

● *Short Communication*

MASS TRANSFER IN CHROMATOGRAPHIC COLUMNS STUDIED BY PFG NMR

ULRICH TALLAREK,*† DAGMAR VAN DUSSCHOTEN,† HENK VAN AS,† GEORGES GUIOCHON,‡ AND
ERNST BAYER*

*Institute of Organic Chemistry, University of Tübingen, Auf der Morgenstelle 18, Tübingen, Germany; †Department of Molecular Physics, Wageningen Agricultural University, and Wageningen NMR Center, Dreijenlaan 3, HA Wageningen, The Netherlands; ‡Department of Chemistry, University of Tennessee, Knoxville, TN and Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Pulsed field gradient (PFG) nuclear magnetic resonance (NMR) is applied to study convective and diffusional transport in chromatographic columns packed with totally porous support particles. Here stagnant zones exist in the particle pores, and diffusional mass-transfer limitations between fluid molecules diffusing in the intraparticle pore network and flowing in the interparticle void space are detected quantitatively. Axial displacement probability distributions were measured for water over a range of Peclet numbers and observation times, with diffusion lengths between 0.15 and 0.91 times the average support particle diameter. The transition towards complete diffusional exchange is demonstrated, thereby also revealing the development of the classical convective dispersion process in a packed bed of (porous) particles. © 1998 Elsevier Science Inc.

Keywords: Transport in porous media; Packed columns; Chromatography; PFG NMR.

Transport processes in chromatographic columns are highly dependent on the porous structure, homogeneity and long-term stability of the packed bed of adsorbent particles, the packing method, as well as on the shape, actual size distribution and porous nature of the support particles. The latter parameter is of special importance regarding (intraparticle) diffusional mass-transfer limitations and slow sorption rates of solute molecules that occur in the stagnant mobile phase of a packed bed of porous particles.¹ Here the effective intraparticle solute diffusivity and the actual flow rate chosen for the separation process critically influence band broadening and resolution in chromatography.²

In this respect, pulsed field gradient (PFG) nuclear magnetic resonance (NMR) techniques are a noninvasive tool to study fluid transport in packed beds of chromatographic columns³ and other porous solids.^{4–7} These methods allow for (quantitative) discrimination between fluid molecules displaced due to externally driven convection and purely diffusive ones, thereby being intimately related to the dynamics within the respective

environments sampled by the fluid particles on the experimental timescale.

Here, we report a set of ¹H PFG NMR measurements obtained for well-consolidated packing in a chromatographic column. The classic convection-driven dispersion process in a packed bed of porous particles and the mass transfer between the intraparticle pore network and the interparticle void space is demonstrated.

MATERIALS AND METHODS

The so-called averaged propagator,⁸ $\bar{P}(\mathbf{R}, \Delta)$, gives the probability that any molecule in the sample will move a dynamic (net) displacement $\mathbf{R} = \mathbf{r} - \mathbf{r}_0$ within the experimentally adjustable observation time Δ .⁹ By applying the PFGs either parallel or perpendicular to the column axis, the axial- or transverse-averaged propagator can be obtained independently based on its Fourier relation with the echo amplitude.^{9,10}

For classic (convective) dispersion of the fluid in the packed bed of particles, correlation between the initial positions \mathbf{r}_0 and \mathbf{r} is completely lost, and the displace-

Address correspondence to Prof. Dr. Ernst Bayer, Institute of Organic Chemistry, The University of Tübingen, Auf der

Morgenstelle 18, D-72076 Tübingen, Germany. E-mail: ernst.bayer@uni-tuebingen.de

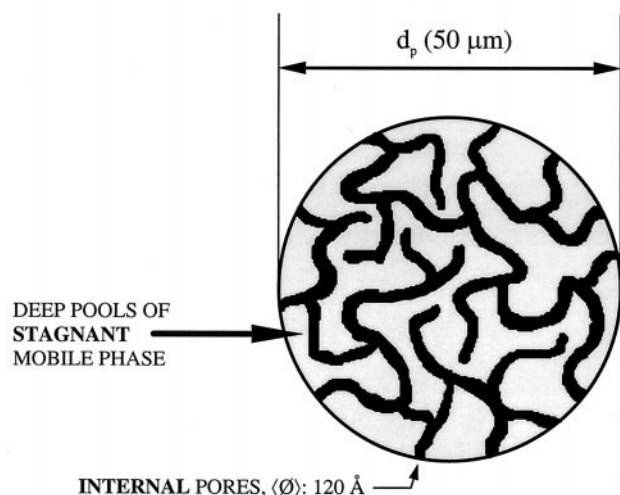


Fig. 1. Spherical shaped, totally porous support particle used in high performance liquid chromatography (HPLC) applications.

ment probability distribution is a Gaussian curve of standard deviation $\sigma = (2D_{ap}\Delta)^{1/2}$, centered at $\bar{u}\Delta$ in displacement space. Here, the cross-sectional average velocity \bar{u} and the apparent (axial or transverse) dispersion coefficient D_{ap} can be extracted from the profile peak center and the profile width, respectively.

The 0.5 T NMR system includes a SMIS console and

custom-built Doty microscopy probe. Measurements are volumetrically averaged over the total column cross-section and *ca.* 40 mm along the axial direction, using the PFG stimulated-echo sequence.⁹ The slurry-packed column^{3,11} (4.4×150 mm) and accessory used in this study is made of poly(arylether ether ketone) (PEEK). The packing support has a narrow particle size distribution and consists of totally porous, nearly spherical shaped (chemically bonded C18) silica particles, with an average particle diameter d_p of $50 \mu\text{m}$ and an average (internal) pore size of 120 \AA (Fig. 1). The iron contamination (Fe^{3+}) is below 10 ppm. Pure, degassed water is continuously pumped through the packing under study.

RESULTS AND DISCUSSION

On their way through the tortuous pore space the water molecules experience different dynamic environments; e.g., they enter into stagnant regions within the porous particles, reside and later exchange again with rapidly moving ones of the flowstreams in the interparticle void space. The dynamics of this stagnant mobile phase mass-transfer resistance largely dominates the overall axial dispersion at high Peclet numbers (Pe) of flow. The actual degree of this exchange is intimately related to the observation time Δ chosen in the respective PFG NMR measurement.

Figure 2 shows axial averaged propagator distribu-

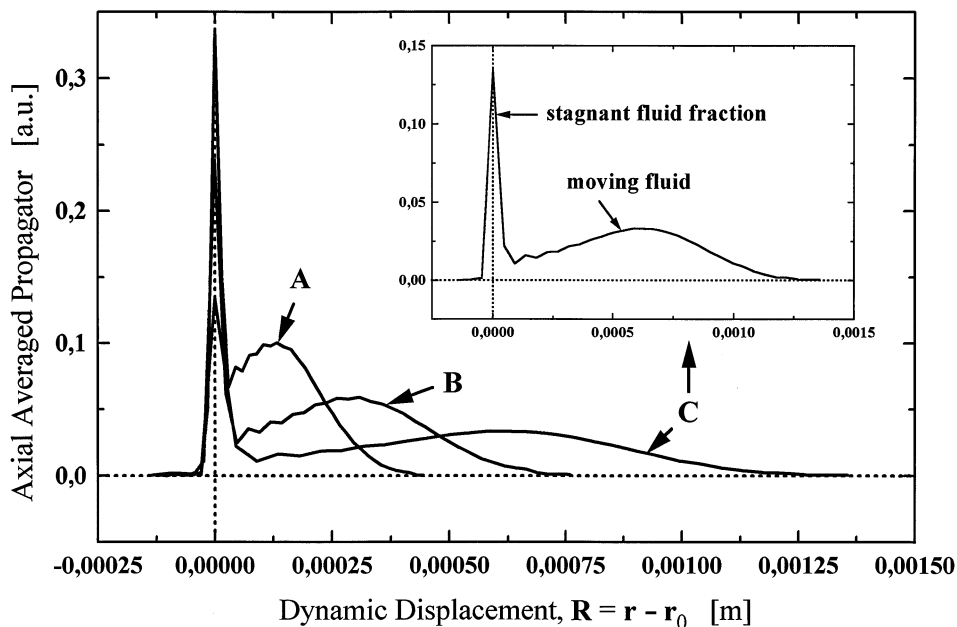


Fig. 2. Axial displacement probability distributions. Flow rate (F_v): (A) 2.2 mL/min, (B) 4.4 mL/min, and (C) 8.8 mL/min. Observation time (Δ) 30 ms. 4.4×150 mm PEEK column packed with totally porous C18 silica particles ($d_p = 50 \mu\text{m}$). Mobile phase: pure water (degassed).

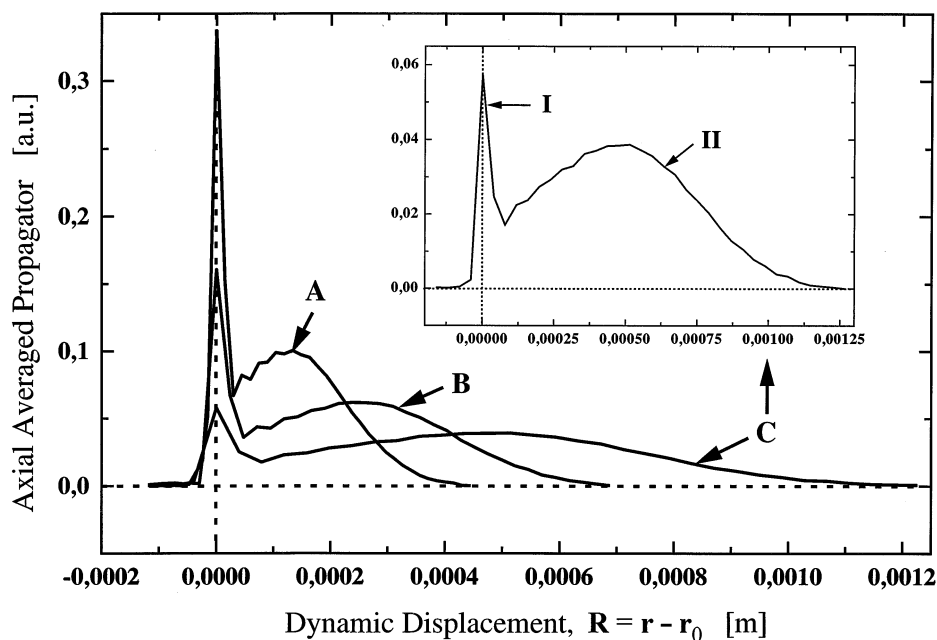


Fig. 3. Axial averaged propagator distributions at constant flow rate ($F_v = 2.2$ mL/min). $\delta = 4.0$ ms. Observation times (Δ): (A) 30 ms, (B) 60 ms, (C) 120 ms. I: stagnant fluid fraction (8.5%); II: moving fluid ($D_{ap} = 3.73 \times 10^{-3}$ cm²/s).

tions obtained for water in the porous column packing. The observation time is fixed and the flow rate is varied. Here convection dominates overall dispersion, but the effect of molecular diffusion still cannot be neglected. At

higher reduced velocities (with $Pe > 300$), convective displacements largely exceed diffusive ones and the complete Gaussian displacement curve characterizing convective dispersion in the medium becomes visible

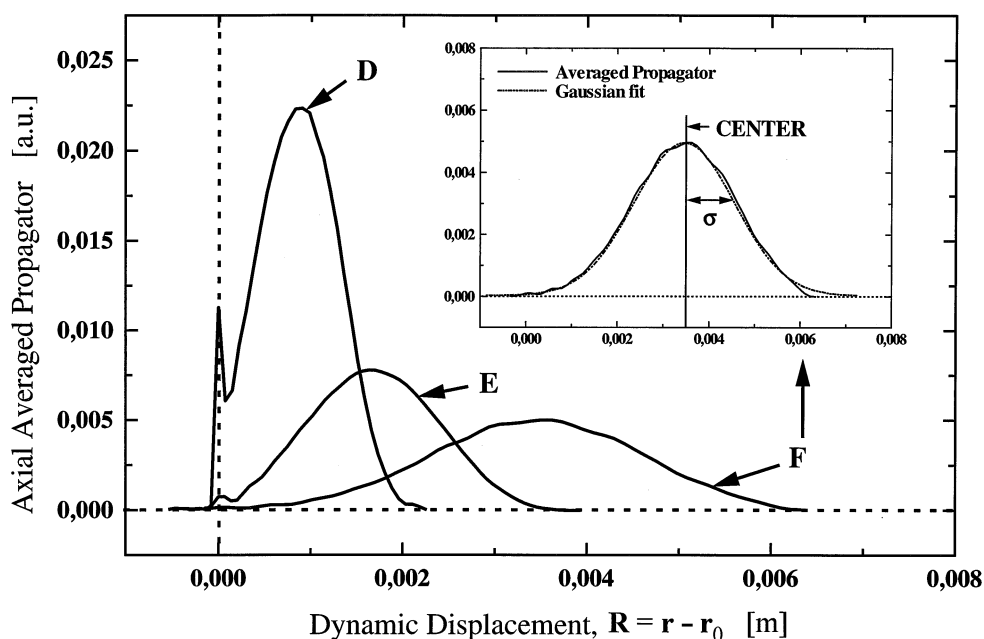


Fig. 4. Axial displacement probability distributions (continued). Observation times (Δ): (D) 240 ms, (E) 480 ms, and (F) 960 ms. Flow rate (F_v) 2.2 mL/min. Gaussian fit (for $\Delta = 960$ ms): center position $\bar{u}\Delta = 3.46 \times 10^{-3}$ m, $\sigma = 1.1 \times 10^{-3}$ m.

(Fig. 2C). However, a second Gaussian distribution is observed. It is exactly centered at zero displacement, i.e., its constituting fluid molecules are stagnant. In addition, this fraction is found to be independent of the flow rate (ca. 21%), with a diffusion coefficient around $1.05 \times 10^{-5} \text{ cm}^2/\text{s}$. It is reduced from D_m to a factor of ca. 2.

When using large porous particles with small constricted pores, deep pools of stagnant mobile phase exist in the particles interior (Fig. 1). Then, the fluid molecules have to diffuse a net, straight distance from the particle center to its boundary (here $d_p/2 = 25 \text{ }\mu\text{m}$) to effect a complete exchange between moving and stagnant fluid! However, the diffusion length of the water molecules covered by an observation time of 30 ms is only $l_D = \sqrt{D_m \cdot \Delta} = 8 \text{ }\mu\text{m}$. The exchange time t_E required for this diffusive process can be estimated by:¹

$$t_E = \frac{(d_p/2)^2}{2 \cdot D_m} \quad (1)$$

On that basis an exchange time of $t_E = 145 \text{ ms}$ is calculated for water. Thus, the stagnant-fluid fraction seen in Fig. 2 mostly arises from water molecules still entrained in the porous particles, and the effective water diffusivity here is reduced from D_m to a degree that depends on the intraparticle tortuosity.

Consequently, the next step was to study the observation time dependence of the stagnant-fluid fraction at a constant flow rate ($Pe = 84$). The results are shown in Fig. 3 and 4. Here, the observation time Δ is increased up to 960 ms ($l_D = 45 \text{ }\mu\text{m}$) and the decrease of the stagnant-fluid fraction can be directly followed. Finally, it has vanished due to complete diffusive exchange and a single Gaussian displacement probability distribution is observed (Fig. 4F). At $\Delta = 120 \text{ ms}$, 8.5% of the water molecules are left being stagnant. Probably due to the highly constricted nature of the small intraparticle channels, they need longer escape times than calculated [see Eq. (1)]. Thus, the technique shows potential for comparative studies of various porous media regarding their diffusion-limited mass-transfer characteristics.

Acknowledgments—This work was supported by an European Union Human Capital and Mobility Grant ERBCHGECT 940061. Dr. Ulrich Trüding (YMC Europe, Schermbeck, Germany) kindly provided the packing material used in this study. We also thank Frank Vergeldt for computational assistance.

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