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Performance characteristics of new superficially porous particles☆

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ABSTRACT

Superficially porous particles (also called Fused-Core, core shell or porous shell particles) show distinct advantages over comparable totally porous particles for separating small molecules. Columns of Fused-Core particles exhibit very high efficiency because of superior eddy dispersion properties (smaller van Deemter A term). The efficiency for columns of 2.7 μm Fused-Core particles actually rivals that for sub-2 μm totally porous particles with only about one-half the back pressure. These Fused-Core particles show special advantages with larger molecules for fast separations at high mobile phase velocities because of superior mass transfer (kinetic) properties (smaller van Deemter C term). This report describes the effect of different particle size and porous shell thicknesses on chromatographic performance for Fused-Core particles. Particle characteristics can significantly affect factors of separation importance. For example, the reduced plate height of packed columns is affected by particle diameter. Interestingly, larger Fused-Core particles show smaller reduced plate heights than smaller Fused-Core particles. Also, porous shell thickness has a strong effect on solute retention as well as separation efficiency, and particle surface area has a direct influence on sample loading characteristics. Fused-Core particles with a wide range of physical characteristics have been developed that allows the preparation of stable, efficient packed columns.

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1. Introduction

The traditional use of totally porous silica particles as support material for preparing columns for high-performance liquid chromatography (HPLC) has recently been undergoing serious changes. The reincarnation of superficially porous (often called Fused-Core®, core shell or porous shell) particles has rapidly resulted in the routine use of these materials because of superior performance for separating both small molecules [1–6] and larger compounds such as peptides [7–9] and proteins [7,10,11]. Better column performance of Fused-Core columns for small molecules is probably based on the higher efficiency of these particles as a result of improved packed bed homogeneity, largely because of very narrow particle size distributions and perhaps higher particle density [1,2]. Advantages in longitudinal diffusion caused by the fused core are also a feature of high column performance. Separations for larger compounds, such as peptides and proteins, are enhanced by the excellent mass transfer (kinetic) properties resulting from the thin shell that surrounds a solid core. Poorly diffusing larger molecules can more rapidly enter and exit the Fused-Core outer shell containing the stationary phase. For totally porous particles where diffusion paths within the porous structure are much longer, poorer mass transfer results in increased peak broadening and decreased column efficiency especially at higher mobile phase flow rates.

In this report, the term superficially porous particles (SPP) is used to designate generic particles with solid cores and porous outer shell. The term Fused-Core particles specifically relates to the materials made by Advanced Materials Technology, Inc. For separating small molecules, superficially porous particles with pores in the 80–100 Å range appear adequate for such solutes to enter the pore structure without restricted access which would denigrate column efficiency. Larger molecules require larger pores for access, and Fused-Core particles with 160 Å have been made available for separating compounds such as peptides [8]. Superficially porous particles with 200–400 Å pores have been used for separating proteins and other larger molecules [10–12]. This report describes for the first time detailed chromatographic data for a series of Fused-Core particles ranging from 2.2 to 5 μm specifically designed for separating small molecules.

The particle size of superficially porous particles can strongly affect the efficiency that can be expected from columns of these materials. Theory predicts that as particle size decreases, column efficiency improves, but the pressure increases more rapidly as a square function of reciprocal particle size. However, there appears to be a practical limit on reducing the size of all particles, both superficially porous and totally porous, since columns with

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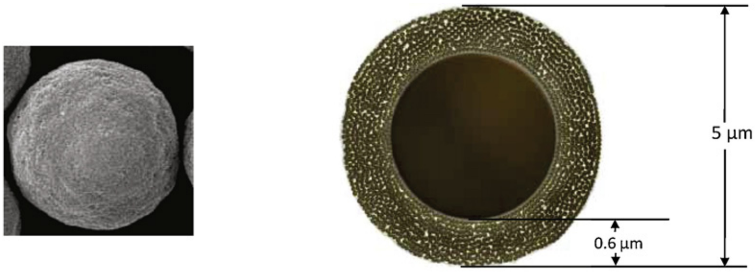

SEM of 5 μm HALO fused-core Graphical representation of 5 μm HALO fused-core

Fig. 1. Graphics of 5 μm Fused-Core particles.

particle sizes of less than about 2 μm diameter typically show lower efficiency than expected from theory [6]. This effect has been said to be a function of increased difficulty for obtaining homogeneous packed beds of these very small particles, especially for smaller diameter columns [6]. The influence of extra-column band broadening and frictional effects that cause inhomogeneity of column cross-sectional flow due to temperature changes also may be an issue.

Currently, the most popular size for superficially porous particles is in the 2.5–2.7 μm diameter range, which involves the usual compromise of chromatographic characteristics (efficiency, back pressure, sample loadability, retention). Superficially porous particles typically have about one-half to three quarters the surface area of comparable totally porous particles, resulting in somewhat smaller capacity factor *k* values for solutes. This feature does not appear to be a practical problem since a small decrease in organic solvent concentration in the mobile phase for reversed-phase separations restores longer retention. Columns of Fused-Core particles in this size range show efficiencies almost equivalent to those containing totally porous sub-2 μm particles, but with only about one-half the back pressure [2,13].

This report presents data on Fused-Core particles in the 2.2–5.0 μm range to illustrate some of the effects on column performance largely caused by changes in particle size and thickness of the outer porous shell. Fused-Core particles with thinner porous shells show marginal improvement in efficiency for small molecules, but can exhibit appreciable efficiency improvement for larger molecules, as predicted by theory. Similar findings have previously been reported by Olah et al. [14] who compared Kinetex SPP particles to Ascentis Express SPP particles and by Omamogho et al. [15] and Gritti et al. [16] in which SPP particles with 0.15, 0.25, or 0.35 μm shells were investigated. An interesting finding of our study was that 4–5 μm Fused-Core particles can be packed into columns with significantly lower reduced plate heights than columns packed with 2.2, 2.7 μm Fused-Core particles. For a comprehensive list of minimum reduced plate heights, minimum plate heights, and maximum plate numbers that have been obtained with modern superficially porous particles, the reader is referred to the recent review of Fekete et al. [17].

2. Experimental

2.1. Chemicals

Compounds used as sample probes and in sample mixtures were from Sigma–Aldrich (St. Louis, MO). Trifluoroacetic acid was obtained from Pierce Chemicals (Rockford, IL) and acetonitrile from EMD (Gibbstown, NJ).

2.2. Columns/chromatographic conditions

Columns of Halo® Fused-Core particles were obtained from Advanced Materials Technology, Inc. (Wilmington, DE). Fig. 1 shows a Scanning electron microphotograph of 5 μm Halo particles and a graphic of the particle with appropriate size measurements. Table 1 gives the physical characteristics of the particles used in this study. Columns of 4.6 mm × 50 mm and 150 mm were used to obtain chromatographic data in this work.

Columns of 5 μm conventional totally porous particles (4.6 mm × 50 mm and 4.6 mm × 150 mm) were obtained from Mac-Mod Analytical (Chadds Ford, PA) and Supelco (Bellefonte, PA). Surface area BET measurements were conducted with a Micromeritics TriStar II instrument (Norcross, GA) using nitrogen. Particle sizes were determined with a Coulter Multisizer 3 instrument (Fullerton, CA). Shell thicknesses were determined by the difference in Coulter counter measurements for the starting solid cores and the final particles. This parameter was confirmed by cross-section microphotographs prepared by Micron, Inc. (Wilmington, DE), who also prepared electron microphotographs of Fused-Core particles.

HPLC separations with 4.6 mm i.d. columns were conducted with an Agilent Model 1100 liquid chromatograph (Palo Alto, CA) with quaternary pump and a pressure limitation of 400 bar. An Agilent Model 1200 SL instrument was used for experiments involving pressures up to 600 bar. Data acquisition and instrument control used Version B.03.02 ChemStation software for experiments conducted with the Agilent 1200SL, while Version B.01.03 ChemStation software was used for experiments with the Agilent 1100. Column stability studies and the NSAID application were performed with a Shimadzu Prominence UFLC XR instrument. Peak widths (Full Width Half Max) were used for measuring plate numbers. No corrections for extra-column band broadening effects were applied to the data obtained in this study since the authors were interested in publishing values that could be easily and conveniently duplicated by interested practitioners with the same instruments.

3. Results and discussion

3.1. Effect of particle size

Theory predicts that as particle size is decreased, the efficiency of a packed bed improves, that is, the plate height H decreases [18]. This effect is shown in Fig. 2A for van Deemter plots of Fused-Core particles ranging in size from 2.2 to 5 μm, all having about the same porous shell thickness (Table 1). These plate height H data are in keeping with theory, with smaller plate heights resulting from smaller particles with the superficial linear mobile phase velocity used. Data for columns of the 2.2 and 2.7 μm Fused-Core

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