

● *Short Communication***SPATIALLY RESOLVED TRANSPORT PROPERTIES IN
RADIALLY COMPRESSED BEAD PACKINGS STUDIED
BY PFG NMR**DAGMAR VAN DUSSCHOTEN,* ULRICH TALLAREK,† TOM SCHEENEN,* UWE D. NEUE,‡ AND
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Pulsed field gradient (PFG) multi-echo (ME) and turbo spin-echo (TSE) imaging is used to study dispersive flow in radially compressed chromatographic columns packed with porous silica beads. By using the pulsed field gradient turbo spin-echo sequence spatially resolved displacement imaging can be accelerated by a factor of 16. The positive effect of homogeneous radial packing on flow velocity and dispersion is demonstrated. Small heterogeneities of only a few percent are shown to cause changes of the dispersion coefficient of up to 50%. © 1998 Elsevier Science Inc.

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INTRODUCTION

The performance of a chromatographic column critically depends on the radial homogeneity of the packing.^{1,2} Local fluctuations in the packing density cause correlative fluctuations of the local porosity, permeability and retention characteristics of a column. As a consequence, column performance deteriorates: the peak resolution in analytical separations, or the production rate in preparative applications, respectively, are reduced. Therefore, it is important to gain insight into the range and position of these local variations in flow velocity, preferably in relation to packing methodology, history of the column, etc.

Nuclear magnetic resonance (NMR) is well suited for these studies because it offers satisfactory spatial resolution combined with a very high sensitivity to motion over a wide range of moieties. We have combined pulsed field gradient (PFG) NMR with both multi-echo (ME) imaging³ and turbo spin-echo (TSE) imaging. The PFG TSE sequence can generate spatially resolved displacement profiles or spectra in less than half an hour. The results of both approaches are treated in this communi-

cation without going into too much detail with regard to the pulse sequences.

Although the PFG TSE is considerably faster than the PFG ME sequence, it is not capable of simultaneously monitoring T_2 , water density and displacement. The multiple echoes of the PFG ME sequence can either be used to enhance the signal-to-noise ratio (SNR), or to enhance the displacement resolution by means of two-dimensional fitting of the combined displacement and T_2 data set.³ It should be noted that motion-induced phase shifts are rotated by 180° pulses and, therefore, displacement profiles of even echoes should be rotated before adding them to odd echo displacement profiles. This effect forces the acquisition of two separate displacement images for TSE, one for the odd and one for the even echoes. When 32 echoes are acquired after the PFGs, 2 motion sensitised images in 8 scans are obtained. The 2 complete displacement data sets can be added after rotation for increased SNR or subtracted without rotation to directly obtain difference propagator images. Details of this experiment are treated elsewhere.⁴

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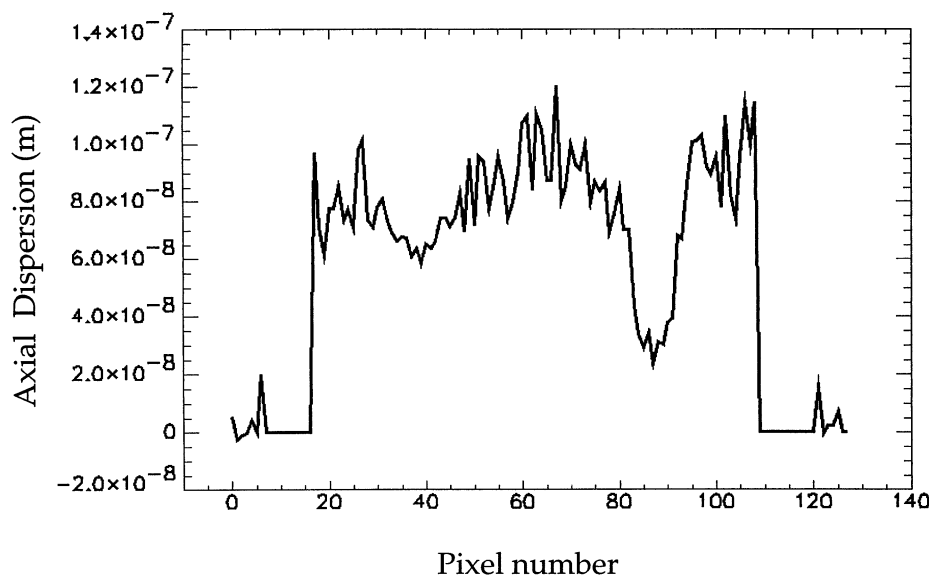


Fig. 1. Sectional plane of an axial dispersion coefficient image of a radially compressed cartridge with totally porous silica beads ($d_p = 55\text{--}105\ \mu\text{m}$) as measured by displacement imaging. Acquired using the PFG ME sequence with FOV = 42 mm, slice thickness = 2.5 mm, $\delta = 3\ \text{ms}$, $\Delta = 32.2\ \text{ms}$.

Recently, displacement studies by PFG NMR have been applied to dispersive flow through porous media⁵⁻⁷ and a theoretical framework is being built to interpret the NMR results and couple them to results from macroscopic studies. The NMR results presented thus far primarily concern uncompressed solid beads. Here we present results of totally porous silica beads which were radially compressed.

RESULTS AND DISCUSSION

Experiments were performed on a 0.5 T imager consisting of a SMIS console in combination with a special design gradient probe (Doty Scientific, Columbia, SC, USA) with a 4.5-cm internal diameter cylindrical gap and radiofrequency coil. Data analysis was performed using locally developed routines written in Interactive Data Language (IDL) (RSI, Boulder, Colorado, USA). Maximum gradient strength was: G_y (vertical) = 500 mT/m, $G_{x,z}$ = 600 mT/m. Typical experimental values were: slice thickness = 2.5 mm, field of view (FOV) = 42 mm, $\delta = 3\ \text{ms}$, repetition time (TR) = 1.5 s, and 4–16 averages resulting in measurement times of about 8 h for the ME sequence and 2 h or less for the TSE sequence (thus obtaining a higher SNR).

For these experiments, we used a radial compression chamber designed to tightly fit into the gradient probe. Two different sizes of totally porous silica beads coated with C-18 were used: $d_p = 55\text{--}105\ \mu\text{m}$ and $d_p = 6\ \mu\text{m}$. Cartridges were placed in an outer jacket with a small air gap between the cartridge wall and the compression

chamber. This was filled with tap water and could be pressurised up to 70 bar with a second high performance liquid chromatography pump, resulting in the radial compression of the cartridge packing. The beads were wetted with acetonitrile before turning to water. Water was degassed with helium to prevent formation of air bubbles within the cartridge and pump head. Flow rates up to 150 mL/min using 30 bar could be sustained for prolonged periods. For the cartridge filled with the larger beads, experiments were performed before and after radial compression.

Firstly, images were acquired using the PFG ME sequence with a 128×128 image matrix and 32 gradient steps. In the case of the larger beads, some small packing density differences, almost invisible in our water density maps, resulted in considerably lower displacements (up to 30%). Here the packing density was slightly higher and, consequently, the permeability, velocity, and therefore dispersion coefficient, are lower. Applying radial compression aggravated these local disturbances and resulted in reduction of the local displacements by more than 50%. A sectional plane of a displacement image including such a local packing density fluctuation is presented in Fig. 1. Note that near the wall, no significantly different flow occurs, a situation that did exist prior to radial compression.

Measurements on the small beads were performed using the PFG TSE sequence that was developed in a later stage of this research project. Measurement time was typically reduced by a factor of four, yet resulted in

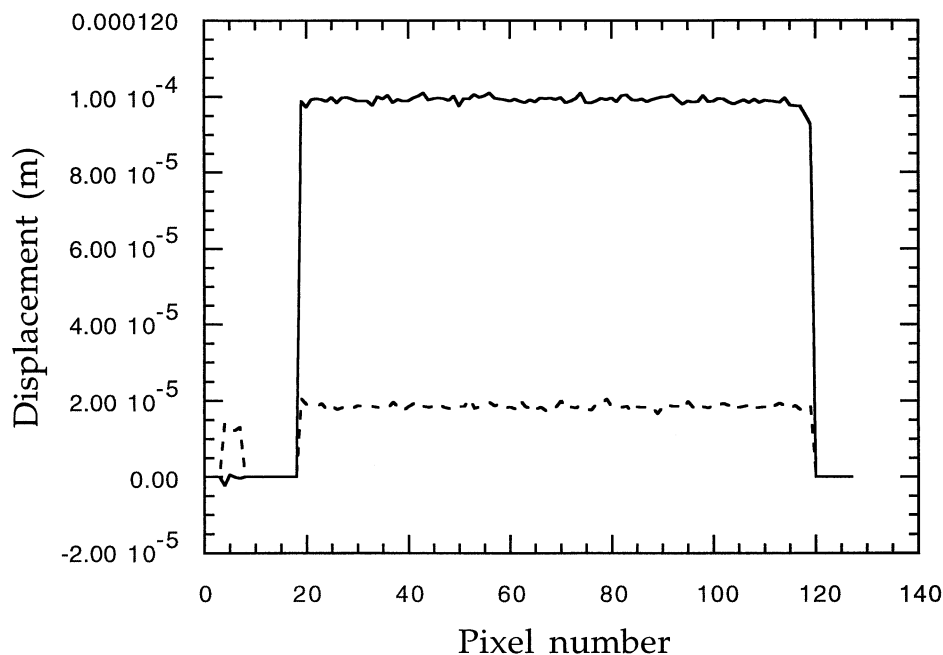


Fig. 2. Sectional planes of an axial displacement and a root-mean-square displacement image of a radially compressed cartridge with totally porous silica beads ($d_p = 6 \mu\text{m}$) as measured by displacement imaging. Acquired using the PFG TSE sequence with FOV = 42 mm, slice thickness = 2.5 mm, $\delta = 3 \text{ ms}$, $\Delta = 32.2 \text{ ms}$.

an increase in the SNR of 2. In this case, the bead size distribution is very narrow, which allows for much more homogeneous packing. Prior to the presented measurements, however, air leaked into the cartridge, which was removed with acetonitrile. Figure 2 presents typical sectional planes through the displacement and dispersion images. Both plots are perfectly flat over the whole width of the column, and the standard deviation is less than 1%. This demonstrates the excellent homogeneous packing of this cartridge. Enhanced flow near the tube wall could not be detected. Of course, it is not unlikely that edge effects do occur on a scale much smaller than the current pixel size of $150 \mu\text{m}$.

The displacement presented in Fig. 2 combined with the flow velocity (as given by the pump computer) resulted in a calculated porosity of 0.44, instead of the expected 0.53. Furthermore, we observed a stagnant phase representing 4% of the total water content in the cartridge. This stagnant phase is not expected because measurements have been performed with $\Delta = 32 \text{ ms}$, and one would expect all bead water to exchange with the flowing water within 10 ms .⁸ Also, the stagnant phase was identical for all observation times. This is contrary to other observations we made using other totally porous beads.⁸ Currently, we do not have an explanation for the difference between the expected porosity and the calculated porosity. For other porous silica beads a good correlation was found.⁸

The above experiments show that the PFG NMR techniques used are excellent tools to study column packing and its effect on dispersive flow and thus, in the end, column performance.

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