PARTICLE SIZE CONSIDERATIONS OF SUPERFICIALLY POROUS PARTICLES

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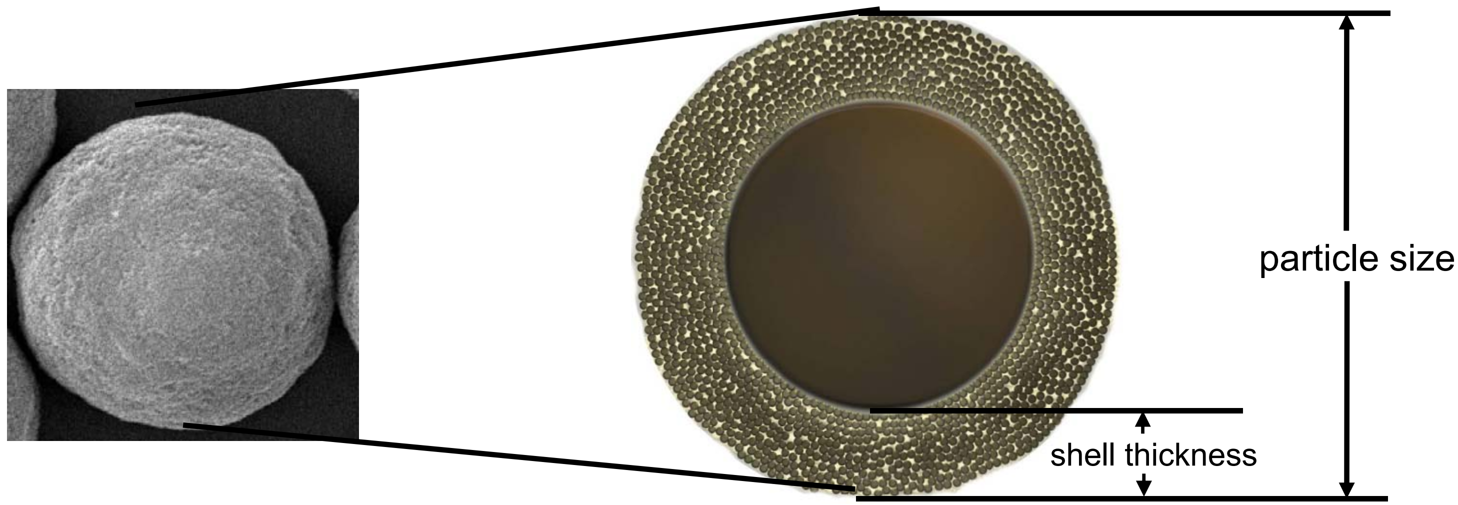
ABSTRACT

Columns of fused-core, superficially porous particles demonstrate higher efficiency than columns packed with totally porous particles of similar size. This result likely is because of superior eddy and longitudinal diffusion properties (smaller van Deemter A and B terms) observed for core-shell particles resulting from exceptionally narrow particle size distributions and higher density contributing to an ability to form homogeneous packed beds. The achievement of efficiencies comparable to those obtained using columns of sub-2-μm totally porous particles without the need for ultra high pressure instrumentation is a distinct advantage of fused-core columns. Fused-core particles with a wide range of uniform particle sizes were synthesized to allow the preparation of stable, efficient packed columns for this study. These columns were used to measure the effects of particle size on chromatographic performance and pressure requirements. This report describes the effect of particle size on several factors of separation importance, including plate heights, reduced plate heights, pressure, and ease of use. Depending on the intended application, certain particle sizes are recommended for use over others. The performance of larger fused-core particles exceeds even the high expectations observed for smaller superficially porous particles, likely because larger particles form more homogeneous packed beds than smaller particles. The utility of larger and smaller superficially porous particles are compared and evaluated for high-speed and high-resolution applications.

HALO® Fused-Core Particles



SEM of HALO Fused-core

Graphical representation of HALO Fused-core

CHARACTERISTICS OF PARTICLES USED IN THIS STUDY

Total Particle Size	Shell Thickness	Core Diameter	Surface Area
2.0 microns	0.5 micron	1.0 micron	100 m^2/g
2.7 microns	0.5 micron	1.7 microns	125 m^2/g
4.1 microns	0.55 micron	3.0 microns	105 m^2/g
4.6 microns	0.6 micron	3.4 microns	95 m^2/g

TEST CHROMATOGRAM

Test Conditions:
Columns: 3.0 x 50 mm
Mobile Phase: 60/40 ACN/H_2O
Flow Rate: varied
Temperature: ambient (ca. 22 ^oC)
Detector: semi-micro UV @ 254nm
Peak Identities:
1. **Uracil (t_0 marker)**
2. **Phenol**
3. **4-Cl-1-nitrobenzene**
4. **Naphthalene (k values 3.3 to 3.8)**

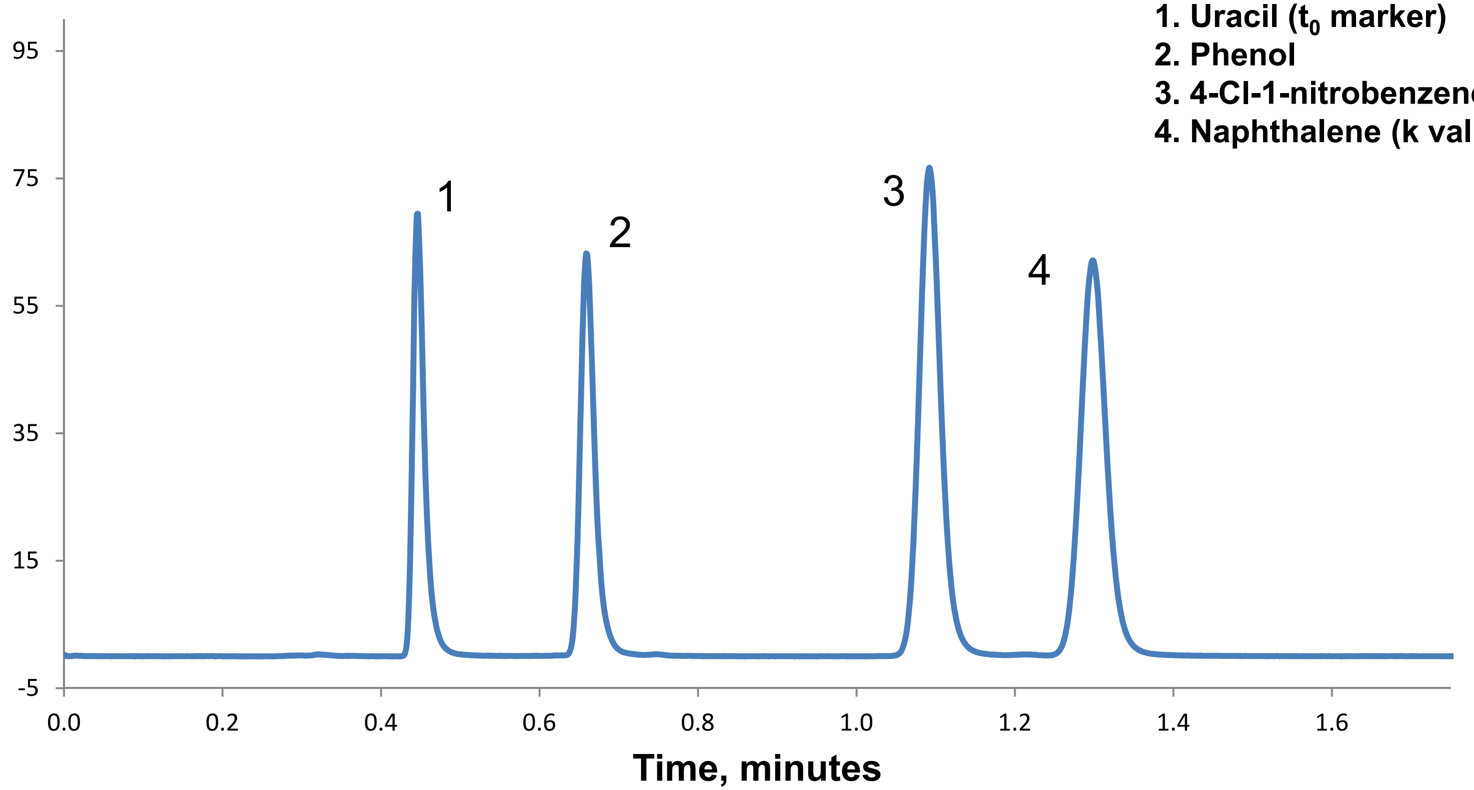
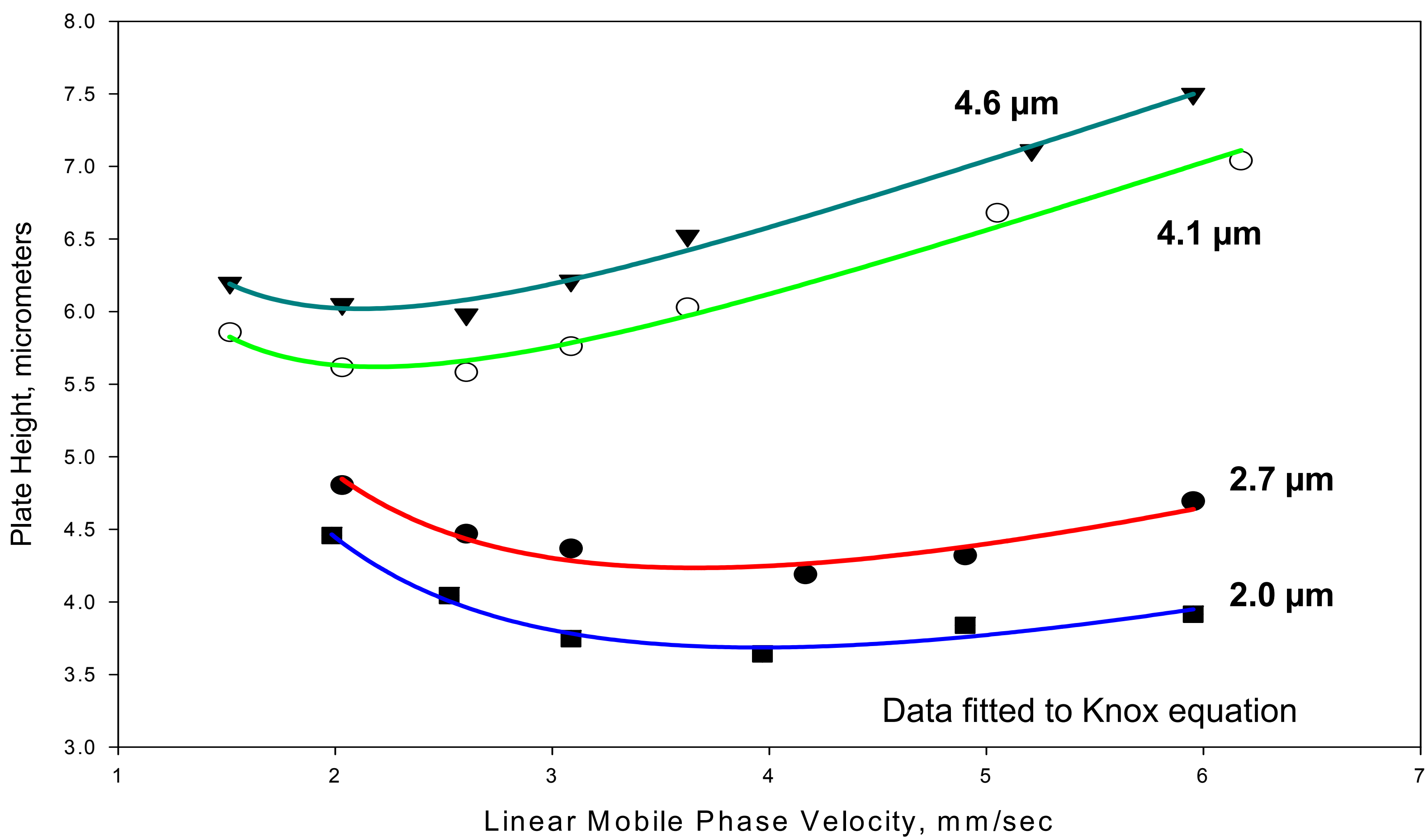
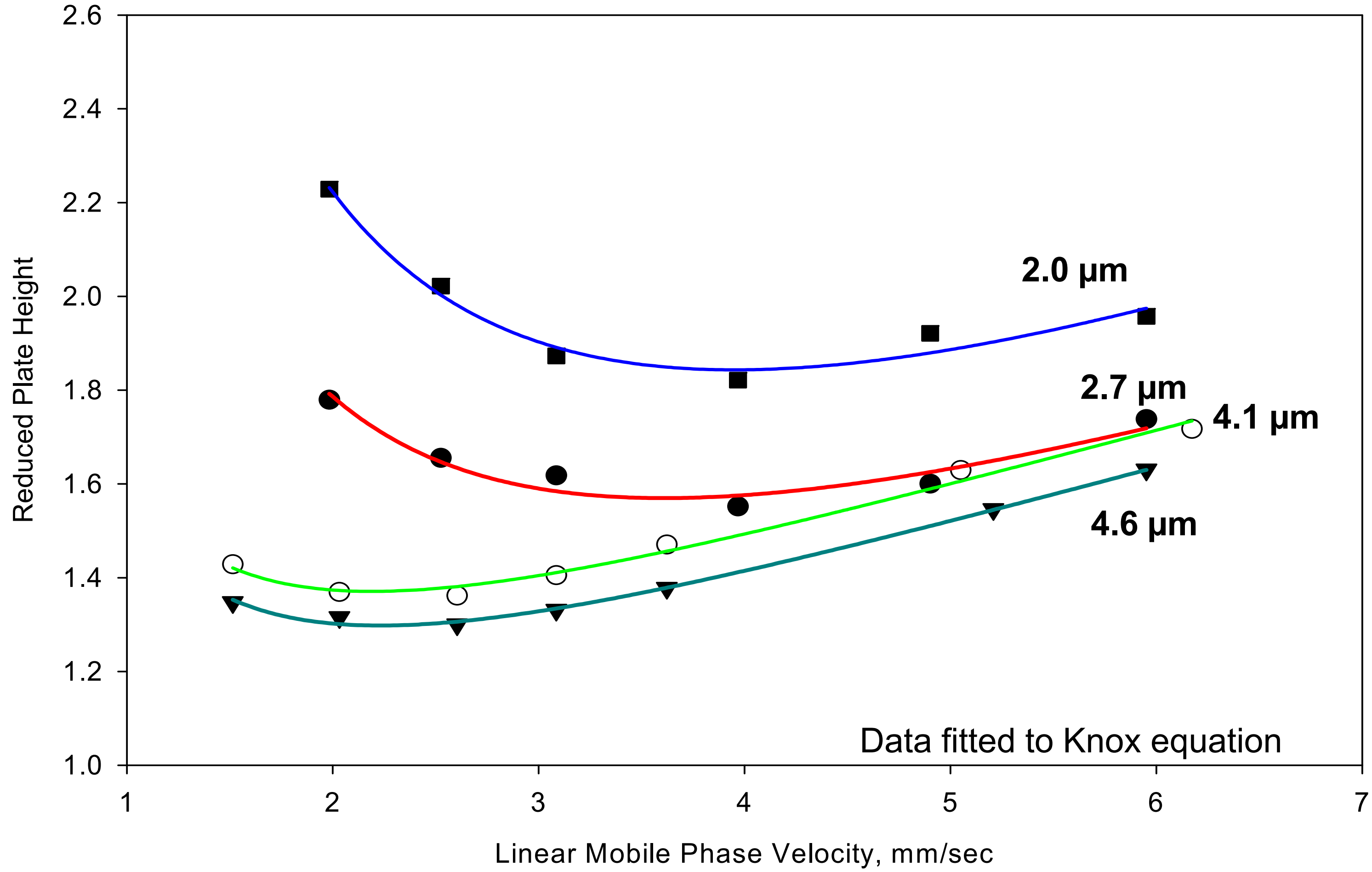


Plate Height Vs Velocity Plots



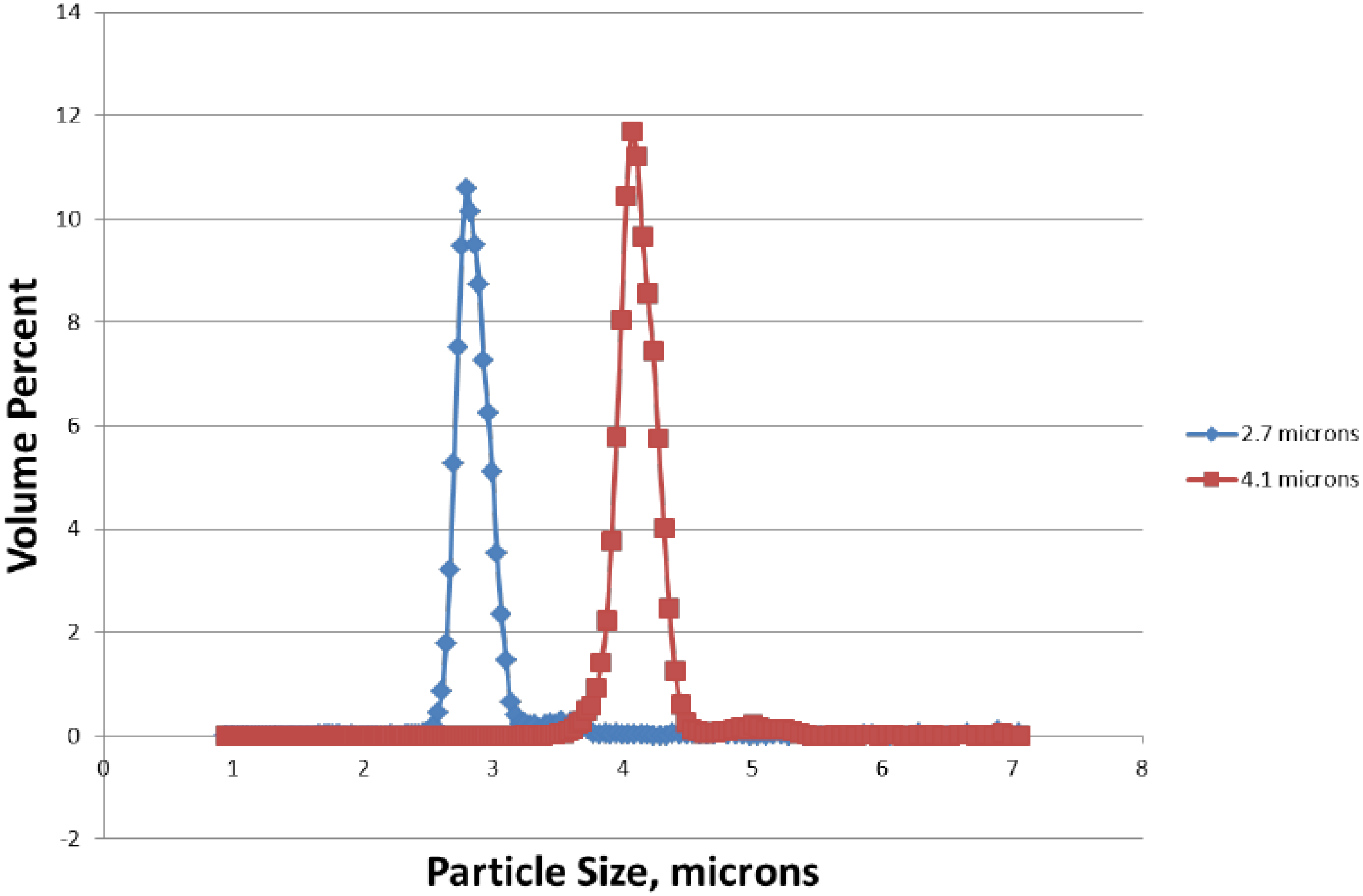
The Plate Heights of columns packed with particles of different sizes, as expected, get smaller as the particle size gets smaller.

Reduced Plate Height Vs Velocity Plots



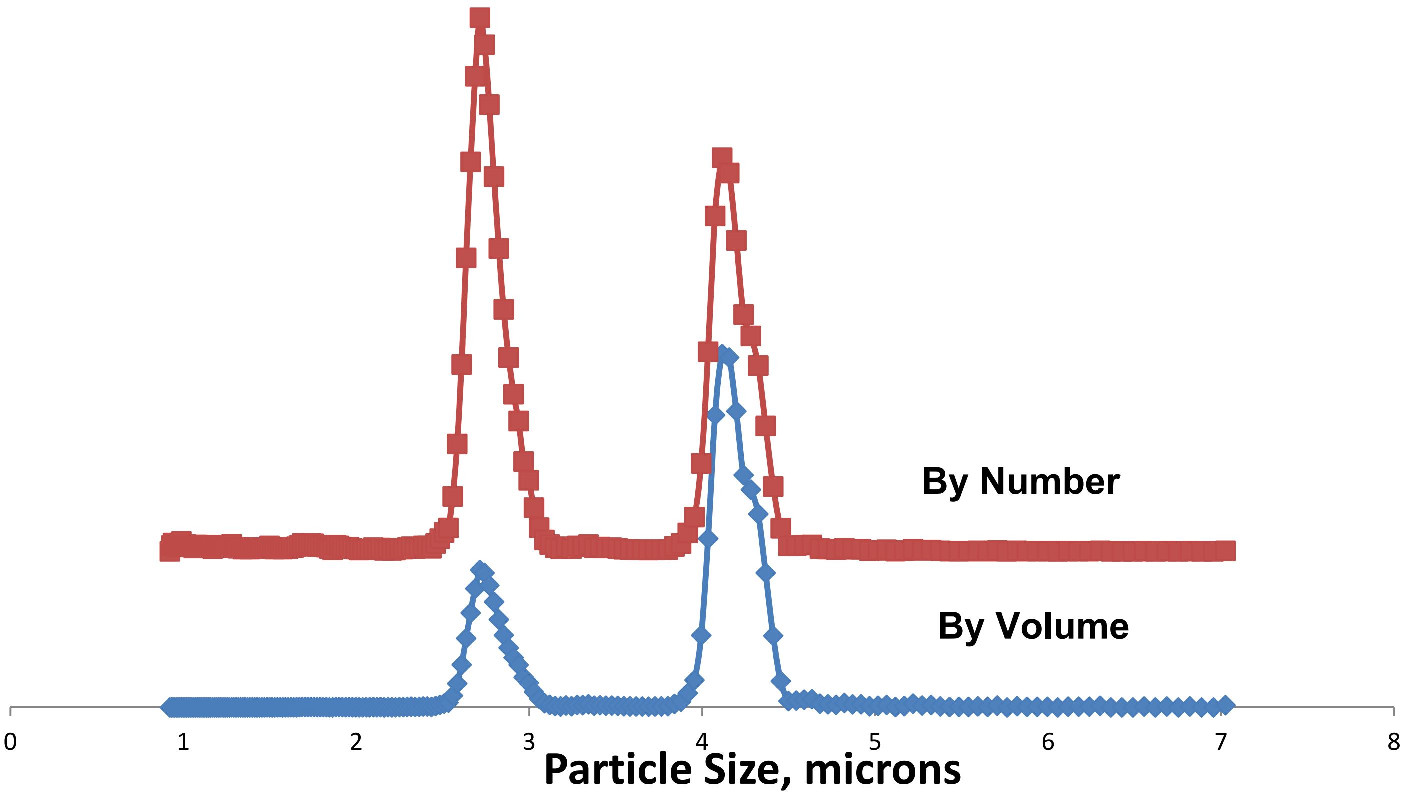
Reduced Plate Heights ($h = H/d_p$) get smaller as the particle size is <u>increased</u>, indicating more homogeneity in packed beds for the larger particles.

Overlay of Size Distributions of Individual Batches of 2.7 µm and 4.1 µm Fused-core Particles



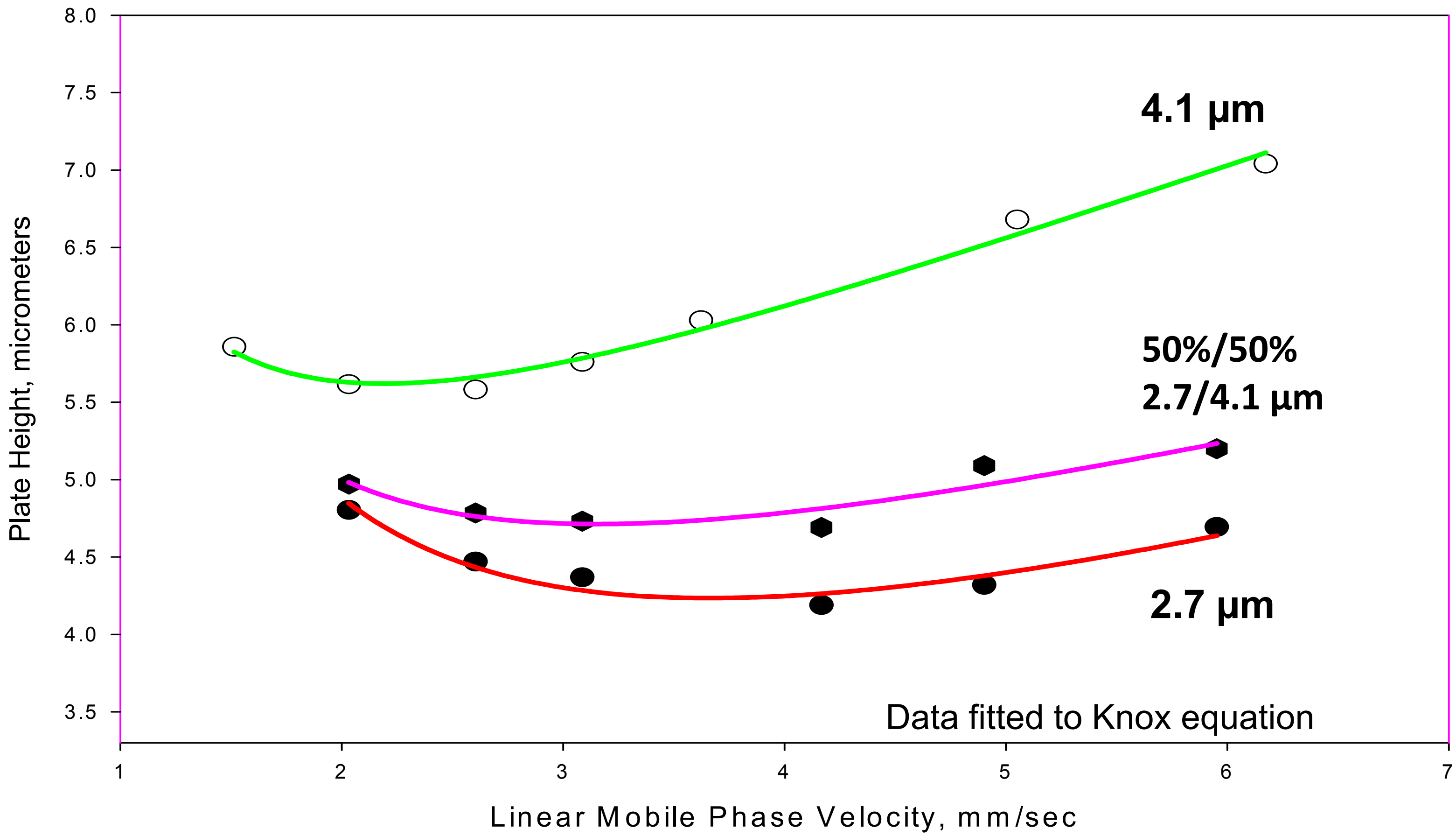
Individual batches of Fused-core particles exhibit very narrow particle size distributions.

Actual Size Distributions of a 50/50 Mixture of 2.7 and 4.1-Micron Particles



- Mixtures of different sized particles can be measured by Coulter Counter and give different values if assessed by number or volume.
- Measurement of particle size by volume is more representative of the contents of a column than is size by number.

Plate Height Vs Velocity Plots Including Mixed Particles



50/50 mix of 2.7 and 4.1 µm particles produces a column with plate heights intermediate to the components of the mixture.

Comparison of Single-Sized Particles and a Mixture

Packing Particles	d_p90[a]	d_p10[b]	d_p90/d_p10	Plate Number (N)*	Plate Height (H)*	Pressure (bar)*	Plates per bar
4.1 µm	4.30	3.89	1.11	8590	5.58	34	253
2.7 µm	3.02	2.69	1.12	11950	4.19	128	93
50/50 mix 4.1/2.7 µm	4.26	2.63	1.62	10650	4.69	94	113

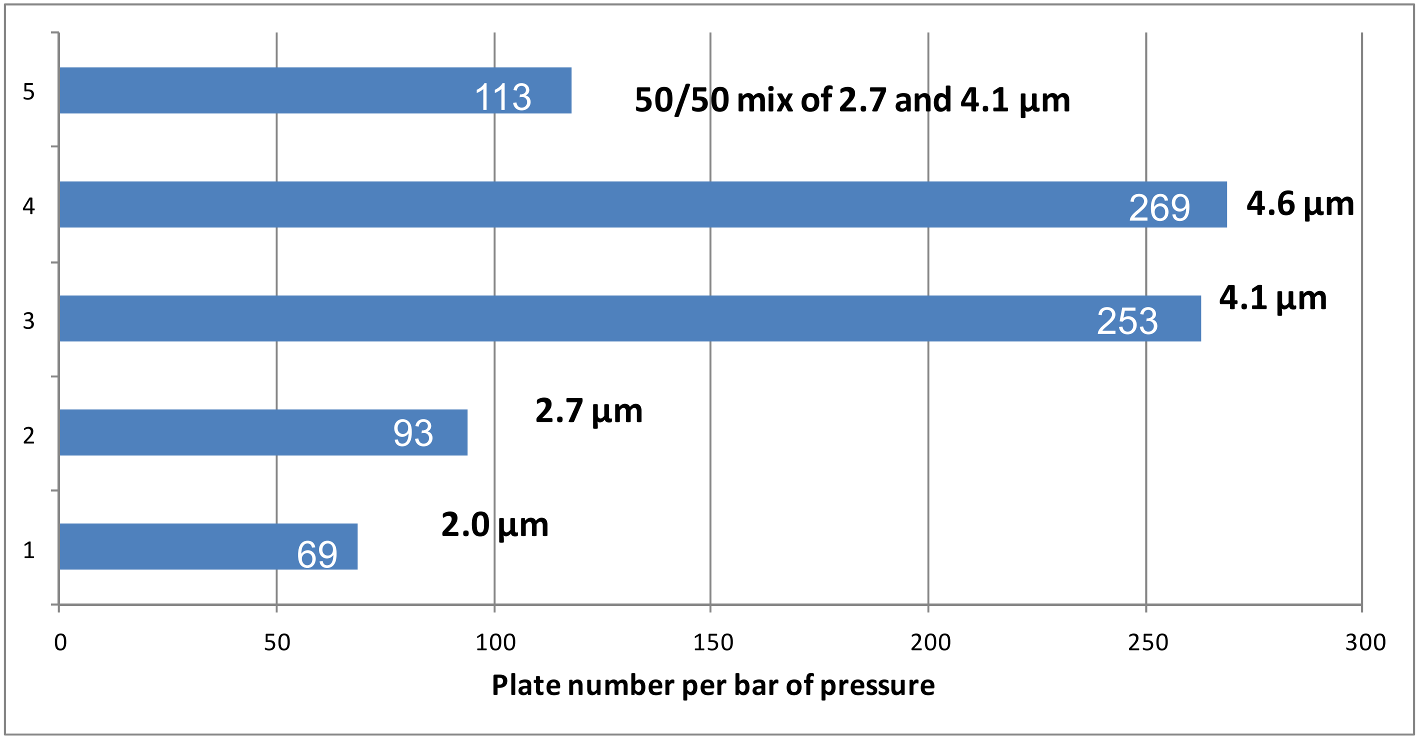
*** Values taken at optimum flow**

[a] d_p90 indicates that 90% of the particles are smaller than the given size
[b] d_p10 indicates that 10% of the particles are smaller than the given size

- High efficiency is still possible for a mixed bed of particles of different sizes, but the pressure increase is not favorable.

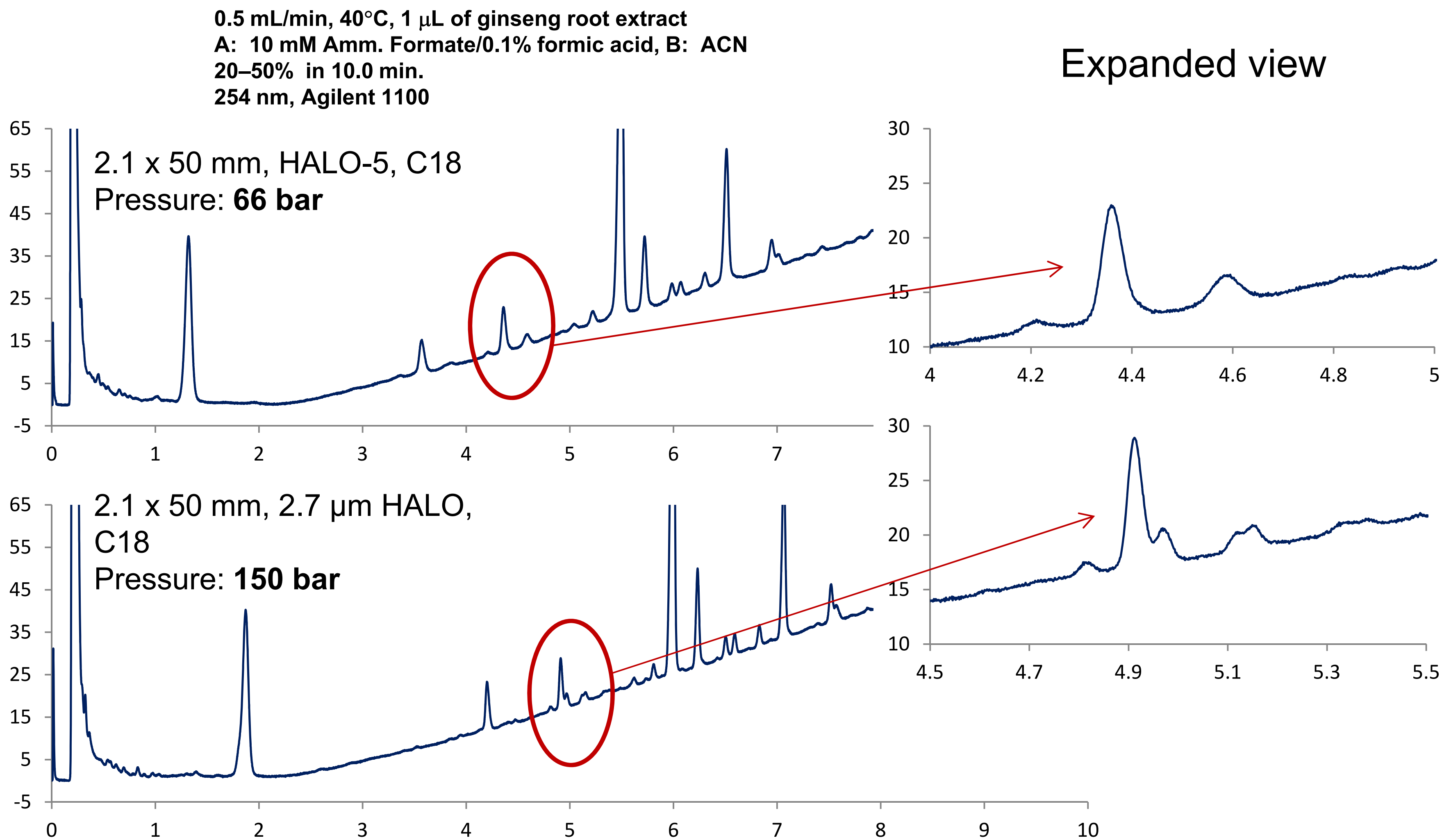
<u>Plate Number Per Unit of Pressure</u>

(Plate number and pressures taken at optimum flow for each particle size)



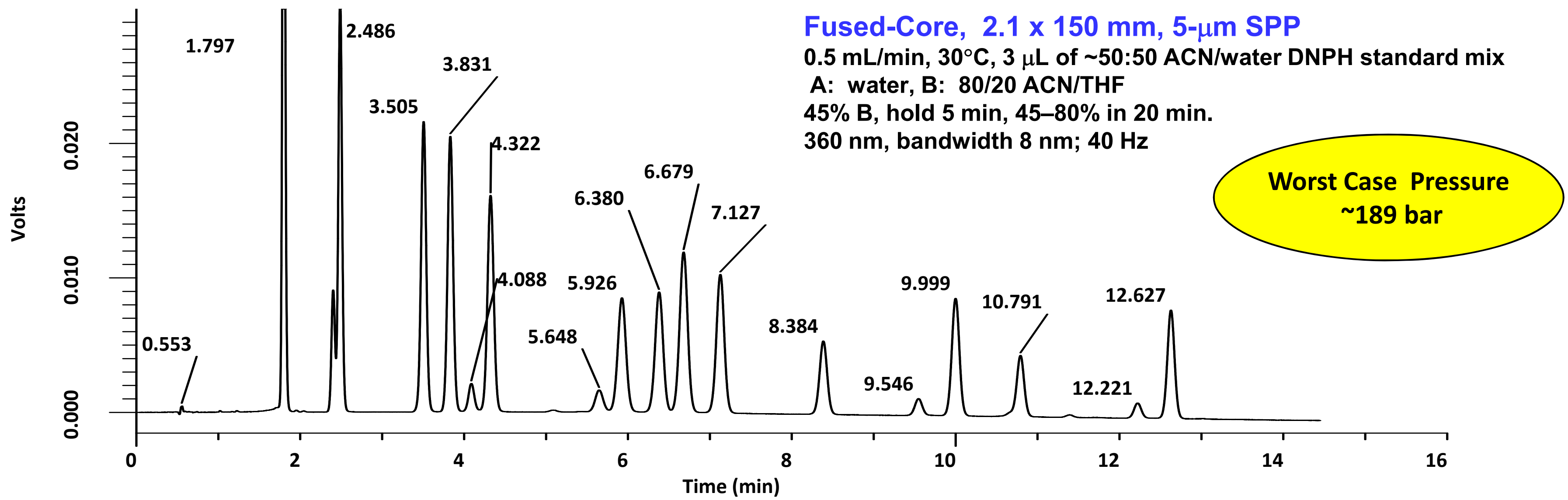
- **The plate number available per unit of pressure greatly increases as the particle size is <u>increased</u>.**
- **The column containing a mixture of large and small particles is not a good compromise of performance features because pressure changes faster than plate number with changes in average particle size.**

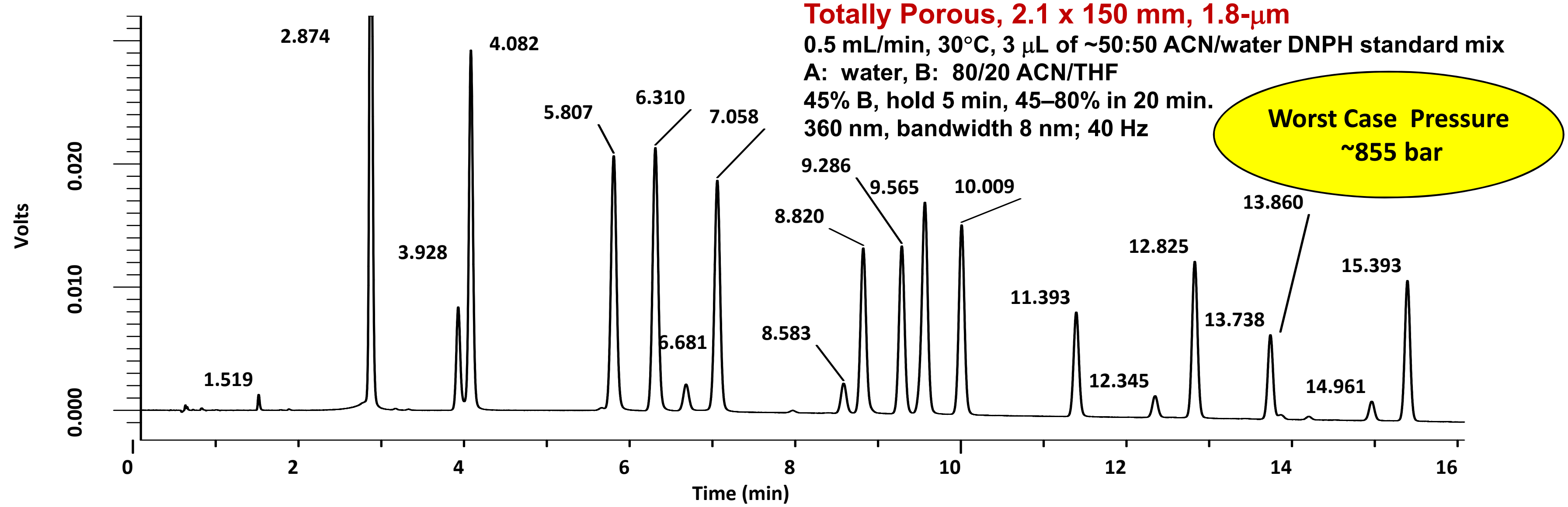
Comparison of 5µm and 2.7µm particle separation



- Use shorter columns for faster separations
- For shorter columns, improved resolution is observed when smaller particles are used

Use 5 µm SPP Columns to Achieve High Resolution at Low Pressure

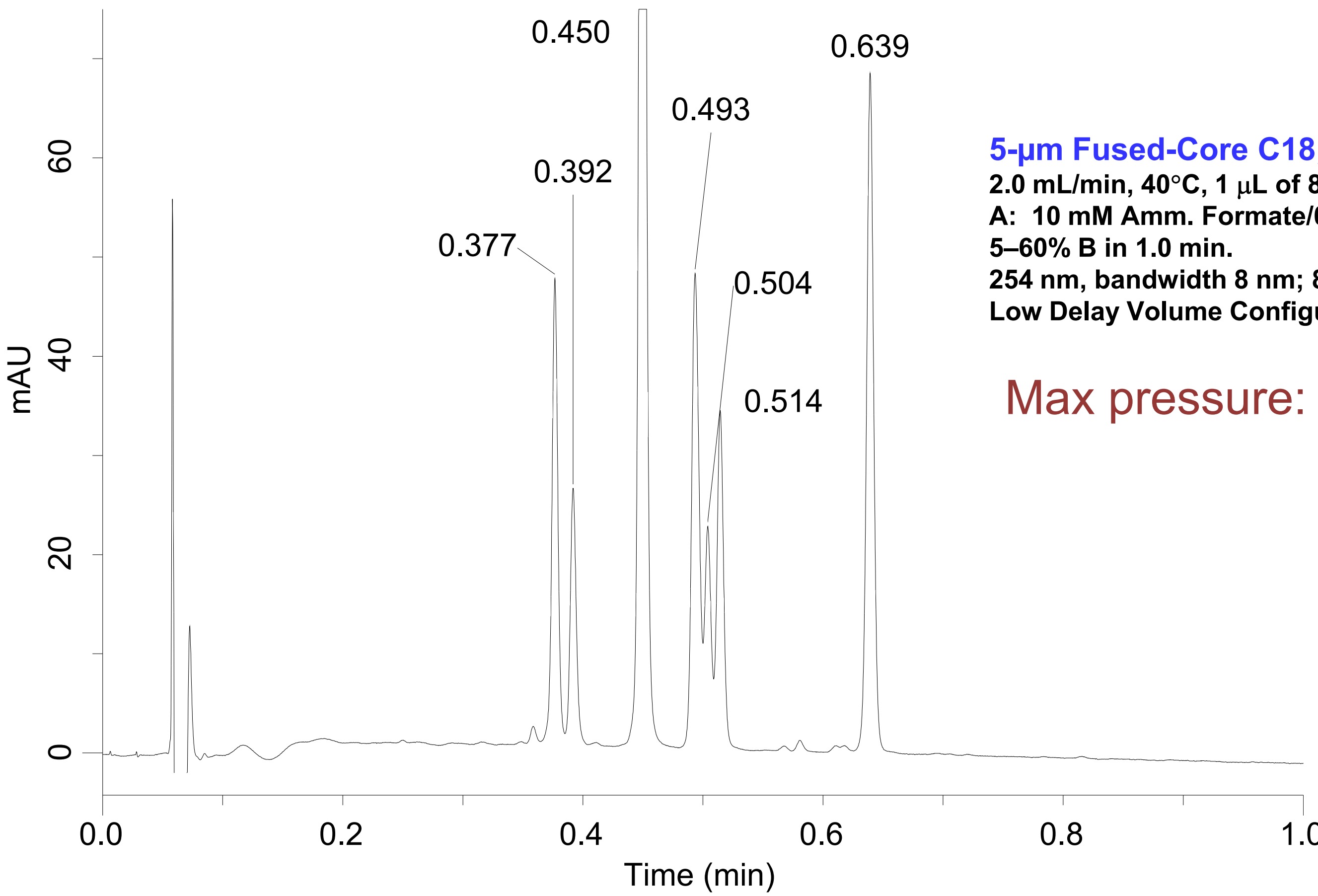




PEAK IDENTITIES (in order): Formaldehyde-2,4-DNPH, Acetaldehyde-2,4-DNPH ,Acetone-2,4-DNPH,Acrolein-2,4-DNPH,Propionaldehyde-2,4-DNPH, Crotonaldehyde-2,4-DNPH, 2-Butanone-2,4-DNPH, Methacrolein-2,4-DNPH, Butyraldehyde-2,4-DNPH, Benzaldehyde-2,4-DNPH,Valeraldehyde-2,4-DNPH,m-Tolualdehyde-2,4-DNPH, and Hexaldehyde-2,4-DNPH

Note: Small peaks preceding labeled aliphatic aldehyde peaks are minor geometric isomers (syn/anti).

Use 5-µm Fused-Core Particles for Ballistic Gradients



5-µm Fused-Core C18, 2.1 x 50 mm
2.0 mL/min, 40°C, 1 µL of 8 flavonoids in MeOH
A: 10 mM Amm. Formate/0.1% formic acid, B: ACN
5–60% B in 1.0 min.
254 nm, bandwidth 8 nm; 80 Hz; Agilent 1200 SL;
Low Delay Volume Configuration ~ 120 µL; ADVR ON

Max pressure: 210 bar

Analytes, in elution order: hesperidin, myricetin , quercetin, naringenin & apigenin (coeluted), hesperetin, kaempferol, biochanin

- **Larger particles enable faster flow rates at lower back pressures**

Conclusions

1. Fused-core particles can be synthesized with different particle diameters to produce columns with high efficiencies.
2. Columns packed with Fused-core particles of different diameters show improvement in Plate Heights as the particle size is reduced.
3. Reduced Plate Heights (column efficiencies normalized for particle size) show the opposite effect – with columns of larger particles having smaller Reduced Plate Heights than smaller particles – indicating larger particles may be easier to pack into homogeneous beds.
4. Mixtures of larger and smaller particles can provide good column performance but the resulting pressure makes this a bad compromise.
5. Narrow particle size distributions for Fused-core packings may not be solely responsible for the exceptionally high performance of columns packed with superficially porous particles.
6. Longer columns of 5μm Fused-core particles are recommended for high resolution separations while short columns of 5μm Fused-core particles are recommended for very fast gradients.

Acknowledgements

Special thanks to Jason Lawhorn for providing the Coulter analysis data and to Jack Kirkland for discussions and help in organizing and graphing the information used in this poster. Additional thanks to Thomas Waeghe for the applications using HALO-5 columns.