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# Study of the Influence of Axial Dispersion on the Band Profile in Nonlinear Chromatography Using the Lax-Wendroff Method

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## Abstract

A comparison is made between the results obtained with the Lax-Wendroff and the characteristic algorithms for the integration of the system of partial differential equations of chromatography. The influence of the diffusion coefficient on the elution profiles is determined in the linear and the nonlinear cases by using two different sets of boundary conditions, and the results are compared. A new phenomenon is predicted in the nonlinear case, which has no equivalent in the linear case; the regressive behavior of the retention time of the band maximum when the diffusion coefficient increases from values near 0 to very high values. On the other hand, it is observed that the elution profiles predicted by the Lax-Wendroff method are relatively independent of the values of the space and time increment chosen for the calculation, the opposite of what has been reported with the characteristic algorithm. This will provide a suitable procedure for the numerical calculation of solutions of kinetic models.

## INTRODUCTION

Molecular diffusion is a physical phenomenon of great importance in both linear and nonlinear chromatography. Different effects are controlled by diffusion, such as the axial dispersion and several of the sources of radial resistance to mass transfer between the stream of mobile phase percolating through the bed of packing material and the stationary phase where the interaction(s) responsible for retention can take place. In this paper, however, we essentially consider the influence on the elution band profiles of the axial dispersion which results from molecular diffusion along the column axis and from the turbulence of the mobile phase stream (*1*). The former is due to the smoothing effect on concentration profiles of the molecular diffusion which, after Fick's law, acts to dampen concentration gradients and also depends on the tortuosity of the column packing. The latter appears in a fluid stream of very low Reynolds number because of the roughness of the channels open to flow between particles. For the same reason, the distribution of the lengths of the various flow lines has a finite width. These various phenomena affect the elution profiles in a complex way. In a first approximation, however, they can be treated as if they were the result of a unique diffusion phenomenon acting along the column axis, the axial diffusion.

In linear chromatography, diffusion affects the value of the retention time of the band maximum. It has been shown that the retention time decreases monotonically with increasing value of the diffusion coefficient (*2*), since the first-order moment of the elution band is $\mu_1 = t_0(1 + FG)$ (where $G$ is the slope of the isotherm at the origin and $F$ is the phase ratio) and the third-order, centered moment of the elution profile, which is related to the skew of the profile, is a function of the mass transfer and the diffusion coefficients and is always positive. Thus, it is only if the axial diffusion coefficient is zero and the mass transfer coefficient is large that the third moment is zero, the profile is symmetrical, and its retention time is equal to the first moment. When the axial dispersion is finite, the retention time of the band maximum is obviously smaller than the first moment; it decreases with increasing value of the dispersion coefficient. In most practical cases of linear chromatography, however, the axial diffusion coefficient is small, and the difference between the first moment and the retention time of the band maximum is small (*1*).

In nonlinear chromatography, the effect of axial dispersion is different. A regressive variation of the retention time with increasing value of the dispersion coefficient takes place. When the dispersion coefficient is decreased from a high initial value, the retention time of the band maximum increases at first (*3–5*). When the coefficient becomes lower than a certain threshold, however, a shock layer (*6*) appears on one side of the profile and becomes thinner and thinner. From then on, the retention time decreases with decreasing axial dispersion coefficient. This phenomenon illustrates the important character of the influence of the axial dispersion on the band profile in nonlinear chromatography, i.e., the coupling between axial dispersion and nonlinear behavior.

The nonlinear behavior of band migration at high concentrations results from the concentration dependence of the velocity associated with each concentration wavelet. This concentration dependence causes the self-sharpening of some part of the profile (e.g., its front in the case of a Langmuir isotherm), while contributing to the broadening of the profile in some other parts (e.g., its rear in the case of a Langmuir isotherm). The extent of the self-sharpening effect depends on the relative magnitude of the isotherm curvature (source of the nonlinear behavior) and the dispersion coefficient (*7*). If the self-sharpening effect is weak, the band becomes unsymmetrical and tails (convex isotherms, e.g., Langmuir, front shock and diffuse tail) or leads (concave isotherms, tail shock and diffuse front). If the effect is large, a concentration shock layer (or even a concentration shock (discontinuity) if the dispersion coefficient is zero) takes place. The effect of molecular diffusion on the band profile is of smoothing and broadening, resulting in more dilution of the sample in the mobile phase, hence changing the migration velocity and the extent of self-sharpening of the profile.

The effect of axial dispersion on the elution profiles of high concentration chromatographic bands has been discussed by several authors (*4*–*9*). Perturbation analysis permitted the study of weak nonlinear behavior (*8*). Houghton (*4*) and Yeroshenkova et al. (*5*) gave a complete solution of the band profile in the case of moderate or strong nonlinear behavior, resulting in the formation of shock layers. The occurrence of these shock layers and the influence of axial dispersion on them affects the peak position and its shape (*6*, *10*). The solution derived by Houghton permits a correct prediction of the variation of the retention time of the band maximum at the onset of nonlinear behavior (*4*, *11*, *12*). This approach involves the replacement of the mass balance equation for the solute by a Burger equation, which can be solved in this case (*4*, *11*). This simplification, however, loses the mass conservation of the profile and prevents the extension of the solution to very high concentrations. An algorithm permitting a numerical solution of one of the possible systems of equations accounting for a kinetic model of chromatography has been discussed previously and some results presented (*13*).

Most of the work previously published on the mathematical properties of the various systems of equations which represent the classical models of chromatography have mainly dealt with the ideal model in which constant equilibrium between the mobile and the stationary phase is assumed (*14*). A detailed, accurate study of the influence of axial dispersion on the band profile and especially on the thickness of the shock layers in a wide range of values of the axial dispersion coefficient, e.g., for $D = 0 \rightarrow 1$, is difficult. Characteristic finite difference methods using an artificial dispersion can be used for the cases when $D$ is small, for example, with $D = 10^{-5}$–$10^{-4}$ cm$^2$/s (*10*). For larger values of $D$, the values of the space and time increments to be used for a proper simulation of the axial dispersion and to satisfy the Courant-Friedrichs-Lewy condition become too large, and unsatisfactory results are obtained. Average center difference and jump point schemes are suitable for large values of $D$.

In the present paper we use a Lax-Wendroff scheme which permits an investigation of the influence of the dispersion coefficient in a large range of values. This approach has allowed the demonstration of the regressive variation of the retention time of the band maximum with increasing dispersion coefficient at constant sample size. We have also examined the influence on the elution band profile of axial diffusion during injection of the sample. Profiles corresponding to different boundary conditions, some more realistic than the classical rectangular pulse injection, have been studied.

## MATHEMATICAL MODEL AND LAX-WENDROFF SCHEME

In the following we discuss the mathematical model of chromatography and its numerical solution in the case of a single component sample. Most observations and comments apply as well to a multicomponent problem. The main difference in the latter case comes from the complexity of the multicomponent isotherm function which must be used to account for the competition between the mixture components.

### 1. Mathematical Model

The mathematical model of chromatography for one compound includes the mass balance equation for this compound:

$$\frac{\partial c}{\partial t} + F\frac{\partial q}{\partial t} + u\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} \qquad (1)$$

In this equation, $c$ and $q$ are the concentrations of the studied compound in the mobile and stationary phase, respectively, $t$ is the time and $x$ the abscissa along the column, $F$ is the phase ratio, $u$ is the local velocity of the mobile phase, and $D$ is the coefficient of axial dispersion which accounts for the molecular diffusion, the tortuosity of the packing, and the so-called eddy diffusion (*1*). The latter is related to the hydrodynamics of the mobile phase stream percolating across the column packing.

We can neglect the mass balance equation for the mobile phase if we assume the proper convention for adsorption (*15*). Equation (1) contains two functions of the time and abscissa along the column, $q$ and $c$. We need another equation to relate these two functions. We use the kinetic equation which accounts for interphase mass transfer:

$$\partial q/\partial t = K[f(c) - q] \tag{2}$$

where $f(c)$ is the isotherm equation of the compound in the phase system investigated, i.e., the concentration of the compound in the stationary phase at equilibrium with the concentration $c$ in the mobile phase. In Eq. (2), $K$ is a rate constant, the coefficient of mass transfer. The kinetic Eq. (2) writes that the rate of change in the concentration of the solute in the stationary phase is proportional to the deviation from equilibrium, which is valid only if the system is always close to equilibrium, i.e., provided that the column efficiency is high.

In order to proceed further, we must complete this system of equations by the initial and boundary conditions. The following condition simulates the pulse injection of a pure compound, at a constant concentration in the mobile phase stream, during a certain period of time:

$$c(0,t) = \begin{cases} c_0, & 0 \leqslant t \leqslant \tau \\ 0, & t > \tau \end{cases} \tag{3}$$

Prior to this injection, the column was empty, which is expressed by the initial condition:

$$q(x,0) = c(x,0) = 0, \qquad x > 0 \tag{4}$$

Equations (1) to (4) constitute the simplest form of the general mathematical model of chromatography. It includes a very simple kinetic equation which, in fact, assumes that the system is always near equilibrium. Otherwise, the kinetics of interphase equilibration would be more complex than given by Eq. (2). As a matter of fact, detailed studies of this kinetics, undertaken within the framework of the linear model, have resulted in extremely complicated sets of equations (*16*, *17*). Besides the adsorption kinetics which is described by Eq. (2), several stages of diffusion are involved, especially the diffusion across the interface between the mobile phase stream percolating through the column packing and the stagnant mobile phase contained within the particles, and the molecular diffusion inside the pores of these particles.

The model just described cannot be solved by an analytical expression of the elution profile. A related model, formulated by Thomas (*18*), has been studied by Goldstein (*19*). Instead of Eq. (2), it uses Langmuir adsorption kinetics. The relation between Eq. (2) and the Langmuir kinetic equation, i.e., between the present model and Thomas', has been discussed by Hiester and Vermeulen (*20*). An analytical solution of the Thomas model has been recently derived by Wade et al. (*21*). In the general case, however, solutions of a kinetic model must be calculated with the help of a computer.

Several general methods are available to calculate numerical solutions of systems of partial differential equations such as the one discussed here. Finite difference methods, finite elements methods, and collocation could be used. Since the problem studied involves only one space dimension, the column length, the computational speed is less critical than with similar three-dimensional problems. We have opted for finite difference methods which do not require fixed boundary conditions for the column exit, as finite element methods do. There are several such methods available, however, and we now compare two of them which we have used.

## 2. Lax-Wendroff Finite Difference Equation

In this case the partial differential Eqs. (1) and (2) are replaced by the following algebraic, finite difference Eqs. (5) and (6), respectively:

$$\frac{c_j^{n+1} - c_j^n}{\tau} + \frac{q_j^{n+1} - q_j^n}{\tau} + u\,\frac{c_{j+1}^n - c_{j-1}^n}{2h} - \left(\frac{u^2\tau}{2h^2} + \frac{D}{h^2}\right)(c_{j+1}^n - 2c_j^n + c_{j-1}^n)$$
$$= 0 \tag{5}$$

and:

$$\frac{q_j^{n+1} - q_j^n}{\tau} = K[f(c_j^n) - q_j^n] \tag{6}$$

A program implementing this numerical solution has been written. The results obtained are discussed in a later section.

## 3. The Characteristic Finite Difference Equation

In previous work we have used another numerical scheme for the calculation of numerical solutions of the mathematical model of chromatography by using the simplifying assumption called the ideal model. This numerical scheme is based on the characteristic equation (*10*).

In the ideal model it is assumed that the column efficiency is infinite, so changes in elution band profiles are due only to the thermodynamics contribution, i.e., to the nonlinear behavior of the equilibrium isotherm. The coefficient $D$ in Eq. (1) is assumed to be zero, and Eq. (2) is replaced by $q = f(c)$. The results of this simulation have been published (*13*), and excellent agreement between these predictions and experimental results have been demonstrated (*22*). The numerical errors made during the calculation and which are due to the finite character of the time and space increments which must be used, act as the contribution of a diffusion coefficient. The conditions to be satisfied in order to permit the simulation of real columns with a finite, albeit large, efficiency have been discussed (*23*). This latter work constitutes the basis of the semi-ideal model of chromatography and justifies the use of a finite difference method for the numerical calculation of solutions of the chromatographic model (*24*).

A finite difference equation, similar to Eq. (5), can be written for the numerical calculation of solutions of Eq. (1). Now, of course, the axial dispersion coefficient is no longer zero. The equation becomes

$$\frac{c_j^{n+1} - c_j^n}{\tau} + F\frac{q_j^{n+1} - q_j^n}{\tau} + u\frac{c_j^n - c_{j-1}^n}{h} - \frac{D}{h^2}(c_{j+1}^n - 2c_j^n + c_{j-1}^n) = 0 \tag{7}$$

Equation (6) is unchanged in this case.

## 4. Comparison between the Lax-Wendroff and the Characteristic Scheme

The major difference between Eqs. (5) and (7) is the introduction in the former of an additional dispersion term which cancels out the effect of the artificial dispersion introduced by the finite character of the time and space increments used for the numerical integration of the partial differential Eq. (1), since

$$u\,\frac{c_j^n - c_{j-1}^n}{h} = u\,\frac{c_{j+1}^n - c_{j-1}^n}{2h} - \frac{uh}{2}\,\frac{c_{j+1}^n - 2c_j^n + c_{j-1}^n}{h^2} \tag{8}$$

and:

$$\left(\frac{uh}{2} - \frac{\tau u^2}{2}\right) = \frac{uh}{2}\left(1 - \frac{u\tau}{h}\right) = \frac{uh}{2}(1 - a) \tag{9}$$

where $a$ is the Courant number and $(uh/2)(1 - a)$ is the artificial dispersion coefficient.

Accordingly, the accuracy of the numerical calculation performed according to Eq. (5) is much better than that made following Eq. (7). The numerical errors made with the Lax-Wendroff scheme are of the second order, i.e., of the order of $(h^2 + \tau^2)$ (*25*). This means that the numerical solutions of the model calculated using the Lax-Wendroff scheme are relatively independent of the numerical values chosen for the time, $\tau$, and the space, $h$, increments. The Lax-Wendroff scheme in the nonlinear case, however, contains an additional term (*25*).

This is a necessary quality in a numerical scheme to be used for the calculation of solutions of the system of Eqs. (1) to (4), since Eqs. (1) and (2) contain the axial dispersion and the resistance to mass transfer responsible for the finite efficiency of chromatographic columns. Then, the characteristic scheme used for the calculation of numerical solutions of the ideal model would give erroneous results. As shown above, this scheme introduces first-order errors which can be adjusted to provide approximate solutions of the ideal model which are in excellent agreement with experimental results, because the first-order errors can be adjusted, by a proper choice of the integration increments, to replace the band-broadening contributions neglected in the ideal model (*13*, *22*). With a nonideal kinetic model, such as the one discussed here, these contributions would be counted twice, which is not acceptable.

## 5. Effect of Different Boundary Conditions

The previous discussion has illustrated the importance of dispersion effects in chromatography. We cannot neglect the influence of axial dispersion on band profiles during the migration of the sample bands along the column. We cannot neglect it during injection either. Proper boundary conditions are required in order to achieve a realistic simulation of the band profile.

Two kinds of boundary conditions are classically used by chemical engineers for problems of that type. The first one of these conditions is the following:

$$c(x = 0,t) = \psi(t) \qquad \text{and } c(x = \infty,t) \text{ is finite} \tag{10}$$

It belongs to the first class of boundary conditions in mathematics. The second type of conditions used is the Danckwerts boundary condition, which belongs to the third class and is written as follows, in the present case:

$$\begin{aligned} c - D\frac{\partial c}{\partial x} &= \phi(t), \qquad x = 0 \\ \partial c/\partial x &= 0, \qquad x = L \end{aligned} \tag{11}$$

While Eq. (10) does not consider diffusion during injection, it is taken into account by Eq. (11). If we use a finite difference method, we may write the first equation in the Condition (11) as follows:

$$uc_1^n - D\frac{c_1^n - c_0^n}{h} = \phi^n \tag{12}$$

If $D = 0$, this condition degenerates into a condition of the first class. From Eq. (12), we have

$$c_0^n = \frac{h}{D}\phi^n - c_1^n\left(1 - \frac{uh}{D}\right) \tag{13}$$

Obviously, different boundary conditions will lead to different band profiles in nonlinear chromatography, since these conditions correspond to different injection bands. They will influence differently the formation of concentration shocks or shock layers, the retention time, and the entire profile. Figure 1 shows the profiles of one first-class injection (i.e., a rectangular pulse with a maximum concentration $C = 5$ m$M$ and a width

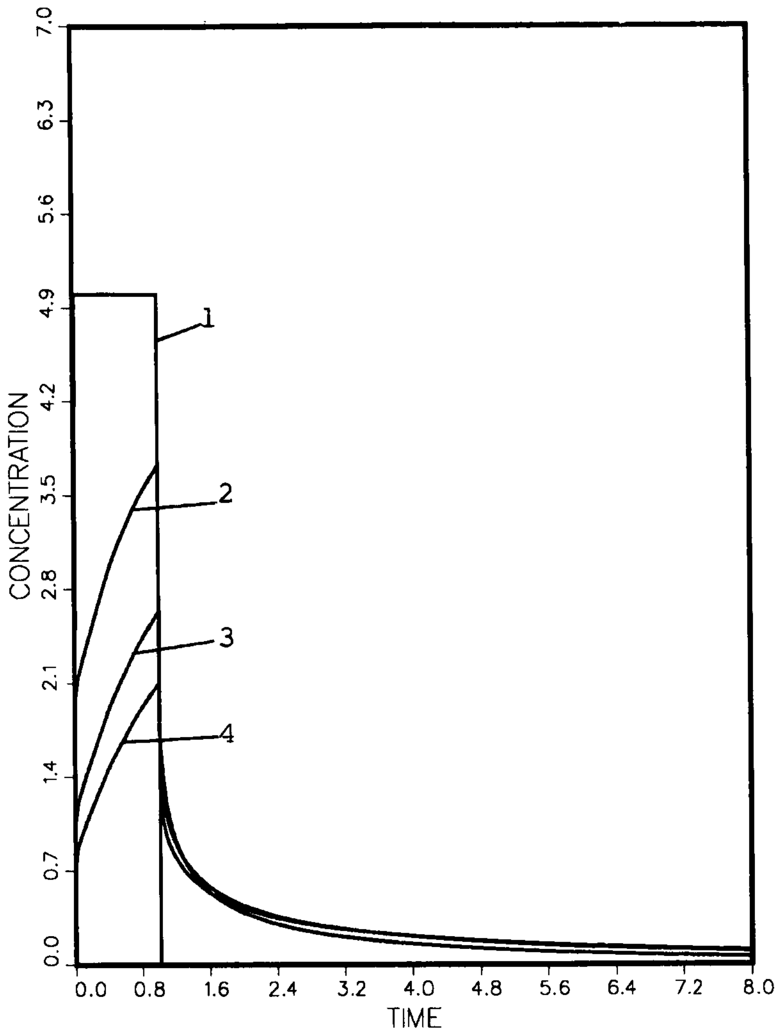

FIG. 1. Injection profiles corresponding to the different boundary conditions used. 1: First-class condition (rectangular pulse). 2: Third-class condition, see Eq. (11), $D = 0.04$ cm$^2$/s. 3: Third-class condition, $D = 0.08$ cm$^2$/s. 4: Third-class condition, $D = 0.12$ cm$^2$/s.

of 1 s) and of three different Danckwerts injections, with increasing values of the diffusion coefficient. The similarity with the profiles actually recorded for injection bands (*26*) is striking.

## RESULTS AND DISCUSSION

The results of different simulations carried out using a program implementing the Lax-Wendroff scheme for the calculation of numerical solutions of the kinetic model of chromatography (Eqs. 1 to 4) discussed above are shown in Figs. 2 to 5. In each case, calculations were made for a constant size sample, with decreasing values of the axial dispersion coefficient. The sample size is large and the retention times are very different whether the isotherm is linear (Figs. 3 and 5) or nonlinear (Figs. 2 and 4). The numerical values of the coefficients used in this work are reported in Table 1. The retention times obtained for the simulated profiles shown in Figs. 2 to 5 are reported in Table 2. Figures 2 and 3 correspond to a first-class boundary codnition; Figs. 4 and 5 to a third-class one.

In all cases, with a linear or a nonlinear isotherm and with a first- or a third-class boundary condition (injection), when starting from very large values of the dispersion coefficient and reducing this coefficient progressively, we observe that the retention time increases with decreasing dispersion coefficient (see Table 2 and Figs. 2 to 5). The major difference between a linear and a nonlinear isotherm is that in the former case the retention time always increases when the dispersion coefficient tends toward zero (Figs. 3 and 5), while in the latter case the retention time begins to decrease when the shock layer appears (see Figs. 2 and 4, axial dispersion coefficient between 0.012 and 0.04 $cm^2/s$) and continues to decrease with decreasing value of the axial dispersion coefficient until this coefficient becomes zero. This last effect is in agreement with the prediction derived from the Houghton equation (*4*, *11*). Nevertheless, the influence of the dispersion coefficient, even in a wide range of variation, is much smaller than that of the mass transfer coefficient (*13*).

Comparison between Figs. 2 and 4 (or Figs. 3 and 5 in the linear case) illustrates the influence of the boundary conditions (injection band profile). With a third-class boundary condition (diffuse injection profile), the retention times of the band maxima are larger than they are with a first-class boundary condition (rectangular pulse) when the dispersion coefficient is large. The effect reverses at low values of the axial dispersion coefficient. The same variation of the difference between the retention times of the bands obtained with a first- and a third-class

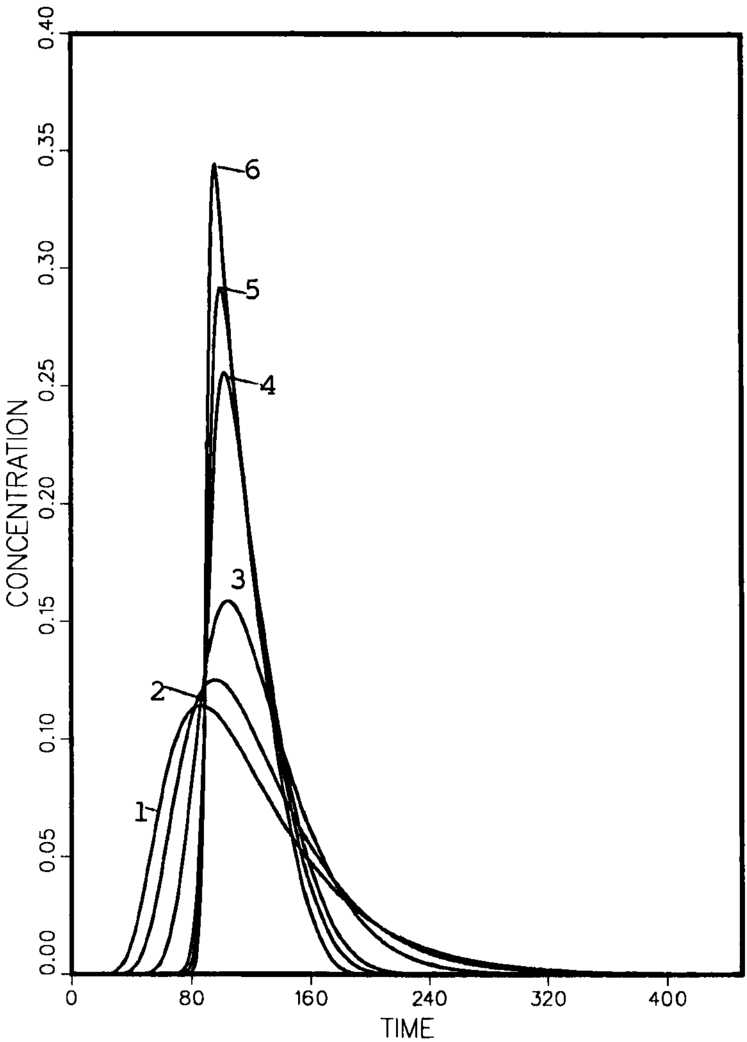

FIG. 2. Band profiles for a nonlinear isotherm. Decreasing values of the axial dispersion coefficient. First-class boundary condition (Eq. 10). Numerical values of the parameters in Table 1. Retention times of the maximum of the bands in Table 2. 1: $D = 0.120$ cm$^2$/s. 2: $D = 0.080$ cm$^2$/s. 3: $D = 0.040$ cm$^2$/s. 4: $D = 0.012$ cm$^2$/s. 5: $D = 0.008$ cm$^2$/s. 6: $D = 0.004$ cm$^2$/s.

TABLE 1
Experimental Conditions for the Simulations Reported in Figs. 2 to 5

| |
|---|
| Column length: 5 cm inner diameter: 4.6 mm; phase ratio: 0.75 |
| Flow velocity: 0.25 cm/s (2 mL/min) |
| Parameters of the Langmuir isotherm: $a = 9, b = (q = ac/(1 + bc))$ |
| Sample size: 0.41 mmol |

TABLE 2
Influence of the Diffusion Coefficient on the Retention Time (s)[a]

| | Linear isotherm | | Nonlinear isotherm | |
|---|---|---|---|---|
| $D$ (cm$^2$/s) | First-class boundary condition | Third-class boundary condition | First-class boundary condition | Third-class boundary condition |
| 0.120 | 106.39 | 117.04 | 86.40 | 98.40 |
| 0.080 | 119.19 | 126.54 | 96.00 | 104.00 |
| 0.040 | 135.20 | 137.96 | 104.00 | 107.20 |
| 0.012 | 147.95 | 147.59 | 102.40 | 101.60 |
| 0.008 | 150.11 | 149.24 | 99.20 | 98.40 |
| 0.004 | 152.79 | 151.20 | 96.00 | 94.40 |

[a] Sample size: 1.53 mmol.

injection function is observed for a linear and a nonlinear isotherm (see Table 2). The change in the sign of this difference is observed for approximately the same value of the axial dispersion coefficient (~0.020 cm$^2$/s) in both cases.

The data in Table 3 show that the same regressive variation of the retention time is observed with a large change of the sample size. The range of retention time varies with the sample size because, with a Langmuir isotherm, the retention time of the band maximum decreases with increasing sample size, but the relative variation of the retention time remains comparable. Obviously, for a linear isotherm there is no change in the direction of variation of the retention time with changing sample size.

As pointed out in a previous section, the Lax-Wendroff scheme includes only second-order errors, which makes the result relatively insensitive to the values selected for the space and time increments in the numerical integration. The artificial, numerical dispersion coefficient

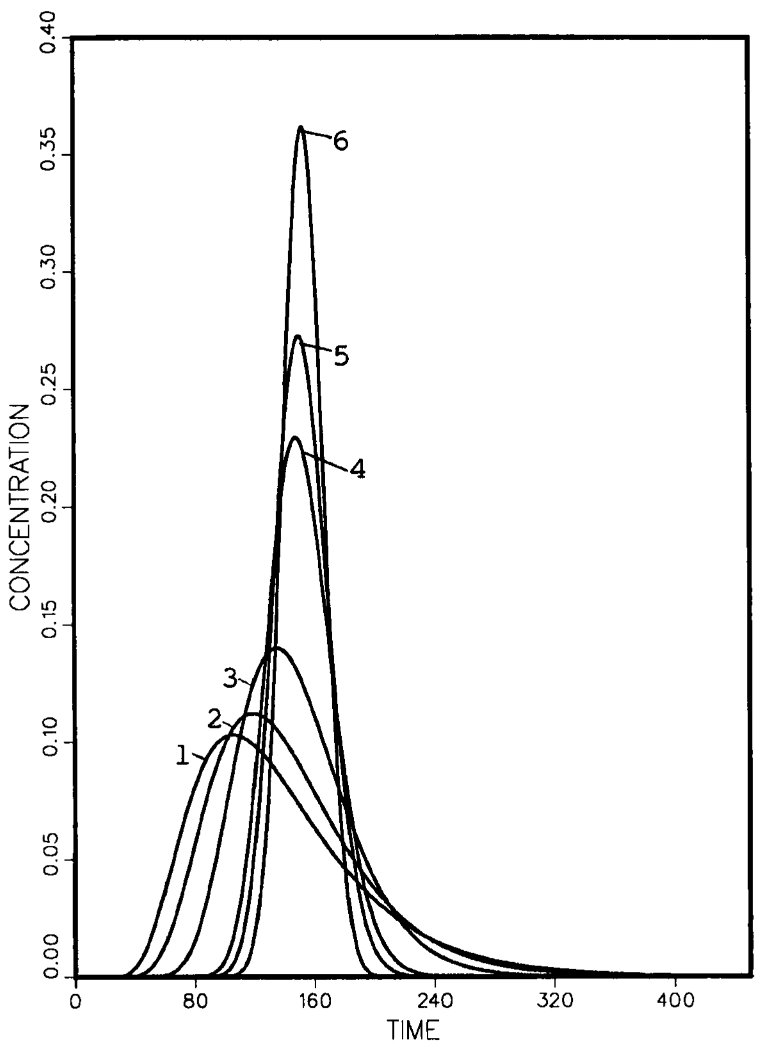

FIG. 3. Band profiles for a linear isotherm. Decreasing values of the dispersion axial coefficient. First-class boundary condition (Eq. 10). Numerical values of the parameters in Table 1. Numbers on curves, see Fig. 2. Retention times of the maximum of the bands in Table 2.

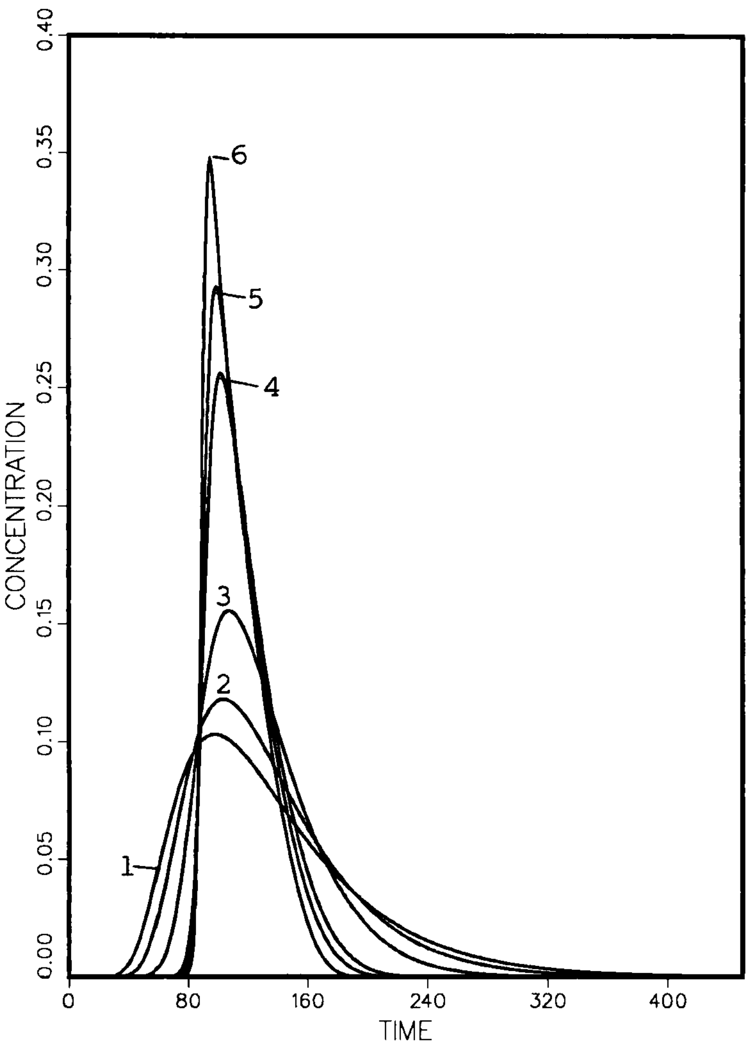

FIG. 4. Band profiles for a nonlinear isotherm. Decreasing values of the dispersion coefficient. Third-class boundary condition (Eq. 13). Numerical values of the parameters in Table 1. Numbers on curves, see Fig. 2. Retention times of the maximum of the bands in Table 2.

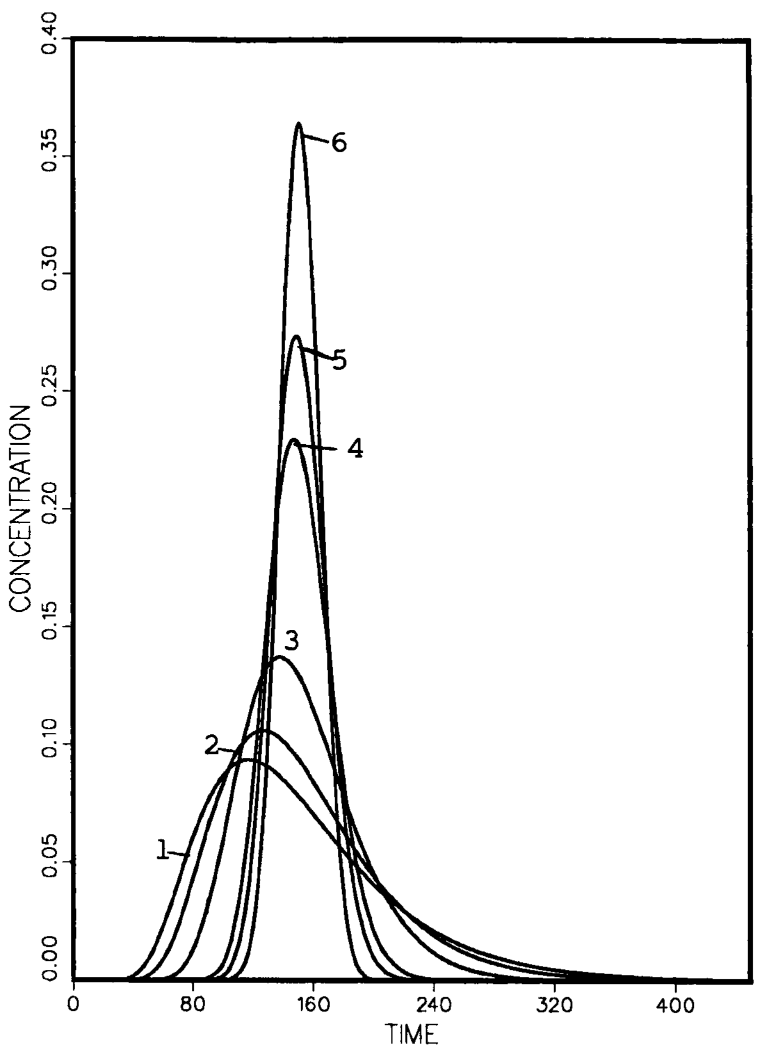

FIG. 5. Band profiles for a linear isotherm. Decreasing values of the dispersion coefficient. Third-class boundary condition (Eq. 13). Numerical values of the parameters in Table 1. Numbers on curves, see Fig. 2. Retention times of the maximum of the bands in Table 2.

TABLE 3
Influence of the Diffusion Coefficient and the Sample Size on the Retention Time (s)[a]

| $D$ ($cm^2/s$) | Sample size (mmol) 0.41 | 1.53 | 3.26 |
|---|---|---|---|
| 0.120 | 100.87 | 86.40 | 70.25 |
| 0.080 | 112.98 | 96.00 | 77.01 |
| 0.040 | 126.49 | 104.00 | 80.88 |
| 0.012 | 133.86 | 102.40 | 75.43 |
| 0.008 | 133.55 | 99.20 | 73.33 |
| 0.004 | 131.20 | 96.00 | 71.20 |

[a] Nonlinear isotherm, first-class boundary condition.

associated with this scheme is zero. The comparison between Figs. 6 and 7 illustrates the difference between the Lax-Wenfroff and the characteristic schemes. A threefold variation in the space increment of integration results in the former case in a small shift of the profile without any change of its shape or width. With the characteristic scheme it results in a wider profile, corresponding to a three times larger column HETP, as already observed (*23*, *24*). This result is important for three reasons.

First, it confirms that the profiles obtained by the procedure described here and which are illustrated by the results shown in Figs. 2 to 5 are accurate. Second, it permits the use of relatively large increments for the calculation of numerical solutions of the equation system, even when the mass transfer kinetics is fast and the axial dispersion is small, i.e., for high or very high efficiency columns. Such simulations were difficult or impossible using the previous, characteristic scheme (*7*) because, in this case, the computing time is proportional to the square of the efficiency of the simulated column and becomes prohibitively long for columns exceeding about 20,000 theoretical plates.

Finally, this method may permit an easy solution of the multicomponent problem. Because there can be only one value used for the space and the time increments during the calculation of the band profiles for a multicomponent sample, the same values must be used for the derivation of the whole chromatogram. On the other hand, the rules for the selection of the values of these increments give different results when applied to the

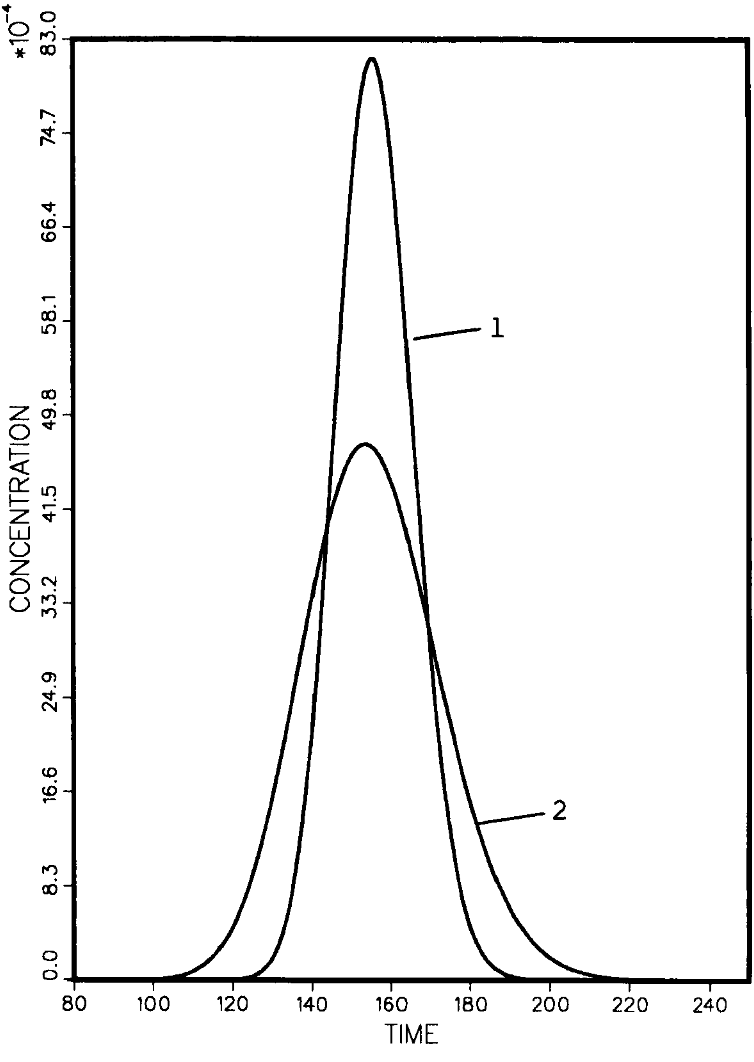

FIG. 6. Profiles obtained with the characteristic scheme for two different sets of integration increments. $\tau = 0.001$ s. 1: $H = 0.02$ cm. 2: $H = 0.06$ cm.

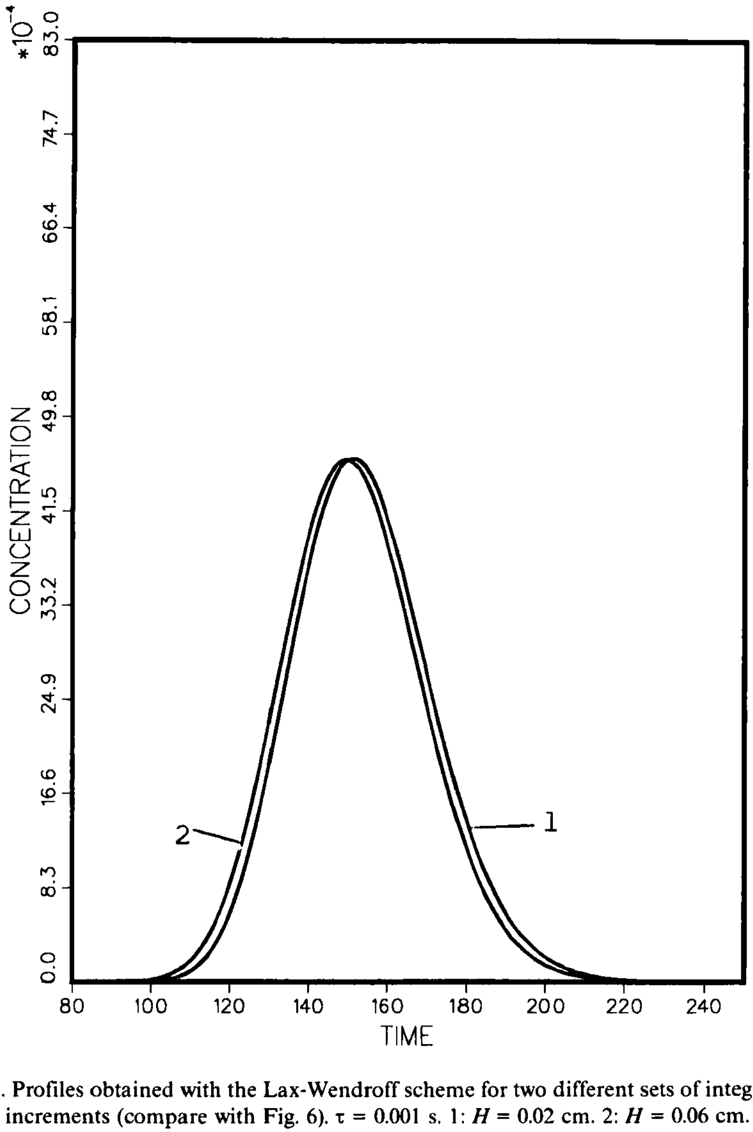

FIG. 7. Profiles obtained with the Lax-Wendroff scheme for two different sets of integration increments (compare with Fig. 6). $\tau = 0.001$ s. 1: $H = 0.02$ cm. 2: $H = 0.06$ cm.

different components of a mixture (*23*). This means that by selecting a single set of values for the calculation, we assume a relationship between the efficiency of the simulated column and the limit retention at infinite dilution of the mixture components (*27*). The problem is minor when the separation of closely eluted components of binary mixtures is investigated, but become serious for the simulation of gradient elution. The use of a Lax-Wendroff scheme permits a solution of this problem. Conversely, this approach is more complex and deliate, as the use of this scheme requires that both the axial dispersion coefficient and a global mass transfer resistance coefficient, which account together for the column efficiency, be selected independently.

Oscillations seem to occur frequently in the numerical solutions of partial differential equations, especially when high accuracy solutions are searched for. The conditions which are prevalent in nonlinear chromatography tend to favorize this phenomenon: discontinuous boundary conditions, very fast mass transfer between phses (or even infinitely fast mass transfers, e.g., in the ideal model), very small values of the axial dispersion coefficient, strongly nonlinear isotherms, and choice of small values of the integration increments because of physical constraints. The Lax-Wendroff scheme we have used here permits the minimization of the oscillations if it uses relatively large integration increments and a continuous boundary condition. Furthermore, the latter makes more physical sense since, whatever care is taken to achieve a rectangular pulse injection, some extent of axial dispersion always takes place in the transfer of the sample to the column. Most injection bands are exponentially convoluted rectangular pulses or Gaussian profiles.

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