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Peak tailing and column radial heterogeneity in linear chromatography

Kanji Miyabe[a], Georges Guiochon[a,b,*]

[a]Department of Chemistry, The University of Tennessee, Knoxville, TN 37996-1600 , USA

[b]Division of Chemical and Analytical Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

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Abstract

The correlation between the radial heterogeneity of a column and the tailing of the elution profiles of chromatographic peaks was studied using a numerical method. A parabolic distribution of the linear flow velocity of the mobile phase and of the column efficiency in the radial direction were assumed. Moment analysis showed that peak tailing takes place under such experimental conditions and that it increases with increasing range of radial variations of the flow velocity and the column efficiency. It was also found that the higher the column efficiency, the larger the effect of a given degree of radial heterogeneity on the extent of peak tailing. Peak tailing behavior of columns having different efficiencies could be correlated with each other by an equation. Some characteristic features of tailing peaks were analyzed in connection with the column radial heterogeneity.

Keywords: Peak shape; Column radial heterogeneity; Column efficiency

1. Introduction

The profiles of elution peaks in chromatography result from the convolution of various contributions. In linear chromatography, it is often assumed that, as a first approximation, peak profiles should be well represented by a Gaussian distribution function. However, tailing profiles are often observed under experimental conditions corresponding to proven linear isotherm. A number of interpretations and models of this behavior have been proposed [1,2]. Early conventional studies on peak tailing have suggested three causes of instrumental origin, a tailing injection profile, a slow detector response, and a dead volume in some tubing connections. In spite of considerable improvements in HPLC instrument design, constant progress in column quality have kept these effects as a lingering source of troubles in physico-chemical studies. Yet, proper care and the use of columns of appropriate size can make these contributions practically negligible.

In addition to these extra-column sources, heterogeneous mass transfer kinetics has been considered as another essential origin of peak tailing. Guiochon et al. [1] and Fornstedt et al. [3,4] made detailed studies on peak tailing phenomena in both linear and nonlinear chromatography by using a transport-dispersive model. They showed that tailing profiles could be comprehensively interpreted by assuming the presence of two different types of adsorption sites with different equilibrium isotherms

*Corresponding author.

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and rates of mass transfer kinetics. The influence of heterogeneity in the mass transfer kinetics on the peak profile may be important when specific interactions take place between the sample components and the stationary phase, such as in the case of chiral separations or in the analysis of strong bases by RPLC.

However, it is not unusual to observe tailing in the profiles of the peaks of nonretained tracers or of compounds capable only of hydrophobic interactions with the stationary phase, indicating that still another source of tailing must be taken into account. Farkas et al. [5,6] and Farkas and Guiochon [7] determined the radial distribution of the flow velocity, the column efficiency (height equivalent to a theoretical plate, HETP), and the concentration of a compound by using fibre optics and on-column local fluorescence detection. It was shown that the flow velocity of the mobile phase was several percent lower in the wall region than in the column centre while the HETP was several times larger in the wall than in the centre region. The radial distributions of the flow velocity and the HETP in a column were parabolic. It was concluded that the radial heterogeneity of a column had to be added as another source of peak tailing [5–7]. This work confirms the results of previous studies using HPLC [8–13] and NMR methods [14–16]. Yun and Guiochon published photographs demonstrating the radial heterogeneity of a large diameter column [17] and proposed a model for calculating nonlinear band profiles in a radially heterogeneous column [18,19].

Radial heterogeneity of chromatographic columns is ubiquitous in all conventional HPLC columns [20], except those in which the ratio of the column to the particle diameter is but a few units. We just do not know how to pack columns and avoid a certain degree of column heterogeneity. Thus, it is useful to elucidate further the influence of the radial heterogeneity of the column on the peak tailing. The goal of this study is to assess through numerical calculations the contribution of the radial distribution of the flow velocity and the column efficiency on the tailing of peak profiles. The derivation of a correlation between column radial heterogeneity and tailing behavior was achieved by analysing some characteristic features of the peaks calculated.

2. Theory

We consider here the profiles of chromatographic peaks under conditions of a linear isotherm. In this first study, we assume that there is no radial dispersion of the compound in the column. We assume also that, in an homogeneous column, these profiles would be Gaussian. To determine the profiles obtained with a heterogeneous column, we divide it into 50 annular columns of constant thickness, equal to 1/50 radius of the column. Each of these annular columns is considered as homogeneous. The overall chromatographic peak will be obtained as the summation of each Gaussian profile, weighed in proportion to the cross-section area of the corresponding annular column. Numerical calculations were carried out with different numbers of annular columns, from 20 to 100. Their results (not shown) confirmed slight changes in band profiles with increasing number of annular columns but practically no differences between the results obtained with 50 and 100 annular columns. These negligible changes do not influence the conclusions of this study.

The profile of the peak leaving each annular column is given by

$$C_{\mathrm{d}} = \frac{1}{\sigma_{\mathrm{d}}\sqrt{2\pi}} \exp\left(- \frac{(1 - t_{\mathrm{d}})^2}{2\sigma_{\mathrm{d}}^2} \right) \tag{1}$$

where C_{d}, t_{d}, and σ_{d} are the dimensionless concentration, time, and standard deviation of the peak, respectively. The first two factors are represented as follows.

$$C_d = \frac{Ct_{\mathrm{R}}}{A_{\mathrm{p}}} = \frac{C\epsilon SL(1 + k_0')}{n} \tag{2}$$

$$t_{\mathrm{d}} = \frac{t}{t_{\mathrm{R}}} = \frac{ut}{L(1 + k_0')} \tag{3}$$

where C is the actual solute concentration, t_{R} its retention time, A_{p} the area of the injected pulse, ε the total porosity of the column, S and L the column cross-sectional area and length, respectively, k_0' the retention factor at infinite dilution, n the amount of solute injected, t the time, and u the interstitial velocity of mobile phase.

The influence of the radial distribution of both the flow velocity and the column efficiency on the peak tailing must now be introduced. According to the experimental results of previous studies [5–7], the radial distribution of the flow velocity and the HETP are represented by the following parabolic functions.

$$u_r = a_u\left(\frac{r}{R}\right)^2 + b_u \quad (4)$$

$$N_r = a_N\left(\frac{r}{R}\right)^2 + b_N \quad (5)$$

where r is the radial distance from the centre of the column, R is the column radius, u_r and N_r are the linear velocity of mobile phase and the number of theoretical plates at a radial position r, respectively, and a_u, b_u, a_N, and b_N are numerical parameters. Since it was experimentally demonstrated that the flow velocity at the centre of the column (u_c) is usually no more than a few percent faster than that near the wall (u_w) [5–7], the ratio of these flow velocities was varied from 0.90 to 1.0. However, the average mobile phase flow velocity, u_{av}, was adjusted so that the first moment of the calculated peaks remained constant and equal to unity (i.e., constant flow rate). The value of u_{av} is given by

$$u_{av} = \int_0^R 2\pi r \frac{u_r}{\pi R^2}\,dr \quad (6)$$

Combination of Eqs. (4) and (6) gives $u_{av}=(a_u/2)+b_u$. From Eq. (4), $u_c=b_u$, and $u_w=a_u+b_u$. Finally, the values of a_u and b_u were chosen so that u_{av} be equal to 1, as explained above. For example, in the case when $u_w/u_c=0.90$, $a_u=-0.10526$ and $b_{u'}=1.0526$. Similarly, the ratio N_w/N_c was varied from 0.2 to 1.0 because the HETP was shown to be several times larger near the wall than at the centre of the column [5–7]. When $N_w/N_c=0.20$ and $N_c=1000$, the coefficients of Eq. (5) are $a_N=-800$ and $b_N=1000$. The calculations of the profiles and its moments were made using a BASIC program.

3. Results and discussion

We studied first separately the influences of a radial distribution of the mobile phase velocity and of a radial distribution of the column efficiency. Finally, we investigated the effect of a combination of these two heterogeneities.

3.1. Influence of the flow velocity distribution alone

Chromatographic peaks were calculated by considering only the flow velocity distribution described earlier (Eq. (4)) and a radially homogeneous column regarding its efficiency. Fig. 1 illustrates the correlation between the ratio of the apparent number of theoretical plates of the elution peak, N, and the value of N at the column centre, N_c, and the amplitude of the fluctuation of flow velocity, u_w/u_c. The influence of the flow velocity distribution is much stronger for high efficiency columns than for low efficiency ones. Fig. 2 shows the influence of the amplitude of the flow velocity distribution on the asymmetry factor of the elution peak. This asymmetry factor is the ratio of the rear half-width of

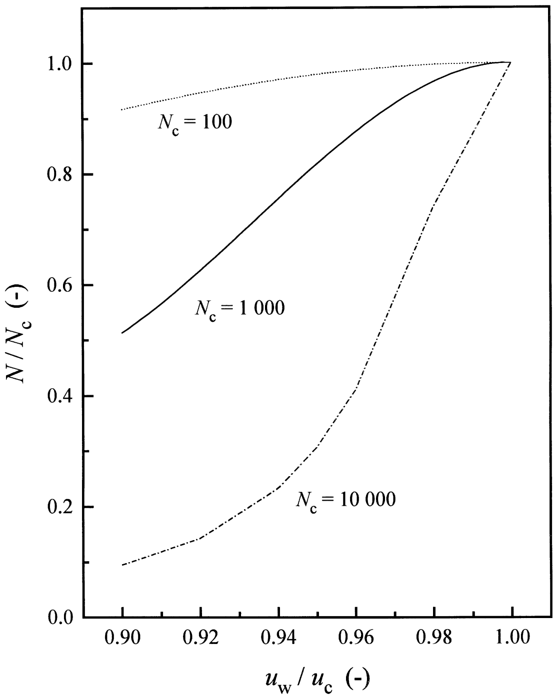

Fig. 1. Influence of a radial heterogeneity of the mobile phase flow velocity distribution on the apparent column efficiency. The radial distribution of the column efficiency is assumed to be uniform.

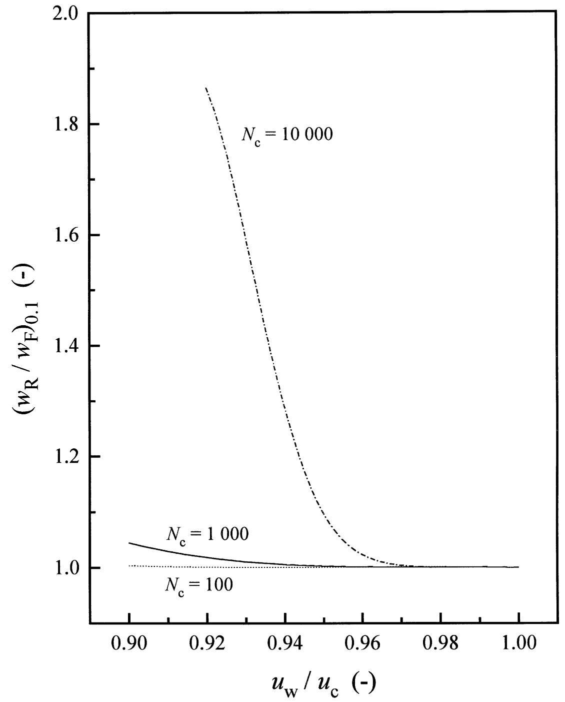

Fig. 2. Influence of the radial heterogeneity of the mobile phase flow velocity distribution on the asymmetry factor of the elution peak. The radial distribution of the column efficiency is assumed to be uniform.

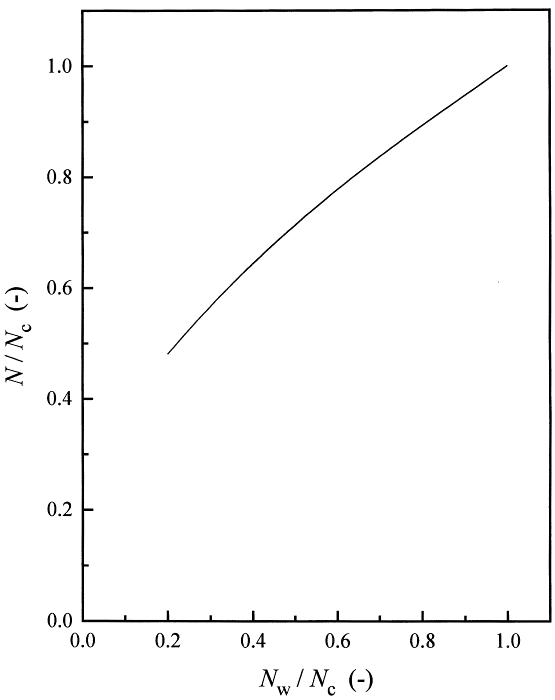

Fig. 3. Influence of the radial heterogeneity of the column efficiency distribution on the apparent column efficiency. The radial distribution of the mobile phase flow velocity is assumed to be uniform.

the elution peak, w_R, to the front half-width, w_F, at 10% of the maximum peak height. The results in Figs. 1 and 2 show that peak tailing would be observed even under experimental conditions for which there would be only a radial distribution of the flow velocity. Again, the effect is more severe on high efficiency columns than on low efficiency ones. Almost no tailing of the profile is predicted at $N_c =$ 100.

3.2. Influence of only column efficiency distribution

By contrast, Fig. 3 shows that, when the mobile phase velocity is distributed homogeneously across the column but not the efficiency, the correlation between the ratio N/N_c and N_w/N_c is the same, irrespective of the value of N_c. In this case, the peak asymmetry factor, $(w_R/w_F)_{0.1}$, is always unity irrespective of the value of N_w/N_c (not shown). Only the peak width increases with increasing width of the efficiency distribution because the distribution of the flow velocity is uniform. This indicates that no tailing peak is expected under this set of conditions.

3.3. Influence of radial distribution of both flow velocity and column efficiency

The combination of the influences of the radial distributions of the mobile phase velocity and the column efficiency gives more complex results. These results depend largely on the value of the column efficiency in the column centre core. Accordingly, we have to discuss successively the cases of a low, a moderate, and a high efficiency column. Similarly to Fig. 1, the correlation between N/N_c and u_w/u_c is illustrated in Fig. 4 in the case of a low efficiency column. The influence of the radial distribution of the mobile phase velocity is nearly negligible as seen earlier (Fig. 1). The influence of the radial distribution of the column efficiency is nearly the same

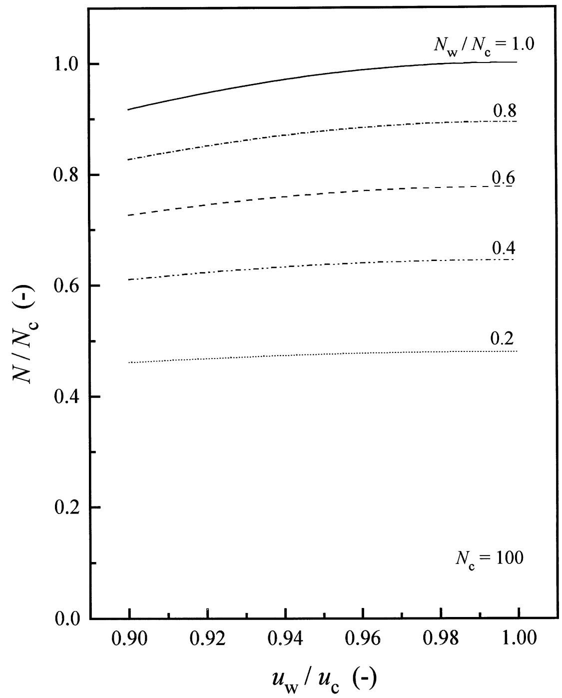

Fig. 4. Influence of the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions on the apparent column efficiency. The column efficiency in the centre region is 100 theoretical plates.

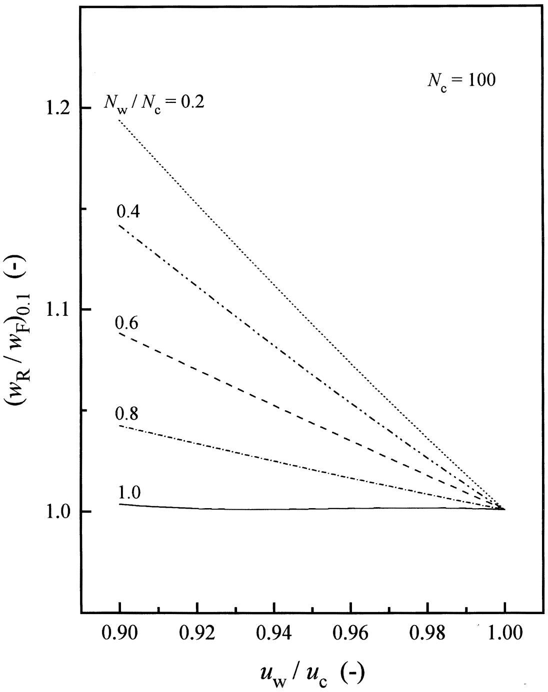

Fig. 5. Influence of the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions on the asymmetry factor of the elution peak. The column efficiency in the centre region is 100 theoretical plates.

as for the case of a flat velocity distribution (Fig. 3). Fig. 5 shows the correlation between $(w_R/w_F)_{0.1}$ and u_w/u_c. As shown in Fig. 2, little tailing is observed in the peak profile given by this column. There is no tailing without a radial distribution of the velocity. The degree of tailing increases slightly with the width of the velocity distribution.

In the case of a moderately efficient column ($N_c =$ 1000), Figs. 6 and 7 illustrate the correlations between N/N_c and u_w/u_c (Fig. 6) and between $(w_R/w_F)_{0.1}$ and u_w/u_c (Fig. 7). Similar plots for a high efficiency column ($N_c = 10\,000$) are reported in Figs. 8 and 9. Comparison of Figs. 4–9 indicates that the higher the column efficiency, the stronger the influence of u_w/u_c on both N/N_c and $(w_R/w_F)_{0.1}$. In Figs. 6 and 7, the open circles indicate the calculation results obtained at $u_w/u_c = 0.9$ and $N_c = 100$. Similarly, the open triangles indicate the numerical results obtained at $u_w/u_c = 0.99$ and $N_c = 10\,000$. The agreement observed between these different values and the corresponding lines at $N_c = 1000$ indicate the following correlation between the correlation curve in Figs. 4–9.

$$\frac{1-\left(\frac{u_w}{u_c}\right)_i}{1-\left(\frac{u_w}{u_c}\right)_j} = \sqrt{\frac{N_j}{N_i}} \qquad (7)$$

This equation indicates that values of u_w/u_c between 0.9 and 1.0 at $N_c = 1000$ correspond to values of u_w/u_c between 0.968 to 1.0 at $N_c = 10\,000$. Similarly, values of u_w/u_c between 0.9 to 1.0 at $N_c = 100$ correspond to values of u_w/u_c between 0.968 and 1.0 at $N_c = 1000$, and to values of u_w/u_c between 0.99 and 1.0 at $N_c = 10\,000$. The results of our calculations show that columns having a high efficiency are more sensitive to the radial heterogeneity of the flow velocity than low efficiency columns. Eq. (7) allows a correlation between the tailing profiles obtained

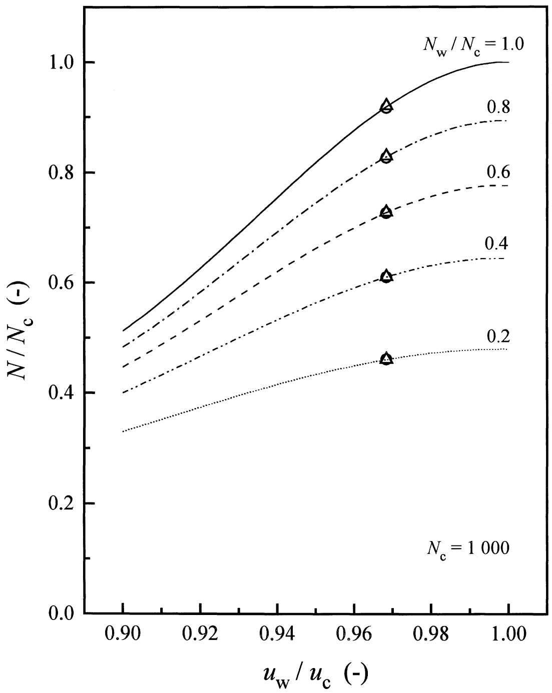

Fig. 6. Influence of the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions on the apparent column efficiency. The column efficiency in the centre region is 1000 theoretical plates. Open circles and triangles indicate calculation results obtained at $N_c = 100$, $u_w/u_c = 0.90$, and at $N_c = 10\,000$, $u_w/u_c = 0.99$, respectively.

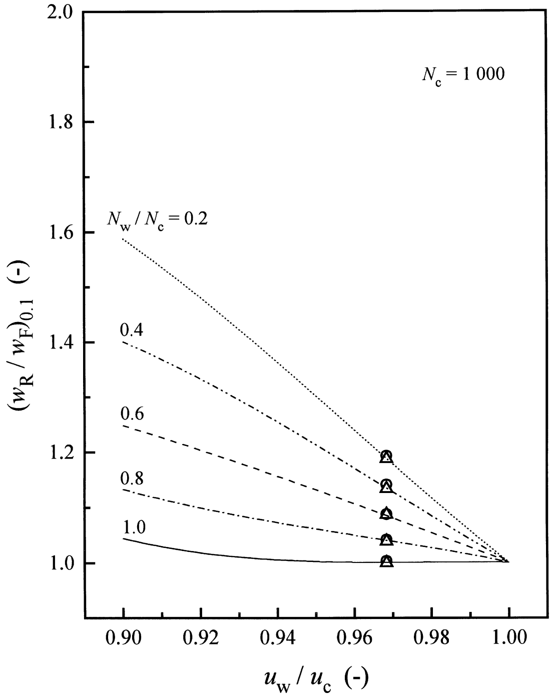

Fig. 7. Influence of the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions on the asymmetry factor of the elution peak. The column efficiency in the centre region is 1000 theoretical plates. Open circles and triangles indicate calculation results obtained at $N_c = 100$, $u_w/u_c = 0.90$, and at $N_c = 10\,000$, $u_w/u_c = 0.99$, respectively.

with columns having different efficiency but similar degree of heterogeneity.

Information about the tailing of peak profiles obtained with a given column can be estimated from similar results obtained with another column having a different efficiency. Experimental data regarding the radial distribution of the flow velocity and the column efficiency have been reported for columns having different efficiency [5–8]. It was observed that the degree of the fluctuations of the flow velocity and the HETP depended on the efficiency of the columns, and that the most uniform flow profiles in the radial direction were observed with the most efficient columns [5]. It is probably possible to apply Eq. (7) directly to compare the degree of the radial fluctuation of the flow velocity between columns having different efficiency.

However, discussing the detailed influence of the column efficiency would be complex. Columns having a wide range of efficiencies, made by packing materials of quite different particle sizes in columns of different lengths are used in HPLC, depending on the difficulty of the separations to perform. The values of the retention time and the peak width depend on the experimental conditions and many sets of parameters should be considered. A more useful comparison of the characteristics of the tailing peaks obtained under this wide variety of experimental conditions can be made more simply by normalizing the peak width in addition to its first moment. So, the results discussed in this study were calculated at $N_c = 1000$.

3.4. Characteristics of tailing peaks.

3.4.1. Retention time

In this study, the average flow velocity of the mobile phase was normalized in such a way that the

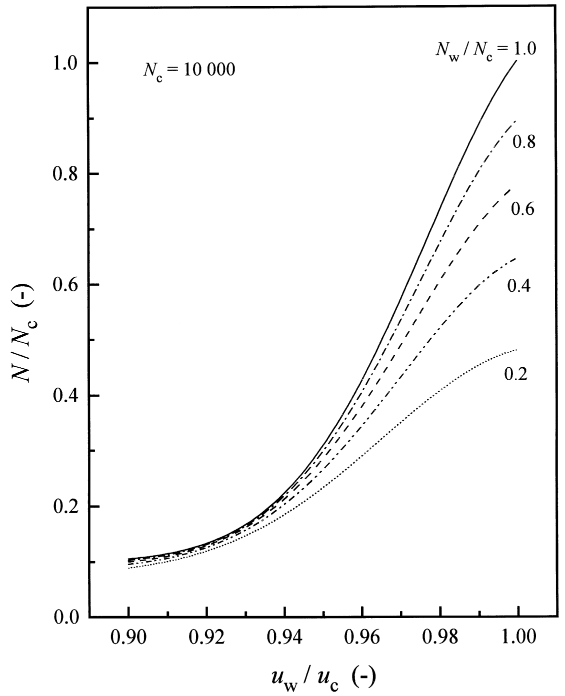

Fig. 8. Influence of the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions on the apparent column efficiency. The column efficiency in the centre region is 10 000 theoretical plates.

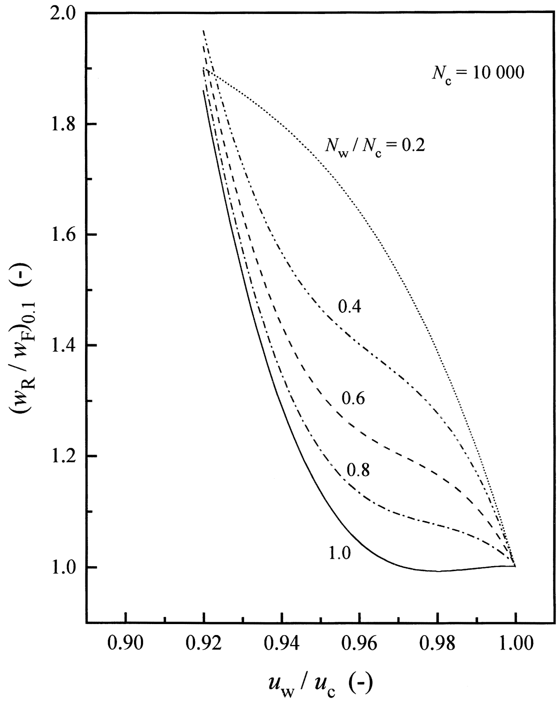

Fig. 9. Influence of the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions on the asymmetry factor of the elution peak. The column efficiency in the centre region is 10 000 theoretical plates.

first moment, μ_1, of all the peaks calculated was equal to unity. Fig. 10 shows the ratio of the peak retention time, t_R, to μ_1 as a function of u_w/u_c. The value of t_R decreases with increasing degree of peak tailing. However, the magnitude of the variation in t_R is not large. The relative variation is approximately 1.5% under such extreme conditions that $u_w/u_c = 0.9$ and $N_w/N_c = 0.2$. As illustrated in Figs. 6 and 7, the peaks obtained under these conditions exhibit considerable tailing, the apparent value of N being reduced to nearly one third of N_c and $(w_R/w_F)_{0.1}$ being equal to approximately 1.6.

3.4.2. Second central moment

Fig. 11 illustrates the influence of the radial distribution of the flow velocity on the second central moment, μ_2'. The ordinate is the ratio of the actual second moment of the elution peak, μ_2', to the moment at the centre of the column, $\mu_{2,c}'$. The moment of the calculated peak is given by

$$\mu_2' = \frac{\int C_d(t_d)(1 - t_d)^2 \, dt_d}{\int C_d(t_d) \, dt_d} \tag{8}$$

where $C_d(t_d)$ is the dimensionless concentration at t_d. In Fig. 11, $\mu_{2,c}' = 1 \cdot 10^{-3}$. Peak spreading increases in the same time as the tailing behavior. The second moment of the elution peak increases by a factor of 3 over $\mu_{2,c}'$ under the extreme conditions selected, $u_w/u_c = 0.9$ and $N_w/N_c = 0.2$.

The apparent variance of an elution peak, σ^2, is conventionally derived from its width at half height, $w_{0.5}$, according to the following equation which assumes a Gaussian profile

$$\sigma_{0.5}^2 = \frac{w_{0.5}^2}{5.54} \tag{9}$$

Fig. 12 shows the correlation between $\sigma_{0.5}^2/\mu_{2,c}'$ and

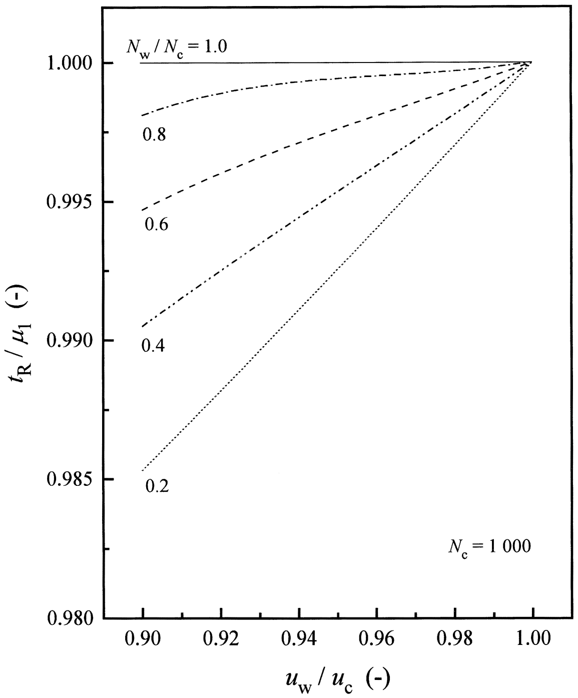

Fig. 10. Ratio of the apical retention time to the first moment of the elution peak as a function of the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions.

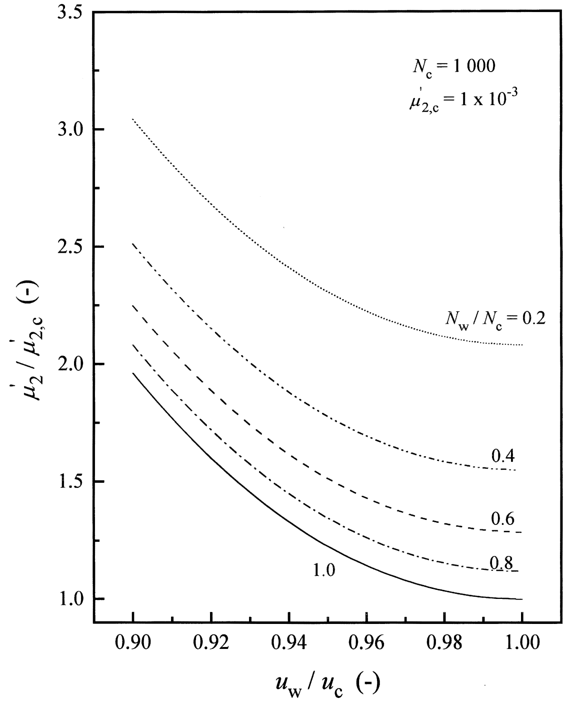

Fig. 11. Dependence of the second central moment of the elution peak on the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions.

u_w / u_c. The same trend is observed in Fig. 12 as in Fig. 11. However, there are differences between the values of μ'_2 and $\sigma^2_{0.5}$ and their variations. These differences become visible when the peak tailing increases. It is frequently observed that the variance calculated from Eq. (9) is smaller than μ'_2 derived from Eq. (8), and that the value of N afforded by Eq. (9) is an overestimate. These effects are well illustrated in Fig. 13 which shows the influence of the peak tailing on the estimation of the column efficiency. The values of N_M and $N_{0.5}$ were calculated by the following equations.

$$N_M = \frac{\mu_1^2}{\mu'_2} \tag{10}$$

$$N_{0.5} = \frac{t_R^2}{\sigma^2_{0.5}} \tag{11}$$

Fig. 13 shows that, depending on the nature and degree of heterogeneity of the column bed, the value of $N_{0.5}/N_M$ may be anywhere between 0.8 and 1.2. When the peak tails, there is no correct definition of the column efficiency and either expression given by Eqs. (10) and (11) can be larger than the other depending on the particular case studied, although, in practice, larger values of $N_{0.5}$ compared to N_M are more frequently reported. Proper application of the contradictory results regarding $N_{0.5}/N_M$ could probably provide original information concerning the radial heterogeneity of a column.

3.4.3. Peak tailing behavior

Fig. 14 illustrates the influence of peak tailing on the variation in the peak width with the fractional height. The ratio $w_{0.5}/w_{0.1}$ is plotted versus the range of variation of the mobile phase velocity, u_w/u_c, for different values of the range of variation of the plate height. This ratio is equal to 0.549 for a Gaussian function. Fig. 15 shows the correlation between the ratio of the asymmetry factors at half-height, $(w_R/w_F)_{0.5}$, and at 10% of the peak height, $(w_R/w_F)_{0.1}$,

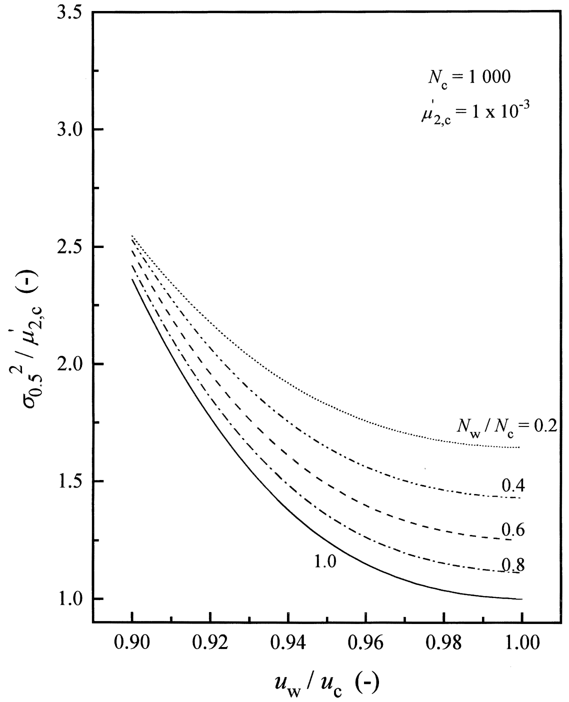

Fig. 12. Dependence of the variance estimated from the peak width at half height on the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions.

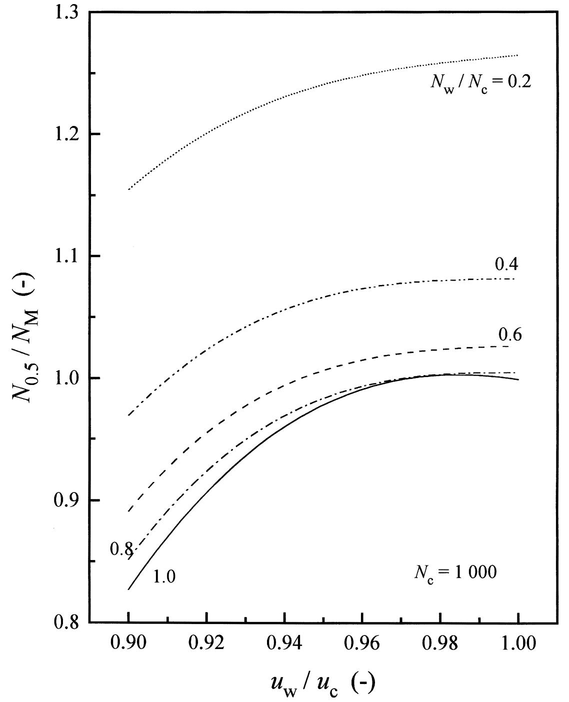

Fig. 13. Influence of the radial heterogeneity of the mobile phase flow velocity and the column efficiency on the estimation of the apparent column efficiency. The column efficiency (number of theoretical plates) was calculated either from the first and the second central moments (N_M), or from the retention time and the peak variance in Fig. 12 ($N_{0.5}$).

with u_w/u_c. The results in Fig. 15 show that $(w_R/w_F)_{0.1}$ is always larger than $(w_R/w_F)_{0.5}$, under all experimental conditions under which chromatographic peaks exhibit tailing profiles.

In order to clarify the characteristic features of the tailing phenomenon, peak profiles were calculated under three limiting conditions, (1) $u_w/u_c = 0.9$, $N_w/N_c = 1.0$; (2) $u_w/u_c = 1.0$, $N_w/N_c = 0.2$; and (3) $u_w/u_c = 0.9$, $N_w/N_c = 0.2$. Fig. 16 shows the three chromatograms calculated. In case (1), there is only a radial distribution of the flow velocity; the column efficiency is uniform across the column. In this case, the results in Figs. 14 and 15 show that the peak exhibits nearly the same asymmetry at both 10 and 50% of the peak height. Also, its ratio of the widths at half-height and 10% of the height is slightly larger than for a Gaussian profile. This is seen in Fig. 16 by comparing the peak profiles under conditions (1) (open circle) and (2) (open triangle). The peak width at 50% height is wider in the former than in the latter, while $w_{0.1}$ is almost same under both conditions.

In case (2), the opposite assumption was made. There is a constant velocity across the column and a radial distribution of the column efficiency and N_c is 5 times larger than N_w. The results in Figs. 14 and 15 indicate that, in this last case, the relative width of the peak close to the baseline is larger than for a Gaussian profile but that the asymmetry factor remains equal to unity under all conditions. Then (Fig. 13), $N_{0.5}$ is always larger than N_M.

Fig. 16 shows also a peak profile calculated under the conditions (3) (open square). The peak profile exhibits some obvious tailing. The retention time of the peak maximum shifts from 1.0 to 0.985. The results in Figs. 14 and 15 show that both the peak width and its asymmetry at 10% height are larger than those at 50% height under the conditions (3).

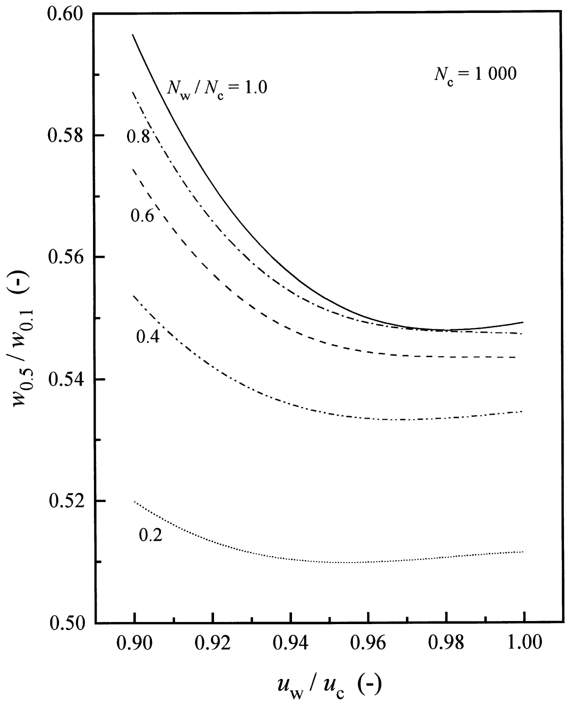

Fig. 14. Correlation between the peak widths at 10 and 50% of the peak height with the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions.

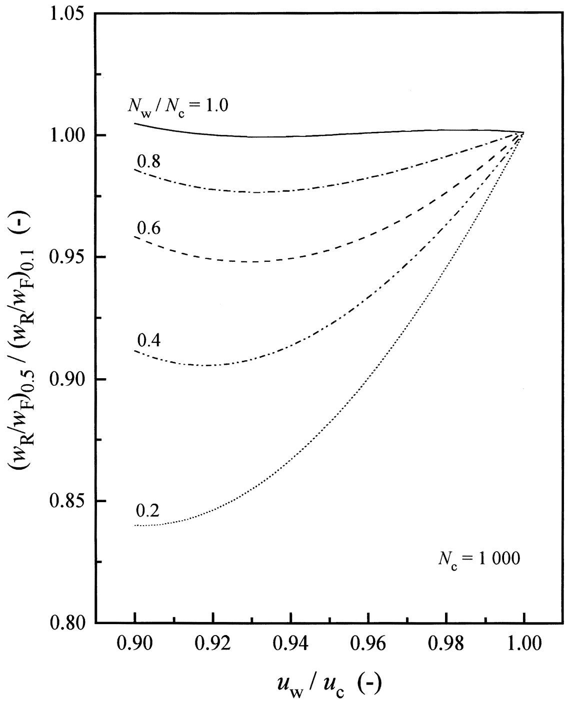

Fig. 15. Correlation between the peak asymmetry factors at 10 and 50% of the peak height with the radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions.

As shown in Fig. 13, $N_{0.5}$ is overestimated by approximately 15% under such conditions (3).

In cases (1) and (2) above, we made the unreasonable assumptions that the radial heterogeneity affected only either the flow velocity distribution (1) or that of the column efficiency (2). Obviously, both should coexist as they originate both from an heterogeneously packed bed [20]. So, there should be a kind of correlation between the radial distributions of the mobile phase flow velocity and of the column efficiency.

4. Conclusion

This numerical study of the influence of the radial heterogeneities of the distributions of the mobile phase flow velocity and of the column efficiency on the characteristics of the tailing of peak profiles in chromatography has confirmed that the radial heterogeneity of the column can cause important peak

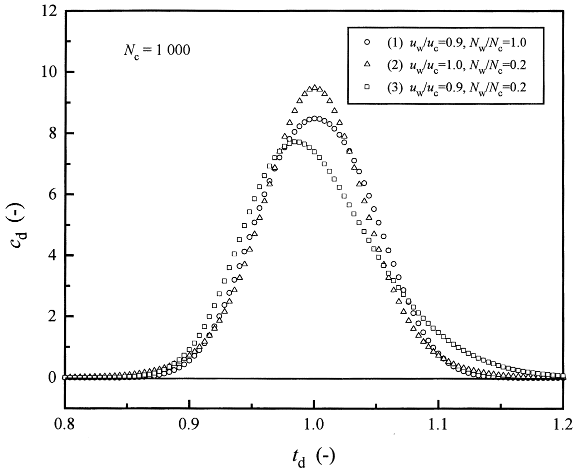

Fig. 16. Peak profiles calculated under three limiting conditions of radial heterogeneity of the mobile phase flow velocity and the column efficiency distributions.

tailing. Peak tailing arises even when there is only a radial distribution of the flow velocity. A radial distribution of the column efficiency enhances the effect of the flow velocity distribution. The influence of the column heterogeneity increases strongly with increasing column efficiency. The tailing behavior resulting from the radial heterogeneity of columns having different efficiencies can be correlated by Eq. (7). Comparison of experimental data with the results of the calculations reported in this study should provide new information regarding this correlation. This subject is currently under investigation.

5. Symbols

a_N	Coefficient in Eq. (5)
a_u	Coefficient in Eq. (4)
A_p	Area of the injected pulse
b_N	Coefficient in Eq. (5)
b_u	Coefficient in Eq. (4)
C	Actual solute concentration
C_d	Dimensionless concentration
kN'_0	Retention factor at infinite dilution
L	Column length
n	Amount of the solute injected
N	Number of theoretical plates
N_M	Defined in Eq. (10)
N_r	Number of theoretical plates at a radial position r
$N_{0.5}$	Defined in Eq. (11)
r	Radial distance from the centre of the column
R	Column radius
S	Column cross-sectional area
t	Time
t_d	Dimensionless time
t_R	Retention time
u	Interstitial velocity of the mobile phase
u_{av}	Average mobile phase flow velocity
u_r	Linear velocity at a radial position r
w	Peak width
w_F	Front half-width of the elution peak
w_R	Rear half-width of the elution peak
w_R/w_F	Asymmetry factor

Greeks

ε	Total porosity of the column
μ_1	First moment
μ'_2	Second central moment
σ	Standard deviation
σ_d	Dimensionless standard deviation

Subscripts

c	At the centre of the column
i	ith column
j	jth column
w	Near the wall of the column
0.1	At 10% of maximum peak height
0.5	At 50% of maximum peak height

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References

[1] G. Guiochon, S. Golshan–Shirazi, A.M. Katti, Fundamentals of Preparative and Nonlinear Chromatography, Academic Press, Boston, MA, 1994.
[2] J.C. Giddings, Dynamics of Chromatography, Marcel Dekker, New York, 1965.
[3] T. Fornstedt, G. Zhong, G. Guiochon, J. Chromatogr. A 741 (1996) 1.
[4] T. Fornstedt, G. Zhong, G. Guiochon, J. Chromatogr. A 742 (1996) 55.
[5] T. Farkas, M.J. Sepaniak, G. Guiochon, J. Chromatogr. A 740 (1996) 169.
[6] T. Farkas, M.J. Sepaniak, G. Guiochon, AIChE J. 43 (1997) 1964.
[7] T. Farkas, G. Guiochon, Anal. Chem. 69 (1997) 4592.
[8] T. Farkas, J.Q. Chambers, G. Guiochon, J. Chromatogr. A 679 (1994) 231.
[9] D.S. Horne, J.H. Knox, L. McLaren, Sep. Sci. 1 (1966) 531.
[10] J.H. Knox, G.L. Laird, P.A. Raven, J. Chromatogr. 122 (1976) 129.
[11] C.H. Eon, J. Chromatogr. 149 (1978) 29.
[12] J.E. Baur, E.W. Kristensen, R.M. Wightman, Anal. Chem. 60 (1988) 2334.
[13] J.E. Baur, R.M. Wightman, J. Chromatogr. 482 (1989) 65.
[14] E. Bayer, E. Baumeister, U. Tallarek, K. Albert, G. Guiochon, J. Chromatogr. A 704 (1995) 37.

[15] U. Tallarek, E. Baumeister, K. Albert, E. Bayer, G. Guiochon, J. Chromatogr. A 696 (1995) 1.
[16] U. Tallarek, E. Bayer, G. Guiochon, J. Am. Chem. Soc. 120 (1998) 1494.
[17] T. Yun, G. Guiochon, J. Chromatogr. A 760 (1997) 17.
[18] T. Yun, G. Guiochon, J. Chromatogr. A 672 (1994) 1.
[19] T. Yun, G. Guiochon, J. Chromatogr. A 734 (1996) 97.
[20] G. Guiochon, T. Farkas, H. Guan–Sajonz, J.-H. Koh, M. Sarker, B.J. Stanley, T. Yun, J. Chromatogr. A 762 (1997) 83.