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STATISTICAL MOMENTS IN LINEAR EQUILIBRIUM CHROMATOGRAPHY

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SUMMARY

The statistical moments of a chromatogram are calculated for the case of a linear equilibrium chromatographic system. For the calculation of the moments, Simpson's rule is adopted to digitize an experimental chromatogram. The parameters that characterize the shape of a chromatogram, such as the mean, relative variance, skewness and excess, are related to the statistical moments. The relationships obtained in this case predict that the skewness and the excess parameters, which should be essentially independent of each other, have a certain functional relationship with the relative variance. This was ascertained experimentally.

INTRODUCTION

There have been many attempts to draw as much information as possible from a chromatogram. Recently, many workers have been interested in the investigation of the statistical moments of a chromatogram[1–9], regarding it as a statistical distribution curve, because the statistical moments have been related to the parameters that are characteristic of an individual chromatogram. Of these moments, the first normal moment, M_1', which represents the retention time of a given solute, and the second central moment, M_2, are related to the height equivalent to a theoretical plate (HETP) by the equation $H = LM_2/(M_1')^2$, where L is the column length, and the third and the fourth moments relate to the shape of a chromatogram, the extent of distortion and sharpness.

In a previous paper[10], we reported the application of the numerical Laplace transform method to the evaluation of these moments from an experimental chromatogram. This paper deals with the third and the fourth moments, which are obtained both theoretically and experimentally in the case of a linear equilibrium chromatographic system, and it is shown that the parameters of distortion and sharpness of a chromatogram are not independent of each other and have a simple relationship with the relative variance.

THEORETICAL

In a linear equilibrium chromatographic system, the following mass balance has been established[11,12]:

$$(1 + k)\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - u\frac{\partial C}{\partial z} \tag{1}$$

where k is the distribution ratio, C is the concentration of the solute in the gas phase, D is the effective diffusion coefficient, u is the linear velocity of the carrier gas flow and z is the distance along the column from the inlet. If the input amount is provided as a pulse, the initial and the boundary conditions for eqn. 1 are

$$\begin{aligned} C(t,0) &= m\,\delta(t) \\ C(0,z) &= 0 \\ C(t,\infty) &= 0 \end{aligned} \tag{2}$$

where m is the input amount measured by a unit of $\delta(t)$ and $\delta(t)$ is Dirac's delta function.

By defining the Laplace transform of the function $C(t,z)$ in the form

$$\tilde{C}(s,z) = \int_0^\infty e^{-st}\, C(t,z)\, dt \tag{3}$$

the solution of eqn. 1 under the conditions of eqn. 2 is expressed by[12]

$$\tilde{C}(s,z) = m \exp\left\{\left[\frac{u}{2D} - \sqrt{\frac{s}{D}(1 + k) + \left(\frac{u}{2D}\right)^2}\,\right] z\right\} \tag{4}$$

On the other hand, the statistical moments, namely the nth normal moment, M'_n, and the nth central moment, M_n, which are defined by

$$M'_n = \frac{\int_0^\infty t^n\, f(t)\, dt}{\int_0^\infty f(t)\, dt} \tag{5}$$

and

$$M'_n = \frac{\int_0^\infty (t - M'_1)^n\, f(t)\, dt}{\int_0^\infty f(t)\, dt} \tag{6}$$

are related to the parameters of a chromatogram in the form

$$\begin{bmatrix} \mu \\ \sigma^2/\mu^2 \\ \alpha_3 \\ \alpha_4 \end{bmatrix} = \begin{bmatrix} M'_1 \\ M_2/(M'_1)^2 \\ M_3/(M_2)^{1.5} \\ M_4/(M_2)^2 - 3 \end{bmatrix} \tag{7}$$

where μ, σ^2/μ^2, α_3 and α_4 are mean, relative variance, skewness and excess parameters, respectively.

As reported previously[10], the statistical moments of the function $\tilde{C}(s,z)$ are given by

$$\begin{bmatrix} M_1' \\ M_2 \\ M_3 \\ M_4 - 3(M_2)^2 \end{bmatrix} = \lim_{s\to 0} \begin{bmatrix} -\mathrm{d}/\mathrm{d}s \\ \mathrm{d}^2/\mathrm{d}s^2 \\ -\mathrm{d}^3/\mathrm{d}s^3 \\ \mathrm{d}^4/\mathrm{d}s^4 \end{bmatrix} \ln \tilde{C}(s,z) \equiv \boldsymbol{M} \tag{8}$$

where we would call $\boldsymbol{M}$ "moment vector".

Substituting eqn. 4 into eqn. 8:

$$\boldsymbol{M} = \begin{bmatrix} z(1+k)/u \\ 2zD(1+k)^2/u^3 \\ 12zD^2(1+k)^3/u^5 \\ 120zD^3(1+k)^4/u^7 \end{bmatrix} \tag{9}$$

Combining eqn. 7 with eqn. 9:

$$\begin{bmatrix} \mu \\ \sigma^2/\mu^2 \\ \alpha_3 \\ \alpha_4 \end{bmatrix} = \begin{bmatrix} z(1+k)/u \\ 2D/zu \\ 3\sqrt{2D/zu} \\ 30D/zu \end{bmatrix} \tag{10}$$

In a general distribution function, these four parameters are essentially independent of each other. However, as can be seen from eqn. 10, only two parameters are independent in this case; in other words, the skewness and the excess parameters are related to the relative variance in the forms

$$\alpha_3 = 3\sigma/\mu \tag{11}$$

$$\alpha_4 = 15\sigma^2/\mu^2 \tag{12}$$

To ascertain these relationships, the skewness and the excess parameters are calculated by two different ways: one according to eqns. 11 and 12, into which the relative variance obtained from an experimental chromatogram is substituted, and another according to Simpson's rule (see below), which gives accurate values of α_3 and α_4 for the same chromatogram:

$$M_0 = \frac{\Delta t}{3}\left(4\sum_{i=1}^{25} \mathrm{f}_{2i-1} + 2\sum_{i=1}^{25} \mathrm{f}_{2i} - \mathrm{f}_{50}\right) \tag{13}$$

$$M_n' = \frac{\Delta t}{3}\left(4\sum_{i=1}^{25} t_{2i-1}^n\, \mathrm{f}_{2i-1} + 2\sum_{i=1}^{25} t_{2i}^n\, \mathrm{f}_{2i} - t_{50}^n\, \mathrm{f}_{50}\right) \tag{14}$$

$$M_n = \frac{\Delta t}{3}\left(4\sum_{i=1}^{25} (t_{2i-1} - M_1')^n\, \mathrm{f}_{2i-1} + 2\sum_{i=1}^{25} (t_{2i} - M_1')^n\, \mathrm{f}_{2i} - (\mathrm{f}_{50} - M_1')^n\, \mathrm{f}_{50}\right) \tag{15}$$

$$\bar{\alpha}_3 = M_3/(M_2)^{1.5} \tag{16}$$

$$\bar{\alpha}_4 = M_4/(M_2)^2 - 3 \tag{17}$$

The detailed procedure for applying these equations to the experimental chromatogram was described in a previous paper[10].

EXPERIMENTAL

The gas chromatographic conditions employed for the measurement of a chromatogram were as follows:

Apparatus: Hitachi GC Model K23, with a thermal conductivity detector.
Column packing: 20% squalane coated on Chromosorb W (60–80 mesh).
Column: spiral glass tube, 4.5 m × 3 mm.
Column and detector temperatures: 50, 55, 60, 65, 70°.
Sample: cyclohexane (3 μl)

The flow-rate of the carrier gas (helium) was adjusted to 18 ± 0.5 ml/min at all temperatures, so that the equilibrium between the gas and stationary phases could be established quickly, and the pressure drop in the column could be reduced to as small a value as possible. The measured value of the pressure drop, P_t/P_0, was 1.36–1.37. The injection port temperature was adjusted to 140°, which was high enough for the input amount to be regarded as a pulse.

RESULTS AND DISCUSSION

The linearity of the distribution isotherm in this experiment was examined according to the established method[13–15]. The result is satisfactory, as illustrated in Fig. 1. The values of relative variance, σ^2/μ^2, which should be substituted into eqns. 11 and 12, are plotted against the column temperature in Fig. 2, which shows a slight dependence on the temperature. Figs. 3 and 4 compare the values of α_3 and α_4 calcu-

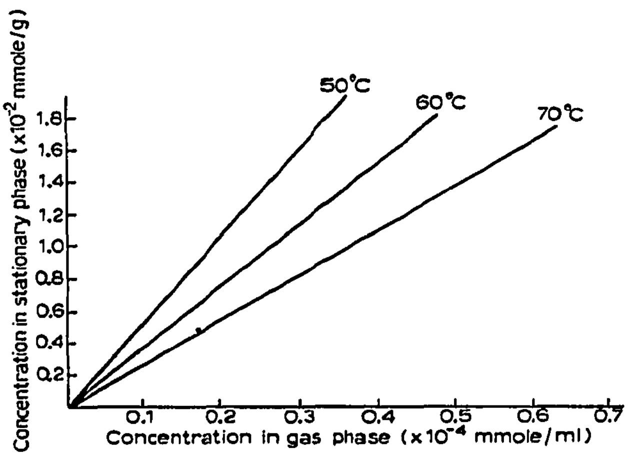

Fig. 1. Distribution isotherms of the squalane–cyclohexane system at 50, 60 and 70°.

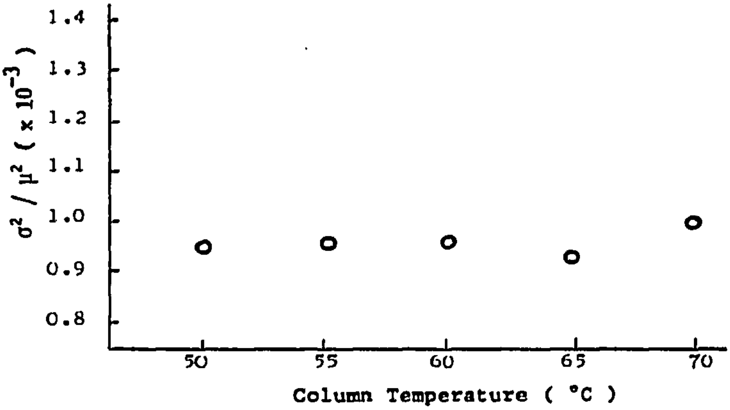

Fig. 2. Plot of σ^2/μ^2 *versus* column temperature.

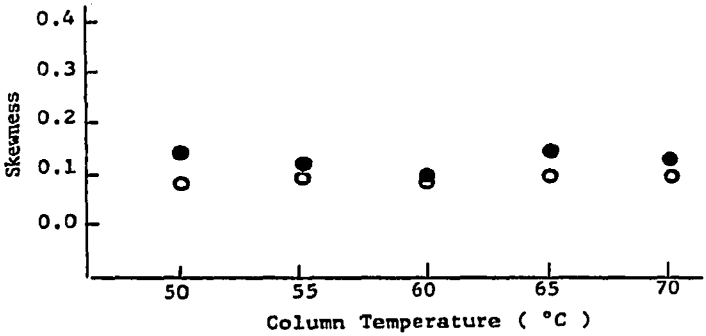

Fig. 3. Plot of α_3 (○) and $\bar{\alpha}_3$ (●) *versus* column temperature.

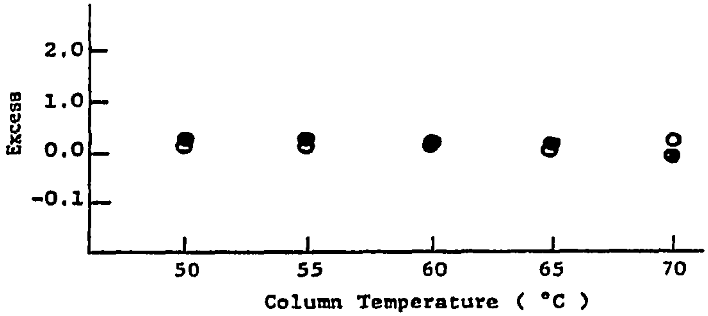

Fig. 4. Plot of α_4 (○) and $\bar{\alpha}_4$ (●) *versus* column temperature.

lated from eqns. 11 and 12 with those of $\bar{\alpha}_3$ and $\bar{\alpha}_4$ from eqns. 16 and 17, respectively. Fig. 3 indicates that the values of $\bar{\alpha}_3$ are larger than those of α_3 at all temperatures, but the differences are small enough to confirm their consistency. The values of the excess parameter α_4, which show a slight scatter as illustrated in Fig. 4, are also found to agree closely with the values of $\bar{\alpha}_4$. The difference between α_4 and $\bar{\alpha}_4$ is acceptable in view of the order of the moment from which α_4 is calculated.

From the above observations, the reliability of eqns. 11 and 12 is confirmed for the linear equilibrium chromatographic system. The present work, dealing with a rather simplified chromatographic system, took no account of the pressure drop in the column, which in general should not be neglected because it has a considerable effect not only on the first moment but also on the higher moments. The theoretical investigation on this aspect will be reported later.

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