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MOMENTS ANALYSIS IN NON-LINEAR CHROMATOGRAPHY

III. THE THIRD MOMENT

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SUMMARY

An approximate expression for the third statistical moment in non-linear chromatography is derived in terms of a series expansion in the non-linearity parameter λC_1. The trends predicted by this model correlate satisfactorily with the results of a computer simulation of the problem.

INTRODUCTION

Skewed peaks is a phenomenon characteristic of non-linear chromatography (*e.g.*, ref. 1); a non-zero value for the third statistical moment, α_3, of a concentration distribution is indicative of the presence of skewness (*e.g.*, ref. 2). It follows that the availability of a mathematical formulation for α_3 in non-linear chromatography would be of importance in the description of this type of chromatogram. This paper is concerned with the mathematical development of such an expression, and a complete list of the symbols used is given at the end of the paper.

THE THEORETICAL MODEL

The mathematical technique used to obtain an expression for the third statistical moment, α_3, defined by

$$\alpha_3 = \frac{1}{m_0} \int_{-\infty}^{+\infty} (z - \langle z \rangle)^3 C \, dz \tag{1}$$

is analogous to that used for the generation of the lower moments[3,4], namely, the application of the third moment operator

$$\frac{1}{m_0} \int_{-\infty}^{+\infty} (z - \langle z \rangle)^3 \, dz \tag{2}$$

to the basic differential equation describing mobile phase mass transport[3]:

$$\frac{\partial C}{\partial t} = -\frac{U}{1+\lambda C}\cdot\frac{\partial C}{\partial z} + \frac{D_e}{1+\lambda C}\cdot\frac{\partial^2 C}{\partial z^2} \tag{3}$$

This results in

$$\frac{d\alpha_3}{dt} = -I + J - \frac{\alpha_3}{m_0}\cdot\frac{dm_0}{dt} - 3\sigma^2\cdot\frac{d\langle z\rangle}{dt} \tag{4}$$

where

$$I = \frac{U}{m_0}\int_{-\infty}^{+\infty}\frac{(z-\langle z\rangle)^3}{1+\lambda C}\cdot\frac{\partial C}{\partial z}\cdot dz \tag{5}$$

$$J = \frac{D_e}{m_0}\int_{-\infty}^{+\infty}\frac{(z-\langle z\rangle)^3}{1+\lambda C}\cdot\frac{\partial^2 C}{\partial z^2}\cdot dz \tag{6}$$

$\lambda = 2k_2/(1+k_1)$ is the non-linearity parameter, where k_1 and k_2 are defined by the non-linear isotherm

$$n = \varepsilon k_1 C + \varepsilon k_2 C^2$$

A series expression for $d\alpha_3/dt$ (for $|\lambda C| < 1$) can be obtained from eqns. 4, 5 and 6 by expanding $1/(1+\lambda C)$ in the binomial series

$$\frac{1}{(1+\lambda C)} = \sum_{n=0}^{\infty}(-1)^n(\lambda C)^n \tag{7}$$

When use is made of the fact that C and $\partial C/\partial z$ tend to zero as $z \to \pm\infty$, substitution of eqn. 7 into the above equation, followed by partial integration, yields

$$\frac{d\alpha_3 m_0}{dt} = I_1 + J_1 + J_2 - 3\sigma^2 m_0\cdot\frac{d\langle Z\rangle}{dt} \tag{8}$$

where

$$I_1 = 3U\sum_{n=1}^{\infty}(-1)^n\frac{\lambda^n}{n+1}\int_{-\infty}^{+\infty}(z-\langle z\rangle)^2 C^{n+1}dz \tag{9}$$

$$J_1 = 6D_e\sum_{n=1}^{\infty}(-1)^n\frac{\lambda^n}{n+1}\int_{-\infty}^{+\infty}(z-\langle z\rangle)C^{n+1}dz \tag{10}$$

$$J_2 = D_e\sum_{n=1}^{\infty}(-1)^{n+1}n\lambda^n\int_{-\infty}^{+\infty}(z-\langle z\rangle)^3 C^{n-1}\left(\frac{\partial C}{\partial z}\right)^2 dz \tag{11}$$

$$\langle Z\rangle = \langle z\rangle - Ut \tag{12}$$

An approximate expression for the $d\langle Z\rangle/dt$ in eqn. 8 has been derived previously[3]. In terms of centre-of-mass coordinates

$$\rho = z - \langle z\rangle \tag{13}$$

This is given by

$$\frac{d\langle Z\rangle}{dt} = \frac{U}{m_0}\sum_{n=1}^{\infty}(-1)^n\frac{\lambda^n}{n+1}\int_{-\infty}^{+\infty}C^{n+1}\,d\rho + \frac{D_e}{m_0}\sum_{n=1}^{\infty}(-1)^{n+1}n\lambda^n\int_{-\infty}^{+\infty}\rho C^{n-1}\left(\frac{\partial C}{\partial\rho}\right)^2 d\rho + \frac{D_e}{m_0}\langle z\rangle\sum_{n=1}^{\infty}(-1)^{n+1}n\lambda^n\int_{-\infty}^{+\infty}C^{n-1}\left(\frac{\partial C}{\partial\rho}\right)^2 d\rho - \frac{\langle z\rangle}{m_0}\cdot\frac{dm_0}{dt} \tag{14}$$

with[3]

$$\frac{dm_0}{dt} = D_e\sum_{n=1}^{\infty}(-1)^{n+1}n\lambda^n\int_{-\infty}^{+\infty}C^{n-1}\left(\frac{\partial C}{\partial\rho}\right)^2 d\rho \tag{15}$$

Substitution of eqn. 15 into eqn. 14 gives

$$\frac{d\langle Z\rangle}{dt} = \frac{U}{m_0}\sum_{n=1}^{\infty}(-1)^n\frac{\lambda^n}{n+1}\int_{-\infty}^{+\infty}C^{n+1}\,d\rho + \frac{D_e}{m_0}\sum_{n=1}^{\infty}(-1)^{n+1}n\lambda^n\int_{-\infty}^{+\infty}\rho C^{n-1}\left(\frac{\partial C}{\partial\rho}\right)^2 d\rho \tag{16}$$

The use of centre-of-mass coordinates transforms I_1, J_1 and J_2 into

$$I_1 = 3U\sum_{n=1}^{\infty}(-1)^n\frac{\lambda^n}{n+1}\int_{-\infty}^{+\infty}\rho^2C^{n+1}\,d\rho \tag{17}$$

$$J_1 = 6D_e\sum_{n=1}^{\infty}(-1)^n\frac{\lambda^n}{n+1}\int_{-\infty}^{+\infty}\rho C^{n+1}\,d\rho \tag{18}$$

$$J_2 = D_e\sum_{n=1}^{\infty}(-1)^{n+1}n\lambda^n\int_{-\infty}^{+\infty}\rho^3C^{n-1}\left(\frac{\partial C}{\partial\rho}\right)^2 d\rho \tag{19}$$

An approximate analytical expression for α_3 can now be obtained from the above equations by evaluating the integrals in C by means of the zeroth-order (*i.e*, $\lambda = 0$) solution of eqn. 3 for an equivalent Gaussian inlet[5], namely

$$C = \frac{m_0}{\sqrt{(2\pi\sigma^2)}}\cdot\exp\left(-\frac{\rho^2}{2\sigma^2}\right) \tag{20}$$

where

$$\sigma^2 = 2D_e t + \frac{w_i^2}{2\pi} \tag{21}$$

Instead of regarding the mass per unit mobile phase cross-section, m_0, as being constant, however, a more realistic description can be formulated by using the approximate zeroth-moment expression obtained previously[3]:

$$m_0 = m_i \left\{ 1 + \frac{\lambda C_i}{2\sqrt{2}} \left[1 - \frac{1}{\left(1 + \frac{4\pi D_e t}{w_i^2}\right)^{1/2}} \right] \right\} \tag{22}$$

The σ^2 term in eqn. 8 will, for mathematical convenience, be approximated by eqn. 21.

Substitution of eqn. 20 into the relevant equations above and rearrangement reduces eqn. 8 to

$$\frac{d(\alpha_3 m_0)}{dt} = 3U \sum_{n=1}^{\infty} (-1)^{n+1} \cdot \frac{n\lambda^n m_0^{n+1}}{(n+1)^{5/2}(2\pi)^{n/2}\ \sigma^{n-2}} \tag{23}$$

which contains no explicit diffusion contribution (see J, eqn. 4).

If terms up to third order in λ are retained, substitution of eqns. 21 and 22 into eqn. 23 and subsequent partial integration results in the following approximation for the third moment in non-linear chromatography:

$$\alpha_3 = \frac{\lambda C_i U m_i w_i^4}{(16\sqrt{2})\pi^2 D_e m_0} \left\{ \left[1 + \frac{4\pi D_e t}{w_i^2} \right]^{3/2} - 1 \right\} +$$

$$+ \frac{(\lambda C_i)^2 U m_i w_i^4}{32\pi^2 D_e m_0} \left\{ \left[1 + \frac{4\pi D_e t}{w_i^2} \right]^{3/2} - 1 \right\} -$$

$$- \frac{(9\sqrt{3} + 16)}{(48\sqrt{3})\pi} \cdot \frac{(\lambda C_i)^2 U m_i w_i^2 t}{m_0} - \frac{(3\sqrt{3} + 16)}{(32\sqrt{6})\pi} \cdot \frac{(\lambda C_i)^3 U m_i w_i^2 t}{m_0} +$$

$$+ \frac{(\lambda C_i)^3 U m_i w_i^4}{(128\sqrt{2})\pi^2 D_e m_0} \left\{ \left[1 + \frac{4\pi D_e t}{w_i^2} \right]^{3/2} - 1 \right\} +$$

$$+ \frac{(3\sqrt{2} + 32 + 3\sqrt{6})}{(128\sqrt{6})\pi^2} \cdot \frac{(\lambda C_i)^3 U m_i w_i^4}{D_e m_0} \left\{ \left[1 + \frac{4\pi D_e t}{w_i^2} \right]^{1/2} - 1 \right\} \tag{24}$$

For comparative purposes, eqn. 24 is rewritten in the following dimensionless form:

$$\alpha_3' = \frac{\alpha_3}{(\lambda C_i)Utw_i^2}$$

$$= \frac{m_i}{(4\sqrt{2})\pi m_0 y}[(1+y)^{3/2}-1] +$$

$$+ \frac{(\lambda C_i)m_i}{8\pi m_0 y}[(1+y)^{3/2}-1] - \frac{(9\sqrt{3}+16)(\lambda C_i)m_i}{(48\sqrt{3})\pi m_0} -$$

$$- \frac{(3\sqrt{3}+16)(\lambda C_i)^2 m_i}{(32\sqrt{6})\pi m_0} + \frac{(\lambda C_i)^2 m_i}{(32\sqrt{2})\pi m_0 y}[(1+y)^{3/2}-1] +$$

$$+ \frac{(3\sqrt{2}+32+3\sqrt{6})}{(32\sqrt{6})\pi}\cdot\frac{(\lambda C_i)^2 m_i}{m_0 y}[(1+y)^{1/2}-1] \quad (25)$$

where

$$y = \frac{4\pi D_e t}{w_i^2} \quad (26)$$

is the dimensionless time parameter.

MODEL EVALUATION

Eqn. 3 was solved numerically with a digital computer by means of methods described in studies on the lower moments[3,4]. A graphical comparison is presented in Figs. 1–4 for different combinations of λC_1, D_e and w_1 values.

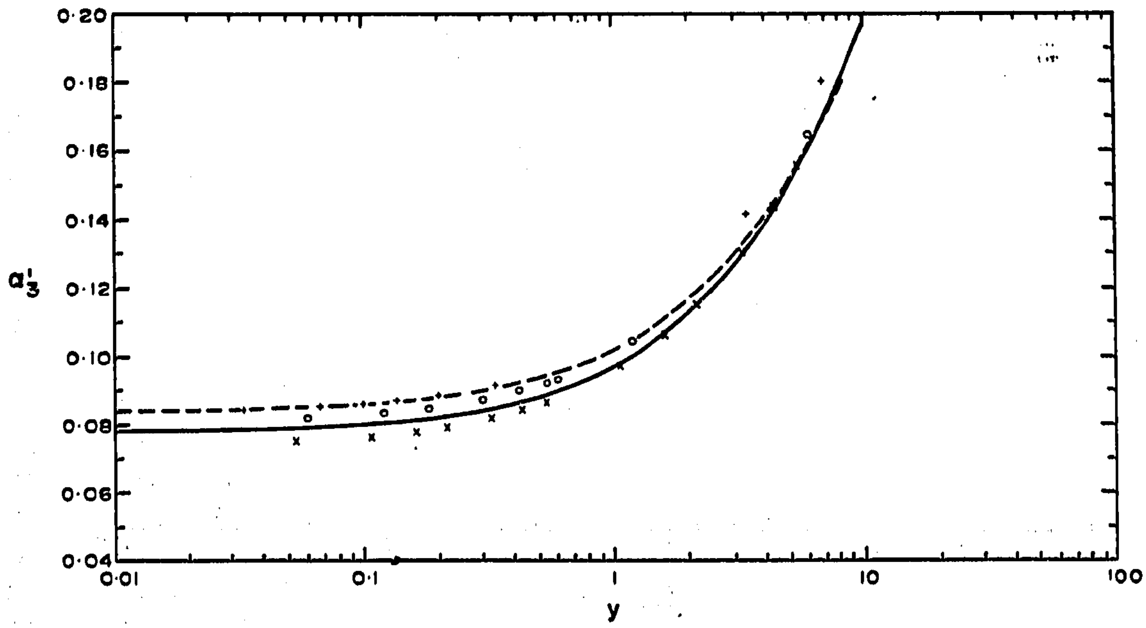

Fig. 1. Illustration of the time-dependence of the third moment. $\lambda C_1 = 0.1$; $u = 1$ cm/sec; $k_1 = 20$. – – – –, First-order approximation; ———, second-order approximation. Simulation results: ×, $D_e = 0.01$, $w_1 = 4.8$; ○, $D_e = 0.110567$, $w_1 = 4.8$; +, $D_e = 0.110567$, $w_1 = 6.4$.

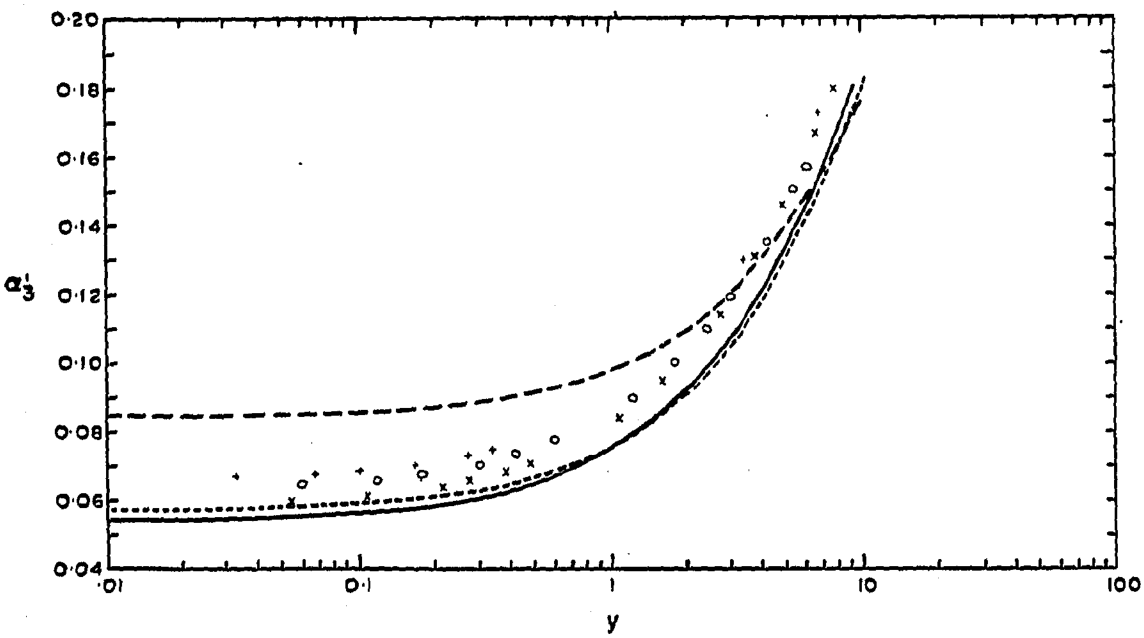

Fig. 2. Illustration of the time-dependence of the third moment. $\lambda C_1 = 0.5$; $u = 1$ cm/sec; $k_1 = 20$. – – – –, First-order approximation; ———, second-order approximation; - - - - -, third-order approximation. Simulation results: ×; $D_e = 0.01$, $w_1 = 4.8$; ○, $D_e = 0.110567$, $w_1 = 4.8$; +, $D_e = 0.110567$, $w_1 = 6.4$.

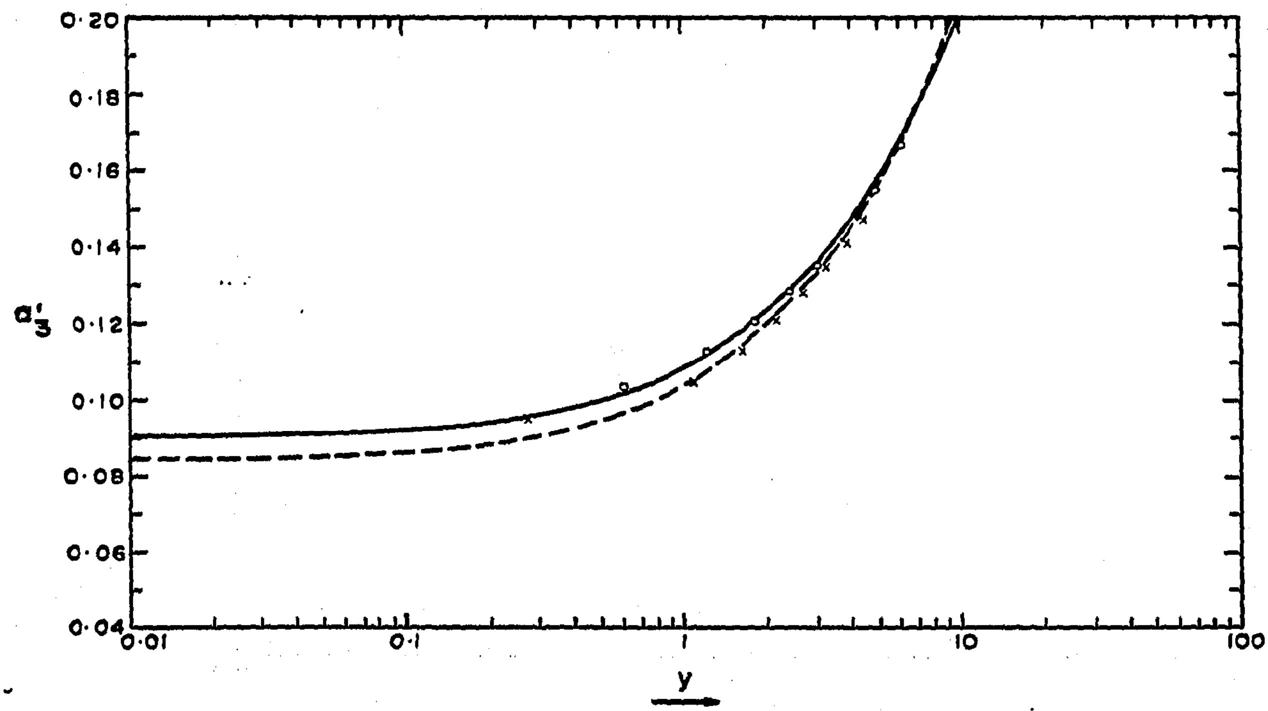

Fig. 3. Illustration of the time-dependence of the third moment. $w_1 = 4.8$; $\lambda C_1 = -0.1$; $u = 1$ cm/sec; $k_1 = 20$. – – – –, First-order approximation; ———, second-order approximation. Simulation results: ×, $D_e = 0.01$; ○, $D_e = 0.110567$.

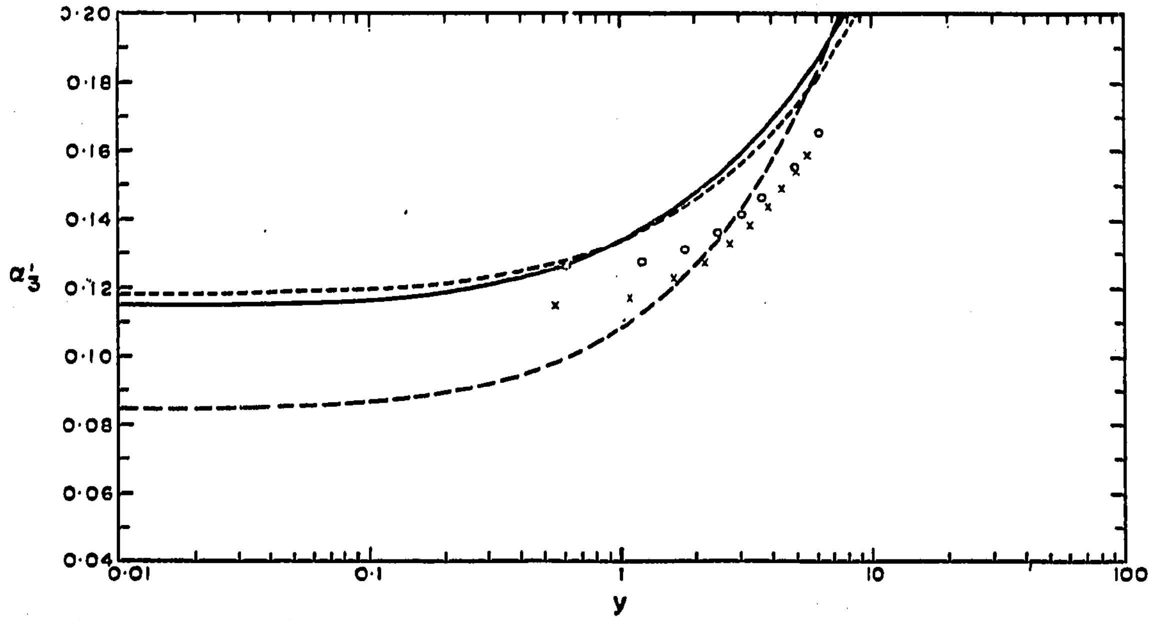

Fig. 4. Illustration of the time-dependence of the third moment. $w_l = 4.8$; $\lambda C_l = -0.5$; $u = 1$ cm/sec; $k_1 = 20$. – – – –, First-order approximation; ———, second-order approximation; - - - - -, third-order approximation. Simulation results: ×, $D_e = 0.01$; ○, $D_e = 0.110567$.

The general trends are seen to be satisfactorily predicted by the theoretical model; although deviations become larger as $|\lambda C_l|$ increases, terms of higher than second order will normally not be required. The observed dependence of α'_3 on D_e, which is not predicted by the model is probably due to a transient inlet effect and is not considered to be sufficiently significant to merit further investigation.

SYMBOLS

C = mass of solute per unit mobile phase volume
C_l = value of C at $t = 0$ at the inlet
D_e = $D_p/(1 + k_1)$
D_p = effective diffusion coefficient
I = convenient parameter, eqn. 5
I_1 = convenient parameter, eqn. 9
J = convenient parameter, eqn. 6
J_1 = convenient parameter, eqn. 10
J_2 = convenient parameter, eqn. 11
k_1 = parameter in adsorption isotherm
k_2 = parameter in adsorption isotherm
m_0 = zeroth moment
m_l = mass of solute per unit cross-section of the mobile phase at inlet at time $t = 0$
n = mass of solute adsorbed per unit column volume
t = time
U = $u/(1 + k_1)$
u = carrier flow velocity
w_l = width of plug inlet sample profile

y = $4\pi D_e t/w_1^2$; dimensionless time parameter
z = axial coordinate
$\langle z \rangle$ = first moment of concentration–distance distribution
Z = $z - Ut$; relative axial coordinate
$\langle Z \rangle = \langle z \rangle - Ut$

Greek symbols
α_3 = third central moment of concentration–distance distribution
α'_3 = dimensionless third- moment parameter (eqn. 25)
ε = void fraction
λ = non-linearity parameter
ρ = $z - \langle z \rangle$; centre-of-mass coordinate
σ^2 = total variance

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