

Note

Chromatogram statistical moments from columns of finite length

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(Received December 30th, 1987)

The usual expressions for the column elution chromatogram or its statistical moments have been derived using both discrete and continuous models. Among the more extensive treatments of the latter are the efforts of Golay¹, Kubin², Kucera³ and Jönsson⁴. These works incorporate important non-equilibrium effects into the dynamic process. The ability to account for non-equilibrium effects has tremendous value in applying precise chromatographic techniques to the determination of physicochemical quantities⁵⁻⁸.

In this article, we wish to discuss a boundary condition associated with the continuous model of chromatography on a column of finite length. This boundary condition influences the elution profile in an important but subtle way. We wish to demonstrate the effect through use of equilibrium linear chromatography, the effect being a change in the elution profile from what has been derived using the unbounded limit. We argue consequently that a more appropriate treatment of boundary conditions ought to be applied to the non-equilibrium case as well.

THEORY

The differential equation describing linear chromatography at *equilibrium* has a particularly simple form given by⁴

$$D \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial z} = (1 + k') \frac{\partial c}{\partial t} \quad (1)$$

or

$$D_e \frac{\partial^2 c}{\partial z^2} - u_e \frac{\partial c}{\partial z} = \frac{\partial c}{\partial t} \quad (2)$$

where $c = c(z, t)$ represents the mobile phase concentration of solute at time t at position z along the column axis; u is the linear flow velocity of the mobile phase; D is an effective diffusion coefficient of the solute in the mobile phase; k' is the capacity factor of the solute on the column; and D_e and u_e are $D/(1 + k')$ and $u/(1 + k')$, respectively.

In order to solve the differential equation or to obtain the solution's statistical moments, appropriate initial boundary conditions need to be invoked. Kucera³, for

example, uses $c(z,t) = 0$ as $z \rightarrow \pm \infty$ and $c(x,0) = \delta(z)$ for an infinitely sharp sample injection pulse at the column origin at time zero. The elution chromatogram for a finite column length L is then taken as the concentration of solute at position $z = L$ as a function of time. Kucera's results for the first several moments are listed in the second column of Table I. These expressions have achieved a wide degree of acceptance and are of immense practical importance. However, upon closer examination, it would appear that they are not as rigorously applicable as previously thought.

TABLE I

STATISTICAL MOMENTS OF THE EQUILIBRIUM ELUTION CHROMATOGRAM FOR A COLUMN OF LENGTH L

	$z < \infty$	$z \leq L$
m_0	1	1
m_1	$\frac{L}{u_c} + \frac{2D_c}{u_c^2}$	$\frac{L}{u_c}$
m'_2	$\frac{2D_c L}{u_c^3} + \frac{8D_c^2}{u_c^4}$	$\frac{2D_c L}{u_c^3}$
m'_3	$\frac{12D_c^2 L}{u_c^5} + \frac{64D_c^3}{u_c^6}$	$\frac{12D_c^2 L}{u_c^5}$
m'_4	$\frac{12D_c^2 L^2}{u_c^6} + \frac{216D_c^3 L}{u_c^7} + \frac{960D_c^4}{u_c^8}$	$\frac{12D_c^2 L^2}{u_c^6} + \frac{120D_c^3 L}{u_c^7}$
m'_5	$\frac{240D_c^3 L^2}{u_c^8} + \frac{3920D_c^4 L}{u_c^9} + \frac{17408D_c^5}{u_c^{10}}$	$\frac{240D_c^3 L^2}{u_c^8} + \frac{1680D_c^4 L}{u_c^9}$

For heuristic purposes, we wish to consider extremely low mobile phase velocities under which circumstance longitudinal diffusion will undeniably be the dominating transport process. We in no way mean to imply that there is necessarily any operational significance to focussing attention at this extreme. It is in this framework, however, that the question at hand becomes clearest.

At low velocities, one can picture the solute molecule as undergoing random, Brownian displacements in any direction in the mobile phase. This motion is superimposed on the drift due to the mobile phase velocity. Viewing a "narrow window" at any position along the column, a given solute molecule, in principle, can make more than one pass into the window. This is particularly obvious in the limit of $u = 0$ when, on the average, half of the solute molecules move forward and half backward at any instant. The boundary condition invoked by Kucera³ and essentially all others as well corresponds to a solute detector that is placed at a particular coordinate L along the unbound column and that does not disturb the transport process. It is indeed what one would have for a passive detector, responding to solute concentration at the detection coordinate L regardless of multiple traversals by solute in either direction in the endless column. Under these or equivalent conditions, the profile moments as given in Table I are correct.

On the other hand, should detection be more appropriately described as one which involves an actual termination of the chromatographic process, as with effluent collection or derivatization, then the usual (Kucera) boundary condition would be inappropriate. A mathematically more fundamental description of this point can be found in the discussion by Cox and Miller⁹ on Markov processes in the continuous state. In particular, the finite length column corresponds precisely to determination of what is called *the first passage time* in a Wiener diffusion process. The first passage time refers to initial arrival at downstream position L , having started at the upstream source. Subsequent crossings of the boundary do not alter the first passage result which is then equivalent to what would be obtained for a sink at L .

Differential eqn. 1 is an example of an unrestricted Wiener process which belongs to a more general set of diffusion equations called Kolmogorov or Fokker-Planck equations⁹. Through the use of Laplace transforms, Cox and Miller⁹ obtain $\gamma(z_0)$, the moment generating function for first passage times to point $z = L$ for a sample starting at z_0 (equal to zero in our case) and unrestricted in the upstream direction.

$$\gamma(z_0) = \exp [z_0 - L\theta_2(s)]$$

where s is the time Laplace transform parameter and

$$\theta_2(s) = [-u_e + (u_e^2 + 2s\sigma^2)^{1/2}]/\sigma^2$$

and

$$\sigma^2 = 2D_e$$

Calculation of time moments m_n from the moment generating function $\gamma(z_0)$ is quite straightforward⁹. The pertinent relationship is

$$\sigma(z_0) = 1 + \sum_{n=0}^{\infty} (-s)^n m_n(z_0)/n! \quad (3)$$

from which the various order moments in the first passage time can be calculated through operation on eqn. 3 by $(-1)^n d^n/ds^n$ and subsequent evaluation at $s = 0$. The results are listed in the third column of Table I. For orders greater than 1, the central moments, $m'_n = \langle (t - m_1)^n \rangle$, are used.

DISCUSSION

When elution chromatography on a column of finite length L is such that the various processes in effect on the column have ceased at position L , the column-end boundary condition usually invoked is inappropriate. The elution profile is correctly calculated by determining the time profile at which solute *initially* arrives at the detector or collector. The statistical moments for the finite system ($z \leq L$) are compared to those from the infinite system ($z < \infty$) in Table I for a linear system at

equilibrium. It is particularly noteworthy that the two sets of moments agree exactly in the limit of high velocity when longitudinal diffusion becomes less influential. One should also be aware that a recent discussion of short chromatographic columns by Underhill¹⁰ gave a result identical to the one derived here for m_1 , the mean residence time on a column, in which the detector "acted as a perfect sink for sorbate". Underhill used a geometrical argument to show also that the retention mean is independent of the degree to which equilibrium is attained.

With the effect of finite column length derived here, there is no longer need to resort to neglecting higher order terms in D/u when discussing (i) chromatogram peak centroids and (ii) the otherwise exact relationship between the second statistical moment and height equivalent to a theoretical plate^{6,8}.

The effect of imposing the finite column length restraint will be further examined for non-equilibrium scenarios in a future work.

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