# Influence of the choice of the boundary conditions on the results of the dynamic chromatography model

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## ABSTRACT

An investigation of the influence of the choice of the boundary conditions on the shape of the band profile obtained by simulation of the elution process using the classical model of semi-ideal chromatography is presented. As the boundary condition represents the perturbation created at the column inlet, it influences the response of the column. It is shown that the peak area is conservative only if certain conditions are satisfied. Among other approximations, the Houghton equation does not fulfil these requirements. Contour plots are used to illustrate the band migration process and the properties of these bands in non-linear chromatography.

## INTRODUCTION

The choice of the boundary conditions for the integration of the partial differential equations which constitute the dynamic model of chromatography is important. These conditions must represent correctly the physical phenomena involved in the introduction of the sample. The boundary condition at the column inlet translates into mathematical terms the injection profile of the sample. At the column outlet, the boundary condition indicates whether and how reflection of the propagating wave takes place.

In this paper, we present an analysis of the influence of the boundary conditions on the zeroth-order moment of the elution of the band, *i.e.*, on its area. A discussion of the travelling character of the band during the elution process inside the column is also included. The results obtained by a series of computer simulations and a comparison with various experimental results are also described.

As the boundary condition represents the perturbation created at the column inlet by the injection of the feed, different boundary conditions must result in different band profiles. The mathematical and physical aspects of the problem are investigated and compared.

MASS OF A COMPOUND AND THE ZEROTH MOMENT OF ITS BAND

*Mass balance equation*
     The mass balance for a compound in a slice of a chromatographic column (slice thickness, d$x$), can be derived from the principle of continuity [1], which is written as

$$\frac{\partial \rho}{\partial t} + \text{div } \vec{J} = 0 \tag{1}$$

where $\rho$ is the total concentration of the compound in the slice considered:

$$\rho = C + Fq \tag{2}$$

$C$ is the concentration in the mobile phase, $q$ the concentration in the stationary phase and $F$ the phase ratio, *i.e.*, the ratio $(1-\varepsilon)/\varepsilon$, where $\varepsilon$ is the porosity of the column packing. $\vec{J}$ is given by

$$\vec{J} = \vec{u}C - D\nabla C \rightarrow uC - D\frac{\partial C}{\partial x} \tag{3}$$

Further discussion of the properties of this equation requires a relationship between the mobile and stationary phase concentrations of the compound studied. It is most convenient here to continue the discussion within the framework of the semi-equilibrium models. The ideal model assumes constant equilibrium between the two phases, which is tantamount to assuming that the column has an infinite efficiency. In practice, it has been shown that the results obtained with the ideal model are an excellent first approximation of the chromatograms actually observed [2]. It has been shown also, both theoretically [3–5] and experimentally [6,7], that excellent band profile predictions are obtained with a mass balance equation which assumes constant equilibrium between the two phases and corrects for the finite efficiency of the real column by using a proper value of the coefficient of axial dispersion. This apparent diffusion coefficient, $D_a$, is equal to $Hu/2$, where $H$ is the height equivalent to a theoretical plate of the real column and $u$ the velocity of the mobile phase.
     This semi-equilibrium model of chromatography permits an accurate description of the behavior of a band in a chromatographic system, its migration, broadening and change in profile, as long as the mass transfer kinetics are not very slow [2,8,9]. In this case, we have the following equation system:

$$\frac{\partial C}{\partial t} + F\frac{\partial q}{\partial t} + u\frac{\partial C}{\partial x} = D_a\frac{\partial^2 C}{\partial x^2} \tag{4}$$

with
$$q = f(C) \tag{5}$$

where $f(C)$ is the equilibrium isotherm of the compound studied between the two phases. The combination of eqns. 4 and 5 is the classical mass balance equation of the semi-ideal model of chromatography.

*Mass and zeroth-order moment*

The mass, $m$, of substance contained in the column can be derived from eqn. 2 and is given by

$$m = \int \rho dv = S \int_0^L (C + Fq)dx \qquad (6)$$

where $v$ is the volume of mobile phase, $L$ is the column length and $S$ the cross-sectional area of the column fraction accessible to the solute, *i.e.*, the product of the geometrical volume and the total column porosity. The mass flow across a section perpendicular to the column axis is

$$S\left(uC - D_a \frac{\partial C}{\partial x}\right) \qquad (7)$$

Integrating eqn. 1 or 4 along the column gives

$$\frac{dm}{dt} = S\left(uC - D_a \frac{\partial C}{\partial x}\right)_0 - S\left(uC - D_a \frac{\partial C}{\partial x}\right)_L \qquad (8)$$

which is exactly the integrated mass balance for the whole column. Since at the end of an experiment the column is usually left under the same conditions as it was at the beginning, we have $m(t = \infty) - m(t = 0) = 0$, which can be written as

$$S \int_0^\infty \left(uC - D_a \frac{\partial C}{\partial x}\right)_0 dt = S \int_0^\infty \left(uC - D_a \frac{\partial C}{\partial x}\right)_L dt \qquad (9)$$

Equation 9 indicates that, if we wait long enough, the whole sample will be washed out of the column.

In the particular case when the mobile phase velocity is constant and $D_a = 0$, the mass of compound injected is

$$Su \int_0^\infty Cdt|_{x=0} \qquad (10)$$

and the mass of the same compound eluted from the column is

$$Su \int_0^\infty Cdt|_{x=L} \qquad (11)$$

In this case, the area of the injected profile, the area of the profile $C(t)$ recorded at any position along the column and the area of the elution profile are all equal and proportional to the sample mass. In other words, when the diffusion coefficient is 0 and $u$ is constant, the zeroth moment is conserved and is proportional to the sample mass. In liquid chromatography, the molecular diffusion coefficient, $D_m$, is of the order of $1 \cdot 10^{-5}$ cm$^2$/s, but the apparent dispersion coefficient is larger, typically of the order of $1 \cdot 10^{-3}$ cm$^2$/s and $u$ is kept constant, so the condition stated above applies, and the previous analysis holds for the real world of liquid chromatography.

When $D_a$ is significantly different from 0, however, a more complicated analysis of the implications of the classical boundary and initial conditions is required.

VARIATION OF PEAK AREA WITH COLUMN LENGTH

Eqn. 4 is a second-order partial differential equation. The solution of a well posed problem involving such an equation requires an initial and a boundary condition. In fact, the main difficulty in the use of a dispersion model of chromatography is in choosing a proper set of initial and boundary conditions which describe properly the actual physical problem. Three types of boundary conditions are used most often [10]:

First type: the injection profile is given by the equation

$$C(x = 0, t) = \psi_1(t) \tag{12}$$

Second type: the derivative of the injection profile is given by

$$\left. \frac{\partial C}{\partial x} \right|_{x=0} = \psi_2(t) \tag{13}$$

Third type: the following condition applies:

$$\alpha C(x = 0, t) + \beta \left. \frac{\partial C}{\partial x} \right|_{x=0} = \Psi_3(t) \tag{14}$$

From the uniqueness theorem, one knows that any one of these conditons can be used to determine a solution of the eqn. 4, and that the solution obtained is unique. If one attempts to use two or more conditions simultaneously, the problem is overdetermined and has no solution.

In the case of chromatography modeling, the following initial conditions are most often preferred:

$$C(x, t = 0) = q(x, t = 0) = 0 \tag{15}$$

and the boundary conditions are of the first or the third class.

As pointed out by Danckwerts [10], a boundary condition of the third class must be used when the diffusion coefficient, $D_a$, is not zero, and the column length is finite. A boundary condition of the first class may be used only if the column length is long enough so that the condition: $4D_a/Lu \ll 1$ is satisfied. Kreft and Zuber [11] introduced two definitions of the concentration (the resident and the flux concentrations), both at injection and detection, to specify the various initial and boundary conditions. Jönsson [12] discussed several assumptions and compared the solutions of the mass balance equation in linear chromatography for two types of first class boundary conditions, an infinitely sharp pulse in the time domain and an infinitely sharp pulse in the space (i.e., column) domain.

In the following, we derive the value of the zeroth-order moment of the elution profile obtained as solution of eqn. 4 when using a boundary condition of the third or the first class, and we discuss the meaning of the result obtained.

*General properties of the peak area*
   Integrating eqn. 4 with respect to time, from the beginning of the experiment
(*i.e.*, between $t = 0$ and $t = \infty$), gives

$$\int_0^\infty \frac{\partial C}{\partial t}\, dt + F \int_0^\infty \frac{\partial q}{\partial t}\, dt + u \int_0^\infty \frac{\partial C}{\partial x}\, dt = D_a \int_0^\infty \frac{\partial^2 C}{\partial x^2}\, dt \tag{16}$$

or

$$(C + Fq)|_\infty - (C + Fq)|_0 + u \frac{dA(x)}{dx} = D_a \frac{d^2 A(x)}{dx^2} \tag{17}$$

where

$$A(x) = \int_0^\infty C(x,t)dt \tag{18}$$

$A(x)$ is the local peak area. Our problem now is to show that it is independent of $x$,
under certain conditions.
   Since

$$(C + Fq) = 0 \text{ when } t = \infty \tag{19}$$

and

$$(C + Fq) = g_i(x) \text{ when } t = 0 \tag{20}$$

where $g_i(x)$ is the initial condition. Eqn. 17 becomes

$$-g_i(x) + u \frac{dA}{dx} = D_a \frac{d^2 A}{dx^2} \tag{21}$$

$g_i(x)$ represents the initial distribution of the compound in the column, before the
injection is made. If $g_i(x) = 0$, the condition is called homogenized. This is the
condition which applies in almost all practical aplications of chromatography.
   The solution of eqn. 21 is

$$A(x) = C_1(x)\exp(ux/D_a) + C_2(x) \tag{22}$$

Using the classical method of the variation of constant, we obtain

$$\frac{dC_1(x)}{dx} \frac{u}{D_a} \exp(ux/D_a) = - \frac{g_i(x)}{D} \tag{23}$$

and:

$$\frac{dC_1(x)}{dx} \exp(ux/D_a) + \frac{d}{dx}C_2(x) = 0 \tag{24}$$

The solutions of eqns. 23 and 24 are

$$C_1(x) = -\frac{1}{u}\int_0^x g_i(x)\exp(-ux/D_a)dx + C_{1,0} \tag{25}$$

and

$$C_2(x) = \frac{1}{u}\int_0^x g_i(x)dx + C_{2,0} \tag{26}$$

Combining eqns. 22, 25 and 26 gives

$$A(x) = C_{1,0}\exp(-ux/D_a) + C_{2,0} - \frac{1}{u}\exp(ux/D_a)\int_0^x g_i(x)\exp(-ux/Da)dx +$$

$$+ \frac{1}{u}\int_0^x g_i(x)dx \tag{27}$$

Eqn. 27 is the fundamental result in this paper. It represents the variation of the peak area during its migration along the column. It shows that the peak area depends on the boundary conditions, through the constants $C_{1,0}$ and $C_{2,0}$, and on the initial condition, through $g_i(x)$. In fact, $S\int_0^L g_i(x)dx = m(t=0)$.

*Peak area under third class boundary condition*
        The boundary conditions used in this case are formulated as follows, at the column inlet:

$$uC - D_a\frac{\partial C}{\partial x} = uC_k, x = 0 \tag{28}$$

and at the column outlet:

$$\frac{\partial C}{\partial x} = 0, x = L \tag{29}$$

where $C_k$ is a constant concentration. This is the Danckwerts boundary condition [10]. Integrating eqn. 28 between the beginning and the end of the experiment gives

$$D_a\frac{dA(x)}{dx}\bigg|_{x=0} = uA(0) - uA_k \tag{30}$$

where $A_k = \int_0^\infty C_k \mathrm{d}t$. Integrating the other boundary condition (eqn. 29) gives

$$\left.\frac{\mathrm{d}A}{\mathrm{d}x}\right|_{x=L} = 0 \tag{31}$$

Combining eqns. 27, 28, 30 and 31 permits the calculation of the constants $C_{1,0}$ and $C_{2,0}$ in eqns. 25 and 26:

$$C_{1,0} = \frac{1}{u}\int_0^L g_i(x)\exp(-ux/D_a)\mathrm{d}x \tag{32}$$

and

$$C_{2,0} = A_k \tag{33}$$

Finally, equation 27 becomes:

$$A(x) = \frac{1}{u}\exp(ux/D_a)\int_x^L g_i(x)\exp(-ux/D_a)\mathrm{d}x + \frac{1}{u}\int_0^x g_i(x)\mathrm{d}x + A_k \tag{34}$$

From eqn. 34, we can derive the value of the function $A$ at both ends of the column:

$$A(0) = A_k + \frac{1}{u}\int_0^L g_i(x)\exp(-ux/D_a)\mathrm{d}x \tag{35}$$

and

$$A(L) = A_k + \frac{1}{u}\int_0^L g_i(x)\mathrm{d}x \tag{36}$$

Accordingly,

$$A(L)-A(0) = \frac{1}{u}\int_0^L g_i(x)[1 - \exp(-ux/D_a)]\mathrm{d}x \tag{37}$$

Obviously, when $g_i(x) = 0$, which is true in chromatography, we have $A(L) = A(0)$. This demonstrates that the zeroth-order moment of the band remains constant during its migration throughout the column if the initial condition is homogeneous (*i.e.,* if dthere is nothing in the column before the injection is made).

*Peak area under first class boundary condition*
    The boundary conditions are now written as follows, at the column inlet:

$$c(x,t) = \psi(t), x = 0 \tag{38}$$

and at the column outlet, for an infinitely long column:

$$c(x,t) \text{ is finite when } x \to \infty \tag{39}$$

From eqn. 38, we have

$$A(0) = \int_0^\infty \psi(t)dt \tag{40}$$

Combining eqns. 27 and 40 gives (see also eqn. 22):

$$C_{1,0} + C_{2,0} = \int_0^\infty \psi(t)dt \tag{41}$$

From eqns. 27 and 39, it results that, in order to have $C(x,t)$ and hence $A(x)$ finite, we *must have*

$$C_{1,0} = 0 \tag{42}$$

and

$$C_{2,0} = \int_0^\infty \psi(t)dt \tag{43}$$

Combination of eqns. 27, 42 and 43 gives

$$A(x) = \int_0^\infty \psi(t)dt - \frac{1}{u}\exp(ux/D_a)\int_0^x g_i(x)\exp(-ux/D_a)dx + \frac{1}{u}\int_0^x g_i(x)dx \tag{44}$$

From eqn. 44, we derive the value of $A$ at both ends of the column:

$$A(L) = \int_0^\infty \psi(t)dt - \frac{1}{u}\exp(uL/D_a)\int_0^L g_i(x)\exp(-ux/D_a)dx + \frac{1}{u}\int_0^L g_i(x)dx \tag{45}$$

and

$$A(0) = \int_0^\infty \psi(t)dt \tag{46}$$

and, finally,

$$A(L) - A(0) = -\frac{1}{u}\exp(uL/D_a)\int_0^L g_i(x)\exp(-ux/D_a)dx + \frac{1}{u}\int_0^L g_i(x)dx \tag{47}$$

Eqn. 47 is identical with eqn. 37. We have

$$A(L) = A(0), \text{ if } g_i(x) = 0$$

In chromatography, the zeroth-order moment remains constant all along the column if the initial condition is homogeneous.

*Peak area in the case of the Houghton approximate equation*
    Houghton [13] obtained an analytical solution of the mass balance equation of chromatography (eqn. 4) by making two assumptions. First, he assumed a parabolic isotherm, *i.e.*, replaced the isotherm by its three-term expansion around the origin (see eqn. 53). Second, he used the Cole–Hopf transform [1] in order to replace the mass balance equation (eqn. 4) by a Burger equation, for which an analytical solution can be obtained [13–16]. This requires, however, another assumption, that the factor $(1 + \lambda C)^{-1}$ (see eqn. 50) in the mass balance equation can be replaced by 1. As a consequence of these two assumptions, the analytical solution obtained has physical significance only for small concentrations. Potentially more troublesome, however, is the fact that the Burger equation (*i.e.*, the equation really solved) has lost the conservation property of eqn. 4, because of the simplification made. Since the non-conservation behavior of the Houghton equation has been reported [17,18], it is interesting to apply the same analysis as above and to investigate the extent of the variation of the zeroth-order moment of the band profile during the band migration. The equation derived by Houghton [13] may be written as

$$\frac{\partial C}{\partial t} - \lambda U C \frac{\partial C}{\partial \xi} = E_0 \frac{\partial^2 C}{\partial \xi^2} \tag{48}$$

with

$$U = \frac{u}{1 + \dfrac{K_1}{\varepsilon}} \tag{49}$$

$$\lambda = \frac{2K_2/\varepsilon}{1 + \dfrac{K_1}{\varepsilon}} \tag{50}$$

$$E_0 = \frac{D_a}{1 + \dfrac{K_1}{\varepsilon}} \tag{51}$$

$$\xi = x - Ut; \; x = \xi + Ut \tag{52}$$

where $1/\varepsilon = F$ and $K_1$ and $K_2$ are the coefficients of the parabolic adsorption isotherm, which is used for the investigation of the onset of column overload behavior. This isotherm is written as

$$q = K_0 + K_1 C + K_2 C^2 \tag{53}$$

where $K_0$ is constant and usually equal to 0. The initial and boundary conditions assumed by Houghton [13] are

$$C(0,x) = g_{1,i}(x) = C_0 \ \text{if} \ |x| < L_0/2$$
$$C(0,x) = 0 \ \text{if} \ |x| > L_0/2 \tag{54}$$

and

$$q(0,x) = g_{2,i}(x) = K_1 C_0 + K_2 C_0^2 \ \text{if} \ |x| < L_0/2$$
$$q(0,x) = g_{2,i}(x) = 0 \ \text{if} \ |x| > L_0/2 \tag{55}$$

In eqn. 48, we have $\partial C/\partial t = \partial C/\partial t \big|_{\xi=\text{constant}}$. Further, we know that

$$\left. \frac{\partial C}{\partial t} \right|_{\xi} = \left. \frac{\partial C}{\partial t} \right|_{x} + U \frac{\partial C}{\partial x} \tag{56}$$

and

$$\left. \frac{\partial C}{\partial x} \right|_{t} = \left. \frac{\partial C}{\partial \xi} \right|_{t} \tag{57}$$

Combining eqns. 48, 56 and 57 gives

$$\left(1 + \frac{K_1}{\varepsilon}\right) \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} - \lambda u C \frac{\partial C}{\partial x} = D_a \frac{\partial^2 C}{\partial x^2} \tag{58}$$

Eqn. 58 is the Houghton approximate equation in the $(x, t)$ space coordinate. Hence the differential of the mass density represented by the Houghton equation can be written as

$$\frac{\partial \rho}{\partial t} = \left(1 + \frac{K_1}{\varepsilon} + \frac{2K_2 C}{\varepsilon}\right) \frac{\partial C}{\partial t} \tag{59}$$

Combining eqns. 58 and 59 gives

$$\frac{\partial \rho}{\partial t} = -u \frac{\partial C}{\partial x} + D_a \frac{\partial^2 C}{\partial x^2} + \lambda^2 u C^2 \frac{\partial C}{\partial x} + \lambda D_a C \frac{\partial^2 C}{\partial x^2} \tag{60}$$

It is obvious that the solution of the Houghton equation is different from that of the mass balance equation (eqn. 1). The difference is due to the terms $\lambda^2 u C^2 \; \partial C / \partial x$ and $\lambda D C \; \partial^2 C / \partial x^2$. Since $\lambda C \ll 1$, $\lambda^2 C^2$ is still smaller and the term in $\lambda^2 C^2$ can be ignored.

Integrating eqn. 60 with respect to $x$ and $t$, multiplying the two sides by the cross-sectional area, $S$, and ignoring the term in $\lambda^2 C^2$, we obtain

$$m(t = \infty) - m(t = 0) = Su[A(L) - A(0)] +$$
$$+ \; SuD_a \int_0^\infty \left[ \left( \frac{\partial C}{\partial x} \right)\Big|_L - \left( \frac{\partial C}{\partial x} \right)\Big|_0 \right] dt \; + \; Su\lambda D_a \int_0^\infty \int_0^L C \frac{\partial^2 C}{\partial x^2} \, dx \, dt \tag{61}$$

From partial integration of eqn. 61, we obtain

$$\int_0^L C \frac{\partial^2 C}{\partial x^2} \, dx = \int_0^L Cd \frac{\partial C}{\partial x} = \left( C \frac{\partial C}{\partial x} \right)\Big|_0^L - \int_0^L \left( \frac{\partial C}{\partial x} \right)^2 dx \tag{62}$$

We combine eqns. 61 and 62 and consider that $m(\infty) - m(0) = 0$. Since in the case of the Houghton equation the injection is very narrow, $L_0/2$ is small and the initial condition is still a Dirac $\delta$ pulse. Therefore, we may integrate from $x = L_0/2$ and the boundary condition is still homogeneous. Thus, we have

$$A(L) - A(0) = D_a \int_0^\infty \left[ \left( \frac{\partial C}{\partial x} \right)\Big|_L - \left( \frac{\partial C}{\partial x} \right)\Big|_0 \right] dt \; +$$
$$+ \; \lambda D_a \int_0^\infty \left( C \frac{\partial C}{\partial x} \right)\Big|_0^L dt \; - \; \lambda D_a \int_0^\infty \int_0^L \left( \frac{\partial C}{\partial x} \right)^2 dx \, dt \tag{63}$$

For the finite column, the Danckwerts condition (eqns. 28 and 29) can be considered. This gives

$$A(L) - A(0) = -D_a \int_0^\infty \left( \frac{\partial C}{\partial x} \right)\Big|_{x=0} (1 - \lambda C_0) dt - \lambda \int_0^\infty \int_0^L \left( \frac{\partial C}{\partial x} \right)^2 dx \, dt \tag{64}$$

Since we have $\lambda C \ll 1$, we can write:

$$A(L) - A(0) = -D_a \int_0^L \lambda \int_0^L \left( \frac{\partial C}{\partial x} \right)^2 dx \, dt - D_a \int_0^\infty \left( \frac{\partial C}{\partial x} \right)_0 dt \tag{65}$$

Usually, $\partial C / \partial x$ is large in non-linear chromatography, at least in some concentration range, e.g., on the front of elution bands when the isotherm is Langmuirian. Thus, we may expect the absolute value of the term $\lambda \int_0^L (\partial C / \partial x)^2 dx$ to be larger than that of $(\partial C / \partial x)_{x=0}$. Therefore, the sign of the difference $A(L) - A(0)$ is determined by the sign of $\lambda$.

When the isotherm is convex, such as with a Langmuir isotherm, $\lambda < 0$ and the eluted band has a lower area than the injected band. In fact, the area of the eluted band decreases with increasing column length [5]. The opposite is true for a concave or an S-shaped isotherm. This loss or gain of zeroth moment, which should not be mistaken

for an apparent loss or gain in sample mass, occurs because the analytical solution of eqn. 48 is not a solution of eqn. 4, owing to the simplification introduced in the derivation of eqn. 48.

When $\lambda = 0$, we have linear chromatography and eqn. 58 is identical with eqn. 4. Comparison between eqn. 9 and eqns. 37 and 47 shows that when $g_i(x) = 0$,

$$\int_0^\infty \left(\frac{\partial C}{\partial x}\right)\Big|_0 \, \mathrm{d}t = \int_0^\infty \left(\frac{\partial C}{\partial x}\right)\Big|_L \, \mathrm{d}t$$

and, from eqn. 63, we have always $A(L) = A(0)$.
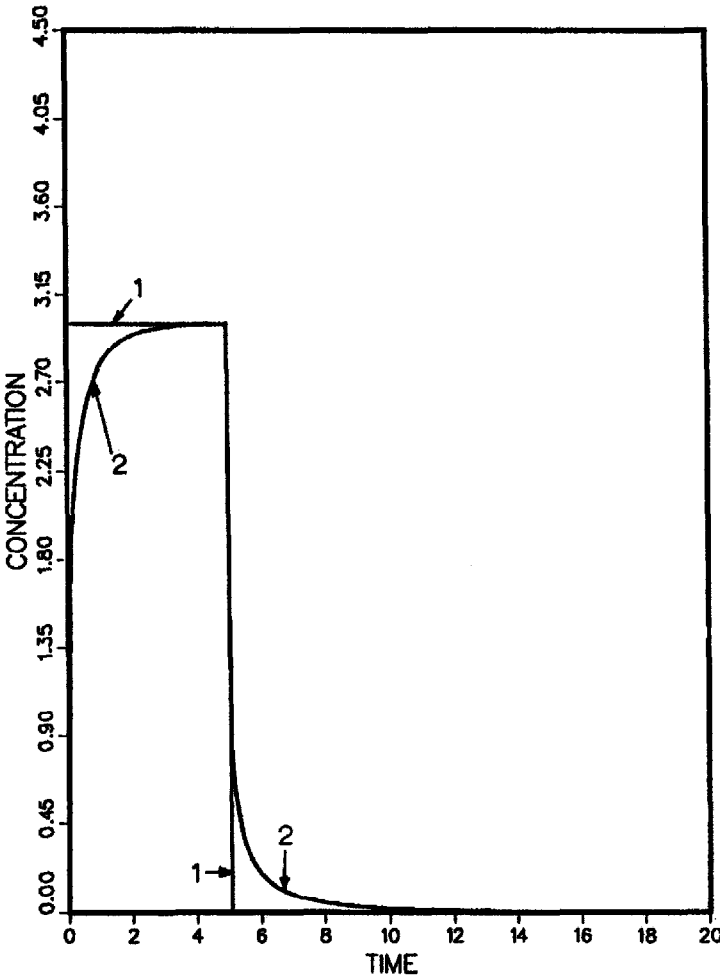


Fig. 1. Injection profiles corresponding to two different boundary conditions. 1 = plug (first kind) condition; 2 = Danckwerts (third type) conditions. Time in seconds, concentrations in m$M$.

INFLUENCE OF BOUNDARY CONDITIONS ON BAND MIGRATION

The previous discussion has shown that the peak area (*i.e.*, the zeroth-order moment) is not necessarily a quantity conserved by eqn. 4, contrary to general belief. Even for rigorous solutions of eqn. 4, the zeroth moment may change and this change still remains consistent with the mass conservation law. Hence the peak area does not always represent the mass of the compound analyzed. The band area is related to the mass of compound injected, however, and under certain conditions it remains constant during the migration of the band.

The choice of the boundary conditions has an effect on the retention time and the profile of the eluted band. Fig. 1 shows the injection profiles corresponding to the pulse (first type) and the Danckwerts (third type) boundary conditions. In the latter instance, the boundary condition includes a diffusion term (see eqn. 28), and Fig. 1 shows the plot of $C(t)$ at the column inlet which corresponds to that condition. The differences in the front and tail of the injection profiles are significant and explain why different profiles may be recorded for the injection of the same amount of sample using one boundary condition or the other, if the width of the injection pulse profile and especially the rise and decay times of the Danckwerts boundary condition are significant compared with the retention time. The Danckwerts condition is certainly much more realistic than the pulse condition.

To illustrate the influence of the boundary conditions, we determined the contour plots of the band migration, using a computer program previously developed to calculate numerical solutions of eqn. 4 [19] and suitably modified to include the boundary conditions required. These contour plots are the isoconcentration contours projected on a $(t, x)$ plane. A section of these plots by a vertical plane at $t = $ constant gives the concentration profile of the band inside the column at that given time. A section of the same contour plot by a vertical plane at $x = $ constant gives the elution profile through the column section at that abscissa. The contour plot gives the trail of a concentration wavelet in the column, from its entrance to its exit.

Fig. 2 shows the contour plot for a very small diffusion coefficient and a linear isotherm. Then the wavelet moves linearly. The slope of the trajectories of the different wavelets are the same, as they have all the same velocity. Figs. 3–5 show the contours in the case of a non-linear isotherm. Fig. 3 corresponds to a plug injection (first type of boundary conditions), and Figs. 4 and 5 correspond to the same Dankwerts boundary condition and to different values of the axial dispersion coefficient in the column. As the isotherm is not linear, the velocity of a wavelet, *i.e.*, the velocity associated with a concentration [20], depends on this concentration and the trails are not linear. The parallel lines in the upper part of the figures correspond to the migration of the shock layer of the band [20]. The lines which leave the time axis beyond *ca.* 1 min and diverge correspond to the band tail, *i.e.*, the non-sharpening part of the profile. In each instance, the inner curvilinear triangle, at the bottom left of the figures, corresponds to the decay of the injection profile plateau. Beyond that first profile, the apex of each curvilinear triangle corresponds to a band maximum. These apices mark the trajectory of the band maximum and its decay.

The location of the countour lines in Figs. 3 and 4, which differ only by the boundary condition, are slightly different and the overall effect is small. The influence of the axial dispersion on the contour map is illustrated by a comparison between Figs.
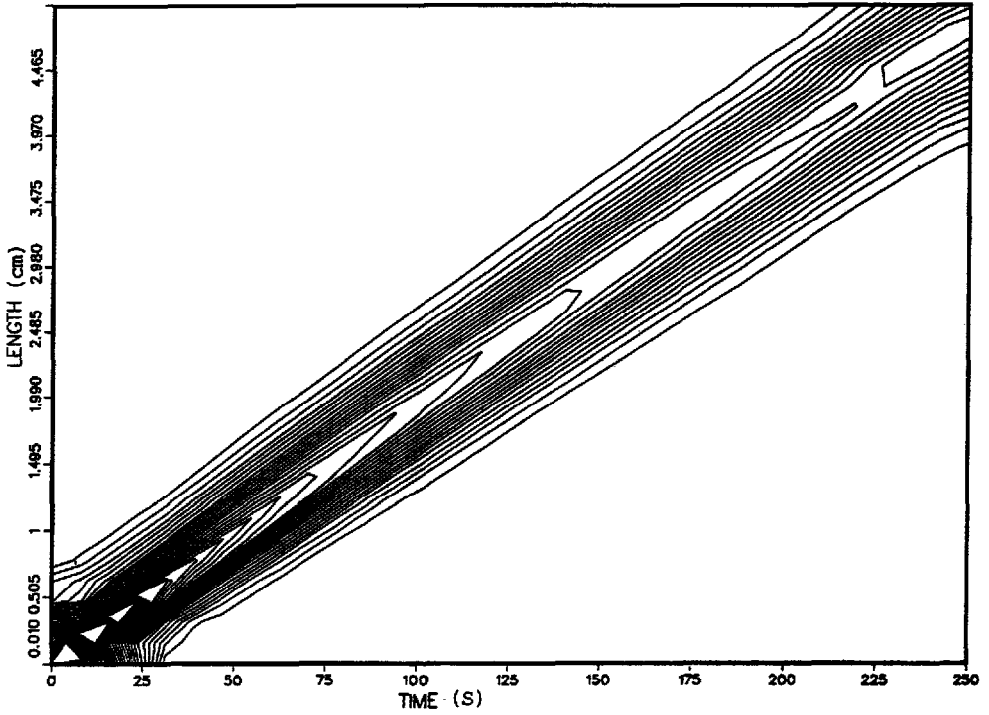
Fig. 2. Concentration contour plots corresponding to a linear isotherm. The moire effect around the origin is a graph artefact. Note the parallel lines corresponding to isokinetic concentration trajectories. Pulse injection (see Fig. 1). Apparent dispersion coefficient, $D_a = 0.0012 \text{ cm}^2/\text{s}$.
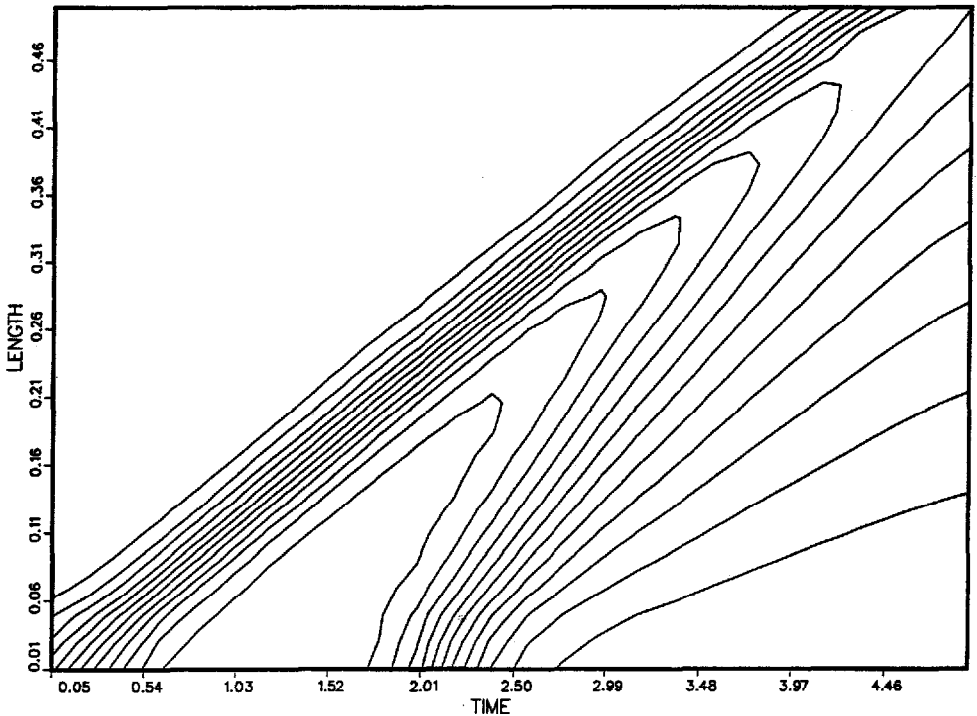


Fig. 3. Concentration contour plots corresponding to a non-linear isotherm and to a first type inlet boundary condition (see Fig. 1). Same conditions as for Fig. 2.
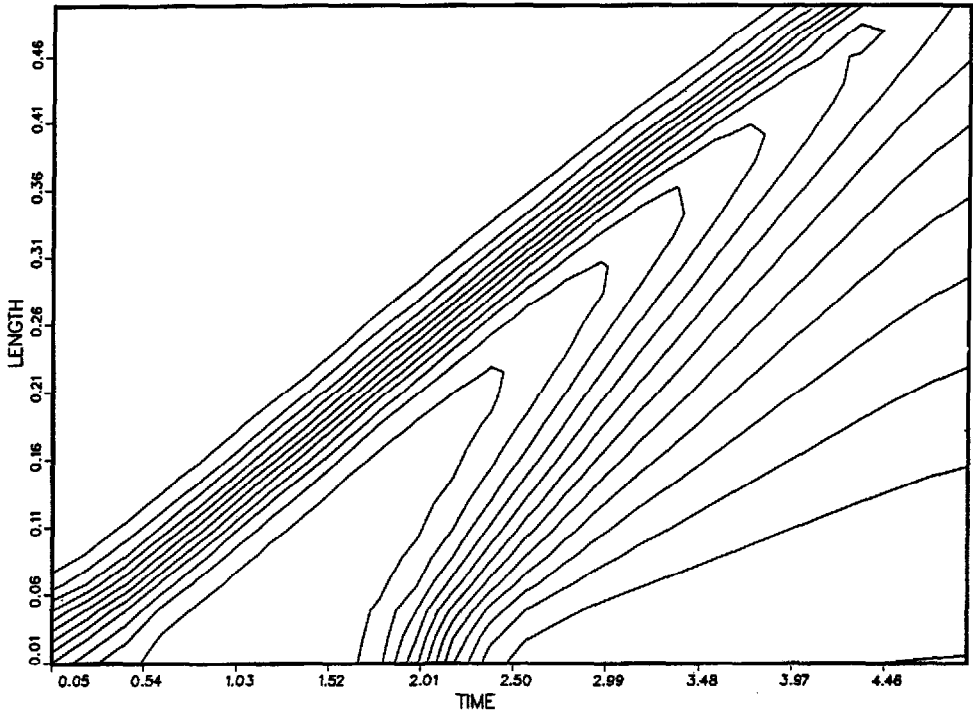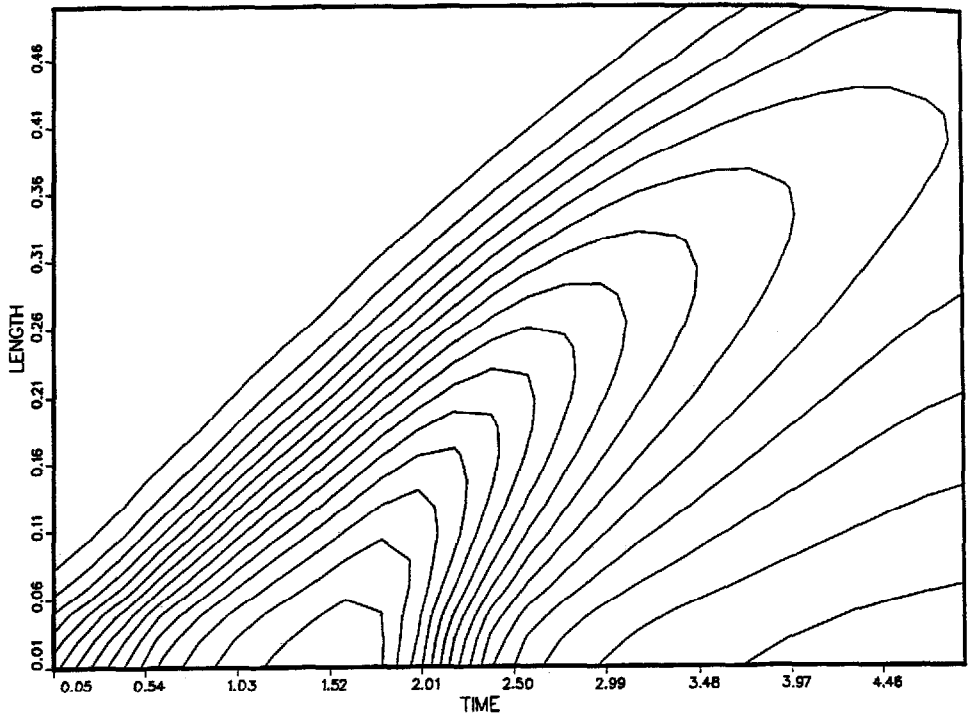
Fig. 4. Concentration contour plots corresponding to a non-linear isotherm and to a third type (Danckwerts) inlet boundary condition (see Fig. 1). Same conditions as for Fig. 2.



Fig. 5. Concentration contour plots corresponding to a non-linear isotherm and to a third type (Danckwerts) inlet boundary condition. Same conditions as for Fig. 2, except $D_a = 0.012$ cm$^2$/s.

4 and 5. In the latter figure (axial dispersion ten times as large as for Fig. 4), the self-sharpening effect on the band front is much less acute than in Fig. 4. The shock layer is much thicker.

Fig. 6 shows the elution profiles corresponding to the two boundary conditions at the end of a 5-cm long column (see injection profile in Fig. 1). The effect is important. The retention time is longer and the profile is wider, shorter and tails longer with the Danckwerts boundary condition than with the pulse injection. Such an effect should be expected on comparing the two profiles in Fig. 1. This phenomenon arises because of the influence of diffusion on the injection profile. In practice, the Danckwerts injection is a more realistic model than the plug injection.
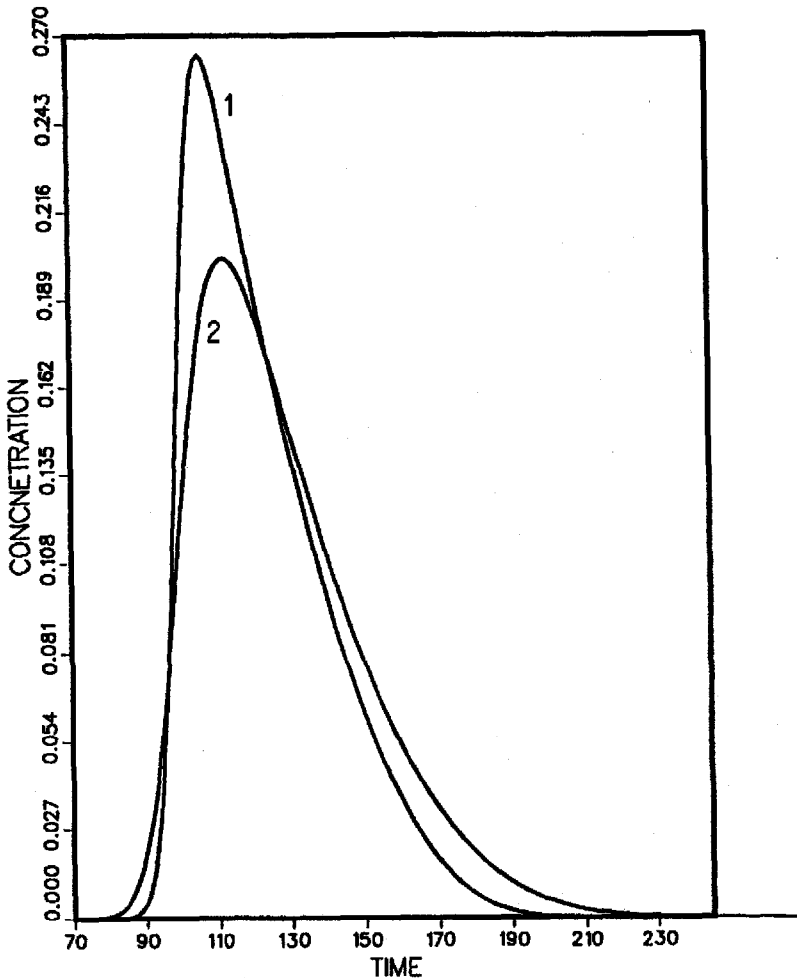


Fig. 6. Effect of the nature of the inlet boundary condition on the retention time and the shape of the elution profile. Both profiles were generated with $h = 0.01$ cm, $\tau = 0.01$ s, $L = 5$ cm. See injection profiles in Fig. 1. 1 = Plug injection; 2 = Danckwerts condition.
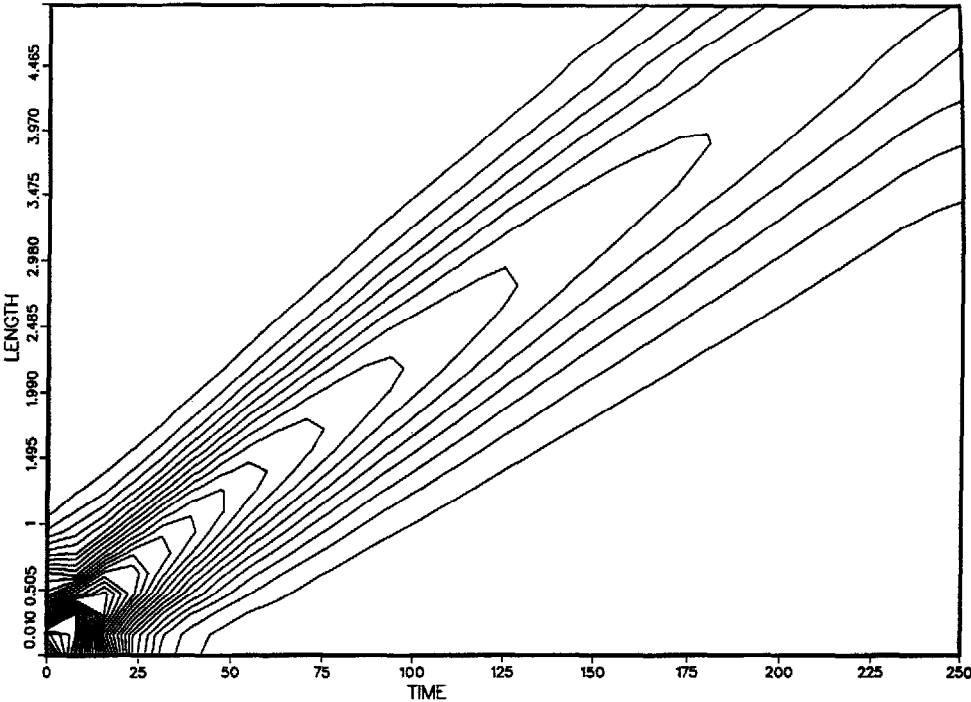
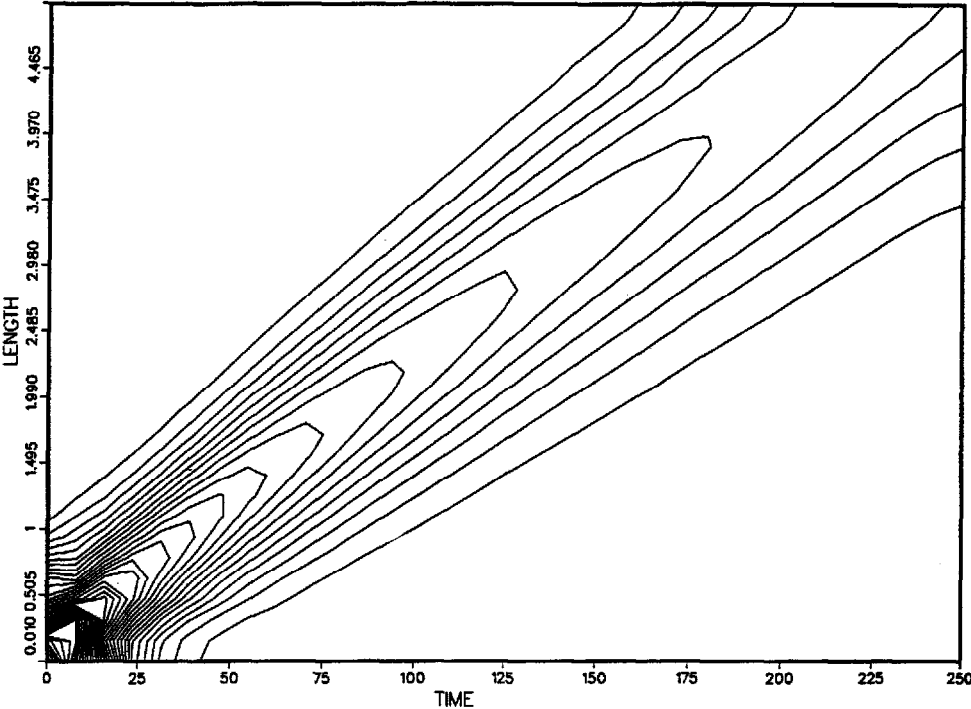Fig. 7. Same as Fig. 2, except infinite outlet boundary condition.



Fig. 8. Same as Fig. 2, except finite outlet boundary condition.

Finally, Figs. 7 and 8 compare the effects of the outlet boundary conditions. In Fig. 7 the boundary condition assumes an infinite column length. In Fig. 8, the column length is finite, *i.e.*, $\partial C/dx|_L = 0$. In the latter instance, the contour lines are bent upwards near the column exit. The choice of a correct outlet boundary condition appears to be relevant when simulating the behavior of chromatographic columns and looking for the determination of the optimum column length for maximum production under some constraint of product purity [21].

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