Journal of Chromatography A, 1368 (2014) 70–81

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Assessment and numerical search for minimal Taylor–Aris dispersion in micro-machined channels of nearly rectangular cross-section

Manly Callewaert[a,b], Wim De Malsche[a], Heidi Ottevaere[b], Hugo Thienpont[b], Gert Desmet[a,*]

[a] Department of Chemical Engineering, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel, Belgium
[b] Brussels Photonics Team, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel, Belgium

ARTICLE INFO

Article history:
Received 24 May 2014
Received in revised form 29 August 2014
Accepted 3 September 2014
Available online 16 September 2014

Keywords:
Taylor–Aris dispersion
Pillar array column
Etching limitation
Computational fluid dynamics
Rectangular cross section
Dispersion reduction

ABSTRACT

A mathematical procedure using the Matlab® PDE toolbox to calculate the numerical constant appearing in the general Taylor–Aris expression for the dispersion in a laminar flow through open-tubular conduits with a variety of quasi-rectangular cross-sectional shapes is described. The procedure has been applied to assess the effect of some of the most frequently occurring etching imperfections (linear or curved tapering of the inter-pillar distance along the depth coordinate, occurrence of local notches) in etched pillar array columns. In addition, covering a broad range of possible geometries, a number of new shapes and optimal geometries to minimize the dispersion in open-tubular microchannels and pillar array columns have been proposed. Making a full shape-sensitivity study, it was also found that, whereas the proposed designs can theoretically reduce the dispersion up to a factor of 8, relatively small deviations from this ideal shape can however again dramatically increase the dispersion. Designers should therefore be very careful before implementing an optimized shape and should first aim at solving the etching imperfection problems.

1. Introduction

During the last decade, so-called pillar array columns have been evaluated as an alternative for the particle and monolithic columns conventionally used to perform liquid chromatography [1–11]. Because of the maximal degree of uniformity with which micro-pillar arrays can be fabricated, they seem ideally suited to conduct chromatographic separations, as this is a separation method where any degree of band broadening caused by disorder and heterogeneity directly translates into a considerable loss in performance. Stimulated by promising 2D computational fluid dynamics (CFD) simulations [12–14], a series of extensive axial dispersion (band broadening) measurement studies has been conducted and reported upon in literature [1–3,10,11]. When the measurements were performed in non-porous silicon pillar array columns with a small depth, i.e., with a small depth over pillar spacing (distance between pillars, e.g. pillar spacing = 1 in Fig. 1) aspect ratio (aspect ratio = A in Fig. 1), the observed degree of band broadening could be perfectly predicted by adding a so-called top–bottom contribution to the 2D dispersion predicted by the CFD simulations [6,14–16]. This top–bottom contribution is needed to correct for the flow-arresting effect of the top and bottom wall. Compared to the theoretical 2D array case considered in most simulations, the top and bottom walls are needed in reality to close-off the pillar array. The presence of these walls leads to a local deviation of the flow field from that in the central part of the flow, in turn leading to an additional source of dispersion, very similar to the unexpectedly large contribution of the short side-walls to the dispersion in laminar flows through conduits with a flat-rectangular cross-section [17–21]. In a 2D calculation, such top and bottom walls are not present because the flow field is assumed to be uniform in the direction of the pillar's central axis. In [22], it was shown that the presence can be represented by an extra C-term contribution (=extra plate height term varying linearly with the velocity) whose magnitude can be fully predicted using the side-wall effect theory for flat-rectangular channels.

A significant deviation (factor 1.25 increase) from this theoretical expectation was however measured when testing deeper pillar arrays, i.e., with a larger pillar aspect ratio [10,11]. In these cases, SEM pictures of the employed channels revealed a small vertical taper of the distance between the pillars, typically decreasing from the top to the bottom of the array, and typically on the order of some 5–10% (some 50 nm in absolute values). This taper is in practice

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

http://dx.doi.org/10.1016/j.chroma.2014.09.009
0021-9673/

List of symbols

D_{mol}	molar diffusion coefficient [m^2/s]
D_{ax}	axial molar diffusion coefficient [m^2/s]
κ_{Aris}	geometry dependent numerical constant [–]
t	time [s]
x, y, z	coordinates [m]
C	concentration [mol/m^3]
u	speed [m/s]
u_{av}	average speed [m/s]
P	pressure [Pa]
μ	dynamic viscosity [Pa s]
d	hydraulic diameter [m]
L	length [m]
Γ	boundary
S	surface [m^2]
χ	dispersion potential [–]
ϕ	concentration potential [–]
h	dimensionless plate height [–]
ν	dimensionless speed/Peclet number [–]
A	height over width aspect ratio [–]
W, H, T, P, B, N	geometrical parameters (see Fig. 1) [–]

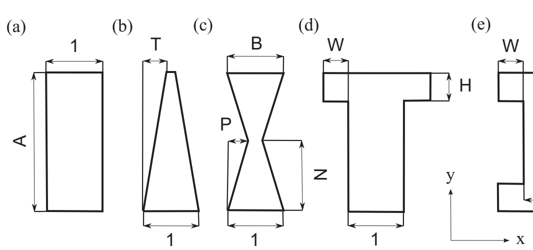

Fig. 1. Considered geometries: (a) rectangular-duct, (b) tapered-duct, (c) pinched-duct, (d) T-duct, (e) I-duct.

difficult to avoid and is caused by minor unbalances between etching and passivation during the Bosch etching process. This taper can be expected to inevitably lead to an additional velocity gradient extending over the depth of the channel.

In a recent paper [23], where smaller dimensions could be achieved with advanced deep UV lithography, the employed 1.25 μm spacing (32 μm depth) resulted in a plate height of 2.0 μm, which was roughly two times higher than what can be expected based on work with a spacing twice as large [10,11]. This was attributed to the occurrence of vertical differences in throughpore width, in turn caused by the vertical taper that is inevitably present on the diameter of the etched pillars. It was speculated that these vertical differences in throughpore width give rise to vertical velocity gradients. Since the taper on the pillar diameter is absolute in nature, its relative contribution becomes more and more important if smaller inter-pillar distances are pursued, which would explain why poorer performances are obtained with pillar array columns with a smaller through-pore size. A similar effect was observed in [9], where it was concluded that any further efforts to reduce the dimensions of pillar array columns are useless without first improving the tapering of the structures. Estimating the magnitude of this effect is one of the aims for the present study.

Other etching imperfections that have been noticed from SEM pictures of photolithographically etched micro-pillar arrays are the occurrence of local notches at the very top and bottom of the pillars, as well as the occurrence of a more lense-shaped taper profile, reaching a maximal inter-pillar distance midway the depth of the array. Examples are Fig. 4 in [24] and Fig. 2 in [1]. To find out

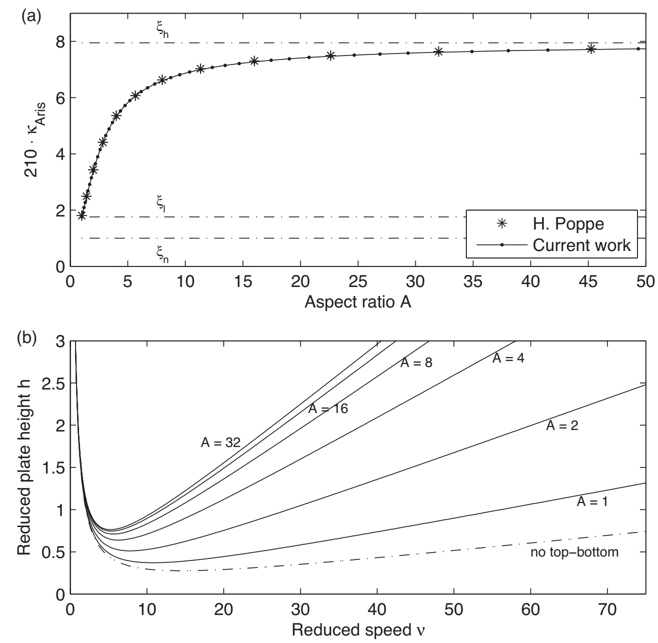

Fig. 2. (a) κ_{Aris}-coefficient as function of the aspect ratio A of a tube with a rectangular cross-section. The dots indicate the values calculated in this work. The asterisks show the values calculated by Poppe [21]. (b) Effect on the plate height, expressed as a reduced van Deemter plot Eq. (1.2).

whether this additional velocity could explain the observed additional band broadening, flow simulations are needed.

In the present paper, the potential effect of such etching imperfections has been assessed by numerically calculating the numerical constant (κ_{Aris}) appearing in the classic Taylor–Aris expression for the dispersion in laminar flows through open-tubular channels with a uniform cross-section for a wide variety of channels with a quasi-rectangular shape (cf. Fig. 1 further on). A fast numerical method, based on the calculation of κ_{Aris} (see Eq. (1.1)) has been implemented in Matlab® that allows to calculate a full scan of geometries in a matter of minutes (calculating κ_{Aris} for a single quasi-rectangular consumes about 1 s of computational time). Although the assumption of a constant cross-section does not strictly hold for the flow-through pores in a pillar array column (because of the continuously changing distance between the pillars in the flow direction), it has been shown by 3D-computational fluid dynamics calculations in [14] that the constant cross-section assumption provides a very close approximation. Since pillar array columns with non-rectangular channels still have a uniform depth, it can be inferred that there still would be no vertical convective component, such that no diffusive-convective coupling effects can be expected, similar to the case studied in [14].

The problem of the axial dispersion in a rectangular channel is a classic problem that has been studied and solved by, amongst others, Taylor, Aris, Chatwin and Poppe [17,20,21,25–27]. They showed that the axial dispersion is in the long time limit (i.e., the limit where D_{ax} is no longer a function of the time after the extinction of the transversal concentration gradients) given by:

$$\frac{D_{ax}}{D_{mol}} = 1 + \kappa_{Aris} \cdot \nu^2 \quad (1.1)$$

wherein ν is the dimensionless velocity (=Peclet-number in engineering literature) based on the characteristic size of the channel (shortest side in present contribution). In the area of chromatography, axial dispersion is most often described in terms of a theoretical plate height, which, in its dimensionless form can