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Calculation of the Pressure Drop Effect in Gas Chromatography

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Summary

Analysis by statistical moments permits the effect of pressure drop on the performance of a gas chromatography column to be understood more clearly. Through the use of the first three statistical moments, exact equations are derived for both the standard deviation and the skewness of the breakthrough curve following a pulse input. Higher statistical moments can be derived and by their use the breakthrough curve can be determined to any desired accuracy.

The effect of pressure drop on the breakthrough curve is one of the fundamental problems of gas chromatography. A very general solution to this problem is possible through the use of the method of statistical moments. This procedure is described in detail in this report; a second report is being prepared in which the pressure effects in various types of gas chromatography columns are tabulated and compared.

Here the method of statistical moments (*1*) is applied to an isothermal column in which the mechanisms of mass transfer are interparticle molecular diffusion, interparticle eddy diffusion, and intraparticle diffusion. Additionally, it is assumed that (a) the adsorption (or absorption) isotherm is linear, and (b) the adsorbent (or absorbent) consists of uniform spheres in which (c) the intraparticle diffusion coefficient is independent of pressure. (d) The mobile phase consists of a laminar flow of an ideal gas. There is a finite pressure drop and a finite increase in carrier gas velocity across the column, and these changes can be calculated from Poiseuille's law.

1. DIVISION INTO INCREMENTS

The gas chromatography column can be divided into increments, each with a nearly constant pressure. The output from the *i*th increment following a unit pulse (delta function) input into the column is given by:

$$C_i(t) = \int_0^t c_i(\tau) C_{i-1}(t-\tau)\, d\tau \tag{1}$$

where c_i is the response of the *i*th increment to a unit delta function input, and C_{i-1} is the response, as measured by the output of the $i - 1$ increment, of the preceeding sections of the column to a unit delta function input.

Applying the Laplace transform to Eq. (1) gives:

$$\bar{C}_i = \bar{c}_i * \bar{C}_{i-1} \tag{2}$$

and following successive application of Eq. (2), $\bar{C}_n$, the Laplace transform of the output of the entire column (assuming division of the column into n increments), is found to be:

$$\bar{C}_n = \prod_{i=1}^{n} \bar{c}_i \tag{3}$$

2. RESPONSE OF THE INCREMENTS

The Laplace transform for the response of the *i*th section of the column is given by:

$$\bar{c}_i = \exp\left\{-\frac{(\Delta L)V_i}{2D_i}\left[\left(1 + \frac{4D_i\rho K\lambda}{V_i^2}\right)^{1/2} - 1\right]\right\} \tag{4}$$

where ΔL is the length of the *i*th increment, V_i is the superficial carrier gas velocity in the *i*th increment, D_i is the effective interparticle diffusion coefficient in the *i*th increment in cm^2/sec, K is the transform for the effective bulk adsorption coefficient in cm^3/g, ρ is the bulk density of the sorbent in g/cm^3, λ is the coefficient of the Laplace transform, and

$$K = \frac{\epsilon}{\rho} + \left(K_0 - \frac{\epsilon}{\rho}\right)\frac{12D_p}{\lambda d_p^2}\left[\left(\frac{\lambda d_p^2}{4D_p}\right)^{1/2}\coth\left(\frac{\lambda d_p^2}{4D_p}\right)^{1/2} - 1\right] \tag{5}$$

where K_0 is the effective bulk adsorption coefficient, as measured statically, in cm^3/g, D_p is the intraparticle diffusion coefficient in cm^2/sec, ϵ is the fractional interparticle void volume, dimensionless, d_p is the sorbent particle diameter, and also

$$D_i = \epsilon\gamma Dm_i + \lambda_p V_i d_p \tag{6}$$

where γ is the tortuosity factor for interparticle molecular diffusion, dimensionless, Dm_i is the coefficient for molecular diffusion of the sorbate in the carrier gas in the ith increment in cm^2/sec, and λ_p is the coefficient for eddy diffusion, dimensionless.

The development of Eqs. (4), (5), and (6) has been discussed earlier (*2*).

3. LOCAL PARAMETERS

The factors V_i and D_i depend upon their position within the column. Specifically for V_i (*3*),

$$V_i = \frac{V_0}{\sqrt{(P_i/P_0)^2 - \frac{x}{L}\{(P_i/P_0)^2 - 1\}}} \tag{7}$$

where x = distance from inlet of the column in cm, L = length of the column, P_i = input pressure, P_0 = output pressure (both P_i and P_0 in the same units), and V_0 = superficial carrier gas velocity at the end of the column in cm/sec.

Then

$$V_i = V_0/\sqrt{} \tag{8}$$

where

$$\sqrt{} = \sqrt{(P_i/P_0)^2 - \frac{x}{L}\{(P_i/P_0)^2 - 1\}}$$

If it is assumed that the molecular diffusion coefficient varies inversely with the pressure (and further, that γ and λ are constant), then

$$D_i = D_0/\sqrt{} \tag{9}$$

where D_0 is the effective interparticle diffusion coefficient at the outlet.

4. THE GENERATING FUNCTION

From Eqs. (3) and (4)

$$\bar{C}_n = \exp\left\{-\sum \frac{\Delta L_i V_i}{2D_i}\left[\left(1 + \frac{4D_i\rho K\lambda}{V_i^2}\right)^{1/2} - 1\right]\right\} \tag{10}$$

which becomes in the limit

$$\bar{C} = \exp\left\{-\int_0^L \frac{V}{2D}\left[\left(1 + \frac{4D\rho K\lambda}{V^2}\right)^{1/2} - 1\right] \mathrm{dx}\right\} \tag{11}$$

where V and D are functions of x.

Expanding the last equation in powers of λ gives:

$$\bar{C} = \exp\left\{-\int_0^L \left[\left(\frac{\lambda\rho K_0}{V}\right) - \lambda^2\left(\frac{\rho\left\{K_0 - \frac{\epsilon}{\rho}\right\} d_p^2}{60 D_p V} + \frac{\rho^2 K_0^2 D}{V^3}\right)\right.\right.$$
$$+ \lambda^3\left(\frac{\rho\left\{K_0 - \frac{\epsilon}{\rho}\right\} d_p^4}{2520 D_p^2 V} + \frac{\rho^2 K_0\left\{K_0 - \frac{\epsilon}{\rho}\right\} d_p^2 D}{30 D_p V^3} + \frac{2\rho^3 K_0^3 D^2}{V^5}\right)$$
$$\left.\left. + \text{higher terms in } \lambda\right] dx\right\} \tag{12}$$

Carrying through the indicated integration gives:

$$\bar{C} = \exp\left\{-\left[\frac{P_1 \lambda \rho K_0}{V_0} - \lambda^2\left(\frac{P_1 \rho\left\{K_0 - \frac{\epsilon}{\rho}\right\} d_p^2}{60 D_p V_0} + \frac{P_2 \rho^2 K_0^2 D_0}{V_0^3}\right)\right.\right.$$
$$+ \lambda^3\left(\frac{P_1 \rho\left\{K_0 - \frac{\epsilon}{\rho}\right\} d_p^4}{2520 D_p V_0} + \frac{P_2 \rho^2 K_0\left\{K_0 - \frac{\epsilon}{\rho}\right\} d_p^2 D_0}{30 D_p V_0^3}\right.$$
$$\left.\left.\left. + \frac{2 P_3 \rho^3 K_0^3 D_0^2}{V_0^5}\right) + \text{higher terms in } \lambda\right]\right\} \tag{13}$$

where

$$P_n = \frac{\int_0^L \left(\sqrt{(P_i/P_0)^2 - \frac{x}{L}\{(P_i/P_0)^2 - 1\}}\right)^n dx}{L} \tag{14}$$

$$= \frac{\{(P_i/P_0)^{n+2} - 1\}}{(n/2 + 1)\{(P_i/P_0)^2 - 1\}} \tag{15}$$

The exponent in Eq. (13) can be expanded as:

$$e^{-Z} = 1 - Z + \frac{Z^2}{2} - \frac{Z^3}{6} + \text{higher powers of } Z \tag{16}$$

where Z is the negative exponent in Eq. (13).

But the Laplace transform is also given by:

$$\bar{C} = m_0 - \lambda m_1 + \frac{\lambda^2 m_2}{2} - \frac{\lambda^3 m_3}{6} + \text{higher terms in } \lambda \tag{17}$$

where

$$m_n = \int_0^\infty t^n C(t)\, dt$$

and $C(t) = L^{-1}(\bar{C})$ is the breakthrough curve following a unit delta function input into the column.

Carrying out the expansion given by Eq. (16) and summing the results in terms of powers of λ shows that:

$$m_0 = 1 \tag{18}$$

$$m_1 = \frac{P_1\rho K_0 L}{V_0} \tag{19}$$

$$m_2 = \left(\frac{P_1\rho K_0 L}{V_0}\right)^2 + \frac{P_1\rho\left(K_0 - \frac{\epsilon}{\rho}\right)d_p^2 L}{30D_pV_0} + \frac{2P_2\rho^2K_0^2D_0L}{V_0^3} \tag{20}$$

$$\begin{aligned} m_3 = {} & \left(\frac{P_1\rho K_0 L}{V_0}\right)^3 + \frac{P_1^2\rho^2K_0\left(K_0 - \frac{\epsilon}{\rho}\right)d_p^2L^2}{10D_pV_0^2} + \frac{6P_1P_2\rho^3K_0^3D_0L^2}{V_0^4} \\ & + \frac{P_1\rho\left(K_0 - \frac{\epsilon}{\rho}\right)d_p^4L}{420D_p^2V_0} + \frac{P_2\rho^2K_0\left(K_0 - \frac{\epsilon}{\rho}\right)d_p^2D_0L}{5D_pV_0^3} \\ & + \frac{12P_3\rho^3K_0^3D_0^2L}{V_0^5} \end{aligned} \tag{21}$$

5. SIGNIFICANCE OF THE RESULTS

Zeroth Moment

$m_0 = 1$. The zeroth moment is equal to one, which is consistent with the assumption that all of the unit input fed into the bed passes through the bed; no fraction of the input is retained permanently or chemically reacted in the bed.

First Moment

The first moment, which gives the mean retention time, is:

$$m_1 = \frac{2}{3}\frac{\{(P_i/P_0)^3 - 1\}}{\{(P_i/P_0)^2 - 1\}}\frac{\rho K_0 L}{V_0} \tag{22}$$

The effect of pressure on the mean retention time is identical to that derived earlier by James and Martin (*3*).

Second Moment

$$m_2 = \left(\frac{P_1\rho K_0 L}{V_0}\right)^2 + \frac{P_1\rho\left(K_0 - \frac{\epsilon}{\rho}\right)d_p^2 L}{30D_pV_0} + \frac{2P_2\rho^2K_0^2D_0L}{V_0}$$

Using the second moment in conjunction with the first, we can describe the spreading of the output. If the average height of a theoretical plate, h_{av}, is defined as:

$$h_{av} = \frac{L}{d_p}\left(\frac{m_2}{m_1^2} - 1\right) \tag{23}$$

then

$$h_{av} = \frac{3}{2}\frac{\{(P_i/P_0)^2 - 1\}}{\{(P_i/P_0)^3 - 1\}}\left(\frac{2\epsilon\gamma}{v} + 2\lambda_p\right) + \frac{9\{(P_i/P_0)^4 - 1\}\{(P_i/P_0)^2 - 1\}}{8\{(P_i/P_0)^3 - 1\}^2}\left\{\frac{\left(K_0 - \frac{\epsilon}{\rho}\right)Dm_0 v}{30\rho K_0 D_p}\right\} \tag{24}$$

where Dm_0 is the coefficient for molecular diffusion of the sorbate at the outlet in cm^2/sec, and v is defined as $V_0 d_p/Dm_0$.

This last equation predicts a standard deviation which is identical in form to that given by Giddings (*4*). However, it is seen here that Giddings' equation accurately describes the broadening effects of mass transfer without the restriction of a Gaussian output (a restriction implied in his use of the van Deemter equation).

From the third moment we can, indeed, calculate the skewness of the output. If we define the skewness as:

$$\beta = \frac{\gamma_3}{\gamma_2^{3/2}} \tag{25}$$

where γ_n is the nth central moment,

$$\gamma_2 = m_2 - m_1^2 \tag{26}$$

$$\gamma_3 = m_3 - 3m_1m_2 + 2m_1^3 \tag{27}$$

Then

$$\beta = \frac{\dfrac{P_1\rho\left(K_0 - \frac{\epsilon}{\rho}\right)d_p^4}{420D_p^2V_0} + \dfrac{P_2\rho^2K_0\left(K_0 - \frac{\epsilon}{\rho}\right)d_p^2D_0}{5D_pV_0^3} + \dfrac{12P_3\rho^3K_0^3D_0^2}{V_0^5}}{\sqrt{L}\left(\dfrac{P_1\rho\left(K_0 - \frac{\epsilon}{\rho}\right)d_p^2}{30D_pV_0} + \dfrac{2P_2\rho^2K_0^2D_0}{V_0^3}\right)^{3/2}} \tag{28}$$

It is now possible to calculate more accurately the skewness of the output from a gas chromatography column across which there is a significant pressure drop. More importantly, the higher moments of the breakthrough curve can also be derived, and once a sufficient number of moments are known, numerical values for the breakthrough curve can be determined by their use to any desired accuracy. Thus the effect of pressure drop on gas chromatographic behavior can be determined to a high degree of accuracy.

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