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Moment Theory of Band Spreading, Skewness, and Resolution in Programmed Temperature Gas Chromatography

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Abstract

Expressions for first, second, and third moments are developed for a simple model of gas–liquid partition chromatography with linear temperature programming. The results show how increased heating rate causes increased sharpening of output peaks, even though resolution is decreased. Second and third central moments are nearly inversely proportional to heating rate.

Programmed temperature gas chromatography (PTGC) allows separation of a wide boiling point range of solutes in a shorter time than can be realized with isothermal operation (*1*). The column temperature, uniform along the entire length, is increased with time so that the more volatile solutes are eluted at low temperatures and the heavier solutes at higher temperatures. A linear increase of temperature during a run leads to the elution of uniformly spaced peaks in a homologous series such that the plot of retention time versus number of carbon atoms is nearly linear (*2*). With isothermal operation, on the other hand, the retention time increases nearly exponentially with the number of carbon atoms, so that the separation of the more volatile fractions is larger than necessary at the temperature that separates the heavier fractions. With PTGC each solute is eluted at a temperature near the optimum temperature for that fraction alone (*3*).

Although the difference in retention times (*4*), or first moments, is the main consideration in optimizing resolution in PTGC, the widths, or second moments, of the output pulses are of interest as well. The present work reproduces the well-known results for first moments (*1–3*), but extension to higher moments requires a reexamination and reworking of the foundations of the theory. In this paper we derive relationships for the second and third central moments, μ_2 and μ_3, in PTGC, and show how band spreading and skewness depend on the rate of temperature change and on enthalpy difference between gas and liquid. The major result is that μ_2 and μ_3 are nearly inversely proportional to heating rate. In spite of the sharpening effect of PTGC, resolution decreases with heating rate because of the decrease in retention time.

The method that implements these results is the moment technique. The results are developed for a simple model of gas–liquid partition chromatography (*5*) that ignores details of intraparticle and liquid diffusion. Although the analytical solutions are restricted in application by the assumptions of the model, the method could be used with numerical integration to achieve a more accurate representation of real chromatographic processes. The basic ideas also have potential for application to other programming and gradient procedures in separation processes.

INTEGRATION OF MOMENTS

The temperature of the column is uniform and increasing with time, $T(t)$, so that in general equilibrium coefficients, rate parameters, mass transfer coefficients, and intraparticle and axial dispersion coefficients are functions of time. The time-moment expressions are in the form that the difference of a moment at two different locations in a column, $\Delta\mu$, is proportional to the distance between these points, Δz.

For the normalized first moment, defined as

$$\mu_1'(z) = \frac{1}{m_0}\int_0^\infty c(t, z)t\,dt \tag{1}$$

with the zeroth unnormalized moment

$$m_0 = \int_0^\infty c\,dt \tag{2}$$

we may write

$$\Delta\mu_1' = f(t)\Delta z \tag{3}$$

We have assumed in Eq. (3) that the time for the peak to traverse the distance Δz is short enough that the temperature has not changed significantly. The form that $f(t)$ takes will depend on the particular model adopted to describe the geometry and equilibrium behavior in the column. Since the first moment locates the average time position of the peak, $\Delta\mu_1'$ represents how long it takes for the peak to move the distance Δz. For an infinitesimally small distance, $\Delta z \to dz$, we let $\Delta\mu_1' \to dt$; therefore from Eq. (3) we have

$$dz = dt/f(t) \tag{4}$$

This expression may be integrated between the entrance, $z = 0$, and exit, $z = L$, of a column of length L. We may choose $t = 0$ as the time when the peak enters the column; thus $\mu_1'\ (z = 0) = 0$. The integration of Eq. (4) yields

$$L = \int_0^{\mu_1'(L)} dt/f(t) \tag{5}$$

where $\mu_1'(L)$ may be identified as the retention time. Equation (5) has the same general form as other equations in the PTGC literature (*1–3*) relating column length to retention time. If the temperature is constant, then $f(t)$ is constant and may be removed from under the integral to give a familiar equation similar to Eq. (3) with L replacing Δz.

The normalized second central moment, defined as

$$\mu_2(z) = \frac{1}{m_0}\int_0^{\infty} (t - \mu_1')^2 c(z, t)\, dt \tag{6}$$

changes over the small distance Δz according to

$$\Delta\mu_2 = g(t)\Delta z \tag{7}$$

where $g(t)$ depends upon the transport processes, as well as geometry and equilibrium behavior, in the column. In the differential limit we have

$$\frac{d\mu_2}{dz} = \frac{d\mu_2}{dt} f(t) = g(t) \tag{8}$$

Integration between the values of moments at either end of the column yields

$$\mu_2(L) - \mu_2(0) = \int_0^{\mu_1'(L)} dt\, g(t)/f(t) \tag{9}$$

which is a measure of band spreading between the column inlet and outlet.

The normalized third central moment, which is a measure of band skewness, is defined as

$$\mu_3(z) = \frac{1}{m_0}\int_0^\infty (t - \mu_1')^3 c(z, t)\, dt \tag{10}$$

and changes proportionally with the distance Δz,

$$\Delta\mu_3 = h(t)\Delta z \tag{11}$$

Again we have

$$\frac{d\mu_3}{dt} f(t) = h(t) \tag{12}$$

so that

$$\mu_3(L) - \mu_3(0) = \int_0^{\mu_1'(L)} dt\, h(t)/f(t) \tag{13}$$

The definite proportionality between moments and column length exhibited by Eqs. (3), (7), and (11) is known to hold for the adsorption model of Kubin (*6*), as well as the model examined in the present paper. This proportionality, which holds at least for the first and second moments for some other models (*7*, *8*), is a consequence of the reversible nature of the transport and reaction phenomena that take place in the column.

MODEL FOR GAS-LIQUID PARTITION CHROMATOGRAPHY

The model we propose for concrete investigation of the magnitude of the effect on chromatographic peaks of temperature programming applies to gas-liquid partition chromatography (*5*, *9*). The model includes the equilibrium distribution constant and the axial dispersion coefficient, but neglects intraparticle diffusion. In terms of the column void fraction α, the average gas velocity v_0, and the axial dispersion coefficient D_0, we have the differential equation for the space and time dependence of the concentration of solute $c(z, t)$:

$$\alpha(1 + k)\partial c/\partial t + v_0 \partial c/\partial z - D_0 \partial^2 c/\partial z^2 = 0 \tag{14}$$

Here k is the partition ratio, which may be written as

$$k = K/\beta \tag{15}$$

in terms of $K = c_{\mathrm{liq}}/c$, the equilibrium partition coefficient, and β, the ratio of volume of gas to volume of liquid in the column. The initial and boundary conditions take the form

$$c(z, t = 0) = 0 \tag{16}$$

$$c(z = 0, t) = c_0(t) \tag{17}$$

$$c(z \to \infty, t) = \text{finite} \tag{18}$$

The moments for this system may be calculated from the solution of Eqs. (14) to (18) in the Laplace domain which is

$$\bar{c}(z) = \bar{c}_0 \exp(\lambda z) \tag{19}$$

where

$$\lambda = \frac{v_0}{2D_0}[1 - (1 + 4\alpha D_0 s/v_0^2)^{1/2}] \tag{20}$$

where s is the Laplace transform parameter. Using the identity relating the unnormalized moments to the Laplace transform of concentration,

$$m_n = \lim_{s \to 0} (-1)^n d^n\bar{c}/ds^n \tag{21}$$

we readily calculate the moments (*9*) according to Eqs. (3), (7), and (11):

$$f(t) = \alpha(1 + k)/v_0 \tag{22}$$

$$g(t) = 2D_0\alpha^2(1 + k)^2/v_0^3 \tag{23}$$

$$h(t) = 12D_0^2\alpha^3(1 + k)^3/v_0^5 \tag{24}$$

The temperature dependence of the partition ratio is given by

$$k = k_1 \exp(-\Delta G/RT) \tag{25}$$

and since the standard free energy change from the gas to the liquid ($\Delta G < 0$) has the temperature dependence

$$\Delta G = \Delta H - T\Delta S \tag{26}$$

therefore we may write

$$k = k_0 \exp(-\Delta H/RT) \tag{27}$$

where $k_0 = k_1 \exp(\Delta S/R)$. We assume that the enthalpy and entropy change from gas to liquid, ΔH and ΔS, are independent of T.

For a satisfactory chromatographic separation, the partition ratio k cannot be too small. If k is negligible compared to unity, we see from the governing differential Eq. (14) that there is no mechanism for resolving solutes except for possible slight differences in axial dispersion. Thus we are not entirely unjustified in restricting the subsequent calculations to the case $k \gg 1$; otherwise we would not be able to obtain analytical expressions for moments in PTGC. Giddings (*2*) makes the same approximation in writing his Eq. (6). The approximation is equivalent to ignoring the dead space, an assumption discussed by Harris and Habgood (*1*).

LINEAR PROGRAMMED TEMPERATURE

Our objective is to obtain analytical expressions for the moments $\mu_1'(L)$, $\mu_2(L)$, and $\mu_3(L)$. Following earlier work (*2*) we assume that gas expansion and pressure drop in the column are negligible, so that average velocity v_0 is constant. When temperature is programmed to increase linearly with time, we write

$$T(t) = T_0 + \varepsilon t \tag{28}$$

where T_0 is the starting temperature. The integrations in the moment expressions can be performed analytically when $k \gg 1$ or when $\varepsilon\mu_1'(L)/T_0 \ll 1$. The latter inequality, which would apply for small temperature gradients and short retention times, is of less interest and is not considered further.

Combining (5), (22), and $k \gg 1$, we obtain

$$L = \frac{v_0}{\alpha k_0}\int_0^{\mu_1'(L)} e^{\Delta H/RT}\,dt = \frac{v_0}{\varepsilon\alpha k_0}\int_{T_0}^{T_R} e^{\Delta H/RT}\,dt \tag{29}$$

where we have substituted the retention temperature

$$T_R = T_0 + \varepsilon\mu_1'(L) \tag{30}$$

Integrating by parts, we find

$$L = \frac{v_0}{\varepsilon\alpha k_0}\frac{\Delta H}{R}F_1 \tag{31}$$

where

$$F_1 = \frac{e^{-X_0}}{X_0} - \frac{e^{-X_R}}{X_R} - E_1(X_0) + E_1(X_R) \tag{32}$$

which is equivalent to well-known results (*1–3*). Here we define $X_R = -\Delta H/RT_R > 0$, $X_0 = -\Delta H/RT_0 > 0$, and we use the following notation for the exponential integral (*10*),

$$-Ei(-x) = E_1(x) = \int_x^\infty \frac{e^{-t}}{t}\,dt, \qquad \text{for} \quad x > 0 \tag{33}$$

Combining Eqs. (9) and (23) and integrating, we have for the second moment with $k \gg 1$,

$$\mu_2(L) - \mu_2(0) = \frac{2D_0\alpha k_0}{\varepsilon v_0^2}\int_{T_0}^{T_R} e^{-\Delta H/RT}\,dt \tag{34}$$

We have assumed D_0 to be independent of T_0 temperature; i.e., that the temperature dependence of the axial dispersion coefficient is much weaker than that of the partition ratio k. The integrand in Eq. (34) is the same as in Eq. (29) except that ΔH is replaced with $-\Delta H$. Thus using the relation (33) between the two exponential integrals, we find

$$\mu_2(L) - \mu_2(0) = \frac{2D_0\alpha k_0}{v_0^2}\frac{\Delta H}{R}\frac{F_2}{\varepsilon} \tag{35}$$

where

$$F_2 = \frac{e^{X_0}}{X_0} - \frac{e^{X_R}}{X_R} - Ei(X_0) + Ei(X_R) \tag{36}$$

We can test the approximation that $D_0(T)$ has a relatively small effect on $\Delta\mu_2$. A significant part of the temperature dependence of the axial dispersion coefficient $D_0(T)$ will be due to the contribution of the gas diffusion coefficient $D_{AB}(T)$, which increases with T as the 1.7 or 1.8 power (*1*). However, the convective, or eddy, contribution to $D_0(T)$ will also have an effect. For our purposes it will suffice to consider $D_0(T)$ increasing as the first or second power.

If

$$D_0 = \delta_1 T \tag{37}$$

then we have instead of Eq. (34)

$$\begin{aligned}\Delta\mu_2 &= \frac{2\alpha\delta_1 k_0}{\varepsilon v_0^2}\int_{T_0}^{T_R} Te^{-\Delta H/RT}\,dT \\ &= \frac{2\alpha\delta_1 k_0}{\varepsilon v_0^2}\left(\frac{\Delta H}{R}\right)^2\int_{X_0}^{X_R}\frac{e^X}{X^3}\,dX \\ &= \frac{2\alpha\delta_1 k_0}{V_0^2}\left(\frac{\Delta H}{R}\right)^2\frac{F_2^{(1)}}{\varepsilon}\end{aligned} \tag{38}$$

where

$$F_2^{(1)} = -e^{X_0}\left(\frac{1}{X_0^2} + \frac{1}{X_0}\right) + e^{X_R}\left(\frac{1}{X_R^2} + \frac{1}{X_R}\right) + Ei(X_0) - Ei(X_R) \tag{39}$$

The integral in Eq. (39) may be developed by integration by parts, or simply by using a suitable table of integrals (*11*).

If

$$D_0 = \delta_2 T^2 \tag{40}$$

then by the same procedure

$$\Delta\mu_2 = \frac{\alpha\delta^2 k_0}{3v_0^2}\left(\frac{\Delta H}{R}\right)^3 \frac{F_2^{(2)}}{\varepsilon} \tag{41}$$

where

$$F_2^{(2)} = -e^{X_0}\left(\frac{2}{X_0^3} + \frac{1}{X_0^2} + \frac{1}{X_0}\right) + e^{X_R}\left(\frac{2}{X_R^3} + \frac{1}{X_R^2} + \frac{1}{X_R}\right) + Ei(X_0) - Ei(X_R) \tag{42}$$

Combining Eqs. (13) and (24) and integrating, we have for the third moment with $k \gg 1$,

$$\mu_3(L) - \mu_3(0) = \frac{12D_0^2\alpha^2k_0^2}{v_0^4}\int_{T_0}^{T_R} e^{-2\Delta H/RT}\,dT \tag{43}$$

Since the integrand is the same as in Eq. (36) except that ΔH is replaced with $2\Delta H$, we have

$$\mu_3(L) - \mu_3(0) = \frac{24D_0^2\alpha^2k_0^2}{v_0^4}\frac{\Delta H}{R}\frac{F_3}{\varepsilon} \tag{44}$$

where

$$F_3 = \frac{e^{2X_0}}{2X_0} - \frac{e^{2X_R}}{2X_R} - Ei(2X_0) + Ei(2X_R) \tag{45}$$

RESULTS AND DISCUSSIONS

It is necessary to calculate the quantities F_1, F_2, $F_2^{(1)}$, $F_2^{(2)}$, and F_3 for various retention temperatures to estimate the relative effect of temperature programming on the moments. Such calculations are shown

TABLE 1

Calculations Showing Effect of Retention Temperature on Moments

X_R	F_2	F_2	$F_2^{(1)}$	$F_2^{(2)}$	$-F_3$
0.1	7.225	302.0	192.3	2359	1.362×10^6
0.2	2.871	296.3	106.6	367.9	1.362×10^6
0.5	6.533×10^{-1}	292.2	78.53	60.85	1.362×10^6
1.0	1.485×10^{-1}	290.2	72.63	34.01	1.362×10^6
2.0	1.877×10^{-2}	288.1	69.68	27.47	1.362×10^6
5.0	1.992×10^{-4}	278.9	64.52	22.84	1.361×10^6
6.0	5.264×10^{-5}	270.6	61.54	21.23	1.360×10^6
7.0	1.439×10^{-5}	254.5	56.63	18.97	1.354×10^6
8.0	3.880×10^{-6}	221.6	47.89	15.48	1.32×10^6
9.0	8.792×10^{-7}	151.8	31.57	9.747	1.14×10^6
10.0	0	0	0	0	0

in Table 1 for $X_0 = 10$, which corresponds to $T_0 = 300$°K and $\Delta H = -6000$ cal/mole. Qualitative conclusions are not affected by changing X_0 within realistic limits. Values for exponential integrals come from tabulations in Ref. *10*. Note that the case $X_R = X_0 = 10$ in Table 1 refers to a zero-length column where $\mu_1'(L) = 0$; to recover the steady temperature moments, where $\varepsilon = 0$, one can apply l'Hospital's rule to Eqs. (31), (35), and (44).

The results for F_1 in Table 1 merely reproduce results already known (*2*). The interesting new information in Table 1 is the relative constancy of F_2 and F_3. This implies that $\Delta\mu_2$ and $\Delta\mu_3$ are nearly inversely proportional to ε, see Eqs. (35) and (44), so that band spreading and skewness are reduced for larger heating rate. This is illustrated by Fig. 1 where the moments are plotted. If the inlet mixture is a very thin pulse, then we may approximate it with a delta function at time zero, so that $\Delta\mu_1'$, $\Delta\mu_2$, and $\Delta\mu_3$ may be replaced with μ_1', μ_2, and μ_3. We have assumed for Fig. 1 that $\alpha = 0.4$, $L = 400$ cm, $v_0 = 8$ cm/sec, $D_0 = 0.1$ cm^2/sec, $k_0 = 0.01$, $\Delta H_A = -10{,}000$ cal/mole and $\Delta H_B = -6{,}000$ cal/mole. The calculations for second and third central moments are performed by finding T_R at the given value of ε [e.g., by using a graph similar to Giddings' (*2*) Fig. 3], *computing* X_R *from* T_R, using Table 1 or its graph to get F_2 and F_3, and then using Eqs. (35) and (38) to calculate $\Delta\mu_2$ and $\Delta\mu_3$. The first moment μ_1' is simply $(T_R - T_0)/\varepsilon$. The values at $\varepsilon = 0$ are calculated from Eqs. (7) and (11), with Δz replaced by L; this procedure is a consequence of the application of l'Hospital's rule to Eqs. (31), (35), and (44).

The effect of the temperature dependence was estimated by setting

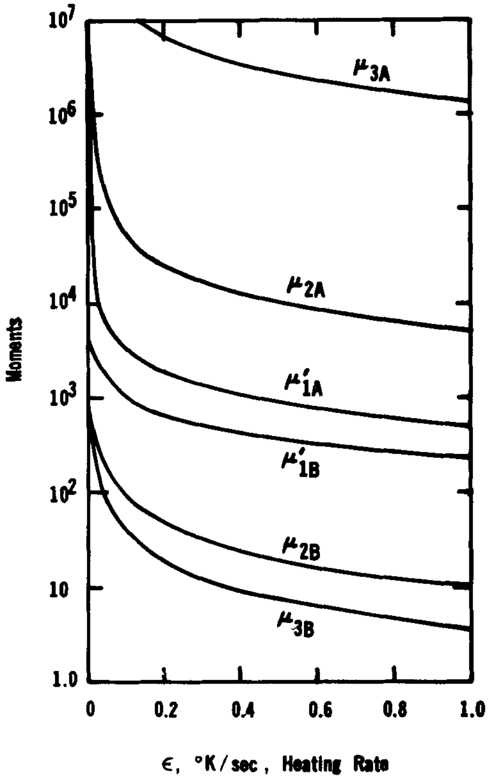

FIG. 1. Effect of heating rate ε on first, second, and third moments of components A and B, $\Delta H_A = -10{,}000$ cal/mole and $\Delta H_B = -6{,}000$ cal/mole.

$D_0 = 0.1$ cm^2/sec for $T_0 = 300$°K and calculating $\delta_1 = 3.33 \times 10^{-4}$ cm^2/sec°K and $\delta_2 = 1.11 \times 10^{-6}$ cm^2/sec°K^2. Values of $F_2^{(1)}$ and $F_2^{(2)}$ were interpolated graphically for $\Delta H_B = -6{,}000$ cal/mole to get values of $\Delta\mu_{2B}$ which are plotted in Fig. 2. The increase in $\Delta\mu_{2B}$ at $\varepsilon = 1.0$ was 15% for $D_0 \propto T$ and 36% for $D_0 \propto T^2$. The percent increase was less for smaller values of ε, and was, of course, zero where $\varepsilon = 0$. This increase of $\Delta\mu_2$ is small enough that it is not plotted in Fig. 1.

The sharpening of the pulse by increased heating rate can be qualitatively explained as follows. For higher heating rates the retention time of each peak is reduced. Therefore absorption, which is the main broadening effect, has less time to act. In addition, at higher temperatures, absorp-

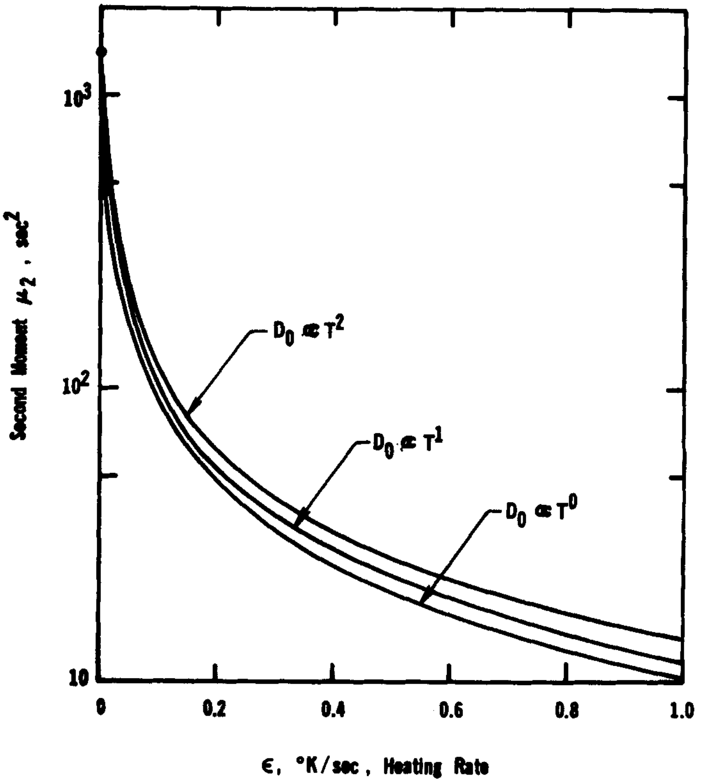

FIG. 2. Influence of temperature dependence of the axial dispersion coefficient D_0 on plot of second moment μ_{2B} versus heating rate ε.

tion is reduced because of the temperature dependence of the equilibrium partition coefficient. However, resolution is not increased for larger ε despite the band sharpening, because spacing between first moments is decreased.

To illustrate this behavior, we plot resolution (7), defined in terms of moments as

$$R_S = \frac{\mu'_{1A} - \mu'_{1B}}{\sqrt{\mu_{2A}} + \sqrt{\mu_{2B}}} \qquad (46)$$

versus heating rate in Fig. 3. The resolution is entirely satisfactory even at $\varepsilon = 1.0$, and a large reduction in retention time is achieved. These results

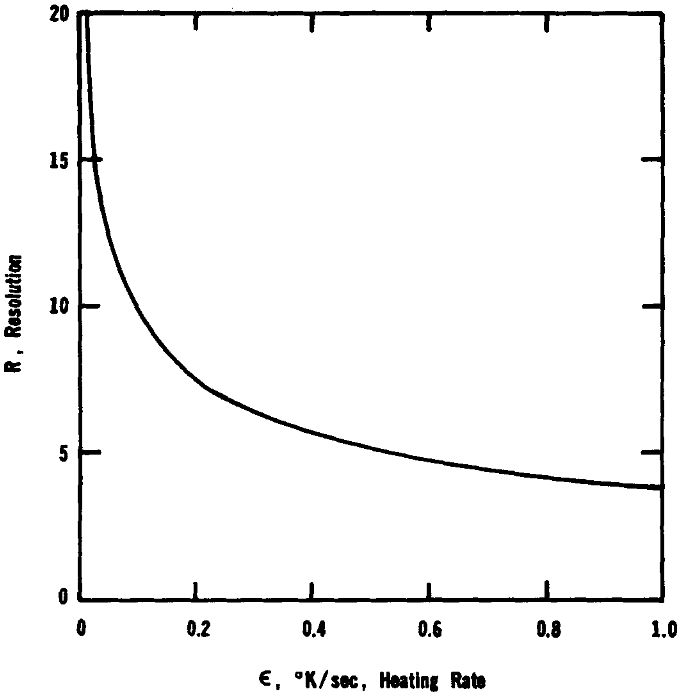

FIG. 3. Effect of heating rate ε on resolution of components A and B.

are obviously conditional on the large difference in ΔH for Components A and B that was chosen for this calculation.

CONCLUSION

The key to this paper's development of a theory for band broadening and skewness is the realization of the differential expressions for the moments, Eqs. (4), (8), and (12). The integration of the first moment reproduces well-known results. The second moment shows how pulse sharpening occurs for larger heating rates. The decrease in the third moment shows how the peak becomes more symmetric as it narrows. Using the first and second moment results, we are able to demonstrate how resolution decreases with increased heating rate, although retention time is reduced. The temperature dependence of the axial dispersion coefficient can be included and is a secondary effect.

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