Peak tailing and mass transfer kinetics in linear chromatography Dependence on the column length and the linear velocity of the mobile phase

Gustaf Gotmar[a], Torgny Fornstedt[a], Georges Guiochon[b],*

[a]*Department of Analytical Pharmaceutical Chemistry, Uppsala University, BMC Box 574, S-751 23 Uppsala, Sweden*
[b]*Department of Chemistry, The University of Tennessee, Knoxville, TN, 37996-1600 and Division of Chemical and Analytical Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

Abstract

Although peak tailing in analytical (i.e., linear) chromatography is often considered to be associated merely with slow mass transfer kinetics, we show that it results rather from the use of too short a column, at too high a mobile phase velocity, under such conditions that the mass transfer kinetics is insufficiently fast. The phenomenon is characterized by the dimensionless Stanton number, $St = k_f L/u$ (with k_f the rate coefficient of mass transfer, L the column length, and u the linear velocity of the mobile phase) which relates the average residence time of the molecules in the stationary phase ($1/k_f$) and the column hold-up time ($t_o = L/u$). If there is only one retention mechanism (e.g., in adsorption chromatography, if the surface of the adsorbent phase is homogenous), there is a critical range of Stanton numbers around 1 (depending slightly on the retention factor). If $St < 1$, a split peak effect is observed. For $1 < St < 10$, the peak tails severely and the asymmetry factor, asf_{10}, is equal to or larger than 1.2. For $St > 1000$, the peak profile is Gaussian and $asf_{10} = 1.0$. If there is a mixed mechanism (e.g., with a heterogenous adsorbent surface), the relationship between peak shape and Stanton numbers is more complex as it also depends on the relative contribution of both mechanisms to retention. The peak may tail severely for values of the smaller Stanton number between 10 and 100 and asf_{10} may be large. Split peak effect may arise at Stanton numbers below 10.   © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Peak tailing; Mass transfer kinetics; Column length; Mobile phase velocity; Linear velocity

1. Introduction

Peak tailing has a nefarious effect in analytical chromatography. It reduces, often considerably, the resolution between analytes, it causes band interference (hence preventing an accurate interpretation of UV spectra), and it decreases the accuracy of quantitative results because it confuses the area allocation between the compounds involved. This problem has received much attention, but has not been solved.

Some of the statements in the literature on analytical chromatography regarding peak tailing, mass transfer kinetics, and the contribution of active sites are discordant with the present state of theoretical knowledge. The goal of this paper is to attempt to clarify the relationships between the extent of tailing observed experimentally and the characteristics of the column and phase system used, so as to derive some practical rule which may help in reducing the consequences of excessive band tailing.

In a series of papers published nearly 20 years ago, Weiss cast serious doubts regarding the conven-

*Corresponding author.

tional interpretation of peak tailing through slow mass transfer kinetics [1–3]. Admittedly, it is true that homogeneous kinetics cannot account for the profiles of the tailing peaks encountered in most practical cases but that it is necessary to assume heterogeneous kinetics to achieve profiles bearing strong similarities with those of conventional experimental peaks [4–6]. However, the objection of Weiss is apparently more profound. He claimed '... that an isolated peak will [always] approach the Gaussian form at sufficiently long times.' [2,3]. This is certainly correct, the asymptotic solution of linear chromatography is a Gaussian profile [7]. The confusion arises from the fact that, in any applications of chromatography, we are never dealing with infinitely long columns and we do not have the possibility to wait for an infinite period of time and then record the elution band. Peak tailing arises because of this time limitation, because the elution band has not achieved its asymptotic profile. This conclusion is quite in agreement with the statements of Weiss [1–3] although, sometimes, it has been construed otherwise.

In previous publications, we have illustrated the consequences of slow mass transfer kinetics on the elution of chromatographic bands under linear [4] or nonlinear [5] conditions. Slow, homogeneous kinetics results in broad, unsymmetrical peaks and, eventually, for very low mass transfer rate coefficients, in the phenomenon of split peaks in which most of the sample is eluted as a highly efficient, unretained narrow peak and the rest in a long tail while the first moment of the band remains the one corresponding to the initial slope of the isotherm [4]. It is only when phase equilibrium and kinetics are heterogeneous that the conventional unsymmetrical peak observed in chromatography on 'active' stationary phases can be observed. Such phases contain two types of adsorption sites, with different retention factors and different mass transfer kinetics. Under the proper set of conditions, we observe narrow, tall, efficient peaks with a long tail affecting only the base of the peak but lasting for a large number of standard deviations of its quasi-Gaussian main mode [4]. We have also shown in an example, obtained under experimental conditions in which the existence of two different types of sites could be demonstrated, the importance of separating these two contributions [6].

This earlier study neglected, however, the influence of the rate of convection along the column. Obviously, if the band migrates slowly, it is possible that quasi-equilibrium between the mobile and the stationary phases be reached with a slower mass transfer kinetics than that necessary for bands migrating much faster. So, the aim of this paper is to show the role of the convection rate on the extent of peak tailing.

2. Theory

Peaks or band profiles are either concentration profiles along a column (i.e., $C(z)$ at constant t, during the migration of the band) or concentration histories at the exit of a column (i.e., $C(t)$ at $z=L$, during the elution of the band). They can be calculated under any set of experimental conditions provided that we have a proper column model, including (1) the differential mass balance equation of the compound(s) involved (2) their mass transfer kinetics (3) the equilibrium isotherm relating the component concentrations in the mobile and the stationary phase at equilibrium and (4) a statement of the boundary and initial conditions [7]. We now discuss these four points successively.

2.1. Column model

The differential mass balance equation of each component is the conservation law written for an infinitesimal slice of column

$$u \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + F \frac{\partial q}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \tag{1}$$

where t is the time, z is the axial position in the column, C and q are the local concentrations in the mobile and stationary phase, respectively, u is the mobile phase velocity, F is the phase ratio, and D is the axial dispersion coefficient [7].

Eq. (1) states that the increase of the amount of solute contained in the column slice considered is equal to the balance between the amount that enters into the slice and the one that leaves it, either by convection or by dispersion.

2.2. Initial and boundary conditions

The initial condition characterizes the state of the column when the sample injection is performed. This corresponds to a column empty of sample and containing only the mobile and the stationary phases in equilibrium

$$C(t = 0, z) = 0 \qquad (2)$$

The boundary condition characterizes the way into the sample is introduced into the column. In most practical cases encountered in HPLC, the contribution to column efficiency due to axial dispersion is quite small. Therefore, the dispersion effects can be neglected when writing the boundary condition. The classical Danckwerts boundary conditions [7] can be reduced to a rectangular injection pulse, with a concentration C_0 and a width t_p at the column inlet, as follows

$$C(t, z = 0) = C_0 \qquad 0 \leq t \leq t_p \qquad (3a)$$

$$C(t, z = 0) = 0 \qquad 0 > t \text{ or } t_p < t \qquad (3b)$$

These conditions assume that the column is well packed and exhibits a high efficiency for an unretained peak, so that the contributions of axial and eddy diffusion to band broadening are small, even if the mass transfer kinetic contribution is large.

2.3. Equilibrium isotherms

In this work, we consider only the analytical applications of chromatography, hence we use linear isotherms. This raises no further comment in the case of the adsorption of single components on homogenous surfaces at low concentrations. In the second part of this work, however, we consider cases in which the adsorbent surface is heterogenous. This is the case e.g., in chiral separations [6–12] and in the analysis of basic compounds in RPLC [13,14]. Then, there are two contributions to the apparent retention factor, k', originating from the two mechanisms

$$k' = F(a_1 + a_2) \qquad (4)$$

where F is the phase ratio and a_1 and a_2 are the slopes of the two linear contributions. At infinite dilution, the retention factor of the peak is directly

proportional to the initial slope of the overall isotherm. The two individual contributions cannot be determined separately by any type of analytical (i.e., linear) measurements. The overall equilibrium isotherm must be determined experimentally in order to determine separately the contributions of the two retention mechanisms (this is possible only if the global isotherm is nonlinear) [8].

2.4. Kinetics of mass transfer

The solid film linear driving force model [7] is best suited to account for the mass transfer kinetics in this study. Since we assume an heterogeneous surface, it is consistent to assume that mass transfer kinetics proceeds at different rates on both types of sites. For each type of site, the rate of change of the component concentration in the stationary phase is proportional to the difference between the equilibrium concentration in the stationary phase, $q_i^* = a_i C$, in the presence of the component concentration C in the mobile phase and the actual concentration on the type of sites i on the stationary phase, q_i. This leads to the following set of equations:

$$\frac{\partial q_1}{\partial t} = k_1(q_1^* - q_1) \qquad (5)$$

$$\frac{\partial q_2}{\partial t} = k_2(q_2^* - q_2) \qquad (6)$$

$$q = q_1 + q_2 \qquad (7)$$

Peak tailing will be shown to originate from a lower rate of desorption from the specific type 2 sites than from the nonspecific type 1 sites (i.e., $k_2 \ll k_1$), consistent with the higher adsorption energy on these sites causing an average residence time longer on the selective than on the nonselective sites.

2.5. System in reduced coordinates.

The system of Eqs. (1), (2), (3a), (3b), (4)–(7) constitutes a transport-dispersive model [7] modified to account for heterogeneous kinetics. This system can be rewritten under reduced or dimensionless coordinates. The advantage of this change of variables and parameters is that it will clearly show the interdependence of the parameters which control the

peak profile. We replace the classical parameters by
the following:

$$Pe = \frac{uL}{D_L} \tag{8a}$$

$$St = \frac{k_f L}{u} \tag{8b}$$

$$x = \frac{z}{L} \tag{8c}$$

$$\tau = \frac{ut}{L} \tag{8d}$$

In these equations, Pe and St are the Peclet and the
Stanton numbers, respectively. The Peclet number is
also known in chromatography as the reduced ve-
locity of the mobile phase. In chromatography, the
Stanton number plays the same role with mass
transfer kinetics as the Peclet number with axial
diffusion. Then, Eqs. (1), (2), (3a), (3b), (4)–(7)
become

$$\frac{\partial C}{\partial x} + \frac{\partial C}{\partial \tau} + F \frac{\partial q}{\partial \tau} = \frac{1}{Pe} \frac{\partial^2 C}{\partial x^2}$$

$$\frac{\partial q_1}{\partial \tau} = St_1(q_1^* - q_1) \tag{9}$$

$$\frac{\partial q_2}{\partial \tau} = St_2(q_2^* - q_2)$$

$$q = q_1 + q_2$$

This system of equations was solved numerically,
using the backward–forward finite difference method
as explained by Guiochon et al. [7].

To suit the study of particular cases, several
variants of the system of equations just described
were used. They include two variants of the linear
case, the first with only one rate constant (homogen-
ous, slow kinetics), the second with two rate con-
stants (heterogenous kinetics with a fast and a slow
kinetic components). As shown earlier [4], the latter
system describes a more realistic situation, quite
similar to those encountered either in the case of
enantioselective separations or in the case of RPLC
separations of some strongly polar components, such
as amines or many basic drugs [13,14]. For the sake
of simplicity, the same set of equations and the same
programs were used in the cases of an homogenous
and an heterogenous surface. In the former case, the

parameters of the kinetic equations were set so that
$k_1 = k_2$.

3. Results and discussion

The Stanton number, as defined in Eq. (8b), is the
ratio of the column hold-up time ($t_0 = L/u$) and the
average residence time of the molecules on the
corresponding type of sites (i.e., $1/k_{f,i}$). Thus, a low
Stanton number can be obtained with either a small
rate coefficient (long average residence time) or a
small hold-up time. As shown by the Eq. (9), it is a
more relevant parameter to characterize the degree of
peak tailing of kinetic origin than the mere rate
coefficient.

In the first part of the following discussion, we
consider the influence of the three components of the
Stanton number in the case of an homogenous
kinetics. In the second part, the same is done in the
case of an heterogenous kinetics. In both cases, we
neglect the influence of the axial dispersion due to
molecular and eddy diffusion (i.e., by setting $D = 0$
in Eq. (1)), because, when the mass transfer kinetics
is slow, the contribution of axial dispersion to
column efficiency is small. Then neglecting axial
dispersion is a minor approximation, well justified by
the considerable simplification of the discussion
achieved. Accordingly, the finite column efficiency
arises only from the slow mass transfer kinetics. The
column reduced HETP is given by [7]

$$h = \frac{L}{N d_p} = \frac{L}{d_p} \frac{1}{St} \frac{2k'}{(1 + k')^2} \tag{10}$$

The influence of axial dispersion was considered
in a previous study and was shown to have a
dampening effect on the peak tailing caused by
heterogenous kinetics [4].

In the numerical calculations, we assumed the
following values for those parameters which have no
importance on the results of the discussion. The
column is 4.6 mm I.D., the injection time is $1.0 \cdot 10^{-4}$
min, and the total porosity of the bed, ϵ_T, is 0.8,
giving a phase ratio, F, of 0.25. Although the
discussion is mainly focused on the peak shapes, the
degree of the asymmetry of the bands is also

quantified, by calculating the asymmetry factor at 10% of the peak height (asf_{10}).

3.1. Homogenous mass transfer kinetics

By setting $a_1 = a_2 = 10$ in Eq. (4) and $k_1 = k_2$ in Eqs. (5)–(7), we can use the set of Eq. (9) to account for the homogenous case, with only one type of sites ($a = a_1 + a_2 = 20$, hence $k'' = F (a_1 + a_2) = 5$) and one single rate constant k_f ($= k_1$ or k_2). It is easy to calculate band profiles by changing one by one the values of the mass transfer coefficient k_f, the column length L, and the linear mobile phase velocity u, while obtaining the same series of Stanton numbers. It would be pointless to report these results in detail, however, because it is clear from the system of Eq. (9) that once Pe has been neglected, the band profiles depend only on the value of the Stanton number.

3.1.1. Effect of the Stanton number

In an earlier work [4], we calculated band profiles for a series of values of the mass transfer rate coefficient. This time, we did these calculations for different values of the Stanton number. The correspondence between the value of the Stanton number and that of the different parameters, rate coefficient, mobile phase flow velocity, and column length is discussed in Section 3.1.2. Note that, for a given Stanton number, the value of the retention time of an unretained tracer, $t_0, = L/u$, is a function of both u and L and changes with changing values of these parameters at constant Stanton number. This is why the results are presented as plots of the concentration at the column exit (in arbitrary units) versus the dimensionless retention time, $\tau = t/t_0$ (see Eq. (8d)). With the numerical values chosen for the calculations, the thermodynamic value of the peak reduced retention time, $1 + k'$, is 6.00.

Fig. 1 shows a series of band profiles calculated for increasing values of the Stanton number ranging from 0.1 to 10 000. Table 1 lists the Stanton numbers corresponding to the different peaks in Fig. 1, their retention time, efficiency and degree of asymmetry, expressed as asf_{10}. For peaks 7–11, the Stanton number is equal to or larger than 10 (Table 1). The efficiency of these peaks was derived from the peak width at 50% of the peak height. The data show that

neglecting the axial dispersion is certainly valid for peaks 7–9 but is not so for peak 11. At values of the Stanton number smaller than or equal to 1, the split peak effect is observed. The elution bands 1 to 4 exhibit a narrow peak, eluted at $t = t_0$, with a long tail. This band shape is better illustrated in the enlargement of the first seven peaks in Fig. 2 ($0.1 < St < 10$).

When the Stanton number increases from 0.1 to 10, the initial, unretained peak decays (peaks 1 to 4) and then disappears (peaks 5 to 7). In the same time, the long tail inflates and transforms into the actual peak. Peak 4 ($St = 1$) is the intermediate case. It shows a peculiar shape, the maximum concentration of the 'tail' which has now become the main peak, is higher than that of the first, unretained peak. Note that the retention time of the band maximum increases from peak 4 to peak 8, to remain constant at larger values of the Stanton number (peaks 8 to 11). Also, the asymmetry factor of the peak decreases and becomes smaller than 1.10 for peak 9 and beyond (Table 1). The column efficiency is quite high ($N_{50} = 399$) for the initial, unretained peak (1, at $St = 0.1$). At first, it decreases slightly with increasing rate coefficient, to $N_{50} = 355$ for peak 3 ($St = 0.5$), then it falls dramatically to $N_{50} = 2.3$ for $St = 1$ (peak 4). Then, it increases rapidly with increasing value of St (Table 1).

The reason for this variation is obvious from the enlargement of Fig. 1 provided in Fig. 2. The unretained part of the split peak dominates the profiles of peaks 1–3; the lower the value of St (below 1), the narrower this unretained part, since the peak area remains constant while the area of the tail of this L-shaped peak decreases with decreasing St (cf. Fig. 2). Hence, the lower St, the higher the peak efficiency, since the efficiency is derived from the waist of this narrow peak. For peak 4, however, the unretained split peak is lower than the retained fraction and the efficiency is derived from the width of this retained part. The efficiency is very low because this second peak is very broad. As the value of the St coefficients increases further, the peak efficiency increases, up to $N_{50} = 36\ 100$ at $St = 10\ 000\ min^{-1}$ (see peaks 5–11 in Table 1). Note that, since the efficiency is derived from the peak with at 50% peak height, the peak tailing is not taken into account and the result does not agree with the
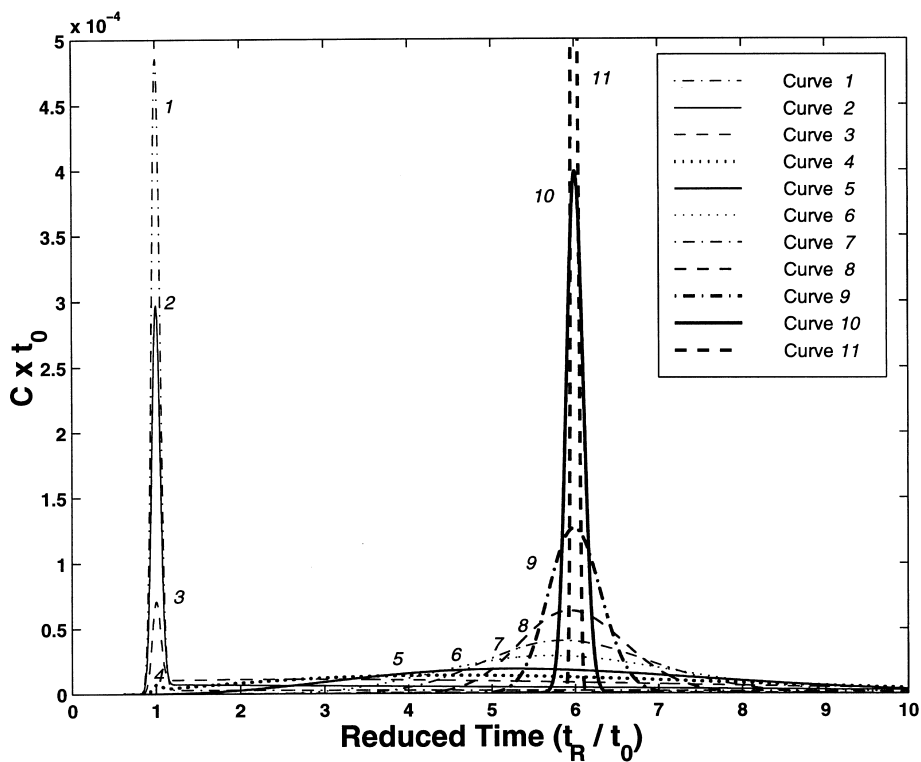
Fig. 1. Peak profiles calculated under linear conditions for an homogeneous mass transfer kinetics. The retention factor was 5, the injection time $1.0 \cdot 10^{-4}$ min, the injected sample concentration was 1.0 M. The Stanton number was varied between 0.1 and 10 000 (Table 1). The numerical values of the retention time, the peak asymmetry factors (at 10% of peak height), and the column efficiency (derived from the peak-width at half the peak height) for each peak are given in Table 1.

Table 1
Influence of the Stanton number on the peak profile in the case of an homogenous surface

Peak no.	St	k_f^a (min^{-1})	L^b (cm)	u^c (cm min^{-1})	t_R/t_o	asf$_{10}$	N_{50}	χ
1	0.1	0.1	1	100	1.00	split	399	$4 \cdot 10^{-4}$
2	0.2	0.2	2	50	1.00	split	split 393	$4 \cdot 10^{-4}$
3	0.5	0.5	5	20	1.00	split	split 355	$1 \cdot 10^{-3}$
4	1	1	10	10	4.40	2.18	2.3	0.68
5	2	2	20	5	5.23	1.69	5.9	0.846
6	5	5	50	2	5.70	1.37	16.7	0.940
7	10	10	100	1	5.85	1.24	35	0.971
8	25	25	250	0.4	5.94	1.15	89	0.989
9	100	100	1 000	0.1	5.99	1.07	359	0.998
10	1 000	1 000	10 000	0.01	6.00	1.04	3 599	1.000
11	10 000	10 000	100 000	0.001	6.00	1.00	36 100	1.001

[a] Value of the rate coefficient for the corresponding Stanton number, with $L = 10$ cm and $u = 10$ cm min^{-1}.
[b] Value of the column length for the corresponding Stanton number, with $k_f = 1$ min^{-1} and $u = 10$ cm min^{-1}.
[c] Value of the mobile phase velocity for the corresponding Stanton number, with $k_f = 1$ min^{-1} and $L = 10$ cm.
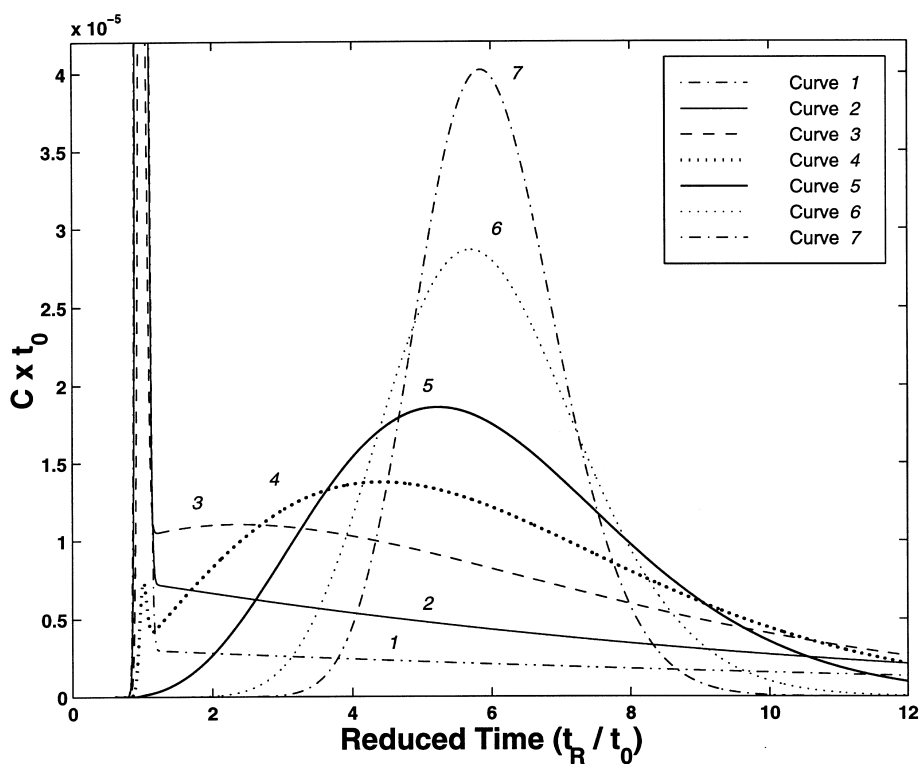
Fig. 2. Same as Fig. 1 but with emphasis on the initial region, in which the peak split effect takes place, and the intermediate region, i.e. on Stanton numbers between 0.1 and 10. The numerical values of the parameters are given in Table 1.

value of the HETP provided by Eq. (10) at low St numbers.

In summary, we can distinguish three regions, depending on the value of the Stanton number. The first region is for $St < 1$. Then, there is split peak or an unretained but tailing peak. The main fraction of the sample is eluted in the unretained peak, followed by a long tail which extends much farther than $t_R = (1 + k') t_0$ (because the first moment of the band is equal to t_R). The second region is for $1 < St < 10$. The split peak disappears. A single band is observed which is very broad and unsymmetrical. The retention time of the band increases and the asymmetry decreases with increasing value of the Stanton number, with values of asf_{10} which are still larger than 1.2 for $St = 10$. The third region is for $St > 10$. The retention time is now independent of the Stanton number but the band width and the peak asymmetry continue to decrease with increasing Stanton number.

In this region, the asymmetry factor asf_{10} is smaller than 1.2 and becomes close to 1 above $St = 1000$.

3.1.2. Comparison of the effects of k_f, L and u

Obviously, as demonstrated by the theoretical analysis, the band profile depends only on the actual value of the Stanton number. However, there are many different combinations of the values of the three parameters, the rate coefficient, the column length, and the mobile phase velocity with which a given Stanton number can be obtained. Some of these possible combinations are indicated in Table 1, where the values of k_f, L and u corresponding to a given Stanton number and given, arbitrary values of the other two parameters are listed. Some of these values are quite unrealistic. The purpose of their inclusion is to illustrate the difficulties which are encountered when one wants to carry out experiments at extreme values of the Stanton number.

3.1.3. Influence of the retention factor

When the retention factor increases, the band spends a longer time in the column, so equilibration can progress farther during its elution. There is a certain ambiguity in the definition of the Stanton number and one might want to replace the mobile phase linear velocity by the band velocity which is $1+k'$ times longer. The influence of the retention factor is illustrated in Fig. 3 which shows the band profiles obtained with St $=1$ for $k' = 0.5$, 1.0, 2.0, 5.0 and 10. The retention factor has a significant influence. The intensity of the split peak effect decreases with increasing value of the retention factor.

At St $=1$, the split peak effect is visible only for $k' = 5$. For $k' = 10$, there is a retained, broad peak (with $\chi = t_R / \mu_1 = 0.85$, Table 2). For $k' < 5$, there is an extremely high, narrow, unretained peak followed by a long tail (see inset in Fig. 3). Obviously, there cannot be any split peak effect if there is no retention. We assume here that the mass transfer between the two fractions of the liquid phase, the one stagnant inside the porous particles and the one percolating across the bed, is instantaneous, the slow mass transfer kinetics being associated only to the adsorption/desorption process. Thus, the unretained peak is nearly a Dirac δ-function, like the injection.

Obviously, with a large retention factor, the split peak would still be observed at values of the Stanton number below 1. With low retention factors, the split peak could also be seen at Stanton number slightly above 1. So, it is not possible to define a clear threshold for the split peak effect. It is observed around St $=1$, at values which increase with decreasing retention factor. This may contribute to explaining the somewhat elusive character of this effect [7].

Since the band moves at the velocity $u/(1+k')$, it could be asked why to refer the Stanton number of the chromatographic column to the mobile phase velocity rather than to the band velocity. In order to clarify this issue and better illustrate the interaction between the Stanton number and the retention factor, profiles were calculated for combinations of St and k' giving nearly equal values of St$(1+k')$. The results are shown in Fig. 4. The characteristics of the peaks are listed in Table 3. They show that bands calculated with a combination of parameters giving close values of St$(1+k')$ have similar profiles. This is the case of the profiles 7 and 10, or 1, 4, 8, 11, and 12 in Fig. 4a or of profiles 2, 5 and 9 or 3 and 6 in Fig. 4b. These groups of profiles are similar. Still they are too different to justify the replacement of the classical St number by a new one, St$(1+k')$. The influence of k' on the profile at constant St is certain but moderate.

3.1.4. Conclusion

When the kinetics are homogeneous, the band profile depends mainly on the Stanton number and slightly on the retention factor. The influence of any abnormally low value of one of the three parameters of this number, the rate coefficient, the column length and the reverse of the mobile phase velocity, can be compensated by a proper choice of the other two, so that nearly symmetrical bands be eluted from any column. Conversely, tailing peaks can be generated even with a high value of any one of these three parameters (e.g., k_f) provided that small enough values of the other two are selected. Similar results were obtained by Villermaux [15] who solved the problem using Laplace transform.

3.2. Heterogenous mass transfer kinetics

The influence of heterogeneous mass transfer kinetics has been studied earlier under different conditions [4]. It was found that peak tailing of kinetic origin arises as a result of an heterogenous surface with two types of sites. On type 1 sites, the adsorption energy is low and the mass transfer kinetics fast. These sites account for the largest fraction of the surface area of the adsorbent. On type 2 sites, the adsorption energy is high and the mass transfer kinetics is slow. These sites account usually for a small fraction of the surface area of the adsorbent. At low values of the second rate coefficient, $k_{f,2}$, a split peak effect took place. At higher values of this coefficient, the peak was broad, unsymmetrical and its maximum eluted before t_R. The peak tended toward a Gaussian profile with increasing value of the second rate coefficient.

This kind of peak tailing seems to constitute the most realistic explanation of the experimental results obtained in modern HPLC separations. It has been used to explain the shape of bands obtained in chiral separations [6], a case in which the slow site is the enantioselective one, and in the RPLC separations of
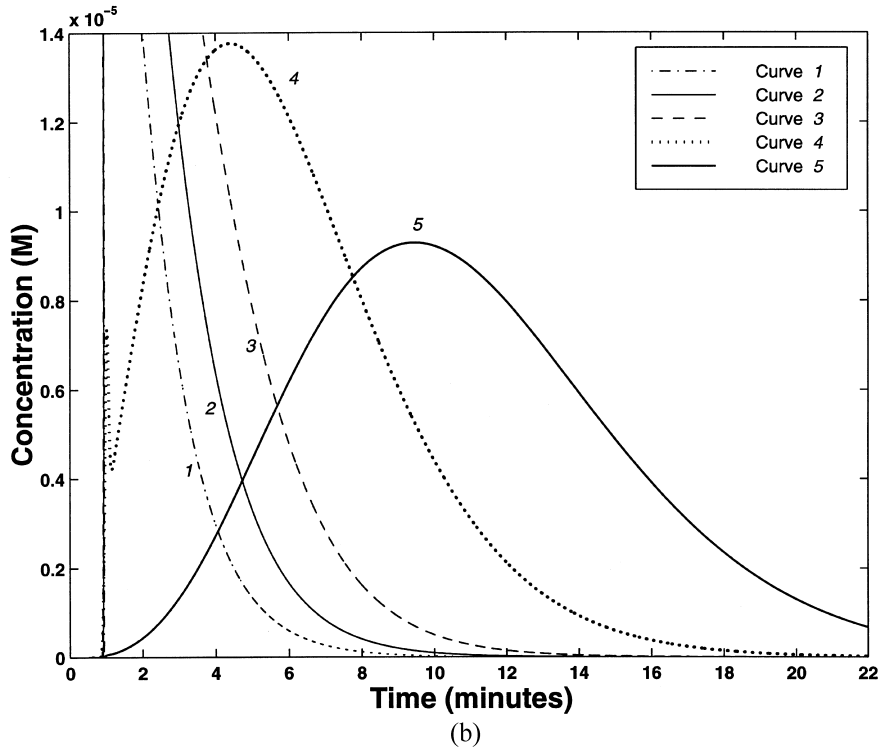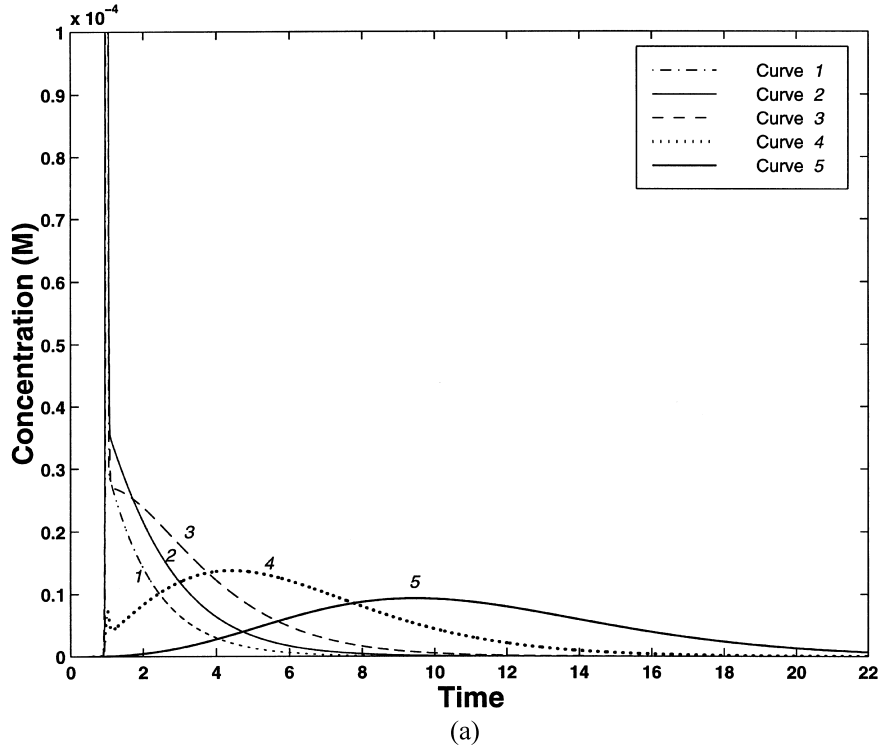
(a)

(b)

Fig. 3. Influence of the retention factor on the peak profile. Same as Fig. 1 except retention factor: peak 1, $k' = 0.5$; peak 2, $k' = 1$; peak 3, $k' = 2$; peak 4, $k' = 5$; peak 5, $k' = 10$. In all cases, St = 1.0; inset, same as the main figure with a different scale.

Table 2
Influence of the retention factor on the characteristics of the peaks obtained with homogeneous kinetics (see Fig. 3)

Peak no. (Fig. 3)	a	$asf_{10\%}$	$\chi = t_R/\mu_1$	$t_R = (1+Fa)t_0$
1	0.5	1.029	0.002	1.001
2	1.0	1.128	0.002	1.002
3	2.0	27.33	0.0025	1.005
4	5.0	2.182	0.68	4.401
5	10	1.694	0.846	9.46

Homogeneous surface. St = 1.0.

many basic amines containing the combination of a strongly hydrophobic region and a strong polar group; a typical example is that of the tricyclic antidepressants [13,14]. In the following we discuss the influence of the column length and the linear velocity on this tailing, utilizing the relationship given by the Stanton number. Note that there are now two Stanton numbers, St_1 and St_2, and that the peak profile will depend on the value of the smaller one (we assume that St_1 is always larger than 100), on the retention, on the relative coverage of the surface by the two type of sites, and, possibly, on the ratio of the two Stanton numbers.

In the present work, we calculated peak profiles under linear conditions, using the transport-dispersive model (Eq. (9)), and assuming an heterogenous mass transfer kinetics. The coefficients of the bilangmuir adsorption isotherm were set at $a_1 = 10$ and $a_2 = 2$, hence $k' = F$ $(a_1 + a_2) = 3$. Three types of calculations were carried out. In the first case, the first Stanton number was set at $St_1 = 10\,000$ and the second Stanton number varied from 10 to 10 000. Then, these calculations were repeated for values of the first Stanton number, $St_1 = 2000$ and 200. In the last series, both Stanton numbers were varied proportionately, their ratio being kept constant at $St_1/St_2 = 1000$ and 100.

3.2.1. Effect of the second Stanton number, St_2

The second Stanton number was varied from 10 to 10 000. The band profiles obtained for values of St_2 between 10 and 250 are shown in Fig. 5. We observe first that, at low values of St_2 (peaks 1 and 2, with $St_2 = 10$ and 25 min^{-1}, respectively, the peak is very broad and unsymmetrical. Although split peak does not take place, the apical reduced retention time

(reduced retention time of the peak maximum) is less than $t_R/t_0 = 1 + k' = 4$ (cf. Table 4). For higher values of the second Stanton number, above 50, the peak becomes narrower and less unsymmetrical. Its retention factor is now nearly constant, at $k' = 4$. However, a slight tailing remains. It did not completely disappear at the largest values illustrated in the figure (Fig. 5, peaks 7 and 8, with $St_2 = 200$ and 250 min^{-1}, respectively). Similarly, the asf_{10} decreases from 2.37 for the first peak to 1.13 for the last two peaks. It becomes less than 1.20 when the Stanton number for the second type of sites becomes larger than 100. This result was unexpected compared to the one obtained in the case of a homogeneous kinetics. It must depend also on the ratio St_1/St_2 because, obviously, if $St_1 = St_2 = 100$, we are in the case of a homogeneous kinetics and the peak should be symmetrical.

3.2.2. Effect of the first Stanton number, St_1

The results in Fig. 5 were obtained for a first Stanton number constant and equal to 10 000. Figs. 6 and 7 show the band profiles calculated for values of the first Stanton number equal to 2000 and 200, respectively, with a second Stanton number between 10 and 250. The characteristics of the peaks obtained are summarized in Table 5 (which contains also data for $St_1 = 500$). The extent of peak tailing depends on the value of the first Stanton number. It decreases markedly with decreasing value of the first Stanton number (Tables 4 and 5). For example, in Fig. 7, it has nearly disappeared with peak 4 ($St_2 = 75$). The variation of the retention time is smaller but still significant. The peak asymmetry becomes lower than 1.10 for $St_2 = 500$ and $St_2 = 75$ with $St_1 = 10\,000$ and 200, respectively.

A ratio of the two Stanton numbers, hence of the two rate constants, very different from unity can cause peak tailing because the efficiencies corresponding to the two mechanisms are too different (Eq. (10)). As a consequence, this effect must also depend on the ratio of the contributions of the two retention mechanisms.

3.2.3. Effect of the Stanton number ratio

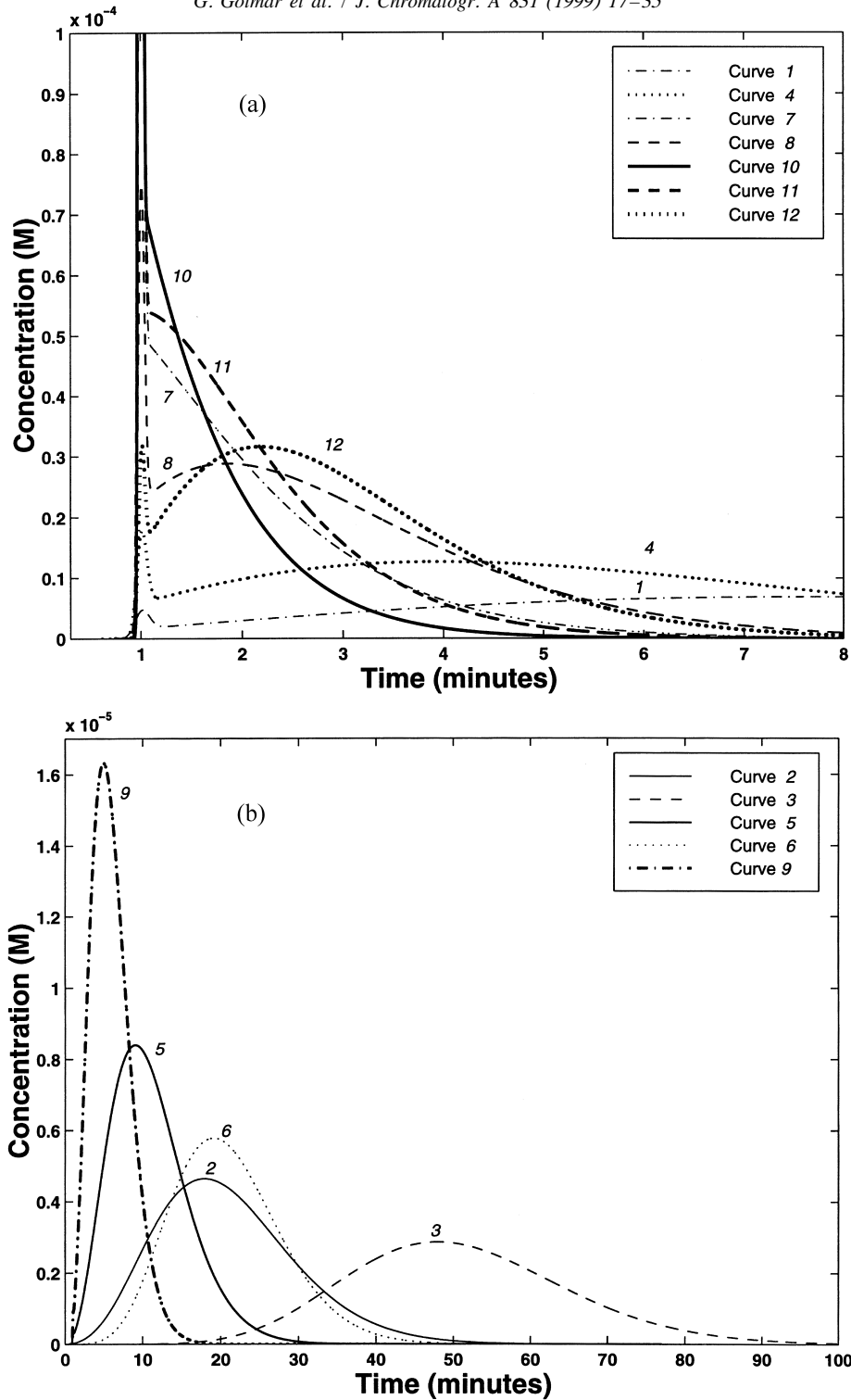The results in Figs. 5–7 were obtained for constant values of the first Stanton number, 200, 2000

Fig. 4. Influence of the product $St(1+k')$ on the peak profile at low values of St. The values of $St(1+k')$, the retention time of the peak maximum, and the peak asymmetry factor corresponding to each curve on the two figures are given in Table 3.

Table 3
Influence of the retention factor on the characteristics of the peaks obtained with homogeneous kinetics (see Fig. 4a and b)

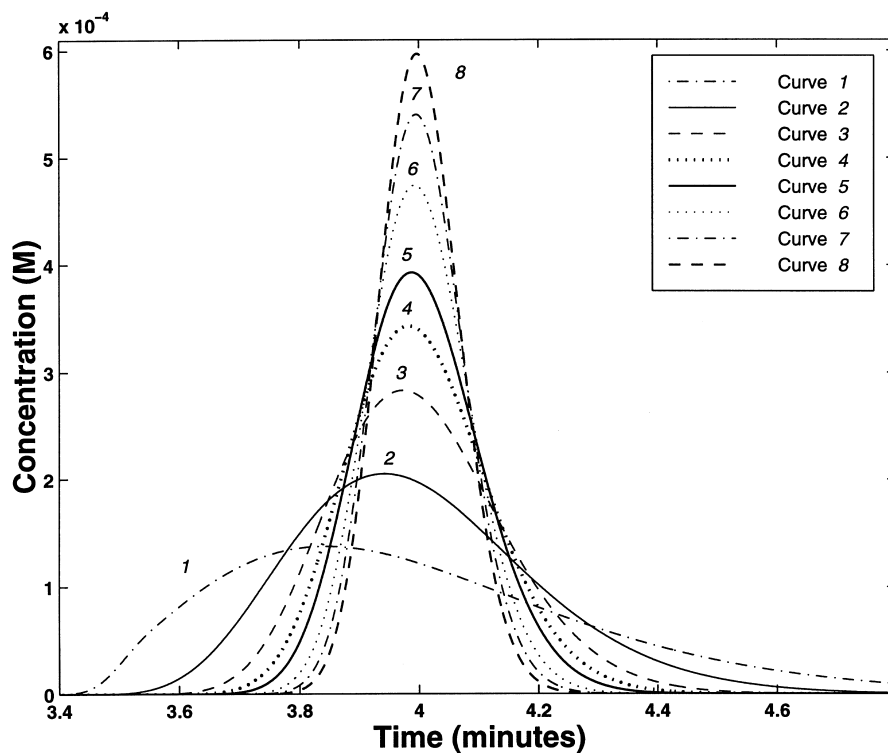| Peak no.	St	k'	$St(1+k')$	t_R/t_0	$asf_{10\%}$	χ
1	0.5	10	5.5	7.80	2.50	0.680
2	0.5	20	10.5	17.92	1.69	0.846
3	0.5	50	25.5	48.0	1.37	0.940
4	0.8	5	4.8	1.01	108.	0.002
5	0.8	10	8.8	9.06	1.83	0.806
6	0.8	20	16.8	19.1	1.49	0.905
7	1.5	1	3	1.00	7.73	0.003
8	1.5	2	4.5	1,01	58.	0.004
9	1.5	5	9.0	4.96	1.88	0.792
10	2	0.5	3	1.00	1.19	0.004
11	2	1	4	1.00	28.	0.004
12	2	2	6	1.01	69.5	0.006

Fig. 5. Peak profiles calculated under linear conditions for an heterogeneous mass transfer kinetics. Parameters; linear isotherm with $k'=3$, column length $L=10$ cm, and linear velocity $u=10$ cm min^{-1}. First Stanton number, $St_1 = 10\,000$. The second Stanton number, St_2 varied between 10 and 250. The values of St_2, the retention time of the peak maximum and the peak asymmetry factor are given in Table 4 for each peak.

Table 4
Influence of the Stanton number for the second type of adsorption mechanism on the peak characteristics (see band profiles in Fig. 5)

Peak no.	St_2	t_R/t_0	asf_{10}	χ
1	10	3.84	2.37	0.947
2	25	3.94	1.57	0.981
3	50	3.97	1.36	0.991
4	75	3.98	1.28	0.994
5	100	3.99	1.22	0.996
6	150	3.99	1.18	0.997
7	200	4.00	1.13	0.999
8	250	4.00	1.13	0.999
9	500	4.00	1.06	1.000
10	1000	4.00	1.06	1.000
11	10 000	4.00	1.00	1.001

and 10 000, respectively. Using these results, it is possible to study the influence of the ratio of the two Stanton numbers on the peak symmetry, as a function of each one of them. Fig. 8 shows band profiles calculated for different values of the Stanton numbers, at constant value of their ratio, St_1/St_2, be-

tween 10 and 200. The characteristics of the peaks obtained and shown in Fig. 8 are summarized in Table 6.

At constant ratio, lowering the second Stanton number (hence, decreasing the first one) always increases the extent of peak tailing (e.g., cf. peaks 1 and 2 or peaks 4 and 5). Decreasing the ratio at constant value of the second Stanton number (the lower one) increases peak symmetry (e.g., cf. peaks 1 and 10 or peaks 2 and 5).

3.2.4. Influence of the retention factors

Both the sum of the two contributions to the apparent retention factor (a_1+a_2) and their ratio (a_1/a_2) are also of importance, besides the two Stanton number (Table 7). Thus, a discussion of the influence of the two retention factors on heterogeneous tailing would involve four parameters and become extremely complex. So, we illustrate merely illustrate the nature and importance of this effect by presenting two sets of results. In Figs. 9 and 10, St_1
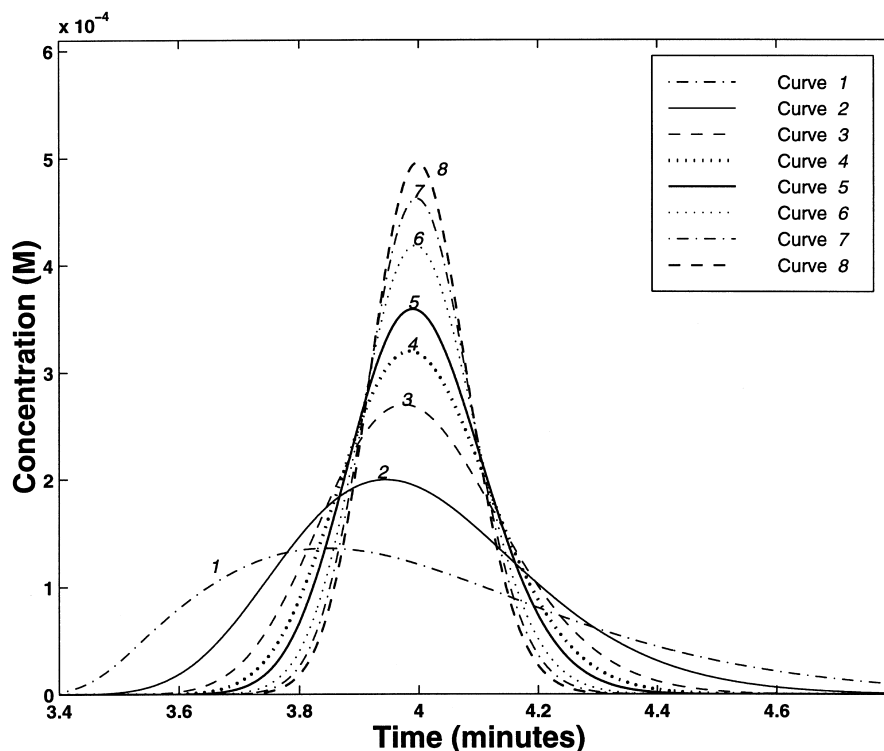

Fig. 6. Same as Fig. 5, except first Stanton number, $St_1 = 2000$. Values of the second Stanton number, St_2, the retention time, and the peak asymmetry factor are given in Table 5.
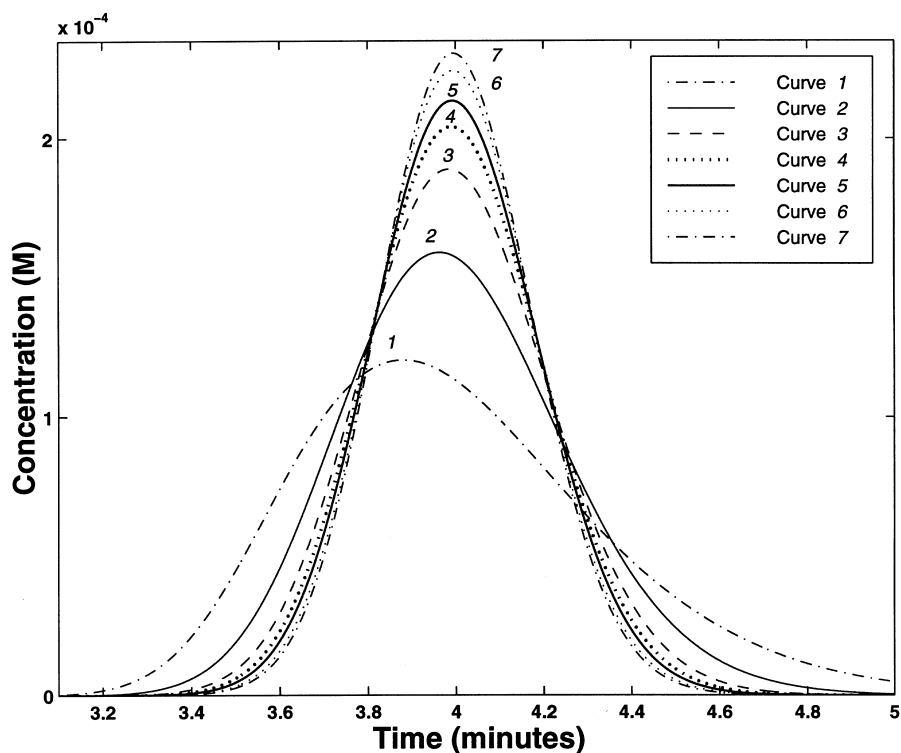
Fig. 7. Same as Fig. 5, except first Stanton number, $St_1 = 200$. Values of the second Stanton number, St_2, the retention time, and the peak asymmetry factor are given in Table 5.

remains equal to 1000. St_2 varies from 10 to 50 and 100, respectively. In Fig. 9, the retention factors are four times larger than they were in this section so far (Figs. 5–8), with $a_1 = 40$ and $a_2 = 8$ ($k' = 12$). In Fig. 10, the apparent retention factor is equal to 3 as earlier but now $a_1 = 10.1$ and $a_2 = 1.09$. All peaks tail significantly in both figures but the effect is more important in Fig. 10 than in Fig. 9. Further calcula-

tions suggest that the tailing is maximum for a ratio of the two contributions around 10 (as in Fig. 10).

3.3. Apparent retention coefficient, the peak asymmetry parameter and the Stanton number

Recently, Farman et al. [16] have suggested a new approach to qualify the asymmetry of an elution

Table 5
Co-Influence of the two Stanton numbers on the peak profile (see peak profiles in Figs. 6 and 7)

| Peak no.	St_2	$St_1 = 2000$			$St_1 = 500$			$St_1 = 200$		
		t_R	asf_{10}	χ	t_R	asf_{10}	χ	t_R	asf_{10}	χ
1	10	3.846	2.25	0.949	3.86	1.96	0.953	3.88	1.68	0.960
2	25	3.944	1.52	0.981	3.954	1.37	0.985	3.96	1.25	0.987
3	50	3.976	1.29	0.992	3.982	1.18	0.994	3.98	1.13	0.995
4	75	3.986	1.21	0.995	3.99	1.12	0.997	3.99	1.09	0.997
5	100	3.99	1.17	0.997	3.994	1.09	0.998	3.99	1.08	0.997
6	150	3.994	1.12	0.998	3.996	1.07	0.999	3.99	1.07	0.998
7	200	3.996	1.10	0.999	3.998	1.05	0.999	3.99	1.07	0.998
8	250	3.998	1.07	0.999	3.998	1.05	0.999			
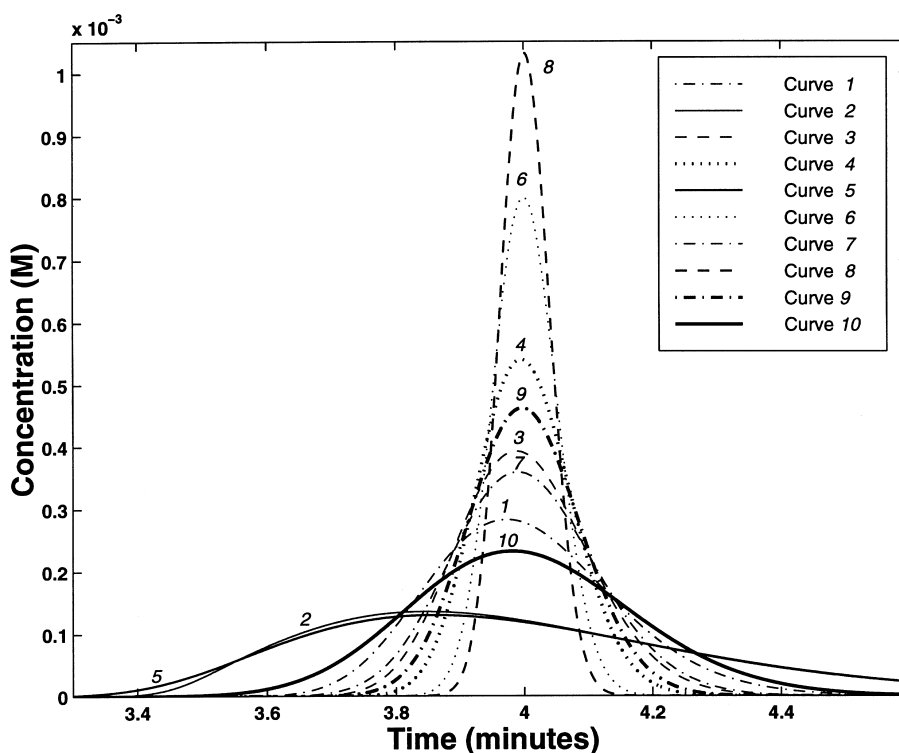
Fig. 8. Comparison of the profiles of peaks obtained with the same ratio of the two Stanton numbers. See peak characteristics in Table 6.

band based on the difference between the apical (or experimental) retention time and the true (or thermodynamic) one. They defined a new parameter, χ, or asymmetry parameter as:

$$\chi = \frac{V_A - V_I}{V_R - V_I} = \frac{t_A - t_I}{t_R - t_I} = \frac{k'_A}{k'_R} \tag{11}$$

where V_A is the 'apparent' retention volume (i.e., the retention volume of the peak maximum), V_I is the column hold-up volume, and V_R is the 'true' or thermodynamic retention volume; the t values are the

Table 6
Influence of the ratio of the stanton numbers on the peak characteristics (see peak profiles in Fig. 8)

Peak no.	St_1/St_2	St_2	t_R	asf_{10}	χ
1	200	50	3.97	1.36	0.991
2	200	10	3.85	2.25	0.949
3	100	100	3.99	1.22	0.996
4	50	200	4.00	1.13	0.999
5	50	10	3.86	1.96	0.953
6	20	500	4.00	1.06	1.000
7	20	100	3.99	1.17	0.997
8	10	1000	4.00	1.06	1.000
9	10	200	4.00	1.10	0.999
10	10	50	3.98	1.18	0.994

Table 7
Influence of the retention factor on peak tailing (see peak profiles in Figs. 9 and 10)

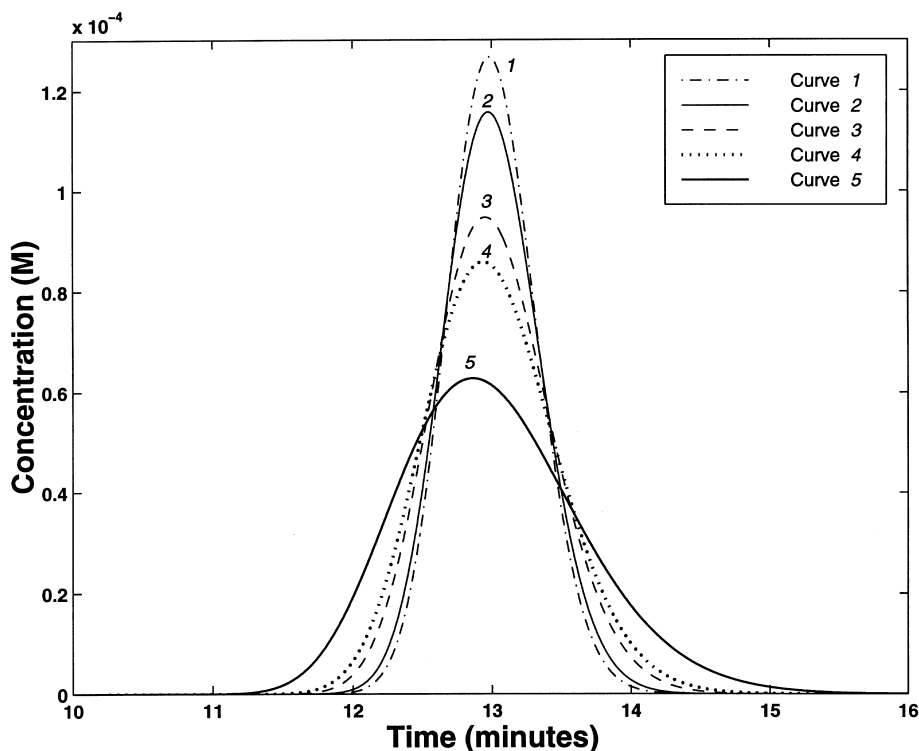| Peak no.	St_2	St_1/St_2	t_R	$asf_{10\%}$	χ
$k' = 12$, $a_1 = 40$, $a_2 = 8$, $St_1 = 1000$					
1	50	20	12.98	1.12	0.998
2	40	25	12.97	1.14	0.997
3	25	40	12.95	1.20	0.996
4	20	50	12.94	1.24	0.995
5	10	100	12.86	1.38	0.988
$k' = 3$, $a_1 = 10.91$, $a_2 = 1.09$, $St_1 = 1000$					
1	100	10	3.99	1.12	0.998
2	50	20	3.98	1.25	0.994
3	40	25	3.98	1.32	0.992
4	25	40	3.95	1.54	0.985
5	20	50	3.94	1.71	0.980
6	10	100	3.85	2.80	0.95

Fig. 9. Influence of the retention factor on peak tailing. See peak characteristics in Table 7. $k' = 12$, $a_1 = 40$, $a_2 = 8$, $St_1 = 1000$.

corresponding retention times and the k values the retention factors.

In practice, the value of the parameter χ is relatively easy to determine for any recorded band profile because the true retention time, t_R, is equal to the first moment of the peak. This method has the great advantage over alternative definitions of an asymmetry coefficient based on the band profile of being much less arbitrary. The maximum of the peak is the only point of the profile where the two phases are actually at equilibrium. So, χ is a coefficient which has some physical meaning, is easy to determine experimentally, and has a practical importance since it gives the relative error made in measuring retention data from the elution time of the band maximum. In their work, Farman et al. [16] studied the relationship between this asymmetry coefficient and the Peclet number in cases in which mass transfer was limited by a low molecular diffusivity, as it often happens in the separation of biopolymers.

The data reported above show that the apical

retention time of the peak maximum increases with increasing Stanton number, in both cases of homogeneous and heterogeneous slow mass transfer kinetics. When the Stanton number increases indefinitely, the retention time tends toward the 'true' retention time, $t_R = t_0 (k' + 1)$. The χ values obtained were plotted in Fig. 11 as a function of the logarithm of St in the homogeneous case (data in Table 1), or of St_2 in the heterogenous case (data in Table 5). Note that the data corresponding to the lowest St values (peaks 1–3 in Table 1) were not included in the figure because these peaks have no maximum for their retained fraction and the definition of χ becomes ambiguous. Fig. 11 shows that, in both cases, the asymmetry coefficient is close to 0.95 for St = 10 and very close to 1.0 for St = 100. However, for St < 10, the asymmetry coefficient decreases rapidly with decreasing St. Note also that, in the heterogenous case and below $St_2 = 10$, the asymmetry coefficient drops more rapidly with decreasing St than it does in the homogeneous case.

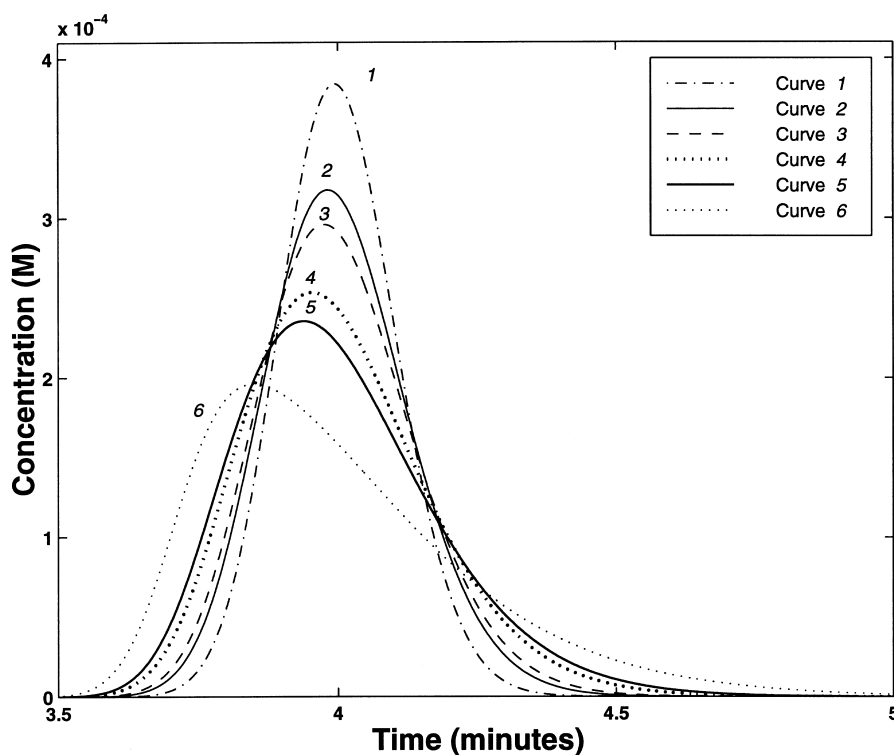The result is qualitatively similar to the depen-

Fig. 10. Influence of the retention factor on peak tailing. See peak characteristics in Table 7. $k' = 3$, $a_1 = 10.1$, $a_2 = 1.09$, $St_1 = 1000$.

dence of χ on the Peclet number reported by Farman et al. [16], However, calculations cannot be carried out at very low values of the Stanton number because of the split peak effect. Thus, it was not possible to achieve values of the asymmetry coefficient below $\chi = 0.68$. This observation could quite probably be used to differentiate between kinetic tailing contributions originating from a low molecular diffusivity of the solute or from a low coefficient of the mass transfer kinetics.

4. Conclusions

The results reported in this paper demonstrate that peak tailing of kinetic origin depends essentially on the value of the Stanton number (homogeneous kinetics) or on that of the smallest Stanton number corresponding to the different retention mechanisms involved in the separation studied (heterogeneous kinetics). However, in the former case, peak tailing is negligible for Stanton number larger than approxi-

mately 10, while in the latter case, significant tailing still takes place when the smallest Stanton number is of the order of 10 to 100, depending on the ratio of the lowest and smallest Stanton numbers and on the value of the contributions of the two mechanisms to the retention factor.

Understanding the critical importance of the Stanton number(s) offers the only, narrow avenue toward the reduction of the tailing extent when deemed necessary to improve analytical results. In most cases, the rate coefficient of mass transfer (or one of them) is small and the first effort of the analyst should be to increase it. Because adsorption on the slow sites is usually accompanied by a high adsorption energy, an increase in the column temperature should be attempted. This should have two positive effects. First it increases the slowest rate coefficient of mass transfer and second it decreases the relative contribution of the active sites to the retention. Most commercial instruments are now supplied with a temperature controlled oven for the column. It has been recognized that this improves
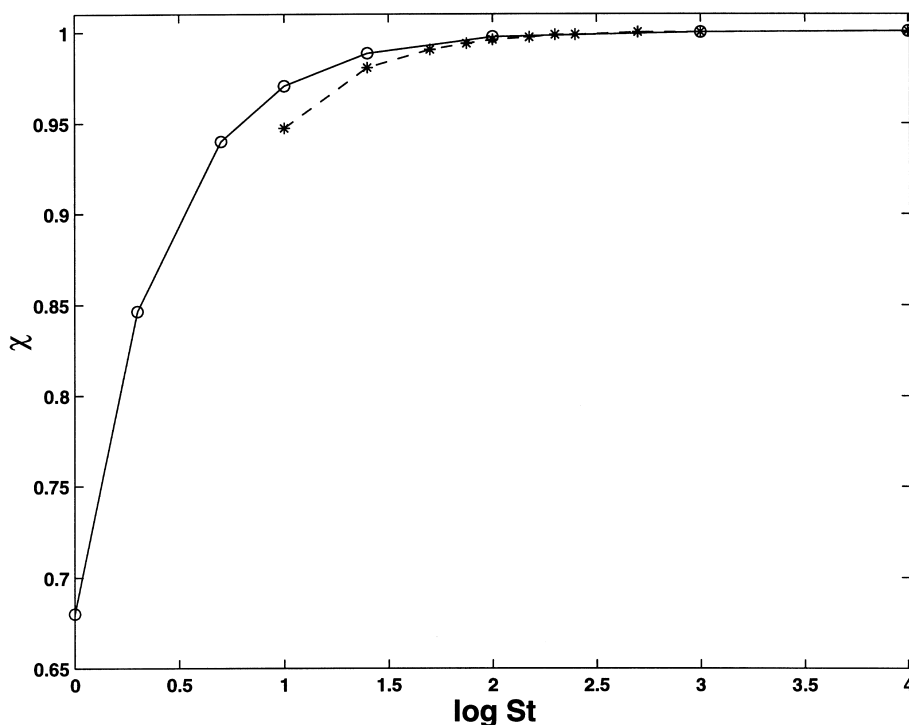
Fig. 11. Plot of the coefficient χ (Eq. (11)) as a function of the logarithm base 10 of the Stanton number in the homogenous case St (circles) and of the Stanton number in the heterogenous case St_2 (asterisks), respectively. The values of χ, St and St_2 are given in Table 1 (St) and in Table 5 (St_2).

significantly the reproducibility of quantitative results. Strangely, analysts are reluctant to perform analyses at temperatures significantly different from ambient. Raising the column temperature is probably the only practical tool to reduce peak tailing. Admittedly, this could reduce the column useful lifetime which is a serious objection.

Finally, analysts must realize that, by physical necessity, efforts devoted to performing faster analyses result in making the tailing problems more serious. Faster analyses require shorter columns and faster mobile phase velocities, two of the three conditions leading to lower Stanton numbers. Since there is always a natural limit to how much faster it is possible to operate a given retention mechanism, tailing will remain a source of trouble [17].

References

[1] G.H. Weiss, Separat. Sci. 5 (1970) 51.
[2] G.H. Weiss, Separat. Sci. Technol. 16 (1981) 75–80.
[3] G.H. Weiss, Separat. Sci. Technol. 17 (1982) 1609.
[4] T. Fornstedt, G. Zhong, G. Guiochon, J. Chromatogr. A 742 (1996) 55.
[5] T. Fornstedt, G. Zhong, G. Guiochon, J. Chromatogr. A 741 (1996) 1.
[6] T. Fornstedt, G. Zhong, Z. Bensetiti, G. Guiochon, Anal. Chem. 68 (1996) 2370.

[7] G. Guiochon, S.G. Shirazi, A.M. Katti, Fundamentals of Preparative and Nonlinear Chromatography, Academic Press, Boston, MA, 1994.

[8] T. Fornstedt, P. Sajonz, G. Guiochon, J. Am. Chem. Soc. 119 (1997) 1254.

[9] S.C. Jacobson, S. Golshan-Shirazi, G. Guiochon, J. Am. Chem. Soc. 112 (1990) 6492.

[10] S.C. Jacobson, S. Golshan-Shirazi, G. Guiochon, AIChE J. 37 (1991) 836.

[11] F. Charton, G. Guiochon, J. Chromatogr. 630 (1993) 21.

[12] F. Charton, M. Bailly, G. Guiochon, J. Chromatogr. A 687 (1994) 13.

[13] A. Sokolowski, K.-G. Wahlund, J. Chromatogr. 189 (1980) 299.

[14] A. Sokolowski, T. Fornstedt, D. Westerlund, J. Liq. Chromatogr. 10 (1987) 1629.

[15] J. Villermaux, J. Chromatogr. Sci. 12 (1974) 822.

[16] D. Farman, D.D. Frey, Cs. Horváth, Biotechnol. Prog. 13 (1997) 429.

[17] R.P.W. Scott, P. Kucera, J. Chromatogr. 169 (1979) 51.