Study of Physical Properties of Superficially Porous Silica on Its Superior Chromatographic Performance

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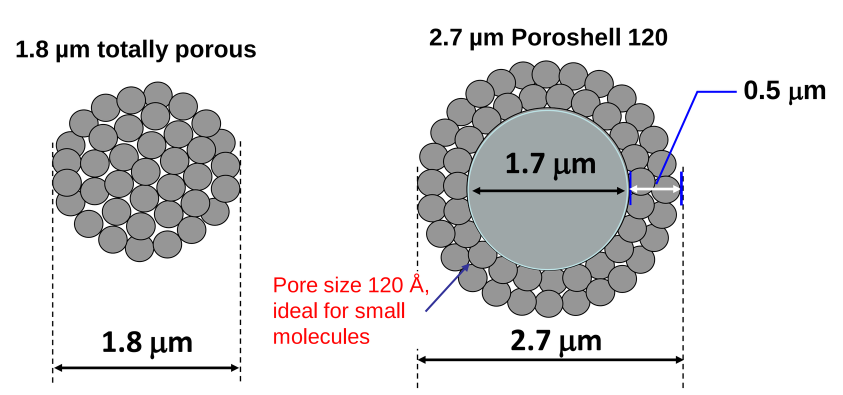
Abstract

2.7 µm superficially porous particles are being seen as an alternative to fully porous sub 2 µm particles for high speed and/or high resolution HPLC separations More recently, we also have developed new the superficially porous silica particles having a 1.7-µm solid core, a 0.5-µm-thick porous shell with 120 –Å pores, called "Poroshell 120", for faster separation of small molecules [1]. These 2.7 µm superficially porous silica particles have very narrow particle size distribution, and show comparable efficiency to fully porous sub 2 µm particles, but only about half of the back pressure of sub 2 µm particles. There are several publications which experimentally and theoretically studied the unique chromatographic performance of these superficially porous particles [2-6].

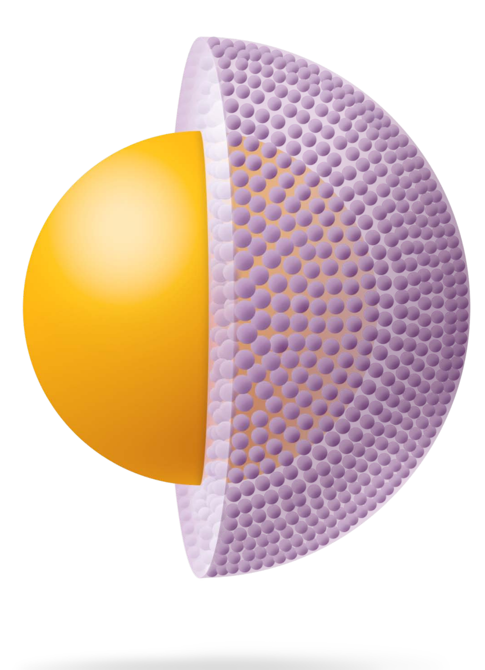
The column of superficially porous particles has a reduced plate height minimum of approximately 1.5, much lower than the value of 2.0, which has been traditionally considered as the "limit" for excellent columns of totally porous particles. The lower reduced plate height minimum is explained by the combination of lower axial diffusion term (due to the solid core in the particle) and a lower eddy dispersion term (due to a narrow particle size distribution) [4]. In this study, we purposely prepared a series of superficially porous particles with the similar particle size, but with different shell thickness and different particle size distribution, studied how shell thickness and particle size distribution affect the column performance regarding the efficiency, back pressure and van Deemter plot, and compared those superficially porous particles with totally porous particles..

Introduction

Totally Porous Particles vs. Poroshell 120

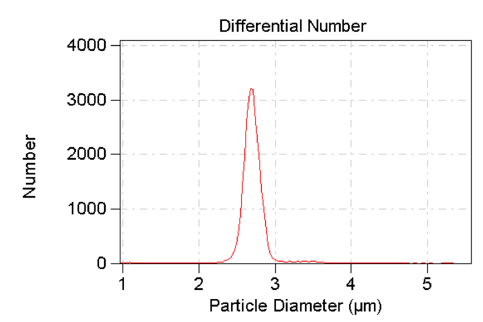


- ➢ The high efficiency of Poroshell 120 particles, similar to sub 2 µm totally porous particles.
- ➢ The high efficiency is due to short mass transfer distance and very narrower particle size distribution.
- ➢ Very low back pressure, 40-60% of sub 2 µm totally porous particles.

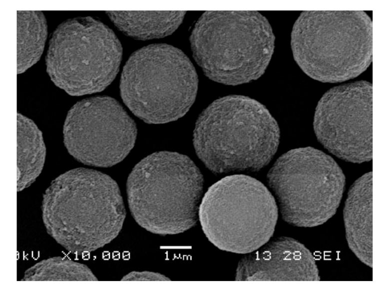


Poroshell 120 Physical Properties

Poroshell 120 Particles Have Very Narrow Particle Size Distribution



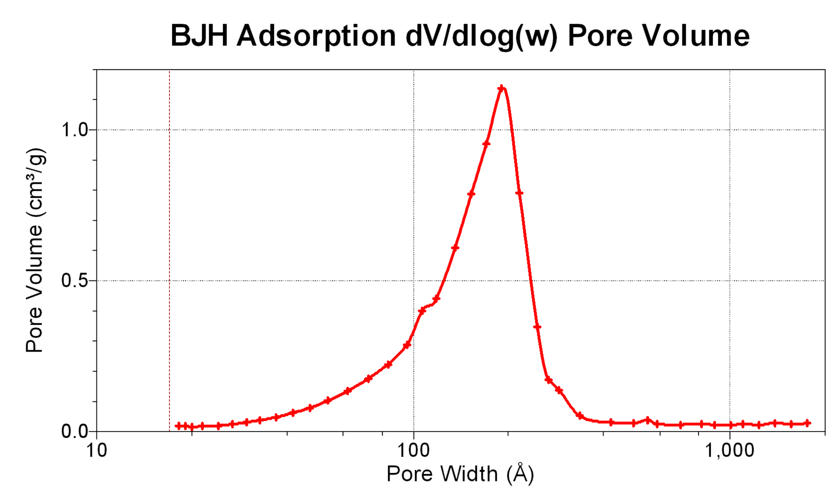
Particle Size Distribution of Poroshell 120



SEM Picture of Poroshell 120

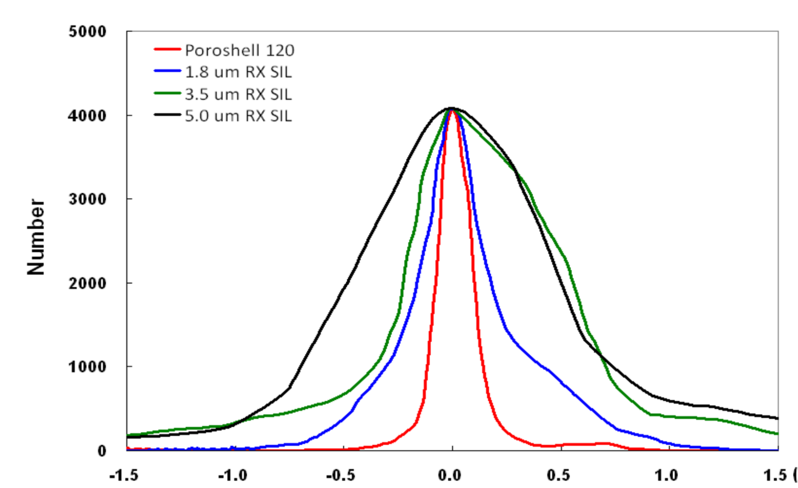
Poroshell 120 particles also show spherical and smooth surface.

Poroshell 120 Pore Size Distribution



Poroshell 120 particles have an average pore size of 120 Å.

A-Term: Compare Particle Size Distribution with Totally Porous Particles



Normalized Particle Size Distribution

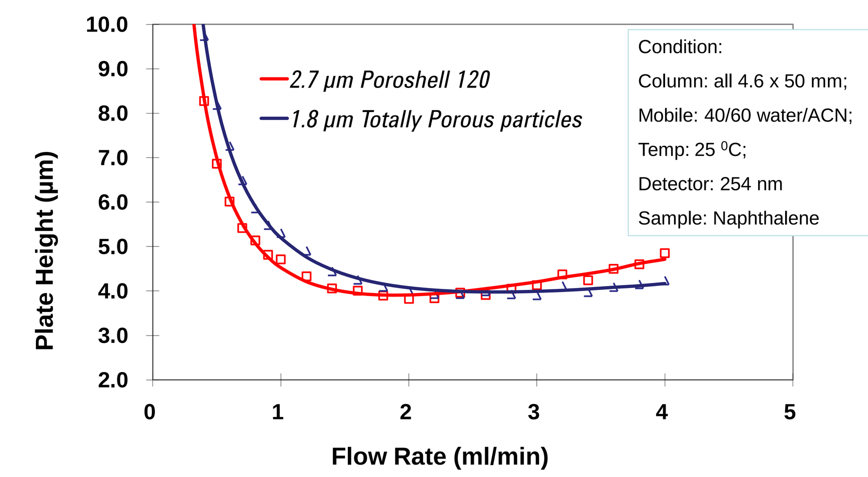
Poroshell 120 Particle Size Distribution is 25% Narrower

	Poroshell 120	Totally Porous Particles		
Particle size	2.70 µm	1.8 µm	3.5 µm	5.0 µm
D_{90}/D_{10}	1.11	1.47	1.45	1.35

- ➢ The 1.8, 3.5 and 5 µm particles all have a normal particle size distribution.
- ➢ A number below 1.5 would be expected for the totally porous particles
- ➢ This narrower particle size distribution improves column efficiency over a totally porous particle.

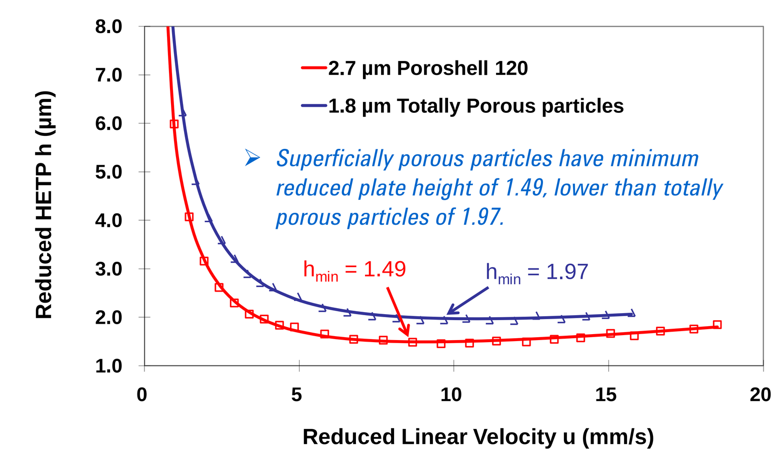
Poroshell 120 Chromatographic Performance

Plate Height Comparison with 1.8 µm Totally Porous Particles

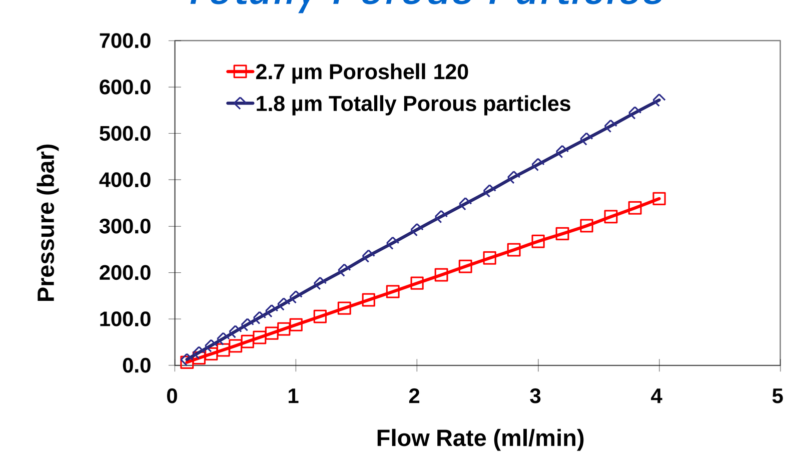


- ➢ 2.7 µm superficially porous particles have similar efficiency as 1.8 µm totally porous particles.

Reduced Plate Height Comparison with 1.8 µm Totally Porous Particles



Back Pressure Comparison with 1.8 µm Totally Porous Particles



- ➢ 2.7 µm superficially porous particles have 40%-50% back pressure of 1.8 µm totally porous particles.

What is Thought about High Efficiency of Superficially Porous Particles

$h = A + B/u + C*u$

- h is reduced HEPT; u is linear velocity
- A term – eddy diffusion and flow distribution
  - Column particle size and column packing quality impact this
  - **Tight particle size distribution improves the A term**
- B term – longitudinal diffusion
  - Impact in superficially porous particle not yet determined
- C term – mass transfer component
  - **Mass transfer is improved by using smaller totally porous particles with shorter diffusion paths, improving the C term**
  - This is improved with a superficially porous particle
  - The C term has more effect on large molecules than on small molecules

Results and Discussions

Objectives of the Study

- ➢ Study how the shell thickness affects performance
  - ➢ Prepare superficially porous particles with the same particle size but different shell thickness
- ➢ Study how the particle size distribution (D_{90}/D_{10}) affects performance
  - ➢ Prepare superficially porous particles with the same size but different particle size distribution
- ➢ Compare 2.7 µm superficially porous particles with 1.8 µm totally porous particles
- ➢ Use van Deemter plot to study how shell thickness and particle size distribution affect A, B and C term

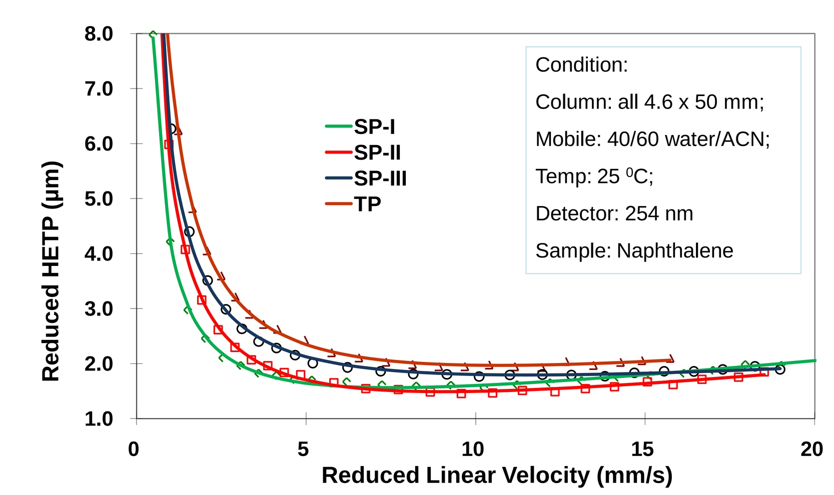
Particles in Study

Particle	Particle Size (µm)	D_{90}/D_{10}	Core Size (µm)	Shell Thickness (µm)	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
TP	1.80	1.40	0	0.9	180	0.383	88
SP-I	2.69	1.17	1.87	0.41	55	0.176	121
SP-II	2.62	1.10	1.57	0.53	122	0.383	113
SP-III	2.80	1.26	1.57	0.62	139	0.433	117

- TP is totally porous particles; SP is superficially porous particles.

- ➢ The superficially porous particle I-III have different shell thickness and different particle size distribution.
- ➢ The superficially porous particle II and III have the same core size; the difference of the particle size and particle size distribution are mainly due to the shell thickness variation.

Van Deemter Plot



Summary of van Deemter Plot

$h = A + B/u + C*u$

h: reduced HETP; $h = H/d_p$, d_p is particle diameter

u is linear velocity; $u = 50$ mm (column length)/t_0

Particle	Particle Size (µm)	D_{90}/D_{10}	Core Size (µm)	Shell Thickness (µm)	A term	B term	C term
TP	2.02	1.47	0	1.01	0.720	6.677	0.058
SP-I	2.69	1.17	1.87	0.41	0.618	3.565	0.063
SP-II	2.62	1.10	1.57	0.53	0.329	5.268	0.064
SP-III	2.80	1.26	1.57	0.62	0.717	5.599	0.049

- TP is totally porous particles; SP is superficially porous particles

Results and Discussions

- ➢ The superficially porous particles having thinner shell (PS-I) exhibit the best reduced plate height at the low end of flow rate.
- ➢ The superficially porous particles having the tightest particle size distribution (PS-II) have the smallest minimum reduced plate height.
- ➢ All the particles show very flat van Deemter plot curves at high flow rate.
- ➢ The totally porous particles have the highest minimum reduced plate height.
- ➢ Superficially porous particles have lower B term value than totally porous particles.
- ➢ Superficially porous particles have similar C term value to 1.8 µm totally porous particles.

Conclusions

- 2.7 µm Poroshell 120 particles have very narrow particle size distribution, and exhibit efficiency of sub-2 µm totally porous particles and about half of the backpressure.
- A term is affected by the particle size distribution (PDS); the particles with larger PDS have the larger A term.
- B term is mostly affected by the shell thickness; the particles with thicker shell seems to have the larger B term.
- For small molecules, the C term doesn't change much for different shell thickness of superficially porous particles.
- There is no much difference of C term between 1.8 µm totally porous particles and 2.7 µm superficially porous particles.
- The superior performance of superficially porous particles for separation of small molecules is mainly due to the combination of narrow particles size distribution (small A term), their thinner shell (small B term due to the core-shell structure), and the similar C term to 1.8 µm totally porous particles.

Reference

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