Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Lin, Bingchang and Guiochon, Georges(1989) 'Numerical Simulation of Chromatographic Band Profiles at Large Concentrations: Length of Space Increment and Height Equivalent to a Theoretical Plate', Separation Science and Technology, 24: 1, 31 — 40

To link to this Article: DOI: 10.1080/01496398908049749

URL: http://dx.doi.org/10.1080/01496398908049749

SEPARATION SCIENCE AND TECHNOLOGY, 24(1&2), pp. 31-40, 1989

Numerical Simulation of Chromatographic Band Profiles at Large Concentrations: Length of Space Increment and Height Equivalent to a Theoretical Plate

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Abstract

It is shown that the numerical integration of the system of partial differential equations accounting for the idea model of chromatography provides the band profiles observed with a column of finite efficiency if the space length increment of the integration is chosen equal to the column HETP for a zero sample size and the time increment is then chosen so that the Courant number is 2.

INTRODUCTION

In a recent paper, Rouchon et al. (*1*) discussed the numerical integration of the system of mass balance equations which accounts for the behavior of a large concentration band in a chromatographic column. The comparison between the profiles predicted by their calculations and the profiles recorded experimentally showed good overall agreement, especially for the largest samples used, but poor rendition of the small or very small samples, the band width of the theoretical profiles being about 40% larger than the width of the experimental ones. Furthermore, their program had no feature permitting an easy adjustment of the efficiency of the simulated column.

It was suggested, however, that carrying out the numerical integration with a space increment equal to the height equivalent to a theoretical plate (HETP) of the column for an extremely small concentration (linear chromatography) should give correct results (*1*).

In a more recent paper, Golshan-Shirazi et al. (*2*) reported the simulation of single solute bands on a chromatographic column and obtained profiles which are Gaussian for very small sample sizes and have a standard deviation corresponding to the HETP of the simulated column, provided the length of the space increment is taken equal to the column HETP. Simulated elution profiles using this program are in excellent agreement with those observed experimentally (*3*). Unfortunately, there is no justification for this choice, which appears so far to be empirical. This could be a serious problem, because the lack of an understanding of the relationship between the space length of the integration increment and the band smoothness casts some legitimate doubt on the validity of the profiles generated by calculating numerical solutions of the system of partial differential equations of chromatography, especially at large concentration loadings where the profiles become extremely steep.

We present here a demonstration of the validity of the choice made in the work by Golshan-Shirazi et al. (*2, 3*) and in other work dealing with the simulation of the separation of binary mixtures (*4–7*).

I. THE SYSTEM OF EQUATIONS OF CHROMATOGRAPHY

The solution of the chromatographic problem, i.e., the prediction of the band profiles in the most general case, can be obtained by writing a system of equations accounting for the mass balances of all the chemical species involved and the kinetics of their mass transfer betwen phase boundaries.

1. Mass Balance Equations

The mass balance equation of Compound i in a slice of column is written (*1*)

$$\frac{\partial C_m}{\partial t} + F\frac{\partial C_s}{\partial t} + u\frac{\partial C_m}{\partial z} = D\frac{\partial^2 C_m}{\partial z^2} \qquad (1)$$

where F = the phase ratio $((1-\varepsilon)/\varepsilon)$
C_m, C_s = the concentration of the solute in the mobile and the stationary phase, respectively
u = the linear velocity of the mobile phase, assumed to be constant
D = the coefficient of molecular (axial) diffusion

There is one equation like Eq. (1) for each compound involved in the experiment, whether a component of the sample studied or of the mobile phase. In order to simplify the system, we may take the convention that the solvent, or the weak solvent in the case of a mixed mobile phase, is not adsorbed (*8*). Since liquids are not compressible and the difference between the partial molar volumes in the mobile and the stationary phases is very small, there is no need for a mass balance equation of the weak solvent. But a mass balance equation is certainly needed for each other component of the mobile phase.

The system of mass balances (Eq. 1 for each compound) is the fundamental part of the chromatographic model. It needs to be completed by a relationship between the concentrations in the mobile and stationary phases or their differentials by respect to time to permit the derivation of a solution of the system.

2. Mass Transfer Kinetics

It is difficult to write a proper relationship between the time differential of the concentration of the Compound *i* in the stationary phase, the experimental parameters, and the local values of its concentrations in both phases. Different models may be assumed to account for the mass transfer, depending on the nature of the problem (*9*). The most simple such equation is

$$\frac{\partial C_s}{\partial t} = -K(C_s - f(C_m)) \qquad (2)$$

where K = a kinetic constant
$f(C_m)$ = the isotherm equation, i.e., it gives the concentration of the corresponding compound in the stationary phase in equilibrium with a concentration C_m in the mobile phase

In the case of a multicomponent problem, the isotherm for each compound is a function of the concentration of all of them in the mobile phase.

The system of partial differential equations obtained by combining Eqs. (1) and (2) written for each compound involved is complex and has not yet received any solution. Preliminary results indicate that a numerical solution may be possible (*9*).

3. The Ideal Model

In most applications of chromatography, however, the mass transfer between phases is extremely fast and these phases are never far from being at equilibrium. We may assume, as a first approximation, that there is constantly equilibrium between the mobile and the stationary phases. This means that the column has an infinite efficiency. Radial mass transfer proceeds at an infinite rate, while axial diffusion proceeds at a zero rate, even when the concentration gradient is infinite. This is the "ideal" model of chromatography (*10–12*). In this case the mass balance equation becomes

$$\left(1 + F\frac{\partial f}{\partial C}\right)\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} = 0 \tag{3}$$

where f is the isotherm equation and C is the concentration in the mobile phase.

It is interesting to observe that a true solution of the system made of Eq. (3) (one for each compound involved, plus a competitive isotherm, $C_s = f(C_m, i)$) should exhibit concentration discontinuities or shocks (*12*), because Eq. (3) can propagate these shocks. Nevertheless, a numerical solution of this system does not exhibit true ideal shocks, but very steep segments of the profiles instead (*2–7*). This is due to the smoothing effect of numerical integration and had already been observed by Rouchon et al. (*1*) and by others (*2–7*). A shock could be obtained only if infinitely small values of the space and time integration increments could be used. This in turn would require an infinite computer time, clearly an unacceptable proposition.

We want to emphasize at this stage, however, that we do not need a solution of the system of equations of the ideal model, since it is an approximation. On the contrary, if we could relate the smoothing effect of the finite character of the integration elements to the effects of a finite rate of mass transfer and of molecular diffusion on strong concentration gradients, we might be able to obtain an approximate solution of the system of Eqs. (1) which would be closer to the exact solution of the problem than an exact solution of the system of Eqs. (3) with the corresponding isotherms.

4. The Semi-Ideal Model

A reasonable alternative assumption could be to write that the rate of mass transfer does not change with concentration. We know that in the range of concentration used in preparative liquid chromatography (up to 5% w/w maximum), the diffusion coefficients do not change much with concentration. In other words, we can assume that the kinetics of mass transfer is accounted for by an apparent diffusion coefficient, D_a, (*13*) such that

$$[\sigma]^2 = 2D_a t_0 = HL \tag{4}$$

where $[\sigma]$ = the standard deviation of the band of a very small sample (Gaussian band observed in linear chromatography)
t_0 = the retention time of a nonretained compound
H = the conventional HETP, which is nearly independent of k' for a given column
L = the column length

D_a, or the height equivalent to a theoretical plate, H, which is another expression of the kinetics of mass transfer, is constant during the experiment because the molecular diffusion coefficients do not vary much with concentration in the range investigated in preparative liquid chromatography.

Equation (1) and the corresponding kinetic equation can be replaced by a combination of

$$\left(1 + F\frac{\partial f}{\partial C}\right)\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} = D_a\frac{\partial^2 C}{\partial z^2} \tag{5}$$

and the isotherm, as given by Eq. (3).

The aim of this work is to relate the error made on the profile determined by numerical integration of the system of Eqs. (3) to the term in the RHS of Eq. (5).

5. Boundary Conditions

We take the classical conditions of elution chromatography. At time $t = 0$ the column contains only the mobile phase, i.e., a constant concentration of those compounds which belong to it. The sample concentration is zero. At the origin of the column ($z = 0$) we assume that the concentration of the sample is zero, except during a well-defined period of time of finite duration, during which it is given by a continuous function which is digitized to satisfy the requirements of the program. In the simple case of a pulse injection, the concentration is different from zero only during one time increment, τ, and the sample size is equal to the product of τ and the concentration of the pulse (and by the mobile phase flow rate, for reasons of homogeneity of the equations).

II. NUMERICAL INTEGRATION

We briefly describe the algorithm used and then discuss the errors introduced by the numerical procedure during the calculation of the profiles.

1. The Explicit Type

We replace the continuous part of the (z, t) plane where the solution is defined by a grid having intervals equal to τ and h in the time and space domains, respectively (*1*). We calculate successively the value of the concentration $C(n, j)$ at each point (n, j) of the grid, starting from the points on the time and space axis for which we know the solute concentrations from the boundary conditions.

We can rewrite Eq. (3) as

$$\frac{\partial C}{\partial z} + B\frac{\partial C}{\partial t} = 0 \qquad (6)$$

with

$$B = 1/u_z$$

and

$$u_z = \frac{u}{1 + F\dfrac{\partial f}{\partial C}} \tag{7}$$

The numerical algorithm used to derive a solution to the system of partial differential equations described above, using the finite difference method discussed by Rouchon (*1*), is given by the following equation (*1*, *5*, *7*):

$$\frac{C_j^{n+1} - C_j^n}{h} + B\frac{C_j^n - C_{j-1}^n}{\tau} = 0 \tag{8}$$

where τ = the time integration increment
h = the space length integration increment
C_j^n = the concentration at the point $(nh, j\tau)$ of the grid

The definition chosen for the derivation of Eq. (8) corresponds to the explicit type (*14*).

2. The Courant Condition

The numerical values of the space length and time increments in Eq. (8) cannot be chosen independently but must satisfy a certain relationship in order for a stable solution to be obtained (*1*, *14*).

In the linear case, if the concentration C_j^n at the point (n, j) of the grid is given by

$$C_j^n = \lambda_j^n \exp(ijk\tau) \tag{9}$$

where $i^2 = -1$ and k is an integer, we obtain

$$\lambda = 1 - a^{-1} + a^{-1}\exp(-ik\tau) \tag{10}$$

where $a = u_z\tau/h$ is the Courant number.

In order to obtain stable results, we must make sure that the time and space length increments are selected in such a way that

$$\|\lambda\| < 1 \tag{10a}$$

This requires that $0 < 1/a < 1$ or $a > 1$. We have chosen a value of a equal to 2.

In the nonlinear case we have (*1*)

$$\operatorname*{Sup}_{C} a^{-1}(c) < 1 \tag{10b}$$

or

$$\frac{\tau}{hC} \inf_{C} u_z(c) > 1 \tag{10c}$$

For any convex function, such as a Langmuir isotherm, inf $u_z = u/(1 + FG)$, where G is the first-order derivative of f at $C = 0$ (i.e., k_0').

3. Artificial Dissipation Coefficient

The use of Eq. (8) to replace Eqs. (6) and (7) entails an error which can be estimated in a first approximation by using Taylor expansions of the concentration (*14*):

$$C_j^{n+1} = C_j^n + h\left(\frac{\partial C}{\partial z}\right)_j^n + \frac{h^2}{2}\left(\frac{\partial_2 C}{\partial z^2}\right)_j^n + \cdots \tag{11}$$

and

$$C_{j-1}^n = C_j^n - \tau\left(\frac{\partial C}{\partial t}\right)^n + \frac{\tau^2}{2}\left(\frac{\partial^2 C}{\partial t}\right)_j^n + \cdots \tag{12}$$

From Eq. (6) and since in a linear approximation B is constant, we can derive

$$\frac{\partial^2 C}{\partial z^2} = B^2 \frac{\partial^2 C}{\partial t^2} \tag{13}$$

Combination of Eqs. (8) and (11)–(13) gives

$$\frac{C_j^{n+1} - C_j^n}{h} + B\,\frac{C_j^n - C_{j-1}^n}{\tau}$$

$$= \left(\frac{\partial C}{\partial z}\right)_j^n + \frac{h}{2}\left(\frac{\partial^2 C}{\partial z^2}\right)_j^n + B\left(\frac{\partial C}{\partial t}\right)_j^n - \frac{\tau}{2B}\left(\frac{\partial^2 C}{\partial z^2}\right)_j^n \tag{14}$$

Comparing Eqs. (8) and (14) gives

$$\frac{\partial C}{\partial z} + B\frac{\partial C}{\partial t} = \frac{h}{2}(a - 1)\frac{\partial^2 C}{\partial z^2} \tag{15}$$

or

$$\left(1 + F\frac{\partial f}{\partial C}\right)\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} = \frac{hu}{2}(a - 1)\frac{\partial^2 C}{\partial z^2} \tag{16}$$

The RHS of Eq. (16) is an artificial dissipation term. The artificial dissipation coefficient is

$$D_r = \frac{hu}{2}(a - 1) \tag{17}$$

The first factor of Eq. (17) ($hu/2 = hl/2t_0$) is best approximated by the apparent diffusion coefficient defined in Eq. (4), assuming that the column efficiency is constant.

4. Space Length Increment and HETP

The HETP in linear chromatography is classically defined by the second relationship in Eq. (4). Accordingly, it is equal to $2D_a t_0/L$, i.e., to $2D_a/u$. Thus, if we take

$$h = H \tag{18}$$

and

$$\tau = \frac{2H}{u_z} \tag{19}$$

we have a Courant number, a, equal to 2. Then, from Eq. (17), the artificial dissipation coefficient becomes equal to the apparent diffusion coefficient. Numerical calculations supply an approximate solution of Eq. (3) which is a correct solution of Eq. (5), i.e., an approximate solution of Eq. (1), the fundamental equation of chromatography. The kinetics of mass transfers between phases has been accounted for by a combination between an equilibrium isotherm and a global, apparent diffusion coefficient. This has been called the semi-ideal model (*4*). The numerical solutions exhibit self-sharpening profiles for large concentrations, characteristic of "overloaded" chromatographic columns. In fact, the apparent diffusion coefficient is different from the coefficient of the corrective term actually introduced by the numerical integration. The former follows a mass conservation law and transfers masses from the high frequency to the low frequency domain of the column response spectrum. The latter is a dissipative coefficient, which smoothes the profiles obtained, but the effect on the profile is similar.

Acknowledgments

We acknowledge fruitful discussions with Patrick Valentin (ELF, Solaize, France), S. Golshan-Shirazi, and Anita Katti (UTK and ORNL).

This work was done with partial support from the National Science foundation (Grant CHE-8519789) and from the cooperative agreement between the University of Tennessee (Knoxville) and the Oak Ridge National Laboratory.

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Received by editor February 8, 1988