Theory of temperature-programmed gas chromatography

The method of moment analysis

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ABSTRACT

For temperature-programmed gas chromatography, it is shown that the first original, the second and the third central moments of a moving zone are additive along all parts of the component passing through in a linear system. Trace expressions for zones moving along the column and expressions for the calculation of the first three moments (retention time, peak variance and third central moment related to peak skew) of peaks according to isothermal data are derived. It is also shown that the definition of local plate height and related equations for peak variance in the literature are not correct. Reasonable definitions of local plate height and related equations are then developed appropriately.

INTRODUCTION

The theory of temperature-programmed gas chromatography (TPGC) was developed by several workers [1–5] and equations for the retention time and peak variance were derived and optimization procedures developed. However, in the literature, trace expressions for components moving along the column length with time have not been considered in detail. Also, the third central moment, which reflects the skew of peaks, and higher order moments have not previously been studied. Additionally, the definition of local plate height and related equations for peak variance in the literature [1,6–8] are not correct, as the actual peak variance in TPGC could not be calculated using these equations with isothermal data.

In the present treatments, equations for the retention time and traces of components moving along the column length are derived. Reasonable definitions of local plate height and related equations for the calculations of peak variance in TPGC are then developed.

In this paper, a new method, moment analysis, is developed for TPGC, in which the retention time, peak variance and higher order moments are dealt with by a common, general, strict and simple method. By using this method, equations for the calculation of different order of moments, including retention time, peak variance and third central moment, in TPGC using isothermal data are developed. Decompression effects of the carrier gas are taken into account.

RETENTION TIME AND TRACE

In this treatment, only systems which satisfy the following assumptions are discussed: columns are homogeneous; columns, or more generally systems, are linear; and carrier gas pressures at the column inlet and column outlet remain constant during analysis.

Considering a component, the position of its zone centre at time t is $z = z(t)$ and the velocity of the zone centre is

$$dz/dt = Rv = v/(1+k) \tag{1}$$

where $k = k(t)$ is the capacity factor and v is the local velocity of the carrier gas.

Darcy's Law is expressed as

$$v = -(K/\eta)dP/dz \tag{2}$$

where K and η are the permeability and viscosity, respectively, of the carrier gas and P is the local pressure of the carrier gas. As the column is homogeneous, at any moment there is no temperature gradient along the column length, and we can write

$$pv = P_i v_i = P_o v_o = \bar{P}\bar{v} \tag{3}$$

where P_i and P_o are the carrier gas pressure at column inlet and column outlet, respectively and v_i and v_o are the corresponding carrier gas velocities. $\bar{P}$ is the distance average of P, i.e.,

$$\bar{P} = (\int_0^L Pdz)/L = P_o/j \tag{4}$$

where

$$j = \frac{3}{2} \cdot \frac{(\alpha^2 - 1)}{(\alpha^3 - 1)} \tag{5}$$

and

$$\alpha = P_i/P_o \tag{6}$$

are constants.

From eqns. 2 and 3, we have

$$\frac{z}{L} = \frac{\alpha^2 - (P/P_o)^2}{\alpha^2 - 1} = \frac{\alpha^2 - (v_o/v)^2}{\alpha^2 - 1} \tag{7}$$

and the time average of v with time is given by

$$\frac{1}{t_0} \int_0^{t_0} vdt = \frac{1}{t_0} \int_0^L dz = \frac{L}{t_0} \tag{8}$$

where

$$t_0 = \int_0^L dz/v = \int_0^L \frac{\sqrt{\alpha^2 - (\alpha^2 - 1)z/L}}{v} \cdot dz = \frac{L}{jv_o} \tag{9}$$

Noting that $\bar{v}$ in eqn. 3 can be written as

$$\bar{v} = v_o P_o/\overline{P} = j\, v_o \tag{10}$$

then $\bar{v}$ is just the time average of v within the dead time t_0, and it is only related to the column temperature, i.e.,

$$\bar{v} = L/t_0 \tag{11}$$

On the other hand, the distance average of v along the column is

$$\bar{\bar{v}} = \frac{1}{L}\int_0^L v\,dz \tag{12}$$

It can be derived that

$$\bar{\bar{v}} = \frac{2\,\bar{v}}{j(\alpha+1)} \tag{13}$$

Combining eqns. 10 and 7 leads to

$$v = \frac{\bar{v}}{j\sqrt{\alpha^2 - (\alpha^2-1)z/L}} \tag{14}$$

This equation relates v (local value) and $\bar{v}$ at an appropriate column temperature.

By combining eqns. 1 and 14, the retention time t_R in TPGC (in this text, subscripts R and r denote TPGC and isothermal processes, respectively) is obtained by the expression

$$\int_0^{t_R} \frac{dt}{t_0\,(1+k)} = 1 \tag{15}$$

This is consistent with the equation derived by Harris and Habgood [3].

The procedure for the calculation of t_R according to isothermal data can be outlined as follows. Experimentally, the dead time can be written as

$$t_0(T) = (A' + B'T)/(P_i - P_o) \tag{16}$$

Recalling that P_i and P_o are constants, this reduces to

$$t_0(T) = A_0 + B_0 T \tag{17}$$

The linear heating programme can be expressed as

$$T = T_0 + rt \tag{18}$$

where T_0 and r are the initial temperature and the heating rate, respectively. It is well known that

$$\ln k = C_0 + D_0/T \tag{19}$$

If the constants A_0, B_0, C_0 and D_0 above are determined by regression to several (more than two) isothermal data, then from eqns. 17, 18, 19 and 15, for any values of T_0 and r, the retention time t_R of each component with temperature programming can be calculated immediately.

The trace expression in TPGC can be obtained by combining eqns. 1 and 14, i.e.,

$$z(t)/L = \frac{\alpha^2}{\alpha^2 - 1} - \frac{1}{\alpha^2 - 1} \left(\alpha^3 - \frac{\alpha^3 - 1}{L} \int_0^t \frac{\bar{v}}{1 + k} \cdot dt \right)^{2/3} \tag{20}$$

Eqn. 14 is then rewritten as

$$v(t) = \frac{\bar{v}}{j} \left(\alpha^3 - \frac{\alpha^3 - 1}{L} \int_0^t \frac{\bar{v}}{1 + k} \cdot dt \right)^{-1/3} \tag{21}$$

Similarly to the calculation of t_R, the position of the zone centre and its velocity (Rv) at any time t can be calculated by eqns. 20 and 21.

As a simple example, in Fig. 1 we give the trace for isothermal processes. The trace expression is obtained according to eqn. 20 as

$$z(t)/L = \frac{\alpha^2}{\alpha^2 - 1} - \frac{1}{\alpha^2 - 1} \left[\alpha^3 - (\alpha^3 - 1) \frac{t}{t_r} \right]^{2/3} \tag{22}$$

As in Fig. 1, actual traces for isothermal processes always fall between the two limiting curves, i.e., the curve $z/L = t/t_r$ $(\alpha \rightarrow 1)$ and the curve $z/L = 1 - (1 - t/t_r)^{2/3}$ $(\alpha \rightarrow \infty)$.

MOMENTS OF LINEAR SYSTEMS

It is well known that moments play an important role in chromatography [9–15], as they are directly related to factors of practical importance, e.g., M_0, peak area; M_1, peak average retention time $(\approx t_r)$; M_2, peak variance $(= \tau^2)$; M_3, peak asymmetry (skew $= M_3/M_2^{3/2}$); M_4, peak flattening (excess $= M_4/M_2^2 - 3$); where M_1 denotes the first original (absolute) moment and M_2, M_3 and M_4 denote the second, third and fourth central moment, respectively.

Basic relationships for moments

The properties of moments are generally discussed as follows [16–18]. First we discuss the moments created by the column itself.
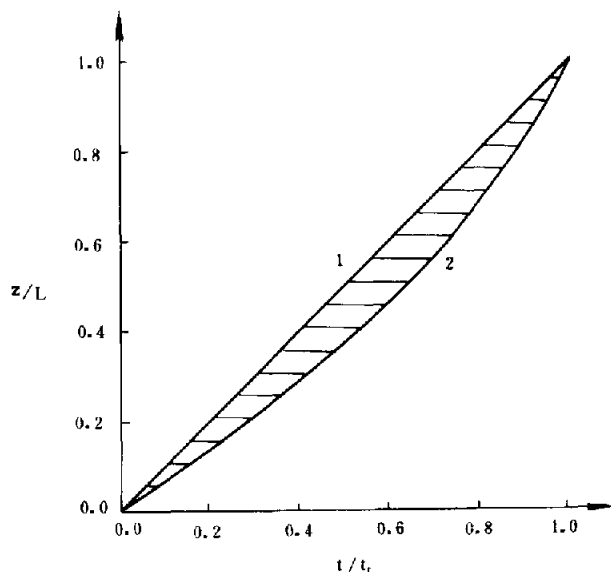
Fig. 1. Traces of components (including air peak) along the column length for isothermal processes. Actual traces always fall between the two limiting curves (shaded area), *i.e.*, curve 1, $z/L = t/t_r$ ($\alpha \to 1$) and curve 2, $z/L = 1-(1-t/t_r)^{2/3}$ ($\alpha \to \infty$).

The whole column can be regarded as many successive short lengths, Δl_1, Δl_2, Δl_3, etc., and we consider the variation of the peak profiles along these column intervals. Suppose individual responding functions of the column intervals are represented by $f_1(t), f_2(t), f_3(t)$, etc., respectively, that is, if a sharp [Dirac $\delta(t)$ function] injection is performed at the inlet of intervals Δl_i ($i = 1,2,3,...$), the profile at the outlet will be depicted by the corresponding function $f_i(t)$.

If the $\delta(t)$ function sampling proceeds at the inlet of the whole column, the profile at the outlet of length interval Δl_i will be $g_i(t)$, where $g_i(t)$ is the convolution of $f_1(t)$, $f_2(t), f_3(t), ...,$ and $f_i(t)$, as the column is assumed to be linear. In the following, we use $\Delta_s M_{ni}$ and M_{ni} denoting the nth moment ($n = 1$ for original moment, $n > 1$ for central moment) corresponding to $f_i(t)$ and $g_i(t)$, respectively, that is,

$$\Delta_s M_{1i} = \int_0^\infty f_i(t)t\mathrm{d}t \tag{23}$$

$$\Delta_s M_{ni} = \int_0^\infty f_i(t)(t - \Delta_s M_{1i})^n \mathrm{d}t \qquad (n = 2,3,...) \tag{24}$$

$$M_{1i} = \int_0^\infty g_i(t)t\mathrm{d}t \tag{25}$$

$$M_{ni} = \int_0^\infty g_i(t)(t - M_{1i})^n \mathrm{d}t \qquad (n = 2,3,...) \tag{26}$$

In TPGC, $f_i(t)$ is a complex function related to the temperature of the interval, because the column temperature is varying during elution and different parts of a zone pass through the column interval at different moments in time, and hence at different temperatures. However, in practice, the time interval is very short when a peak is passing through a very short (infinitesimal) column length interval, provided that the column efficiency is not too low. For example, if the plate number $N = 5.54 (t_R/w_{\frac{1}{2}})^2 = 5.54 \times 10^4$, $w_{\frac{1}{2}} = 1\% t_R$. Assuming that column temperature increases by 100 K during the retention time t_R, the range of temperature variation for the peak passing through an infinitesimal column length will be *ca.* 1 K. Therefore, to a good approximation, we assume that, during the process of a peak moving through an infinitesimal column length interval, the local temperature remains at a certain value that is approximately equal to the temperature of the zone centre passing through. Hence the column can be regarded as many successive length intervals in which each remains at an isothermal temperature while the zone passes through. The time gradient of temperature is then changed into the space gradient of temperature along the column length.

For simplicity, we first consider two intervals, Δl_1 and Δl_2. For a sharp injection into the inlet of the column, *i.e.*, the inlet of the length interval Δl_1, the profile at the outlet of Δl_1 will be $g_1(t) = f_1(t)$, and the profile at the outlet of Δl_2 will be $g_2(t)$, where $g_2(t)$ is the convolution of $g_1(t)$ and $f_2(t)$:

$$g_2(t) = \int_0^t g_1(t') f_2(t - t') dt' \tag{27}$$

Similarly, the profile at the outlet of Δl_3 will be $g_3(t)$, which is the convolution of $g_2(t)$ and $f_3(t)$, etc.

For the first length interval Δl_1,

$$M_{11} = \Delta_s M_{11} \tag{28}$$

$$M_{n1} = \Delta_s M_{n1} \qquad (n = 2, 3, \ldots) \tag{29}$$

The first original moment of $g_2(t)$ is (referring to Fig. 2)

$$M_{12} = \int_0^\infty g_2(t) t \, dt = \int_0^\infty \int_0^t g_1(t') f_2(t - t') t \, dt' dt$$

$$= \int_0^\infty \int_{t'}^\infty g_1(t') f_2(t - t') t \, dt \, dt'$$

$$= \int_0^\infty \int_0^\infty g_1(t') f_2(x) (x + t') dx \, dt'$$

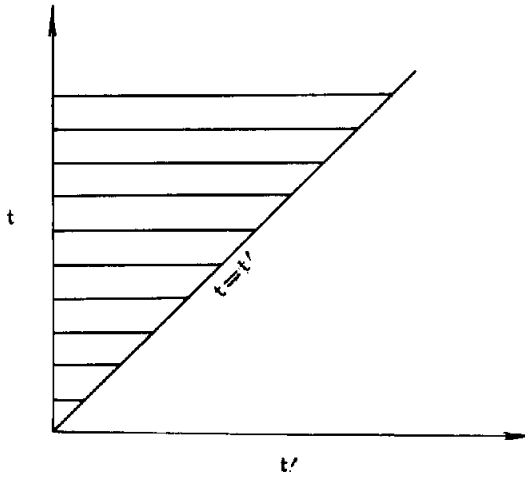$$= \int_0^\infty g_1(t') (\Delta_s M_{12} + t') dt'$$

$$= M_{11} + \Delta_s M_{12} \tag{30}$$

Fig. 2. Integrated field transformation.

The nth central moments of $g_2(t)$ are

$$M_{n2} = \int_0^\infty g_2(t)\,(t - M_{12})^n \mathrm{d}t$$

$$= \int_0^\infty \int_0^t g_1(t')\,f_2(t-t')\,(t-M_{12})^n\,\mathrm{d}t'\mathrm{d}t$$

$$= \int_0^\infty \int_{t'}^\infty g_1(t')\,f_2(t-t')\,(t-M_{11} - \varDelta_s M_{12})^n\,\mathrm{d}t\mathrm{d}t'$$

$$= \int_0^\infty \int_0^\infty g_1(t')\,f_2(x)(x+t'-M_{11} - \varDelta_s M_{12})^n\,\mathrm{d}x\mathrm{d}t'$$

$$= \int_0^\infty \int_0^\infty g_1(t')\,f_2(x)\,\Big[\sum_{k=0}^n C_n^k\,(t' - M_{11})^k\,(x-\varDelta_s M_{12})^{n-k}\Big]\mathrm{d}x\mathrm{d}t' \tag{31}$$

where $n = 2,3,\ldots$,

$$C_n^k = \frac{n!}{k!\,(n-k)!}$$

and $x = t - t'$ (see Fig. 2).

In eqn. 31, for $n = 2,3,\ldots$, we have

$$M_{22} = M_{21} + \varDelta_s M_{22} \tag{32}$$

$$M_{32} = M_{31} + \Delta_s M_{32} \tag{33}$$

$$M_{42} = M_{41} + \Delta_s M_{42} + 6M_{21}\Delta_s M_{22} \tag{34}$$

$$M_{52} = M_{51} + \Delta_s M_{52} + 10(M_{21}\Delta_s M_{32} + M_{31}\Delta_s M_{22}) \tag{35}$$

$$M_{62} = M_{61} + \Delta_s M_{62} + 15(M_{21}\Delta_s M_{42} + M_{41}\Delta_s M_{22}) + 20M_{31}\Delta_s M_{32} \tag{36}$$

The same results can be derived by using the Laplace transformation method.

The first three moments

From eqns. 30, 32 and 33, it can be shown that the first three moments for the whole column are

$$M_1 = \sum_i \Delta M_{1i} = \sum_i \Delta_s M_{1i} \tag{37}$$

$$M_2 = \sum_i \Delta M_{2i} = \sum_i \Delta_s M_{2i} \tag{38}$$

$$M_3 = \sum_i \Delta M_{3i} = \sum_i \Delta_s M_{3i} \tag{39}$$

where the sums are for all column length intervals and Δ is the generally used symbol for increments, *i.e.*,

$$\Delta M_{ni} = M_{ni} - M_{n(i-1)} \tag{40}$$

This illustrates that the first original, the second central and the third central moments are additive along the column length. It is concluded that, for homogeneous conditions along the column length, the moments M_1, M_2 and M_3 are directly proportional to the column length L. This has been confirmed by the results of Grubner [11], Grushka [9] and Chen and Peng [10].

Similarly, the first three moments for the whole system can be shown to be the sums of the appropriate order of moments created by the column itself and that caused by the extra-column devices, that is, the first three moments are additive for every part the component passing through. In the following, we mainly discuss the moments related to the column.

For the original moment, according to eqn. 37,

$$t_R = M_{1R} = \lim_{\Delta z \to 0} \sum_i \Delta_s M_{1i} = \int_0^{t_R} dt = \int_0^L \frac{dz}{Rv} \tag{41}$$

This is only a formal expression. In practice, eqn. 15 is used for calculations.

For the second central moment, for isothermal processes it can be theoretically expressed as

$$M_{2r}^{\text{the}} = \sum_{pq} F_{2pq}(k)\, \bar{v}^{-p}\, [D_q(\bar{v})]^q L \tag{42}$$

where $\sum\limits_{pq}$ denotes the summation for all pairs of p and q and

$$D_g(v) = D_{g0}\, (T/T_{00})^{1.75}\, P_0/P = D_{gT}\, P_0/P = D_{gT}\, jv/\bar{v} \tag{43}$$

in which T_{00} is an arbitrary temperature corresponding to the constant D_{g0}.

The appropriate local expression for M_2 (with $\bar{v}$ and L changed into v and Δz) is

$$\Delta_s M_{2z} = \sum_{pq} F_{2pq}(k)v^{-p}\, [D_g(v)]^q\, \Delta z \tag{44}$$

According to eqn. 32, when $\Delta z \to 0$, this leads to

$$\begin{aligned}
\mathrm{d}M_2 &= \lim_{\Delta z \to 0} \Delta M_{2z} = \lim_{\Delta z \to 0} \Delta_s M_{2z} \\
&= \sum_{pq} F_{2pq}(k)v^{-p}\, [D_g(v)]^q \mathrm{d}z
\end{aligned} \tag{45}$$

Hence the second central moment (observed) for TPGC is

$$\begin{aligned}
M_{2R} &= \sum_{pq} \int_0^L F_{2pq}(k)v^{-p}[D_g(v)]^q \mathrm{d}z \\
&= \sum_{pq} \int_0^{t_R} F_{2pq}(k)v^{1-p}[D_g(v)]^q/(1+k)\mathrm{d}t
\end{aligned} \tag{46}$$

where v is expressed as in eqn. 21.

According to eqn. 46, for isothermal processes (*i.e.*, the special temperature programme with $r = 0$), we obtain the expression for the experimentally observed second central moment, *viz.*,

$$M_{2r}^{\text{obs}} = \sum_{pq} F_{2pq}(k)\bar{v}^{-p}\, j^q D_{gT}^q\, L\, \varphi_{p-q} \tag{47}$$

where φ_{p-q} is the pressure calibration factor, which is defined as

$$\varphi_n = (\bar{v}^n/L) \int_0^L v^{-n}\, \mathrm{d}z \tag{48}$$

with

$$\varphi_0 = 1 \tag{49}$$

$$\varphi_1 = 1 \tag{50}$$

$$\varphi_2 = \frac{1}{2} \cdot j^2 \cdot \frac{\alpha^4 - 1}{\alpha^2 - 1} = \frac{9}{8} \cdot \frac{[(P_i/P_o)^4 - 1] [(P_i/P_o)^2 - 1]}{[(P_i/P_o)^3 - 1]^2} \tag{51}$$

$$\varphi_3 = \frac{2}{5} \cdot j^3 \cdot \frac{\alpha^5 - 1}{\alpha^2 - 1} \tag{52}$$

$$\varphi_4 = \frac{1}{3} \cdot j^4 \cdot \frac{\alpha^6 - 1}{\alpha^2 - 1} \tag{53}$$

$$\vdots$$

$$\varphi_n = \frac{2}{n+2} \cdot j^n \cdot \frac{\alpha^{n+2} - 1}{\alpha^2 - 1} \tag{54}$$

Similarly, for the third central moment, if the theoretical expression is

$$M_{3r}^{\text{the}} = \sum_{pq} F_{3pq}(k) \, \bar{v}^{-p} [D_g(\bar{v})]^q L \tag{55}$$

then the third central moment (observed) for TPGC is

$$M_{3R} = \sum_{pq} \int_0^{t_R} F_{3pq}(k) \, v^{1-p} [D_g(v)]^q/(1+k) \, \mathrm{d}t \tag{56}$$

The expression for the observed third central moment is

$$M_{3r}^{\text{obs}} = \sum_{pq} F_{3pq}(k) \, \bar{v}^{-p} j^q \, D_{gT}^q \, L \, \varphi_{p-q} \tag{57}$$

As an example, we take the theoretical expressions for the second and third central moments in ref. 9, *i.e.* (note: for normal conditions $2D_g/v \ll L$),

$$M_{2r}^{\text{the}} = [2\bar{v}^{-3} D_g(\bar{v})(1+k)^2 + J_1 k/\bar{v}]L \tag{58}$$

$$M_{3r}^{\text{the}} = [12\bar{v}^{-5} [D_g(\bar{v})]^2 (1+k)^3 + J_2 \bar{v}^{-3} D_g(\bar{v})k(1+k) + J_3 k/\bar{v}]L \tag{59}$$

where J_1, J_2 and J_3 are constants related to the parameters of the column.
Under these conditions,

$$M_{2R} = \int_0^{t_R} [2\bar{v}^{-1} j D_{gT}(1+k)/v + J_1 k/(1+k)]\mathrm{d}t \tag{60}$$

$$M_{2r}^{\text{obs}} = [2\bar{v}^{-3} j D_{gT}(1+k)^2 \varphi_2 + J_1 k/\bar{v} \varphi_1]L \tag{61}$$

and

$$M_{3R} = \int_0^{t_R} [12 \bar{v}^{-2} j^2 D_{gT}^2 (1+k)^2/v^2 + J_2 \bar{v}^{-1} j D_{gT} k/v + J_3 k/(1+k)]\mathrm{d}t \tag{62}$$

$$M_{3r}^{\text{obs}} = [12\bar{v}^{-5} j^2 D_{gT}^2 (1+k)^3 \varphi_3 + J_2 \bar{v}^{-3} j D_{gT} k(1+k) \varphi_2 + J_3 k/\bar{v}]L \quad (63)$$

In practice, the moments may be regressed to isothermal data as

$$M_{2r} = A_2 + B_2 t_r + C_2 t_r^2 \tag{64}$$

$$M_{3r} = A_3 + B_3 t_r + C_3 t_r^2 + D_3 t_r^3 \tag{65}$$

where $t_r = t_0 (1+k)$. Additionally, if the decompression effects of the carrier gas are neglected, then we have approximately

$$M_{2R} = (1/L) \int_0^L M_{2r} \mathrm{d}z = \int_0^{t_R} (M_{2r}/t_r) \, \mathrm{d}t \tag{66}$$

and

$$M_{3R} = (1/L) \int_0^L M_{3r} \, \mathrm{d}z = \int_0^{t_R} (M_{3r}/t_r) \, \mathrm{d}t \tag{67}$$

The fourth and fifth central moments

For the fourth central moment, according to eqn. 34 we can write

$$M_{41} = \Delta_s M_{41}$$
$$M_{42} = M_{41} + \Delta_s M_{42} + 6 M_{21} \Delta_s M_{22}$$
$$M_{43} = M_{42} + \Delta_s M_{43} + 6 M_{22} \Delta_s M_{23}$$
$$M_{44} = M_{43} + \Delta_s M_{44} + 6 M_{23} \Delta_s M_{24}$$
$$\vdots$$
$$M_{4(i-1)} = M_{4(i-2)} + \Delta_s M_{4(i-1)} + 6 M_{2(i-2)} \Delta_s M_{2(i-1)}$$
$$M_{4i} = M_{4(i-1)} + \Delta_s M_{4i} + 6 M_{2(i-1)} \Delta_s M_{2i}$$

Adding these equations, we obtain

$$M_{4i} = \sum_{j=1}^{i} \Delta_s M_{4j} + 6 \sum_{j=1}^{i-1} (\sum_{k=1}^{j} \Delta_s M_{2k}) \Delta_s M_{2(j+1)} \tag{68}$$

Similarly, for the fifth central moment it can be shown that (referring to eqn. 35),

$$M_{5i} = \sum_{j=1}^{i} \Delta_s M_{5j} + 10 \sum_{j=1}^{i-1} [M_{2j} \Delta_s M_{3(j+1)} + M_{3j} \Delta_s M_{2(j+1)}]$$
$$= \sum_{j=1}^{i} \Delta_s M_{5j} + 10 \sum_{j=1}^{i-1} [(\sum_{k=1}^{j} \Delta_s M_{2k}) \Delta_s M_{3(j+1)}$$
$$+ (\sum_{k=1}^{j} \Delta_s M_{3k}) \Delta_s M_{2(j+1)}] \tag{69}$$

Referring to eqns. 68 and 69, theoretical expressions for the fourth and fifth central moments may reasonably be written as

$$M_{4r}^{\text{the}} = F_{41} [k, \bar{v}, D_g (\bar{v})] L + F_{42} [k, \bar{v}, D_g(\bar{v})] L^2 \tag{70}$$

$$M_{5r}^{\text{the}} = F_{51} [k, \bar{v}, D_g (\bar{v})] L + F_{52} [k, \bar{v}, D_g(\bar{v})] L^2 \tag{71}$$

Appropriate local expressions can then be written as

$$\Delta_s M_{4z} = F_{41}[k,v,D_g(v)]\Delta z + F_{42}[k,v,D_g(v)]2z\Delta z \tag{72}$$

and

$$\Delta_s M_{5z} = F_{51}[k,v,D_g(v)]\Delta z + F_{52}[k,v,D_g(v)]2z\Delta z \tag{73}$$

According to eqns. 68 and 69, the moments for TPGC will be

$$
\begin{aligned}
M_{4R} = & \int_0^L F_{41}[k,v,D_g(v)]\mathrm{d}z + \int_0^L F_{42}[k,v,D_g(v)]2z\mathrm{d}z \\
& + 6\int_0^L \left\{\int_0^z F_2[k',v',D_g(v')]\mathrm{d}z'\right\} F_2[k,v,D_g(v)]\mathrm{d}z
\end{aligned}
\tag{74}
$$

and

$$
\begin{aligned}
M_{5R} = & \int_0^L F_{51}[k,v,D_g(v)]\mathrm{d}z + \int_0^L F_{52}[k,v,D_g(v)]2z\mathrm{d}z \\
& + 10\int_0^L \left\{\int_0^z F_2[k',v',D_g(v')]\mathrm{d}z'\right\} F_3[k,v,D_g(v)]\mathrm{d}z \\
& + 10\int_0^L \left\{\int_0^z F_3[k',v',D_g(v')]\mathrm{d}z'\right\} F_2[k,v,D_g(v)]\mathrm{d}z
\end{aligned}
\tag{75}
$$

where $k' = k(z')$, $v' = v(z')$, and

$$F_2[k,v,D_g(v)] = \sum_{pq} F_{2pq}(k)v^{-p}[D_g(v)]^q$$

$$F_3[k,v,D_g(v)] = \sum_{pq} F_{3pq}(k)v^{-p}[D_g(v)]^q$$

PLATE HEIGHT AND PEAK VARIANCE

Fundamental aspects of plate height

For arbitrary chromatographic processes (here we still use subscripts R), the plate height for the whole column is defined as

$$H_R = \frac{LM_{2L}}{M_{1L}^2} = \frac{L\tau_L^2}{t_R^2} = \left(\frac{L}{t_R}\right)^2 \frac{\tau_L^2}{L} \tag{76}$$

Similarly, the local plate height should be defined as

$$H_z = \lim_{\Delta z \to 0} \frac{\Delta z \Delta_s M_{2z}}{(\Delta_s M_{1z})^2} = \frac{\mathrm{d}z\mathrm{d}M_2}{(\mathrm{d}M_1)^2} = R^2 v^2 \cdot \frac{\mathrm{d}\tau^2}{\mathrm{d}z} \tag{77}$$

which can also be written as

$$H_z = \lim_{\Delta z \to 0} \frac{R^2 v^2 \Delta_s \tau_z^2}{\Delta z} = \lim_{\Delta z \to 0} \frac{\Delta_s \sigma_z^2}{\Delta z} \tag{78}$$

According to the additivity of the second central moment along the column length, the observed plate height H_R and the local plate height H_z are related by the following expression:

$$H_R = \frac{L}{t_R^2} \int_{(0)}^{(L)} d\tau^2 = \frac{L}{t_R^2} \int_0^L \frac{H_z}{R^2 v^2} \cdot dz \tag{79}$$

For isothermal chromatography, a similar expression was derived by Giddings [6].

In TPGC (or general processes), it is not correct to define the local plate height as [1,6–8]

$$H_z' = \frac{d\sigma^2}{dz} = \lim_{\Delta z \to 0} \frac{\Delta \sigma^2}{\Delta z} \tag{80}$$

because, at any position z, $\sigma = Rv\tau$, where $\sigma = \sigma(z)$, $\tau = \tau(z)$, $Rv = R(z)v(z)$ and

$$\frac{d\sigma^2}{dz} = R^2 v^2 \cdot \frac{d\tau^2}{dz} + \tau^2 \cdot \frac{d(R^2 v^2)}{dz} \tag{81}$$

in TPGC, $d(R^2 v^2)/dz \neq 0$, and hence $d\sigma^2 \neq R^2 v^2 d\tau^2/dz$. Only when the system is under isothermal conditions and the decompression effects of the carrier gas are neglected are the two definitions in eqns. 77 and 80 equivalent to each other.

Since H_z in eqn. 77 and H_r ($= H_R$ for $k = $ constant in eqn. 76) have the same form of definitions (only for different column lengths), an expression for H_z can then be deduced from that for H_r just as that for $\Delta_s M_{2z}$ in eqn. 44 and M_{2r}^{the} in eqn. 42. However, the expression for H_z' in eqn. 80 cannot be deduced from that for H_r; because of their different definitions they are only related in form by the following relationship [1,7,8], which cannot be used for practical calculations:

$$H_R = \frac{L}{t_L^2 R_L^2 v_L^2} \int_0^L H_z' dz \tag{82}$$

It should be made clear that σ^2 discussed above is different from σ'^2 in the equation

$$H_R = \sum_j \sigma_j'^2 / L \tag{83}$$

where $\sigma_j'^2$ is the variance created by independent dispersion processes (ordinary diffusion, eddy diffussion and local non-equilibrium, etc.) of the whole column. However, σ_i^2 discussed above is the variance for different length intervals, and each

involves the effects created by all independent dispersion processes, so certainly they are not independent of each other, that is,

$$\sigma_L^2 = \sum_j \sigma_j'^2 \tag{84}$$

According to eqn. 76, eqn. 83 is valid only for isothermal processes in which the decompression effects are neglected.

Eqn. 79 is a fundamental equation, that is suitable for both TPGC and isothermal processes. This equation is discussed below.

In isothermal chromatography, the variance in distance at the column end is

$$
\begin{aligned}
\sigma_L^2 &= R_L^2 v_L^2 \tau_L^2 = \int_0^L (v_L/v)^2 \, H_z \mathrm{d}z \\
&= \int_0^L (P/P_o)^2 \, H_z \mathrm{d}z = \int_0^L [\alpha^2 - (\alpha^2 - 1)z/L]H_z \mathrm{d}z
\end{aligned}
\tag{85}
$$

This result is the same as that derived by Giddings *et al.* [19]. Under this condition, we have

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = [\alpha^2 - (\alpha^2 - 1)z/L]H_z \tag{86}$$

In TPGC, the variance in distance at the column end is

$$\sigma_L^2 = R_L^2 v_L^2 \int_0^L \frac{H_z}{R^2 v^2} \cdot \mathrm{d}z \tag{87}$$

which is equivalent to

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = R_L^2 \, v_L^2 \cdot \frac{H_z}{R^2 v^2} \tag{88}$$

Obviously, only for isothermal processes and when the decompression effects of the carrier gas are neglected does

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = H_z \tag{89}$$

when H_z is equal to H_z'.

Calculations of plate height and peak variance

A theoretical expression for the plate height for the whole column can be written as

$$H_r^{\text{the}} = A + B \cdot \frac{D_g(\bar{v})}{\bar{v}} + C \cdot \frac{v}{D_g(\bar{v})} + D\bar{v} \tag{90}$$

The local plate height, H_z, will be ($\bar{v} \to v$ in eqn. 90)

$$H_z = A + B \cdot \frac{jD_{gT}}{\bar{v}} + C \cdot \frac{\bar{v}}{jD_{gT}} + Dv \tag{91}$$

The observed plate height in TPGC can then be calculated by eqn. 79.

The observed plate height under appropriate isothermal conditions can be derived as

$$H_r^{obs} = \left(A + B \cdot \frac{j \, D_{gT}}{\bar{v}} + C \cdot \frac{\bar{v}}{jD_{gT}} \right) \varphi_2 + D\bar{v} \tag{92}$$

which was also derived by Giddings *et al.* [19].

The appropriate expressions for peak variance are as follows:

$$M_{2r}^{the} = \frac{M_{1r}^2 H_r^{the}}{L} = \frac{L \, H_r^{the}}{R^2 v'^2} \tag{93}$$

$$M_{2R} = \int_{(0)}^{(L)} dM_2 = \int_0^L \frac{H_z}{R^2 v^2} \cdot dz = \int_0^{t_R} \frac{H_z}{Rv} \cdot dt \tag{94}$$

$$M_{2r}^{obs} = \frac{L \, H_r^{obs}}{R^2 \bar{v}^2} \tag{95}$$

The above illustrates that discussions based on plate height and peak variance are equivalent for calculations.

As an example, for a capillary, we outline the procedures for the calculation of plate height and peak variance in TPGC. Under these conditions, eqn. 90 becomes the Golay equation. Substituting

$$A = 0$$
$$BD_{gT} = B_c T^{1.75}$$
$$\frac{C}{D_{gT}} = C_c \cdot \frac{1 + 6k + 11k^2}{(1+k)^2} \cdot \frac{1}{T^{1.75}}$$
$$D = D_c \cdot \frac{k}{(1+k)^2}$$

into eqn. 92, and regressing to more than three different isothermal data, the regression coefficients B_c, C_c and D_c can be determined. Substituting them into eqns. 91, 79 and 94, the plate height and peak variance in TPGC can then be calculated.

The plate height and peak variance can also be calculated based on other formulations for $H(T,v)$; for example, the deWet and Pretorius [20] formulation may be used for such a purpose.

DISCUSSION

For the Van Deemter equation, some contradictions occur between theory and experiment. For example, experimentally the term A in H may be negative [21,22], and H–v plot as different curves for columns of different length [23]. The reasons may be as follows. $W_{\frac{1}{2}}^2$ is used to replace M_2 and peaks are assumed to be symmetrical; pressure decompression effects are not considered, especially for long columns; extra-column effects are neglected; the systems are not homogeneous; the systems are not linear; and the relationships between H and other factors (v,k,L,D_g, etc.) are only approximately correct.

In practice, extra-column effects generally exist and further it is difficult to determine higher order moments correctly [12–15], so these factors must be considered during confirmation of the theory just developed.

From the above considerations, in TPGC retention time can be calculated by eqn. 15 and peak variance by eqn. 94, 46 or 66. The third central moment can be calculated by eqn. 56 or 67. Plate height and higher order moments can also be calculated by appropriate expressions just developed. The trace for the moving zone position at any moment in time is given by eqn. 20. From these, optimization procedures can then be carried out for TPGC, that is, the optimum initial temperature and heating rate for any temperature programme under the conditions of a given sample and a given column can be predicted according to isothermal data.

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