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From random sphere packings to regular pillar arrays: Analysis of transverse dispersion

Anton Daneyko, Dzmitry Hlushkou, Siarhei Khirevich, Ulrich Tallarek*

Department of Chemistry, Philipps-Universität Marburg, Hans Meerwein Strasse, 35032 Marburg, Germany

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ABSTRACT

We study the impact of microscopic order on transverse dispersion in the interstitial void space of bulk (unconfined) chromatographic beds by numerical simulations of incompressible fluid flow and mass transport of a passive tracer. Our study includes polydisperse random sphere packings (computer-generated with particle size distributions of modern core–shell and sub-2 μm particles), the macropore space morphology of a physically reconstructed silica monolith, and computer-generated regular pillar arrays. These bed morphologies are analyzed by their velocity probability density distributions, transient dispersion behavior, and the dependence of asymptotic transverse dispersion coefficients on the mobile phase velocity. In our work, the spherical particles, the monolith skeleton, and the cylindrical pillars are all treated as impermeable solid phase (nonporous) and the tracer is unretained, to focus on the impact of microscopic order on flow and (particularly transverse) hydrodynamic dispersion in the interstitial void space. The microscopic order of the pillar arrays causes their velocity probability density distributions to start and end abruptly, their transient dispersion coefficients to oscillate, and the asymptotic transverse dispersion coefficients to plateau out of initial power law behavior. The microscopically disordered beds, by contrast, follow power law behavior over the whole investigated velocity range, for which we present refined equations (i.e., Eq. (13) and the data in Table 2 for the polydisperse sphere packings; Eq. (17) for the silica monolith). The bulk bed morphologies and their intrinsic differences addressed in this work determine how efficient a bed can relax the transverse concentration gradients caused by wall effects, which exist in all confined separation media used in chromatographic practice. Whereas the effect of diffusion on transverse dispersion decreases and ultimately disappears at increasing velocity with the microscopically disordered chromatographic beds, it dominates in the pillar arrays. The pillar arrays therefore become the least forgiving bed morphology with macroscopic heterogeneities and the engendered longitudinal dispersion in chromatographic practice. Wall effects in pillar arrays and the monolith caused by their confinement impact band broadening, which is traditionally observed on a macroscopic scale, more seriously than in the packings.

1. Introduction

In chromatography, the height equivalent to a theoretical plate (H) is defined as the slope of the dependence of the variance of an analyte band (σ^2) on its migration distance. In a first approximation, assuming a homogeneous chromatographic bed and an incompressible mobile phase, this slope (hence H) is constant along the column. A similar definition applies to the band broadening in longitudinal (z-) and transverse directions, i.e., parallel and perpendicular with respect to the macroscopic flow direction. Longitudinal and transverse dispersion coefficients D_L and D_T usually discussed in the engineering literature [1] are related to the chromatographic plate heights H_L and H_T by [2]

$$D_L = \frac{H_L u_{av}}{2} = \frac{h_L \nu D_m}{2} = \frac{u_{av}}{2} \cdot \frac{\partial \sigma_L^2}{\partial z}, \quad (1)$$

and

$$D_T = \frac{H_T u_{av}}{2} = \frac{h_T \nu D_m}{2} = \frac{u_{av}}{2} \cdot \frac{\partial \sigma_T^2}{\partial z}, \quad (2)$$

where h is the reduced plate height and ν is the reduced velocity, which characterizes the ratio of longitudinal advective to diffusive transport in a chromatographic bed (u_{av} is the average mobile phase velocity through the bed and D_m is the analyte's diffusion coefficient in the bulk fluid). Importantly, the band broadening in longitudinal direction controls the resolution between the peaks of the different components of the sample and is of paramount importance in all applications of chromatography; band broadening in the transverse

* Corresponding author. Tel.: +49 6421 28 25727; fax: +49 6421 28 27065.
E-mail address: tallarek@staff.uni-marburg.de (U. Tallarek).
URL: http://www.uni-marburg.de/fb15/ag-tallarek (U. Tallarek).

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direction controls the lateral homogeneity of the band and relaxes concentration gradients caused by nonuniform distributions of the local velocity [3,4].

As an analyte zone migrates along a chromatographic bed, it is dispersed in longitudinal and transverse directions by a combination of diffusive and advective processes. When a streamlet hits, e.g., a particle in a randomly packed bed, it splits into several, unequal streamlets that flow around the hit particle, between it and its different neighbors, and merge with other different streamlets of similar origin. Thus, the migration of the mobile phase along a packed column is accompanied by the constant shearing and merger of streamlets. This process is involved in the eddy dispersion contribution to longitudinal dispersion; it is also the essential source of transverse dispersion, because transverse diffusion in the new streamlets and a cascade succession of similar events at each additional particle promote transverse dispersion. In this case, the process is known as "stream-splitting". Because the streamlets are much smaller than the particles between which they flow, transverse dispersion causes rapid local homogenization of the stream composition. However, in the absence of significant transverse advection, homogenization is extremely slow at the column scale, where it relaxes transcolumn concentration gradients that arise from macroscopic variations in the local flow velocity. This implies that at least two fundamental length and time scales exist for eddy dispersion and the associated transverse equilibration between different velocities of the flow field in a confined chromatographic bed: the pore (short-time) scale and the confinement or transcolumn (long-time) scale [5,6].

If a chromatographic bed (e.g., an in situ prepared monolith, a slurry-packed column, or a microfabricated pillar array) is macroscopically inhomogeneous, which is usually related to its confinement, it will show a transcolumn flow heterogeneity. This, in turn, leads to the formation of transverse concentration gradients, which are eventually relaxed with transverse dispersion. Recent work of Gritti and Guiochon [7,8] has provided an in-depth analysis of transcolumn dispersion in packed chromatographic columns. In particular, they demonstrated that transcolumn concentration gradients relax differently depending on whether the bed is made of porous or nonporous particles. When the particles are porous, the analytes can diffuse either through the interparticle void space or through the intraparticle pores (impossible with nonporous particles). The diffusion flux across a particle is the sum of the contributions of diffusion through the mobile phase contained in the pores of the particle and of surface diffusion (along the adsorbent surface) [9,10]. The latter contribution increases rapidly with increasing concentration gradient along this surface, hence the diffusion flux increases rapidly with increasing retention of the analyte. Furthermore, the time spent by the analytes in the column is longer when the particles are porous. Thus, transverse concentration gradients are more effectively relaxed. Gritti and Guiochon [7,8] presented a new model of transcolumn eddy dispersion based on Giddings' coupling theory for diffusive and flow mechanisms [2], in which transcolumn flow profiles were approximated with experimental data and also the importance of surface diffusion (enhancing the rate of mass transfer through porous particles, along the adsorbent surface) was accounted for. To summarize, the impact of transcolumn velocity biases is minimized when the pores of the particles are accessible; it decreases with increasing retention and transverse dispersion coefficient of the analytes.

Transcolumn velocity biases of different origin can be a serious problem with all kinds of chromatographic beds. For example, the presence of two wall effects has been reported for slurry-packed columns [11,12]: (i) Stress and strain that take place in the bed during the slurry packing process and bed consolidation cause the distribution of mobile phase velocities across the column to become heterogeneous [13–15]. Consequently, the sample zones warp during elution and concentration gradients build up [16,17]. This frictional wall effect is traditionally discussed in connection with analytical and preparative columns. (ii) A geometrical wall effect [18,19] dominates the kinetic column performance at low column-to-particle diameter ratio, which becomes important for packed capillaries [20] and microchips [21,22]. In general, both wall effects contribute to the bed morphology, but depending on the actual column-to-particle diameter ratio either wall effect may dominate the macroscopic velocity heterogeneity and transcolumn eddy dispersion.

Compared with packed (particulate) beds, transcolumn velocity biases in silica monoliths are caused by their radial heterogeneity, which is supposed to stem from chemical and/or temperature gradients that form across the column bed during the monolith preparation [23]. Also, strain resulting from the stress caused by the shrinkage of the monolithic rod after formation of a solid network may cause the interface between monolith and column wall to break due to inelastic deformations. The monolith may separate from the wall causing slightly higher local porosities in the wall region. By placing electrochemical detectors at various points of the cross-section at the column exit of semi-preparative (10 mm i.d.) and analytical (4.6 mm i.d.) silica monoliths, Guiochon and coworkers [24,25] found 4% and 1.5% velocity difference, respectively, between the wall and the core region. Even at only a few percent, morphological differences, e.g., in local macroporosity, cause a noticeable loss of separation efficiency. Another, severe form of radial heterogeneity occurs in capillary monoliths: As opposed to larger-diameter monolithic rods, capillary monoliths are prepared directly in the tube then used for chromatographic separations; so that gaps where the bed has snapped back from the wall allow the mobile phase to bypass the bed [26]. Efforts directed against this problem have been reported recently for capillary [27–31] and analytical [32–34] silica monoliths.

Compared to microscopically disordered, macroscopically inhomogeneous packings and monoliths, even microscopically ordered pillar arrays suffer from substantial wall effects as we distort the perfect microstructure by a macroscopic confinement. The concept of pillar arrays as spatially periodic porous media has to be altered when these stationary phases are used as chromatographic supports, because the inevitable confinement engenders a macroscopic heterogeneity, which affects the dispersion behavior and thus the efficiency of the array for separations in liquid chromatography [35]. The effect of a straightforward confinement (resulting in a rectangular bed cross-section and side walls containing a layer of embedded half cylinders) on hydrodynamic dispersion is illustrated with Fig. 1. We employ numerical simulations of the transient normalized longitudinal hydrodynamic dispersion coefficient obtained with a passive (nonadsorbing, nonreacting) tracer in the interstitial void space between nonporous pillars of diameter d_p [35]. Upon confinement of the pillar array, the no-slip velocity boundary condition at the surface of the top and bottom as well as the two side walls causes flow and transport to become macroscopically inhomogeneous. The transcolumn velocity bias is generated parallel to the pillar axis (by the top and bottom walls) as well as perpendicular to it (due to the side walls). To obtain reliable plate height data the dispersion simulations require consideration of the complete three-dimensional geometry of the confined array to take proper account of the four newly created 90°-corners [35]. Starting from an unconfined, i.e., bulk regular pillar array, simulated as a single unit cell with periodic boundary conditions, we first add top and bottom walls (indicated in the upper right panel of Fig. 1 by the semi-transparent faces), and then complete the confinement with the addition of side walls. The two fully confined exemplary pillar arrays in Fig. 1 (with a height of 2.8 d_p each and a width of 28.37 d_p and 112.27 d_p, respectively) are flat, rectangular boxes with channel width-to-height ratios typically found on microchips [36].