and fluometuron—Ciba Ltd.; buturon—B.A.S.F., A.G.; Bayer 43975—Farbenfabriken Bayer A.G.; Benzomarc and Metoxymarc—Péchiney Progil.

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1 J. J. KIRKLAND, *Anal. Chem.*, 34 (1962) 428.
2 W. H. GUTENMANN AND D. J. LISK, *J. Agr. Food Chem.*, 12 (1964) 46.
3 W. H. GUTENMANN AND D. J. LISK, *J. Gas Chromatog.*, 4 (1966) 424.
4 R. W. REISER, *Anal. Chem.*, 36 (1964) 96.
5 D. J. WEBLEY AND C. E. McKONE, *Misc. Rept. 441*, Trop. Pest. Res. Inst., Arusha, Tanzania, 1964.
6 H. G. HENKEL, *J. Chromatog.*, 21 (1966) 307.
7 L. FISHBEIN AND W. L. ZIELINSKI, JR., *J. Chromatog.*, 20 (1965) 9.
8 C. E. McKONE, *Misc. Rept. 536*, Trop. Pest. Res. Inst., Arusha, Tanzania, 1965.

Theory of partition chromatography. V.

In the theory of partition chromatography developed in earlier articles[1-4], the concentration distribution and its moments were expressed as functions of the position coordinates in the column. However, in this form the theory is not applicable to normal experimental conditions, where the concentration is determined as a function of the elution volume. A modification of the theory is therefore desirable and the aim of the present article is to derive relations between the moments of the concentration distribution calculated with respect to the position coordinates in the column and those calculated with respect to the elution volume. As a rule, the notations used here are in agreement with those used in the earlier articles.

To define the problem, we consider specifically a coordinate system fixed in the column, with its x-axis parallel to the axis of the column. We assume that the exit end of the column is at the point $x = a$. We also assume that there is a concentration peak in the column, represented by the distribution function

$$c = f(x,t) \qquad (1)$$

We further introduce a "local" coordinate system "ξ", with its origin fixed at the mean $(x = \mu)$ of the distribution. This coordinate system moves along with the peak at velocity

$$\omega = v\nu \qquad (2)$$

The values of the function $f(x, t)$ at an arbitrary point $x = \mu + \xi$ and at the point $x = a$ are related in the first approximation by the following transformation:

$$f(x,t) = f\left(a, t + \frac{a - x}{\omega}\right) - \frac{\partial f(\xi,t)}{\partial t} \frac{a - x}{\omega} \qquad (3)$$

This implies that the value of the function $f(x, t)$ at point x and time t is equal to the value of the function at point a at a later time $t+(a-x)/\omega$, corrected for the change in the shape of the curve.

Taking the moments in the "ξ" coordinate system, we get for the ith moment Φ_i:

$$\Phi_{i\xi}(t) = \int_{-\infty}^{\infty} f(\mu + \xi,t)\xi^i \, d\xi = \int_{-\infty}^{\infty} f\left(a,t + \frac{a-\mu-\xi}{\omega}\right) \xi^i \, d\xi - \int_{-\infty}^{\infty} \frac{\partial f(\xi,t)}{\partial t} \frac{a-\mu-\xi}{\omega} \xi^i \, d\xi$$

(4)

To evaluate the first integral in the last member of eqn. (4), we make the transformation:

$$t + \frac{a-\mu-\xi}{\omega} = \tau$$

(5)

or

$$\xi = a - \mu + \omega(t - \tau) = a - \omega\tau$$

(6)

Here it is assumed that $\mu = 0$ for $t = 0$, i.e. the peak is at the origin of the "x" coordinate system at zero time. Then $\mu = \omega t$ and the last equality in (6) follows.

With (5) and (6) we get:

$$\int_{-\infty}^{\infty} f\left(a,t + \frac{a-\mu-\xi}{\omega}\right) \xi^i \, d\xi = \omega \int_{-\infty}^{\infty} f(a,\tau)(a - \omega\tau)^i \, d\tau =$$

$$= (-1)^i \omega^{i+1} \int_{-\infty}^{\infty} f(a,\tau) \left(\tau - \frac{a}{\omega}\right)^i d\tau = (-1)^i \omega^{i+1} \Phi_{it}\left(a, \frac{a}{\omega}\right)$$

(7)

where $\Phi_{it}\left(a, \frac{a}{\omega}\right)$ denotes the ith moment with respect to time around the point $t = \frac{a}{\omega}$.

In evaluating the second integral in the last member of (4), we observe that the order of integration and differentiation may be exchanged. Hence:

$$\int_{-\infty}^{\infty} \frac{\partial f(\xi,t)}{\partial t} \frac{a-\mu-\xi}{\omega} \xi^i \, d\xi = \frac{a-\mu}{\omega} \dot{\Phi}_{i\xi}(t) - \frac{1}{\omega} \dot{\Phi}_{i+1\xi}(t)$$

(8)

From (4), (7) and (8) we get:

$$\Phi_{i\xi}(t) = (-1)^i \omega^{i+1} \Phi_{it}\left(a, \frac{a}{\omega}\right) - \frac{a-\mu}{\omega} \dot{\Phi}_{i\xi}(t) + \frac{1}{\omega} \dot{\Phi}_{i+1\xi}(t)$$

(9)

Observing that the moments with respect to ξ are central moments, with $\Phi_{1\xi} = 0$, we get for the zeroth moment, which is a constant:

$$\Phi_{0t}(a) = \frac{1}{\omega} \Phi_{0\xi}(t)$$

(10)

To evaluate the higher moments we first normalize (9) by dividing with the zeroth moment and using (10). Denoting the reduced moments by φ_i, we get:

$$\varphi_{i\xi}(t) = (-\omega)^i \varphi_{it}\left(a, \frac{a}{\omega}\right) - \frac{a-\mu}{\omega} \dot{\varphi}_{i\xi}(t) + \frac{1}{\omega} \dot{\varphi}_{i+1\xi}(t)$$

(11)

For the first moment this yields:

$$0 = -\omega\varphi_{1t}\left(a, \frac{a}{\omega}\right) + \frac{1}{\omega} \dot{\mu}_2(t) = -\omega\varphi_{1t}(a) + a + \frac{2D}{\omega}$$

(12)

Here we have used the relation $\mu_2(t) = 2Dt + \mu_2(o)$ and the definition of $\varphi_{1t}(a,a/w)$ indicated in (7). The mean with respect to time μ_t becomes:

$$\mu_t = \varphi_{1t}(a) = \frac{a}{\omega} + \frac{2D}{\omega^2} \tag{13}$$

For the second moment we get from (11):

$$\mu_2(t) = \omega^2\varphi_{2t}\left(a, \frac{a}{\omega}\right) - \frac{a-\mu}{\omega} 2D + \frac{1}{\omega}\dot{\varphi}_{3\xi}(t) \tag{14}$$

Using (13) we introduce the variance μ_{2t} with respect to time:

$$\varphi_{2t}\left(a, \frac{a}{\omega}\right) = \varphi_{2t}(a,\mu_t) + \left(\frac{a}{\omega} - \mu_t\right)^2 = \mu_{2t}(a) + \frac{4D^2}{\omega^4} \tag{15}$$

Observing that $\mu = \omega t$, we have:

$$\mu_2(t) = \mu_2\left(\frac{\mu}{\omega}\right) = 2D \frac{\mu}{\omega} + \mu_2(o) \tag{16}$$

From (14), (15) and (16) it follows that:

$$\mu_{2t}(a) = \frac{1}{\omega^2}\mu_2\left(\frac{a}{\omega}\right) - \frac{4D^2}{\omega^4} - \frac{1}{\omega^3}\dot{\varphi}_{3\xi}(t) \tag{17}$$

Here $\mu_2(a/\omega)$ is the variance at the time a/ω. The last term in (17) is obviously negligible for peaks which are nearly symmetrical.

Finally, introducing the elution volume V as the independent variable, we have:

$$V = \Theta t \tag{18}$$

where Θ is the flow rate through the column. With V_1, the volume per unit of interphase area of the mobile phase, and σ, the interphase area per unit length of the column, we have σV_1 for the effective cross section of the mobile phase in the column. Hence:

$$\Theta = v\sigma V_1 \tag{19}$$

The ith moment with respect to the elution volume takes the form:

$$\Phi_{iV} = \Theta^{i+1}\Phi_{it} \tag{20}$$

For the reduced moments we get:

$$\varphi_{iV} = \Theta^i\varphi_{it} \tag{21}$$

From these equations and (10), (13) and (17) we get:

$$\Phi_{0V} = \frac{\Theta}{\omega}\Phi_{0\xi} \tag{22}$$

$$\mu_V = \Theta \frac{a}{\omega} + \frac{2D\Theta}{\omega^2} \tag{23}$$

$$\mu_{2V} = \left(\frac{\Theta}{\omega}\right)^2\mu_2\left(\frac{a}{\omega}\right) - \Theta^2\left(\frac{4D^2}{\omega^4} + \frac{1}{\omega^3}\varphi_{3\xi}(t)\right) \tag{24}$$

With the aid of these equations, the results of the original theory may be applied to the case where the concentration distribution is determined as a function of the elution volume. The physical meaning of eqns. (23) and (24) becomes clear when we observe that a/ω is the time it would take the mean of the concentration distribution to reach point a in an uninterrupted column. Thus, apart from a small correction term, μ_V corresponds to the mean of the peak inside the column. Similarly, μ_{2V} corresponds to the variance $\mu_2(a/\omega)$ the peak would have at point a in an uninterrupted column. Finally, eqn. (22) represents an expression for mass balance. If the total mass of the solute is C, then vC is the mass of solute in the mobile phase[4]. Thus, observing that σV_1 represents the cross section of the mobile phase, we have:

$$vC = \sigma V_1 \Phi_{0\xi} \tag{25}$$

On the other hand, the zeroth moment with respect to the elution volume represents the total mass of the solute:

$$C = \Phi_{0V} \tag{26}$$

Combining (25) and (26) we get (22).

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1 H. VINK, *J. Chromatog.*, 15 (1964) 488.
2 H. VINK, *J. Chromatog.*, 18 (1965) 25.
3 H. VINK, *J. Chromatog.*, 20 (1965) 305.
4 H. VINK, *J. Chromatog.*, 25 (1966) 71.