Journal of Chromatography A, 1216 (2009) 1325–1337

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Numerical and analytical solutions for the column length-dependent band broadening originating from axisymmetrical trans-column velocity gradients

K. Broeckhoven, G. Desmet*

Vrije Universiteit Brussel, Department of Chemical Engineering, Pleinlaan 2, 1050 Brussels, Belgium

ARTICLE INFO

Article history:
Received 28 August 2008
Received in revised form 17 December 2008
Accepted 22 December 2008
Available online 27 December 2008

Keywords:
Radial heterogeneity
Band broadening
Plate height model
Column packing
Numerical simulations

ABSTRACT

Trans-column velocity gradients arising from radial variations in packing density or mobile phase temperature lead to a plate height contribution that, in the case of for example a 4.6 mm column, may increase over several tens of centimeters before it reaches a constant value. Considering a wide variety of different trans-column velocity profiles, including Giddings' general polynomial expression and several simplified partially flat profiles, and performing a set of analytical calculations (to establish an expression for the long time-limit constant value H_∞) and numerical simulations (to calculate the band broadening in the transient regime), it was found that the column length-dependent variation of this plate height contribution can be very closely approximated by a simple exponential-law expression. The availability of the latter will greatly simplify the experimental analysis of radial column heterogeneity effects, especially considering that this expression is independent of the radial dispersion, the column diameter, and the average velocity and maximum velocity difference. Surprisingly, the exponential-law expression is to a first approximation also independent of the shape of the velocity profile, provided the velocity profile does not become flat over a substantially large part of the cross-section. In the latter case, the transient curve obeys a more complex law, but can nevertheless still be approximated by an exponential-law expression, though with a different (larger) decay constant.

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1. Introduction

Ever since the classical work of Giddings [1,2], the occurrence of trans-column mobile phase velocity differences (i.e., differences between the central and the outer regions of the column) has been acknowledged as an important source of band broadening in chromatographic columns.

One of the important and practically very relevant sources of trans-column velocity gradients are the radial packing density variations [3–14] that are induced by the relaxation of the packing stresses. These can be countered to a large extent by radial compression [15], but if they are not properly eliminated, they give rise to a slow gradual change of the local velocity (varying from the highest velocity in the center to the lowest velocity to the side-wall). This effect is already present in analytical scale columns, and can of course be expected to be most pronounced in preparative scale columns [16]. Another type of radial packing heterogeneity arises if the thin side-wall layer (usually one to a few particle diameters thick) immediately adjacent to the column wall has a packing density that is different from that in the bulk of the column (so-called geometrical wall effect [6,17–20]). In the past, also other causes of radial heterogeneity have been reported in the literature. When dry packing columns, a segregation of particles by size might occur when they slide down the heaps which form when the material is poured down the column or when radial vibrations are applied during bed consolidation [4]. In slurry packing, a radial heterogeneity can be caused by differential degrees of sedimentation of particles near the wall [4]. It might however very well be that these last two cases are no longer applicable to modern HPLC systems.

Also monolithic columns can be radially heterogeneous for several reasons [21]. The monolithic bed shrinks during the polymerization process causing radial stress at the interface with the encapsulating wall. If the stress causes the bed to separate from the wall, an effect similar to the geometrical side-wall effect is formed. If the bed remains attached to the wall, inelastic deformation of the bed in the wall region may occur due to the higher stress near the enclosing wall [21]. Wide-bore monolithic columns (e.g. $d_c = 4.6$ mm) have to be encapsulated after the polymerization process due to the shrinking of the bed [22], which might cause radial compression and the resulting radial stress and strain [21]. Another cause of radial heterogeneity of monolithic columns is the fact that the polycondensation reaction taking place is exothermal. This results in a radial temperature gradient in the bed during the reaction, resulting in higher temperatures (and thus higher reaction rates) in the center of the bed. The higher reaction rate in turn will result in a distribution of the local external porosity [21].

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* Corresponding author. Tel.: +32 2 629 32 51; fax: +32 2 629 32 48.
E-mail address: gedesmet@vub.ac.be (G. Desmet).

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doi:10.1016/j.chroma.2008.12.065

Nomenclature

a	exponential decay constant used in Eq. (3)
c'	species fraction
C	concentration (mol/m^3)
d_c	column radius (m)
D_{ax}	axial dispersion coefficient (m^2/s)
D_{rad}	radial dispersion coefficient (m^2/s)
f	function describing the trans-column velocity profile, see Eq. (8)
F	polynomial coefficient in excess velocity profile or flow rate (Appendix A) (m^3/s)
G	polynomial coefficient in Giddings' velocity profile (see Appendix B)
H	plate height (m)
H'	dimensionless plate height, as defined in Eq. (2)
H_∞	long time limit plate height (m)
L	column length (m)
m	fraction of column cross-section with constant velocity, See Eqs. (20) and (21)
MOM$_i$	ith order moment
n	power in polynomial function, or number of cross-sections (Appendix A)
p	highest order in polynomial velocity profile function $f(\rho)$
r	radial coordinate (m)
R_{out}	column radius (m)
S	surface (m^2)
t	time (s)
t'	dimensionless time, as defined in Eq. (4)
u	velocity (u_0-velocity in case of unretained marker and u_r-velocity in case of retained component = $u_0/(1+k')$) (m/s)
x	axial position in column (m)
x'	dimensionless axial position in column, $x' = x/L$

Greek letters

α	geometrical constant dependant on shape of trans-column velocity profile
β	parameter relating Δu_{max} with Δu_m, see Eq. (9)
χ	relative velocity difference function, as defined in Eq. (A.10)
δ	side-wall thickness, i.e. $(1-m)\cdot R_{out}$, see Eq. (21) and Appendix C (m)
Δ	excess, finite difference
κ	geometrical Aris constant
ν	relative velocity difference, defined as $\nu = u/u_m$
ρ	dimensionless radial coordinate, $\rho = r/R_{out}$
σ_x^2	spatial variance (m^2)
σ_t^2	temporal variance (s^2)
γ, η, λ, ξ	geometrical constants needed to calculate H_∞ for flat-linear velocity profiles

Subscripts

m	mean, average
w	wall
max	maximum

Another important and practically relevant source of trans-column velocity biases can be encountered in the case of (ultra-)high pressure LC and high-voltage CE and CEC performed in thermostatted columns, where viscous heating or Joule heating inside the column induces radial temperature and velocity profiles [23–31].

All the above mentioned effects lead to a trans-column velocity bias. A distinguishing feature of the latter is that, unlike the other four main sources of velocity bias distinguished by Giddings [2] (transparticle, intra-channel, short-range inter-channel and long-range inter-channel), the time needed for the radial equilibration between the different velocity regions is of the same order or even larger than the typical column residence times during an analysis.

The latter can be understood from the fact that the equilibrium time t_{eq} needed for a species to diffuse over the entire cross-section of a cylindrical column can be calculated according to [8]:

$$t_{eq} = \frac{1}{32}\cdot\frac{d_c^2}{D_{rad}} \tag{1}$$

with d_c the column diameter and D_{rad} the radial dispersion coefficient. In typical HPLC columns ($d_c = 4.6$ mm) and conditions ($u = 1$–3 mm/s, $D_{rad} = 5$–15×10^{-10} m^2/s), this leads to values of t_{eq} between 400 and 1300 s, or equivalently, to columns lengths between 40 cm and 4 m. This implies that the plate height contribution evolving from a trans-column velocity gradient will in a conventional 4.6 mm column depend on the column length for all column lengths less than a few tens of centimeters. This length-dependency obviously complicates the analysis and comparison of columns with different length and it would hence be very helpful to have a mathematical expression at hand that describes this length-dependency.

In [32] it has been shown that if the trans-column flow profile in a chromatographic bed displays a stepwise variation in a small region near the column wall (cf. the geometrical side-wall effect [6]) an additional plate height contribution will arise whose transient can be most conveniently expressed by relating it to its long time limit value, thereby introducing the dimensionless plate height function H'_{loc}:

$$H'_{loc}(t) = \frac{H_{loc}(t)}{H_\infty} \tag{2}$$

The introduction of the subscript "loc" (for "local") is needed here because the existence of a transient implicitly implies that H will vary from time to time (and hence also from position to position). Transient plate heights are for example also observed in the recent work of Khirevich et al. [33].

Starting from the radial two-zone mixing model originally proposed by Berdichevsky and Neue [34] to model eddy dispersion in packed columns, it could be demonstrated in [32] that the H'_{loc}-value evolving from the geometrical side-wall induced velocity profile approximately varies according to

$$H'_{loc}(t') = 1 - e^{-a\cdot t'} \tag{3}$$

wherein a is a decay constant, related to the bed geometry and velocity profile (see [32]) and with t' being a dimensionless time defined as:

$$t' = t\cdot\frac{D_{rad}}{d_c^2} = \frac{x}{u_m}\cdot\frac{D_{rad}}{d_c^2} \tag{4}$$

The shape of Eq. (3) is equivalent to the expression obtained by truncating the Aris-solution for transient dispersion in a laminar flow after its first term (see Eq. (37) of [35]). This truncation also explains why Eq. (3) is only an approximate solution. Eq. (3) however already yields such a very good first estimate that one can easily do without the mathematical complexities of the complete series expansion.

Whereas the study in [32] was limited to profiles with a stepwise jump in the trans-column velocity profile close to the wall, the present study focuses on the time-dependent variation of the plate height contribution originating from more gradual changes of the trans-column velocity, typically spanning the entire column diameter (Fig. 1a).

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