Journal of Chromatography, 100 (1974) 1–9
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CHROM. 7748

MOMENT VECTORS IN LINEAR GAS CHROMATOGRAPHY

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(Received May 24th, 1974)

SUMMARY

The concept of a moment vector is introduced into the theoretical treatment of linear chromatography for convenience in mathematical manipulations. As the moment vector is defined by terms of the first to the fourth cumulants as its elements, additivity can be established between the moment vectors of input distribution, column, and output breakthrough curve. The column moment vector, which is particular to an individual chromatographic system, is given by an integral of the differential moment vector as a function of the column length coordinate for the case where the parameters describing the column characteristics have certain variations down the column. It is found that the column moment vector can be expressed as the product of a matrix and a vector, *viz.*, $M_c = AU$, where A is a (4×7) matrix and U is a vector with seven dimensions for a linear chromatographic system. This equation is applied to two different types of chromatography: one in which matrix A is independent of the column length coordinate and the pressure drop effect on the carrier gas velocity cannot be neglected, and the other in which matrix A depends on the coordinate, for instance with a gradient-loaded column that has a systematic variation of the distribution ratio down the column.

INTRODUCTION

In the development of chromatographic theory, the chromatographic process has been investigated by analogy with the processes of a multi-stage distillation and/or a counter-current distribution, so that the mathematical expressions and even the technical terms of chromatography were derived from these processes and the number of the theoretical plates was regarded as one of the most important quantities[1]. On the other hand, many workers have recently appreciated the use of statistical moments for the mathematical treatment of chromatographic theory[2–10]. In these cases, the conventional chromatographic quantities such as peak area, retention time, plate height, number of theoretical plates and resolution have been related to the statistical moments in the forms

$$S = M_0 \tag{1}$$

$$t_r = M_1' \tag{2}$$

$$N = (M_1')^2/M_2 \tag{3}$$

$$H = L\,M_2/(M_1')^2 \tag{4}$$

$$R = |{}^1M_1' - {}^2M_1'|\,/\,4(\sqrt{{}^1M_2} + \sqrt{{}^2M_2}) \tag{5}$$

where the superscript numerals in eqn. 5 specify the solutes.

It may follow from the above equations that all the conventional quantities involve at most the second statistical moments. However, the use of higher moments added the following newly defined quantities to the conventional quantities:

$$H' = L^2M_3/(M_1')^3 \tag{6}$$

$$H'' = L^3\,[M_4 - 3\,(M_2)^2]/(M_1')^4 \tag{7}$$

These quantities were first introduced by Grubner *et al.*[2], but H'' is defined differently here. Both H' and H'', which we can temporarily call "the second and the third plate heights", respectively, in distinction from the ordinary plate height, are independent of the column length, L, and it is desirable that they should be as close as possible to zero for the optimum column conditions, as well as H. With these new quantities, we can describe column performance more precisely. In this paper, we first introduce the concept of a moment vector, which was suggested by the known equations of statistical moments for some chromatographic systems, and then apply it to determine the effect of pressure drop on the statistical moments and the efficiencies of gradient-loaded columns that have a systematic variation of the distribution ratio down the column.

MOMENT VECTORS

First we define the moment vector as

$$M = \begin{bmatrix} M_1' \\ M_2 \\ M_3 \\ M_4 - 3\,(M_2)^2 \end{bmatrix} \tag{8}$$

where each element is called cumulant. The zeroth moment is not included here because it is significant only for the case where the chemical reaction takes place in the column. From the well known relationship between the statistical moments and a distribution function, f(t), it follows that

$$M = \lim_{s \to 0} \begin{bmatrix} -\partial/\partial s \\ \partial^2/\partial s^2 \\ -\partial^3/\partial s^3 \\ \partial^4/\partial s^4 \end{bmatrix} \ln\,[\int_0^\infty e^{-st}\,\mathrm{f}(t)\,\mathrm{d}t] \tag{9}$$

where s is a complex variable.

In a linear gas chromatographic system, a function describing a breakthrough curve, $f_0(t)$, is given as the convolution of an input distribution, $f_i(t)$, and a column characteristic function, $f_c(t)$:

$$f_0(t) = f_c * f_i(t) = \int_0^t f_c(t-\tau)\, f_i(\tau)\, d\tau \qquad (10)$$

In the case where the input function is Dirac's δ function,

$$f_0(t) = f_c * \delta(t) = f_c(t) \qquad (11)$$

From eqns. 9 and 10, it follows that the moment vectors have the relationship

$$M_0 = M_c + M_i \qquad (12)$$

Starting from the basic mass balance equations, many workers have calculated the statistical moments for various chromatographic systems. In those works, two types of boundary conditions were employed (for instance, see eqns. 8 and 9 in ref. 7). In type I, the input amount is regarded as a pulse in time domain, *i.e.*, $f_i(t) = \delta(t)$ (see also eqn. 20 in this paper), and in type II, a pulse in the column coordinate domain, *i.e.*, $f_i(z) = \delta(z)$. Kučera[6] set the type II of boundary condition for the case of gas chromatography, while Grubner *et al.*[2] assumed that in gas–solid chromatography the terms with higher power of D (diffusion coefficient) and u (carrier gas velocity) in the moment equations could be neglected. This assumption leads to the same results for the moments as are obtained under the type I condition. Thus, we take the type I condition in the present paper. The statistical moments of output quantity, higher ones inclusive, calculated according to type II, involve surplus terms added to those calculated according to type I (for instance, see eqns. 39–42 in ref. 7). Such terms, of course, do not appear if type I is employed. Moreover, such a cross term in the fourth moment, as shown by Kočiřík in eqn. 27 in his paper[7], is cancelled out by the term $3(M_2)^2$ in eqn. 8 in this paper. Thus, eqn. 12 is valid as far as type I considered.

By applying the above discussion to a small segment of the column in the same manner as stated by Giddings[1], the following relationship may be obtained for linear chromatography under the type I condition:

$$\Delta M_c \propto \Delta z \qquad (13)$$

where ΔM_c and Δz are the column moment vector and the length of a small segment of column, respectively.

If we take V_c as a proportional coefficient:

$$\Delta M_c = V_c \Delta z \qquad (14)$$

then the total column moment vector is given as the sum of ΔM_c according to the additivity of the cumulant:

$$M_c = \sum_{i=1}^{n} V_{c,i} \Delta z_i \qquad (15)$$

where n is the total number of the small segments. If V_c is continuous with respect to z over the whole column length, L, then it is possible to transcribe eqn. 15 to

$$M_c = \int_0^L V_c \, dz \tag{16}$$

Hereafter V_c will be called the "differential moment vector".

From the literature dealing with statistical moments in linear chromatography, V_c can be given as a power series of the reciprocal of the carrier gas velocity, u. Thus it may be convenient to express V_c as the product of a matrix and a vector:

$$V_c = A\,U \tag{17}$$

From eqns. 16 and 17:

$$M_c = \int_0^L A\,U \, dz \tag{18}$$

In order to show the examples of matrix A and vector U, we now consider the following set of equations describing the mass balance in a linear chromatographic system[4]:

$$\frac{\partial C}{\partial t} + u \cdot \frac{\partial C}{\partial z} = D \cdot \frac{\partial^2 C}{\partial z^2} - \frac{\alpha}{\varepsilon}(K\,C - C_s) \tag{19}$$

$$\frac{\partial C_s}{\partial t} = \alpha\,(K\,C - C_s) \tag{20}$$

with the type I boundary condition,

$$\begin{aligned} &C(t,0) = \delta(t),\ C(0,z) = 0,\ C(t,\infty) = 0 \\ &C_s(t,0) = 0,\ C_s(0,z) = 0 \end{aligned} \tag{21}$$

where the longitudinal diffusion coefficient, D, is equated to $\gamma D_g + \lambda d_p u$.

From the solution obtained by the Laplace transform of eqn. 19, the first ordinary moment and the second to fourth central moments are calculated in a general way. The moment vector thus obtained is then separated into matrix A and vector U, giving the results

$$A = (a_{ij});\ i = 1, \ldots, 4;\ j = 1, \ldots, 7 \tag{22}$$

where

$$\begin{aligned} a_{11} &= 1 + k \\ a_{21} &= 2k/\alpha \\ a_{22} &= 2\lambda d_p (1 + k)^2 \\ a_{23} &= 2\gamma D_g (1 + k)^2 \\ a_{31} &= 6k/\alpha^2 \\ a_{32} &= 12k\,(1 + k)\,\lambda d_p/\alpha \end{aligned}$$

$$
\begin{aligned}
a_{33} &= 12\,(1+k)\,[(1+k)^2\,(\lambda d_p)^2 + k\gamma D_g/\alpha] \\
a_{34} &= 24\,(1+k)^3\,\gamma D_g\,\lambda d_p \\
a_{35} &= 12\,(1+k)^3\,(\gamma D_g)^2 \\
a_{41} &= 24k/\alpha^3 \\
a_{42} &= 24k\,(3k+2)\,\lambda d_p/\alpha^2 \\
a_{43} &= 24k\,[6\,(1+k)^2\,(\lambda d_p)^2 + \gamma D_g\,(3k+2)/\alpha]/\alpha \\
a_{44} &= 24\lambda d_p\,(1+k)^2\,[5\,(1+k)^2\,(\lambda d_p)^2 + 12k\gamma D_g/\alpha] \\
a_{45} &= 72\gamma D_g\,(1+k)^2\,[5\,(1+k)^2\,(\lambda d_p)^2 - 2k\gamma D_g/\alpha] \\
a_{46} &= 360\,(1+k)^4\,(\gamma D_g)^2\,\lambda d_p \\
a_{47} &= 120\,(1+k)^4\,(\gamma D_g)^3
\end{aligned}
$$

and $a_{ij} = 0$ for $2i - 1 < j$.

$$
U = \begin{vmatrix} u^{-1} \\ u^{-2} \\ u^{-3} \\ u^{-4} \\ u^{-5} \\ u^{-6} \\ u^{-7} \end{vmatrix} \qquad (23)
$$

where u is linear velocity of carrier gas flow.

The number of elements of the vector U is at most seven, provided that type I is employed, while there appears a term u^{-8} when type II is used, as shown in ref. 8. For a homogeneous column, matrix A becomes independent of z, and then

$$
M_c = A \int_0^L U\,\mathrm{d}z \qquad (24)
$$

In the case where the pressure drop is negligible and column characteristic parameters such as diffusion coefficient, D, distribution ratio, k, mass transfer coefficient, α, etc., which are involved in the elements of matrix A, have certain variation down the column,

$$
M_c = \int_0^L A\,\mathrm{d}z \cdot U \qquad (25)
$$

In the following sections, the effect of pressure drop on the plate height, the second and the third plate heights (see eqns. 6 and 7) inclusive, are discussed with the help of eqn. 24, and the efficiency of gradient-loaded columns that have systematic variations of the distribution ratio with respect to z is discussed by using eqn. 25.

EFFECT OF PRESSURE DROP ON THE PLATE HEIGHT

From the well known equations

$$
\mathrm{d}P/\mathrm{d}z = -C_p\,u \qquad (26)
$$

$$
P\,u = P_0\,u_0 \qquad (27)
$$

it follows readily that M_c can be related in a general way to the pressure-corrected carrier gas velocity vector, U_p, in the form

$$M_c = A\,U_p\,L \tag{28}$$

where

$$U_p = \begin{bmatrix} P_1/u_0 \\ P_2/u_0^2 \\ P_3/u_0^3 \\ P_4/u_0^4 \\ P_5/u_0^5 \\ P_6/u_0^6 \\ P_7/u_0^7 \end{bmatrix} \tag{29}$$

and

$$P_j = \frac{2}{j+2}\cdot\frac{(P_I/P_O)^{j+1}-1}{(P_I/P_O)^2-1};\quad j = 1, \ldots, 7 \tag{30}$$

and P_I/P_O is the ratio of inlet and outlet pressures. Thus, according to eqns. 2 and 4, retention time and plate height are given, respectively, by

$$t_r = a_{11}\,P_1\,L/u_0 \tag{31}$$

and

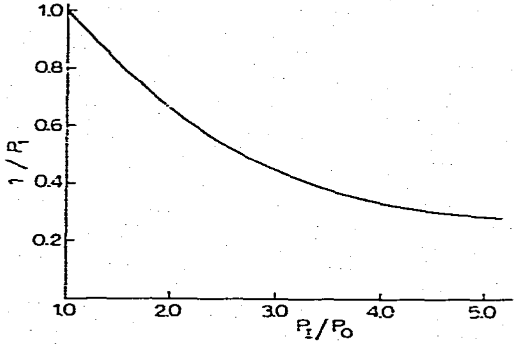
$$H = \frac{a_{21}}{(a_{11})^2}\cdot\frac{u_0}{P_1} + \frac{a_{22}}{(a_{11})^2}\cdot\frac{P_2}{(P_1)^2} + \frac{a_{23}}{(a_{11})^2}\cdot\frac{P_3}{(P_1)^2}\cdot\frac{1}{u_0} \tag{32}$$

Eqn. 32 corresponds to the pressure-corrected Van Deemter equation. Giddings[1] and Underhill[9] presented a similar equation in which the A and B terms in Van Deemter's equation were corrected in combination, not separately. Thus, the correction factor, $P_3/(P_1)^2$, in the last term on the right-hand side of eqn. 32 is first introduced in this paper. Figs. 1, 2 and 3 illustrate $1/P_1$, $P_2/(P_1)^2$ and $P_3/(P_1)^2$ as functions of P_I/P_O respectively. It follows from Figs. 1 and 2 that $P_2/(P_1)^2$ shows only a slight increase with P_I/P_O, while the magnitude of the increase in $P_3/(P_1)^2$ is comparable with that in P_I/P_O. The factor $1/P_1$ in Fig. 3, however, shows a marked decrease with increase in P_I/P_O, *i.e.*, $1/P_1$ contributes to the plate height in a contrary manner to $P_2/(P_1)^2$ and $P_3/(P_1)^2$. The second and the third plate heights defined by eqns. 6 and 7 are also corrected by the pressure drop:

$$\begin{aligned} H' = {} & \frac{a_{31}}{(a_{11})^3}\cdot\frac{u_0^2}{(P_1)^2} + \frac{a_{32}}{(a_{11})^3}\cdot\frac{P_2}{(P_1)^3}\cdot u_0 + \frac{a_{33}}{(a_{11})^3}\cdot\frac{P_3}{(P_1)^3} \\ & + \frac{a_{34}}{(a_{11})^3}\cdot\frac{P_4}{(P_1)^3}\cdot\frac{1}{u_0} + \frac{a_{35}}{(a_{11})^3}\cdot\frac{P_5}{(P_1)^3}\cdot\frac{1}{u_0^2} \end{aligned} \tag{33}$$

$$H'' = \frac{a_{41}}{(a_{11})^4}\cdot\frac{u_0^3}{(P_1)^3} + \frac{a_{42}}{(a_{11})^4}\cdot\frac{P_2}{(P_1)^4}\cdot u_0^2 + \frac{a_{43}}{(a_{11})^4}\cdot\frac{P_3}{(P_1)^4}\cdot u_0$$
$$+ \frac{a_{44}}{(a_{11})^4}\cdot\frac{P_4}{(P_1)^4} + \frac{a_{45}}{(a_{11})^4}\cdot\frac{P_5}{(P_1)^4}\cdot\frac{1}{u_0} +$$
$$+ \frac{a_{46}}{(a_{11})^4}\cdot\frac{P_6}{(P_1)^4}\cdot\frac{1}{u_0^2} + \frac{a_{47}}{(a_{11})^4}\cdot\frac{P_7}{(P_1)^4}\cdot\frac{1}{u_0^3} \qquad (34)$$

Grubner *et al.*[2] used these quantities (Z and F in his work) for the experimental verification of his theory without taking account of the effect of pressure drop on the statistical moments. However, eqns. 33 and 34 still indicate the necessity of the pressure drop correction for these quantities.



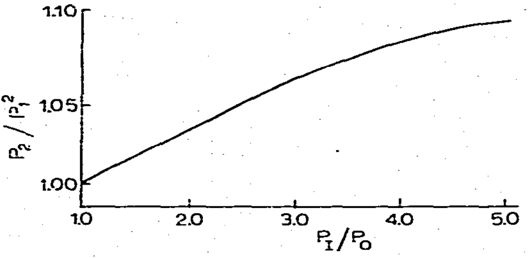


Fig. 1. Plot of $1/P_1$ *versus* P_I/P_O.

Fig. 2. Plot of $P_2/(P_1)^2$ *versus* P_I/P_O.

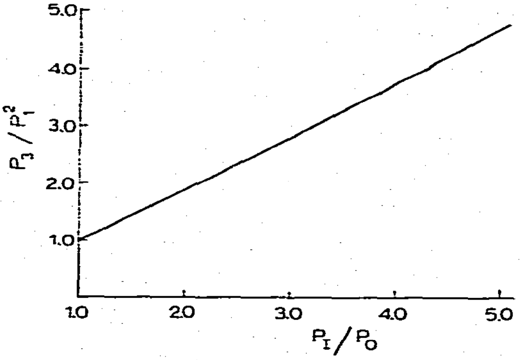


Fig. 3. Plot of $P_3/(P_1)^2$ *versus* P_I/P_O.

EFFICIENCIES OF GRADIENT-LOADED COLUMNS

To illustrate the simplicity of the moment vector expression, we now consider the efficiencies of gradient-loaded columns. The gradient-loaded column, which was first discussed by Meloan and co-workers[11,12], has a certain systematic gradient (linear or exponential) in the distribution ratio k. In such a case, matrix A is a function of z, and M_c can be calculated according to eqn. 25 if the pressure drop is negligible. On the other hand, for the classical column, which involves no such gradient in k, matrix A becomes constant. For the classical column, retention time and the second central moment are given by substituting eqns. 22 and 23 into eqn. 25:

$$t_r^C = L(1+k)/u \tag{35}$$

$$M_2^C = 2Lk_c/\alpha u + 2L(\gamma D_g + \lambda d_p u)\,(1+k_c)^2/u^3 \tag{36}$$

For the gradient-loaded column, k is a function of z, and then similarly

$$t_r^G = \int_0^L (1+k)\,\mathrm{d}z \tag{37}$$

$$M_2^G = 2\int_0^L k\,\mathrm{d}z/\alpha u + 2(\gamma D_g + \lambda d_p u)\int_0^L (1+k)^2\,\mathrm{d}z/u^3 \tag{38}$$

Putting eqn. 35 equal to eqn. 37 in order to compare the efficiencies of both columns which give the same retention time ($t_r^C = t_r^G$) for a given solute,

$$k_c = \int_0^L k\,\mathrm{d}z/L \tag{39}$$

Then, from eqns. 36, 38 and 39,

$$M_2^G - M_2^C = 2L(\gamma D_g + \lambda d_p u)\left[\int_0^L (1+k)^2\,\mathrm{d}z/L - \left\{\int_0^L (1+k)\,\mathrm{d}z/L\right\}^2\right]/u^3 \tag{40}$$

Since Schwartz's inequality proves that the quantity in brackets on the right-hand side of the above equation is always positive,

$$M_2^G > M_2^C \tag{41}$$

It follows from eqns. 4 and 41 that the plate height of a given solute is always larger for the gradient-loaded column than for the classical column if the solute has the same retention time for both columns. Next we consider the resolution of two peaks which are eluted closely next to each other. In such a case, the numerators of eqn. 5 for both columns are almost equal, while the denominator for the gradient-loaded column is obviously larger than that for the classical column, which suggests that the gradient-loaded column gives a worse resolution than the classical column. The foregoing discussion involves the implicit assumption that the gas-phase mass transfer coefficient, α, is independent of k. However, even in the case where α is related to k in the form[13]

$$\alpha^{-1} = c_1\, d_l^2/D_l + c_2\, k\, d_p^2/D_g \tag{42}$$

it will be readily found that an inequality similar to eqn. 41 can be established by substituting eqn. 42 into eqns. 36 and 38. It is understandable from the above discussion that the gradient-loaded column has no special merit for column efficiencies and that the stationary phase should be packed in a column as homogeneously as possible for good column performance.

LIST OF SYMBOLS

L = column length
u = linear velocity of carrier gas
u_0 = linear velocity of carrier gas at column outlet
S = peak area
t_r = retention time
N = number of theoretical plates
R = resolution
H = plate height
H' = second plate height
H'' = third plate height
M_0 = zeroth moment
M_1' = first normal moment
M_n = nth central moment
z = column length coordinate
t = time
C_p = permeability constant
P_j = pressure correction factor
C = solute concentration in mobile phase
C_s = solute concentration in stationary phase
K = distribution coefficient
ε = volume ratio of stationary phase to mobile phase
k = distribution ratio ($= K/\varepsilon$)
D = effective diffusion coefficient in mobile phase
α = mass transfer coefficient
λ = constant concerning regularity of column packing
d_p = average particle diameter of column packing
D_g = molecular diffusion coefficient
P_i = column inlet pressure
P_0 = column outlet pressure
d_l = thickness of stationary phase
D_l = diffusion coefficient in stationary phase
c_1, c_2 = constants

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