances of ± 50%, 8%.

It is seen from the analysis presented that the existence of a distribution of column-packing particle sizes should result in an increased spreading of chromatographic peaks in comparison with columns packed with uniform particles, due to the effects of intraparticle diffusion and fluid-to-particle-surface mass transport. Quantitatively, however, it appears that reasonably narrow particle-size ranges will contribute relatively little to the width of a peak. The effect of particle-size distribution on peak broadening due to variations in axial dispersion is not encompassed in the criterion provided by Equation (12) and needs further study.

NOTATION

c_a = concentration of adsorbing gas adsorbed, mole/g of adsorbent
c_e = concentration of adsorbing gas in the extraparticle volume, mole/cm^3
c_i = concentration of adsorbing gas in the intraparticle pore volume, mole/cm^3
c_0 = concentration of adsorbing gas in input pulse, mole/cm^3
$\mathcal{D}$ = molecular diffusivity of adsorbing gas in gas phase, cm^2/s
D_A = effective axial dispersion coefficient, cm^2/s
D_i = effective intraparticle diffusivity, cm^2/s
$f(R)$ = particle-size distribution function, such that $f(R)\ dR$ is the fraction of the volume, occupied by particles, consisting of particles with radii between R and $R + dR$, 1/cm
k_a = adsorption rate coefficient, cm/s
K_a = adsorption equilibrium constant, cm^3/g
k_m = mass-transfer coefficient for transfer between extraparticle fluid and external particle surface, cm/s
N_{Re} = $2\overline{R}v/\nu$, bed Reynolds number
N_{Sc} = $\nu/\mathcal{D}$, Schmidt number
N_{Sh} = $2\overline{R}k_m/\mathcal{D}$, Sherwood number
r = radial distance from center of a particle, cm
R = particle radius, cm
$\overline{R^n}$ = $\int_0^\infty R^n\ f(R)\ dR$, mean value of R^n
s = Laplace transform parameter, 1/s
t = time, s
t_0 = duration of the input-pulse injection, s
v = average extraparticle axial velocity, cm/s
z = axial distance from column entrance, cm

Greek Letters

α = $\sqrt{\dfrac{s}{D_i}\left(\epsilon_p + \dfrac{\rho_p k_a K_a}{sK_a + k_a}\right)}$
$\delta\mu_2$ = difference between $\Delta\mu_2$ for columns of nonuniform and uniform particles, s^2
$\Delta\mu_2$ = contribution to μ_2 of intraparticle diffusion and of mass transfer between extraparticle fluid and external particle surface, s^2
ϵ_b = bed void fraction, exclusive of intraparticle voids
ϵ_p = intraparticle void fraction
ϕ_e = Laplace transform of c_e
κ = parameter in Equation (13)

$$\lambda = \frac{\epsilon_b v}{2D_A}\left\{1 - \sqrt{1 + \frac{4D_A}{\epsilon_b v^2}\left[s + \frac{1-\epsilon_b}{\epsilon_b}\int_0^\infty \frac{3}{R}\; k_m \frac{\alpha R - \tanh \alpha R}{\alpha R + (k_m R/D_i - 1)\tanh \alpha R} f(R)\, dR\right]}\right\}$$

μ'_1 = first absolute moment of chromatographic output response, s
μ_2 = second central moment of chromatographic output response, s^2
ρ_p = particle density, g/cm^3
ν = fluid kinematic viscosity, cm^2/s

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Relationship of the Two-Level Optimization Procedure to the Discrete Maximum Principle

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We propose to show the relationship between the Discrete Maximum Principle (*1*) and the Two-Level Optimization Procedure (*2* to *5*) as applied to static or discrete time optimization problems. This will indicate the basis on which the Two-Level Optimization Procedure has been developed and will show that it is another method for solving the necessary conditions of the Discrete Maximum Principle. The immediate consequence of this is that the shortcomings of Two-Level Optimization are those of the Discrete Maximum Principle and of all problem solving techniques in which the decision variables appear linearly.

Consider, as a basis for the development of the comparison, the optimal control of sequential, unconstrained problems. (Constraints and recycle do not change the resulting relationship, and we wish to keep the development here as simple as possible.) The problem is to minimize the performance index

$$I[\mathbf{x}(0), N] = \mathbf{C}'\mathbf{x}(N) + \sum_{k=1}^{N} J[\mathbf{x}(k-1), (\mathbf{u}(k-1)] \tag{1}$$

subject to the state equation

$$\mathbf{x}(k) = \mathbf{f}(k) = \mathbf{f}[\mathbf{x}(k-1), \mathbf{u}(k-1)]$$
$$\mathbf{x}(0) \text{ given}; \; k = 1, \ldots, N \tag{2}$$

by means of appropriately choosing the unconstrained control policy $\mathbf{u}(0), \mathbf{u}(1), \ldots, \mathbf{u}(N-1)$.

The Two-Level Optimization approach requires the decomposition of the performance index as

$$I[\mathbf{x}(0), N] = \sum_{k=1}^{N+1} J(k) \tag{3}$$

where

$$J(k) = J[\mathbf{x}(k-1), \mathbf{u}(k-1)]; \; k = 1, \ldots, N$$
$$J(N+1) = \mathbf{C}'\mathbf{x}(N)$$

and the formulation of the Lagrangian function

$$L = \sum_{k=1}^{N+1} J(k) + \sum_{k=1}^{N} \mathbf{p}'(k)\,[\mathbf{f}(k) - \mathbf{x}(k)] \tag{4}$$

The subsequent independent subproblems consist of minimization of the subLagrangians $L(k)$ defined as

$$L(k) = J(k) + \mathbf{p}'(k)\mathbf{f}(k) - \mathbf{p}'(k-1)\mathbf{x}(k-1) \tag{5}$$
$$k = 1, \ldots, N+1$$

with

$$\mathbf{p}(0) = \mathbf{p}(N+1) = \mathbf{f}(N+1) = \mathbf{0}$$

The first level of optimization involves minimizing the subLagrangians of Equation (5) for given values of the decomposition vectors $\mathbf{p}(k)$, $k = 1, \ldots, N$. Necessary *conditions for these minima are the following stationary* conditions

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