Size-Exclusion Chromatography Using Core-Shell Particles

Bob Pirok, Sjoerd van der Wal, Ron Peters, Peter Schoenmakers

Waters GPC Event, September 28th 2016, Amsterdam

B.W.J.Pirok@uva.nl
MAAnIAC

Making ANalytically Incompatible Approaches Compatible
Polymeric Particles

We would like information about the ratio between e.g. (i) the molecular weight distribution (ii) the charge density

- We can only do one at the time
- Solvent incompatibility for LC×LC
- Need to use models

50-200 nm
Stationary Phase Particles

- Fully Porous Particle
- Core-Shell Particle
Core-Shell Particles

Advantages

+ Improved efficiency
+ Much faster analysis times

Disadvantage

- Less pore volume

\[
\frac{V_{\text{core}}}{V_{\text{total}}} = \frac{3.6 \, \text{pL}}{9.2 \, \text{pL}} \cdot 100\% = 40\% \text{ less pore volume}
\]
Calibration curves

Overlay of calibration curves obtained for column 4 (core-shell, 150×4.6 mm, 2.6 μm) at four different flow rates.
Fully porous vs solid-core

- Fully porous
- Core-shell

less pore volume = more narrow SEC domains
Resolution in SEC

The classical definition of resolution is not very useful in SEC, where we do not attempt to separate individual species.

\[ R^*_{sp} = \frac{0.25}{\sigma \cdot b \sqrt{L}} \]

The packing resolution factor allows comparison of different column packings.

\[ \Delta V_e = \frac{\Delta \log M}{b} \]

Resolution in SEC

The packing resolution factor allows comparison of different column packings.

\[ R_{sp}^* = \frac{0.25}{\sigma \cdot b \sqrt{L}} \]

- Length of the column
- Selectivity of the packing material
- Bandwidth of the peak

Band broadening in SEC

How to determine the actual sigma as a result from exclusively column band broadening?

\[ R_{sp}^* = \frac{0.25}{\sigma \cdot b \sqrt{L}} \]

The width of the analyte(s) band includes:

- Column band broadening
- Extra-column band broadening
- Polydispersity of the polymer

Van Deemter curves

The very good reduced plate heights known from literature for core-shell columns were confirmed by experimental data.

Examples of duplicate van Deemter curves obtained for two columns featuring solid-core packings. Mobile phase: acetonitrile; analyte: Sudan IV; detection at 500 nm.
Core-shell packings can give rise to similar or better resolution factors...

\[
R_{sp}^* = \frac{0.25}{\sigma \cdot b \sqrt{L}}
\]

Overlay of plots of the normalized specific resolution (\(R_{sp}^*\)) against the relative nominal mass (\(M_r\)) for several columns.
Comparison of packing materials

Core-shell packings can give rise to similar or better resolution factors... in much less time!

\[ M_r = 100,000 \]

80% less!

0.35 minutes

2.5 minutes

This is a log scale!
Comparison of packing materials

Core-shell packings can give rise to similar or better resolution factors... in much less time!

This is a log scale!
Conclusions

- Core-shell particles can be used for size-exclusion chromatography
- Packing resolution factors are similar or better relative to fully porous stationary phase particles
- Using core-shell particles for SEC, analysis times can be greatly reduced, unlocking powerful modulation times in LC×LC.

My other work

- Characterization of Synthetic Dyes by Comprehensive 2D-LC
  Pirok et al. *J. Chromatogr. A*, 1436, 2016, 141-146

- Program for Interpretive Optimization of Two-dimensional Resolution