Temperature Gradients in Packed Column SFC

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Speed, Pressure Drop and Efficiency in SFC

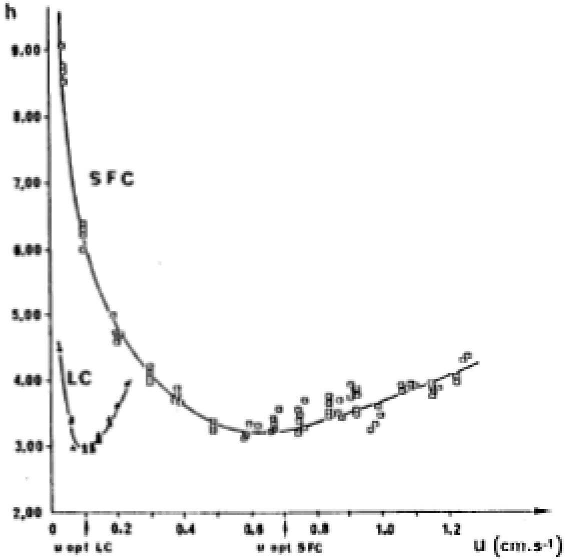


Fig. 1

Reduced plate height h v. mobile phase linear velocity ν for HPLC and SFC.

Column: 15 × 0.46cm i.d. stationary phase: 5μm octadecyl bonded silica. Mobile phase: (△) methanol-water (80-20 v/v); (□) CO_2. Temperature: (△) 25°C; (□) 50°C; average column pressure: 240 bar.

Solute: phenanthrene.

SFC is 5 times faster than HPLC

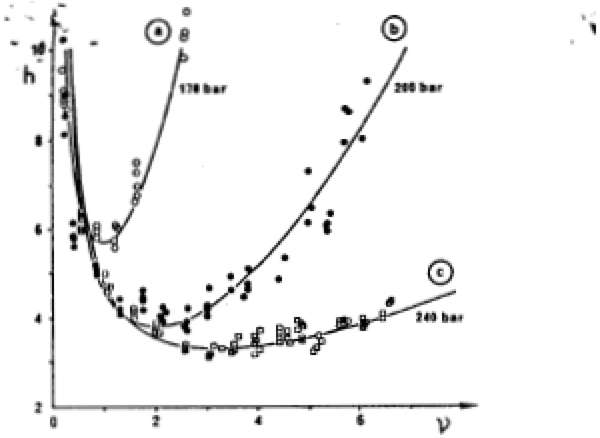


Fig. 6

Reduced plate height h v. CO_2 reduced velocity for phenanthrene at various mean pressures.

Column and stationary phase as Fig. 1. Temperature: 50°C; Average column pressure: (a) 170 bar; (b) 200 bar; (c) 240 bar.

At lower pressures, large pressure drops may cause excessive loss of efficiency

P.A. Mourier, M.H. Caude, R.H. Rosset, Chromatographia 23 (1987) 21.

Conditions Producing Poor Efficiency

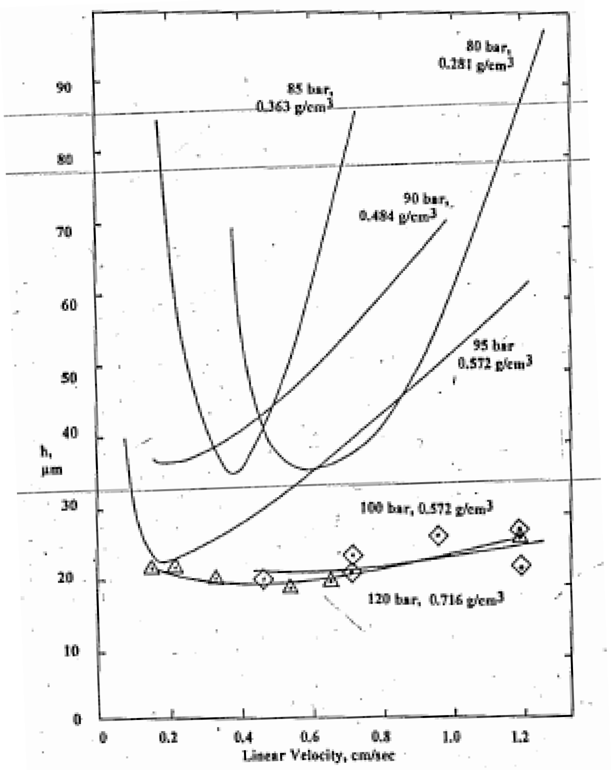
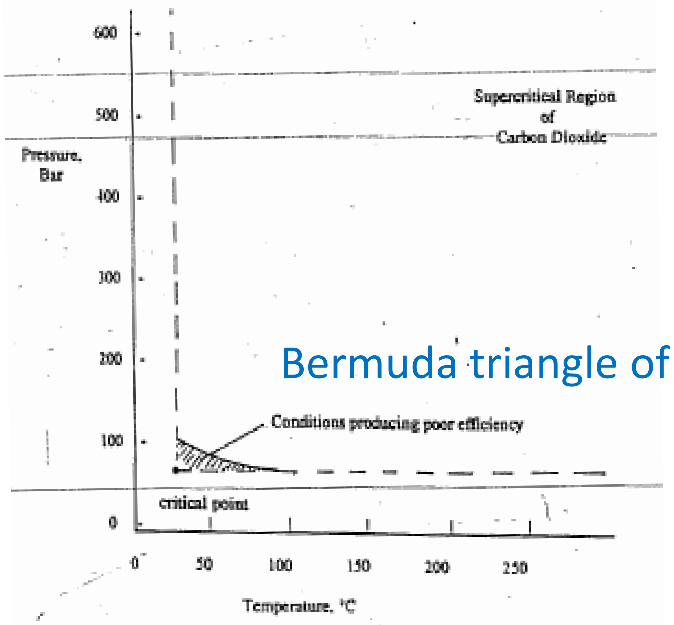


Figure 12

Van Deemter plots for fluoranthene at 6 different outlet pressures, using carbon dioxide at 40 °C. Pressures and densities are listed beside each set of data. The solid lines are approximate average values such as found in Figures 9 through 11. Data points around the bottom two curves indicate the much narrower data scatter at higher pressures (i.e. 100 and 120 bar). Column same as in Figure 4. Note the similarities to Figures 7 and 8, indicating increased D_M and increased stationary phase film thickness at lower densities.

Excess efficiency loss at outlet pressure < 100 bar



Bermuda triangle of SFC

Figure 3

The shaded region indicates the approximate combinations of temperatures and pressures producing unexpectedly poor efficiency.

- Excess efficiency loss occurs at low pressure and temperature
- Solution: Keep outlet pressure ≥ 120 bar

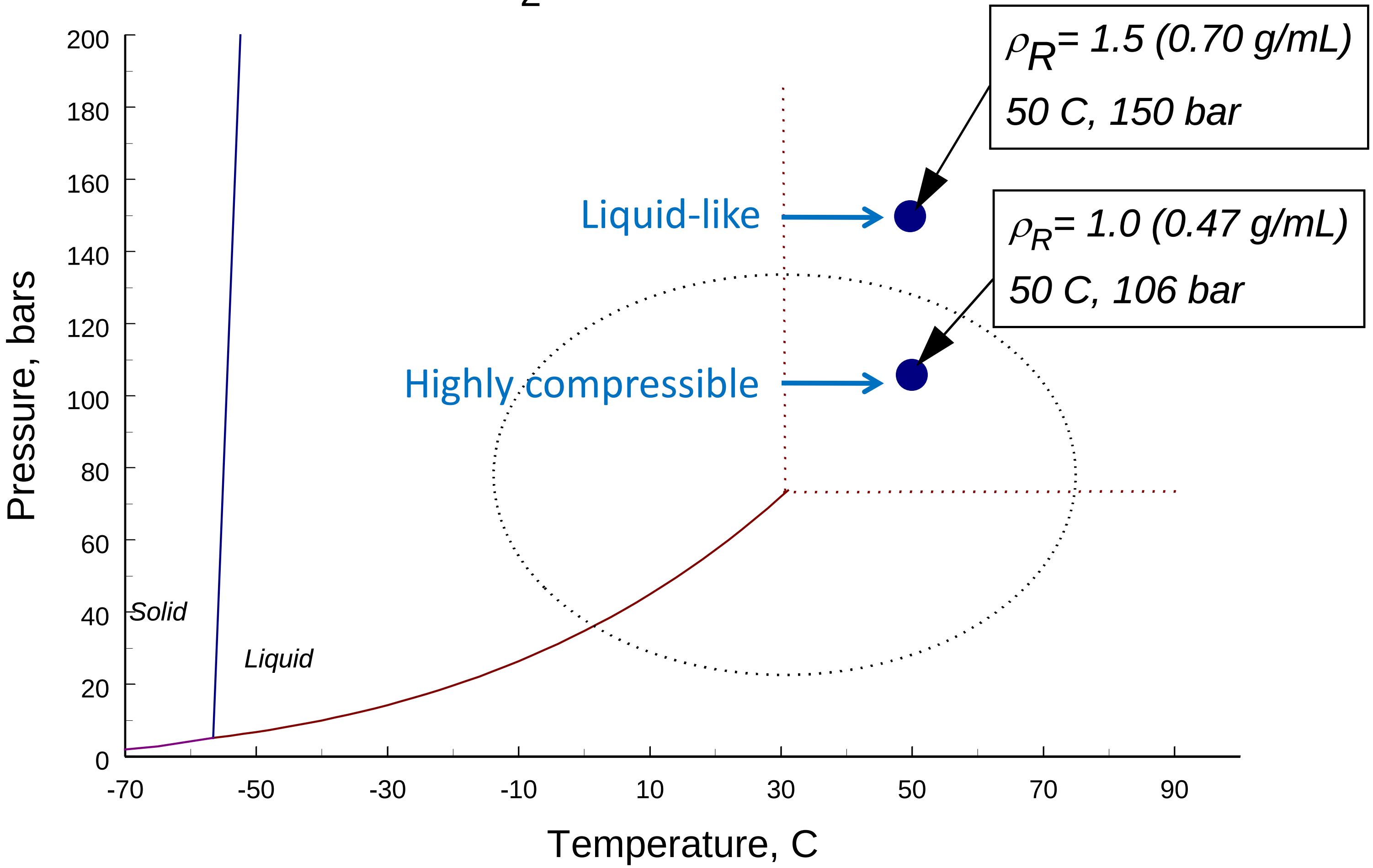
T.A. Berger, Chromatographia 37 (1993) 645.

Large pressure drops give highly nonuniform conditions

- Density gradients
- REALLY HUGE TEMPERATURE GRADIENTS!

CLAIM: EXCESS EFFICIENCY LOSS IS DUE TO ENTHALPIC EXPANSION OF CO_2

CO_2 Phase Diagram



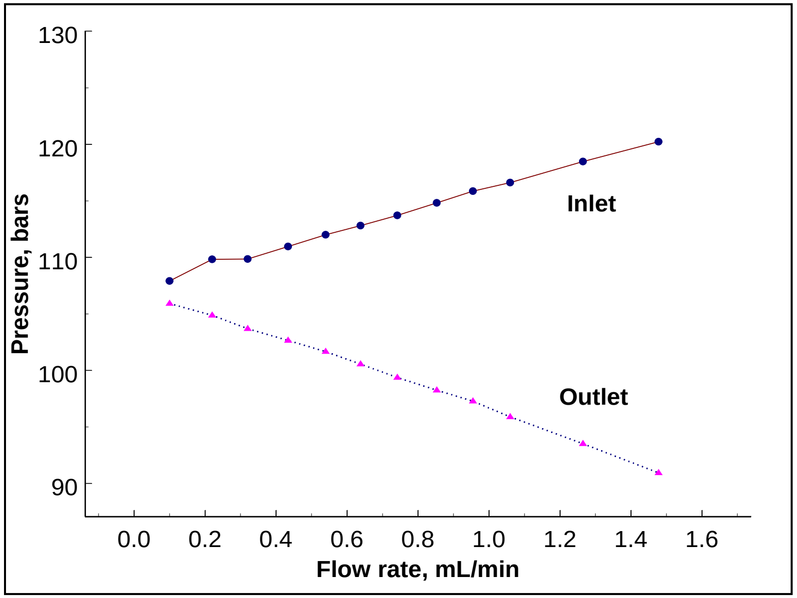
Liquid-like

ρ_R = 1.5 (0.70 g/mL)
50 C, 150 bar

Highly compressible

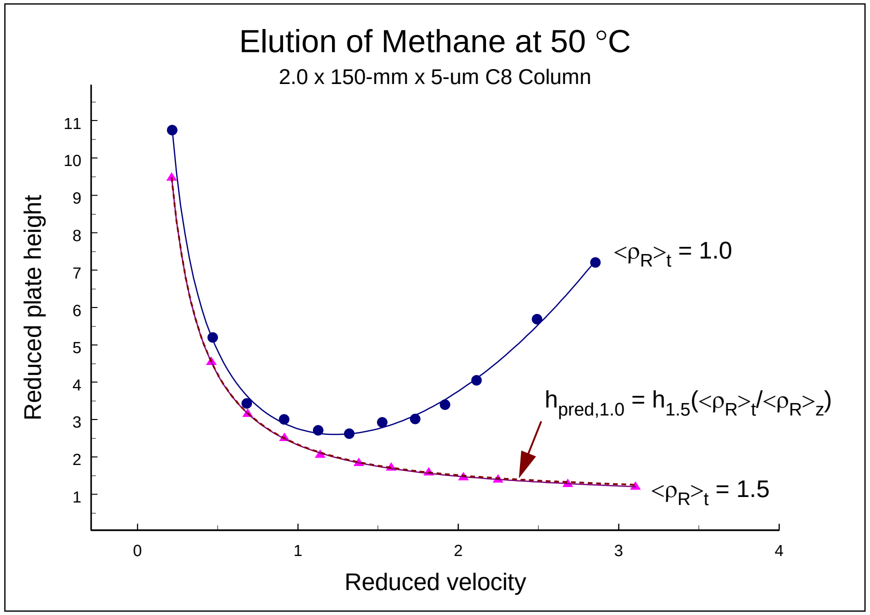
ρ_R = 1.0 (0.47 g/mL)
50 C, 106 bar

Isopycnic Plate Height Curves for an Unretained Solute at Constant Density



Pressure settings for $<\rho>_t$ = 1.0 at 50 °C, isothermal conditions.

Column: 150 x 2.0 mm x 5 μm

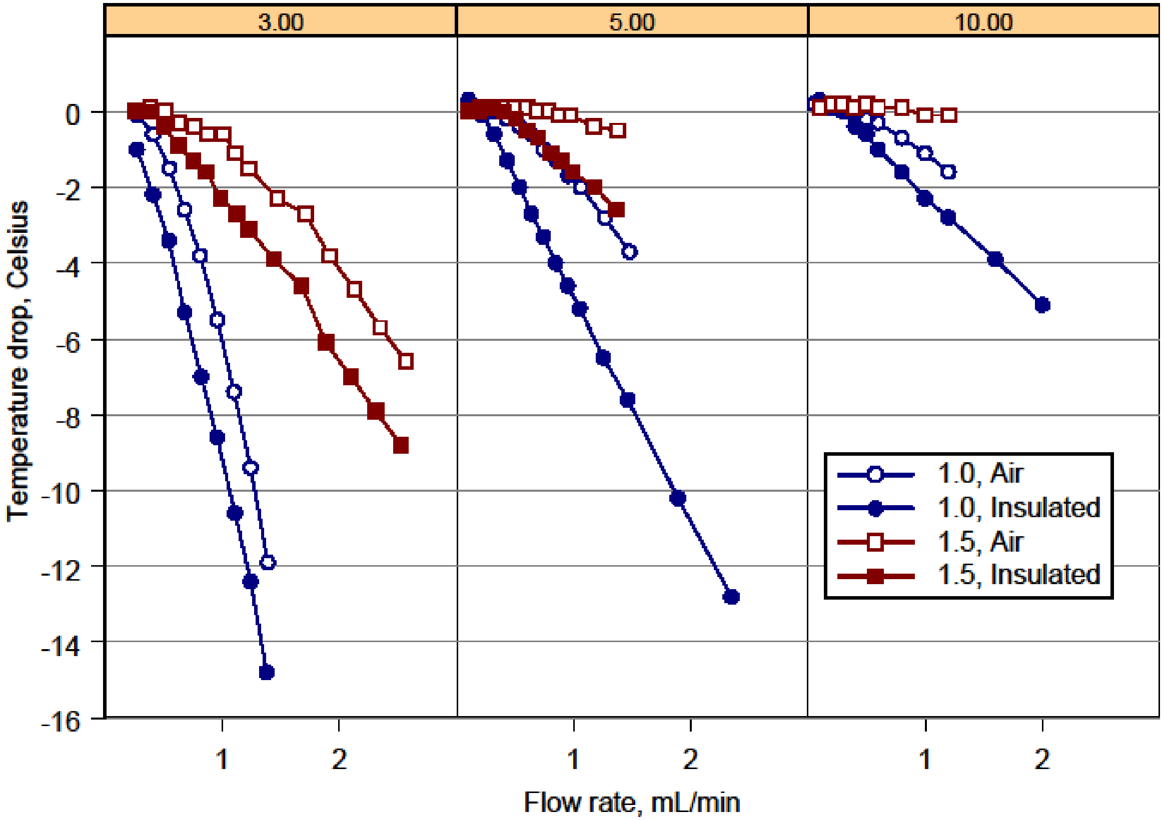


Efficiency for elution of an unretained solute at RD = 1.0 and 1.5

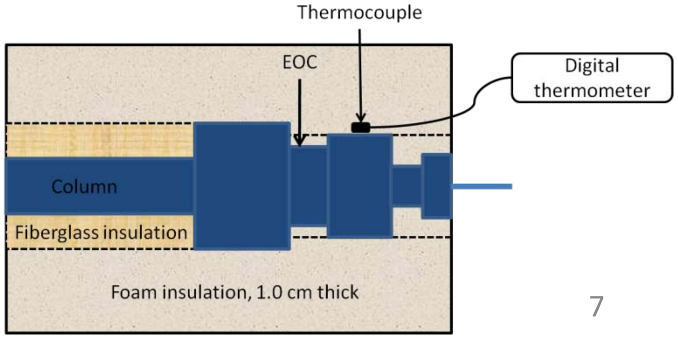
$$\hat{h} \cong \frac{\langle \rho \rangle_t}{\langle \rho \rangle_z} h_{uniform}$$

Poe et al, J. Chromatogr. A, 2005

Temperature Drop and Thermal Condition



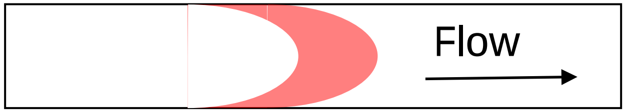
Columns: 150 x 2.0 mm. Particle size in top panel. Neat CO_2 at 50 °C.



Radial Temperature Gradient

HPLC

- Frictional heating results in temperature gradients with higher temperature and lower viscosity at center of column.
- Velocity is greatest near center of column.

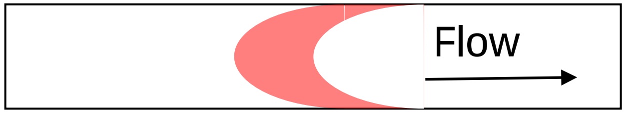


$$T_c - T_w = \frac{-u \frac{\partial p}{\partial z} R^2}{4\overline{\lambda}_{rad}}$$

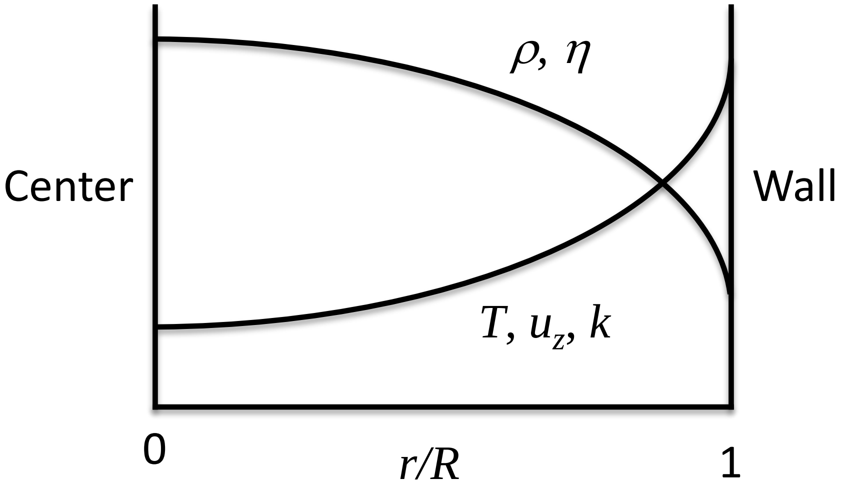
H. Poppe et al, *Chromatographia*, **1981**, 14, 514

SFC

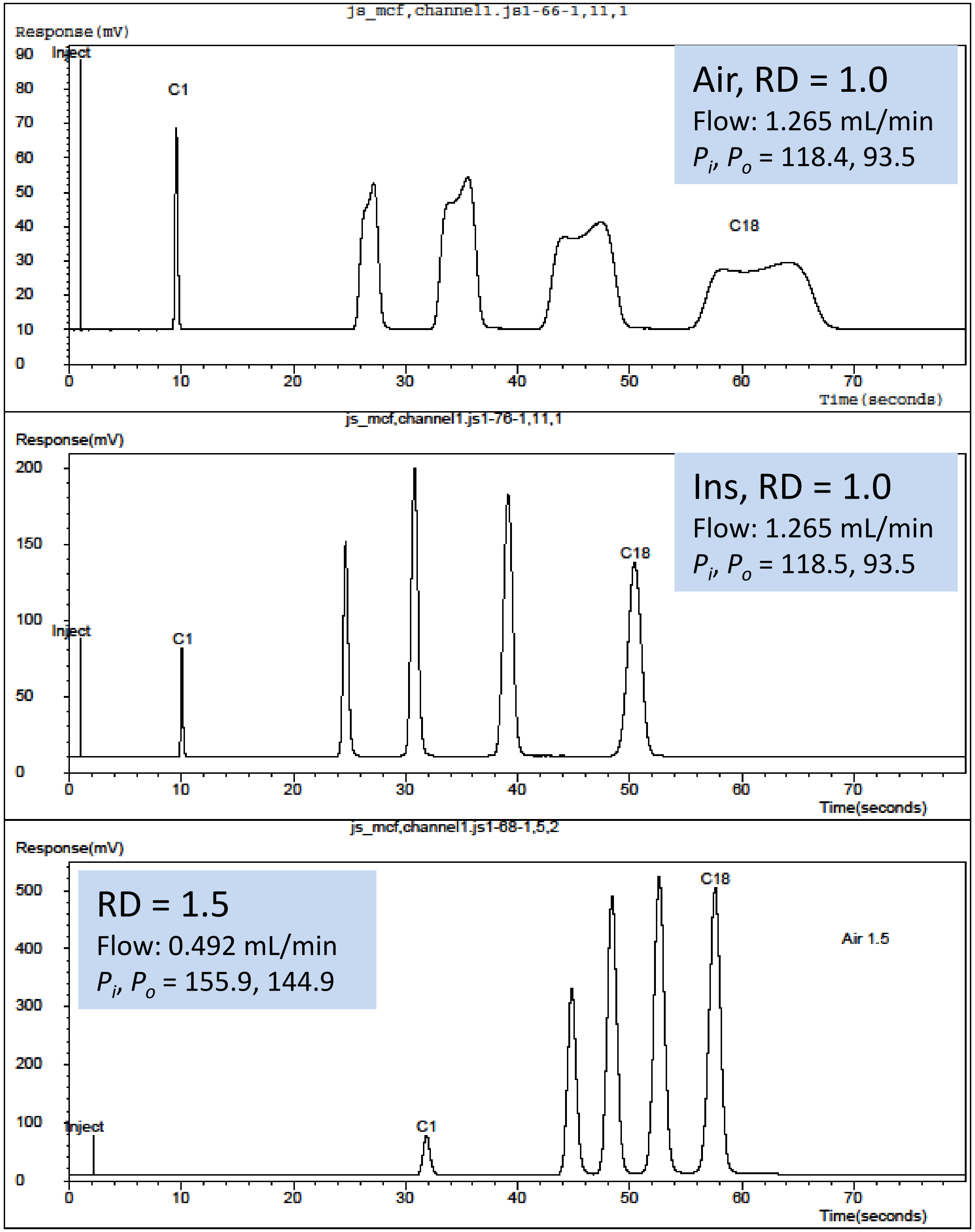
- Enthalpic expansion results in temperature gradients with lower temperature and higher viscosity at center of column.
- Velocity is greatest near wall.



Radial Distribution of Physico-Chemical Properties in SFC



Effect of Density and Thermal Conditions



Air, RD = 1.0
Flow: 1.265 mL/min
P_i, P_o = 118.4, 93.5

Ins, RD = 1.0
Flow: 1.265 mL/min
P_i, P_o = 118.5, 93.5

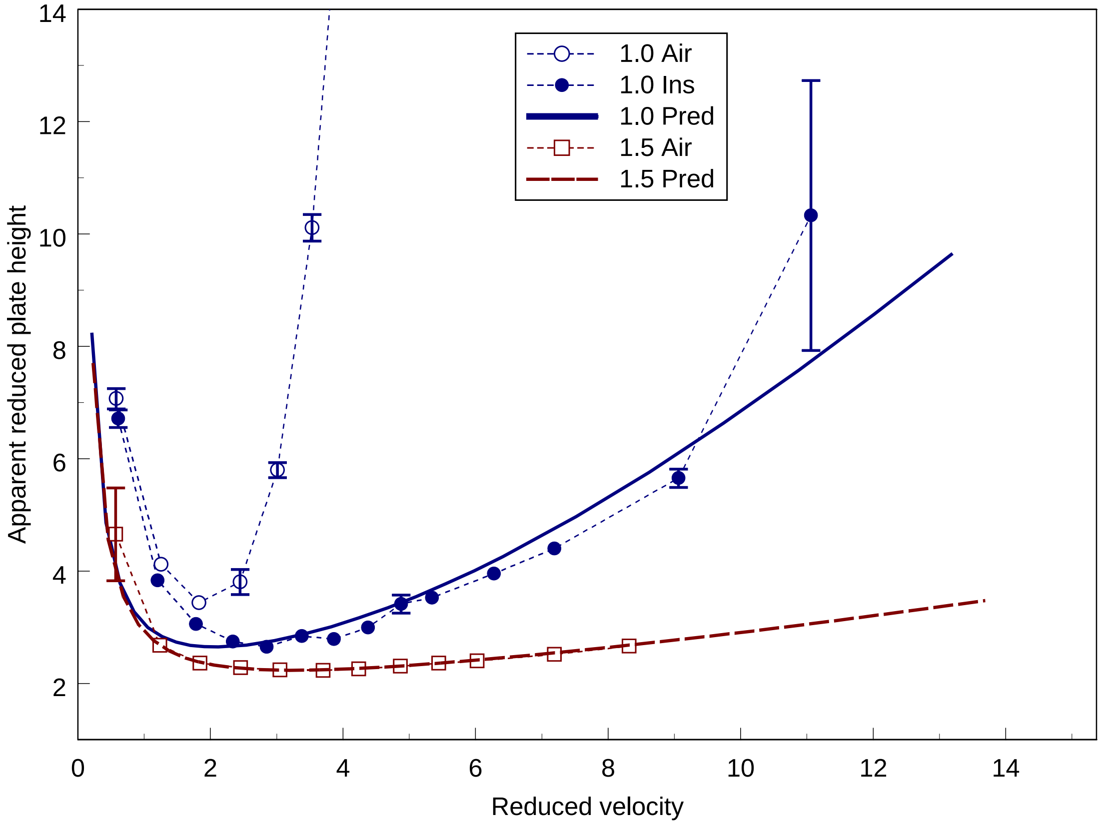
RD = 1.5
Flow: 0.492 mL/min
P_i, P_o = 155.9, 144.9

- Column: 150 x 2.0 mm, 5-um Spherisorb C8
- Neat CO_2 at 50 ^{o}C
- Solutes: n-alkanes in CO_2

Thermal insulation at low densities

- decreases t_r (cooling)
- restores lost efficiency by elimination of radial temperature gradients

Effect of Density and Thermal Conditions



- Column: 150 x 2.0 mm, 5-um Spherisorb C8
- Neat CO_2 at 50 °C
- Solutes: n-alkanes in CO_2

At RD = 1.0, relative to RD = 1.5,

- some efficiency loss for
  - isothermal case (predicted)
  - insulated case
- excessive efficiency loss for air-thermostatted case

Predicted plate height for isothermal column

$$\hat{h} = \frac{\left\langle h(1+k')^2 \rho \right\rangle_t}{\left\langle 1+k' \right\rangle_t^2 \left\langle \rho \right\rangle_z} = \frac{1}{\left\langle 1+k' \right\rangle_t^2 \left\langle \rho \right\rangle_z} \left\{ \begin{aligned} &\left\langle D_m \rho^2 (1+k')^2 \right\rangle_t \frac{B}{(\dot{m}_o/\varepsilon_t) d_p} + \left\langle (1+k')^2 \rho \right\rangle_t A \\ &+ \left\langle (\phi_K + k')^2 / D_m \right\rangle_t C_k (\dot{m}_o/\varepsilon_t) d_p \end{aligned} \right\}$$

Poe and Schroden 2009

Sources of band spreading in SFC

- **Normal chromatographic dispersion processes**

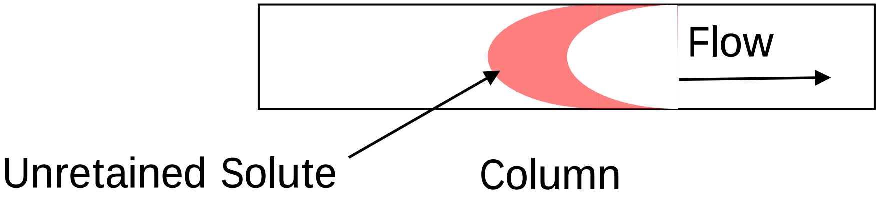
  $$H = B/u + A + Cu$$

- **Nonuniform conditions.**
  - ***Axial density/temperature gradients***

$$\hat{H} = \frac{\left\langle H(1+k)^2 \rho \right\rangle_t}{\left\langle 1+k \right\rangle^2 \left\langle \rho \right\rangle_z}$$

Poe and Martire, J. Chromatogr. A, 1990

  - ***Radial temperature gradient*** generates parabolic flow profile.



Poe and Schroden, J. Chromatogr. A, 2009

Modeling Peak Profiles in SFC

PROVING THE CLAIM

Modeling Peak Profiles in SFC

Overall model combines three separate models

- a model of heat transfer

$$\left(\varepsilon_t c_p^m + (1-\varepsilon_t)c_s\right)\frac{\partial T}{\partial t} - \varepsilon_t T\alpha\frac{\partial P}{\partial t} + c_p^m u_z\frac{\partial T}{\partial z} + c_p^m u_r\frac{\partial T}{\partial r}$$
$$= \frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda_{r,ef}\frac{\partial T}{\partial r}\right) - u_z\left(1-\alpha T\right)\frac{\partial P}{\partial z}$$

- a model of mass transfer (equilibrium-dispersive model)

$$\frac{\partial C}{\partial t} + F\frac{\partial q}{\partial t} + \frac{\partial\left(w_z C\right)}{\partial z} = \frac{\partial}{\partial z}\left(D_{z,a}\frac{\partial C}{\partial x}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{r,a}\frac{\partial C}{\partial r}\right)$$

- a model of mobile phase velocity distribution

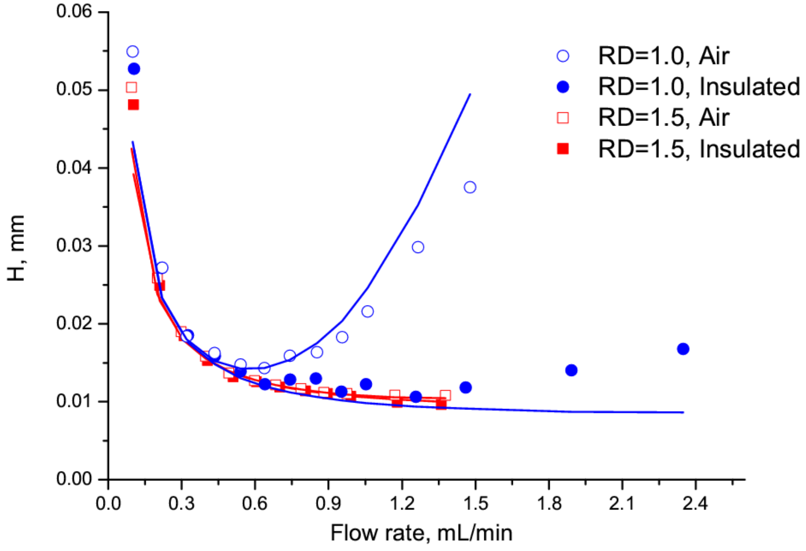
$$u_z\left(r,z\right) = \frac{u^\circ \rho^\circ}{\eta\left(r,z\right)\left(\overline{\rho/\eta}\right)_z}$$

The three models are based on those developed for VHPLC. They are solved simultaneously, using experimental data and accurate models for calculation of various physico-chemical parameters.

J. Kostka, F. Gritti, G. Guiochon, K. Kaczmarski, J Chromatogr A, 1217 (2010) 4704.
K. Kaczmarski, D. Poe, G. Guiochon, J Chromatogr A, 1217 (2010) 6578.

Efficiency for Elution of an Unretained Solute

Column: 150 x 2.0 mm, 5-um Spherisorb, 50 ^{o}C, neat CO_2



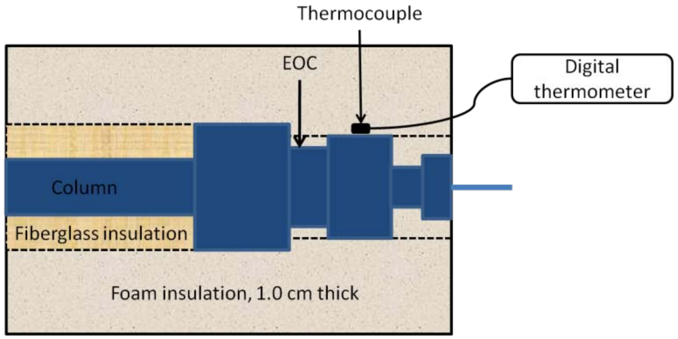
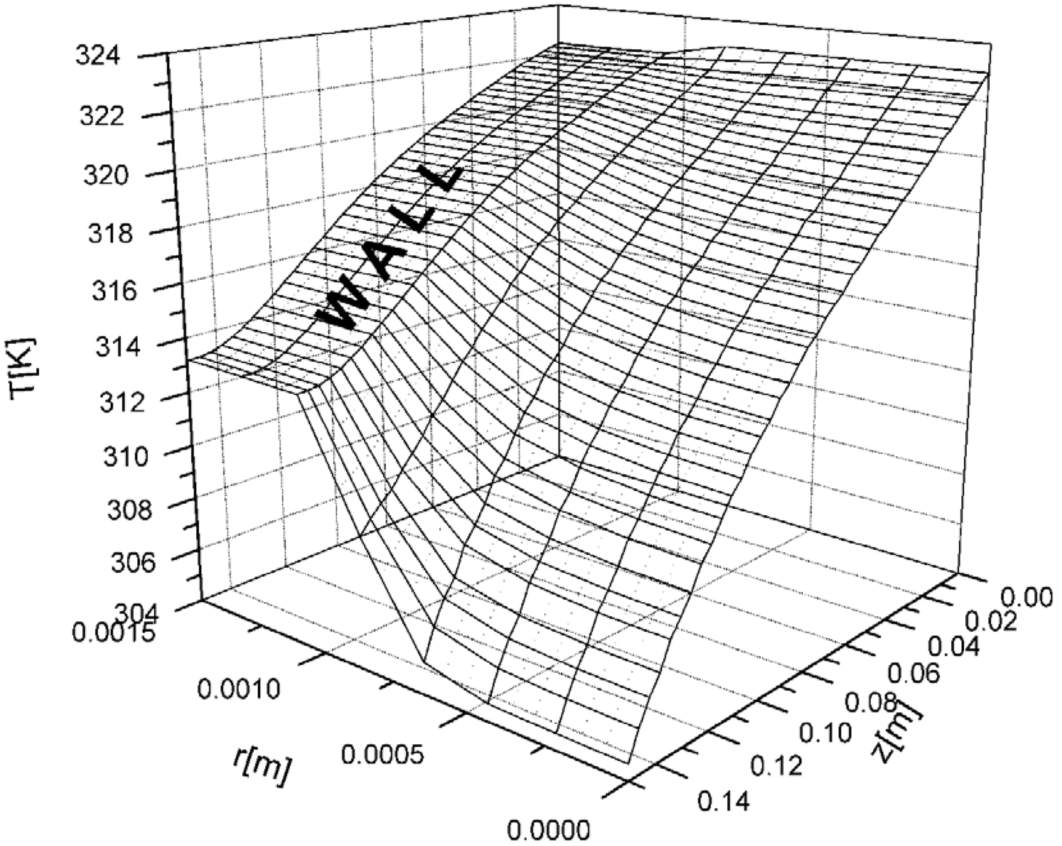


Plate height for methane and flow rate

Temperature Distribution

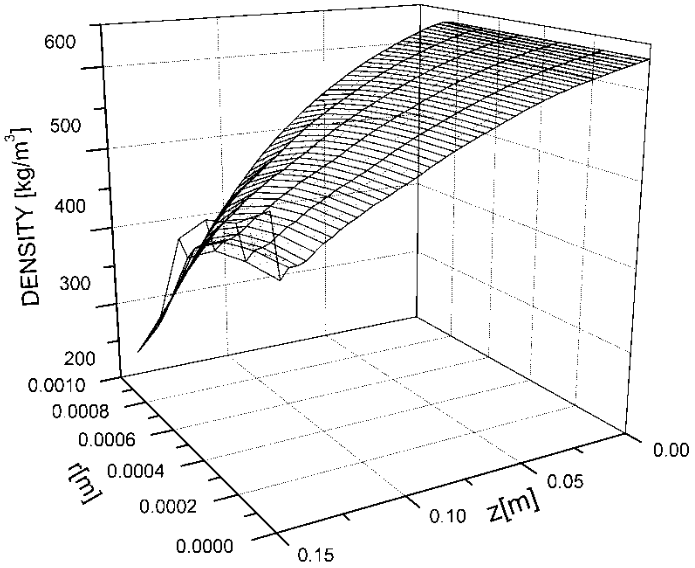
Column: 150 x 2.0 mm, 3-μm Spherisorb-C8. 50 °C, 1.245 mL/min, RD = 1.0

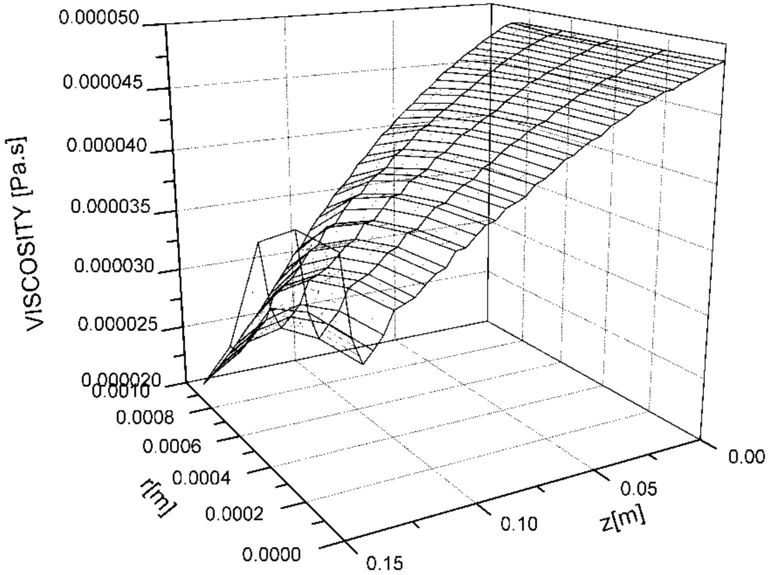


Temperature is higher near the wall.
Radial temperature gradient near outlet is ≈ 8 K/mm.

Density and Viscosity

Column: 150 x 2.0 mm, 3-μm Spherisorb-C8. 50 °C, 1.245 mL/min, RD = 1.0

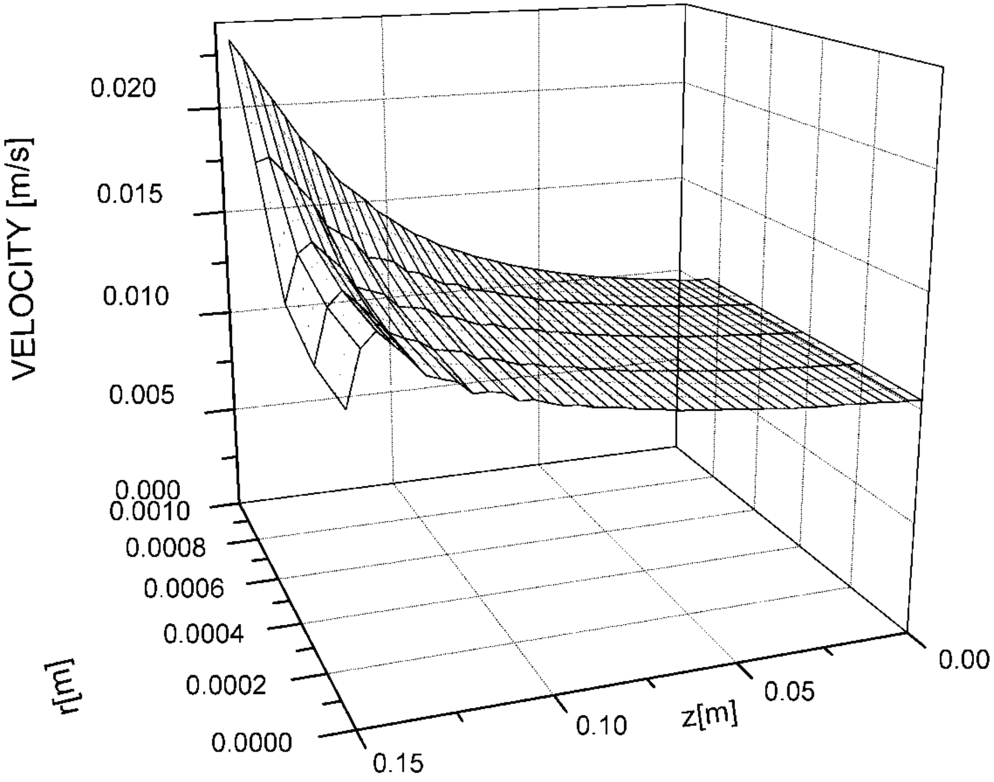




Density and viscosity are lowest at the wall near outlet

Velocity Distribution

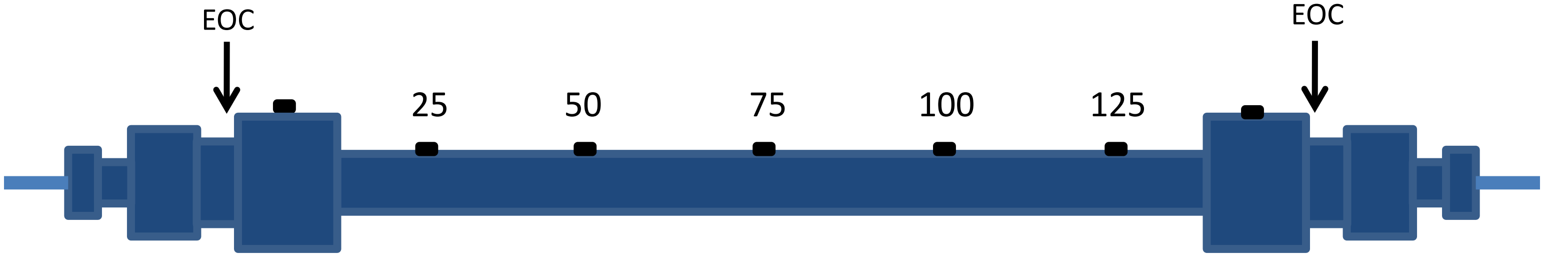
Column: 150 x 2.0 mm, 5 um Spherisorb-C8. 50 ^{o}C, 1.245 mL/min



Velocity is greatest at outlet and near the wall n-Alkanes on 5-um Spherisorb, neat $CO_{2.}$ *J. Chromatogr. A, accepted July 2011.*

MODELING RETAINED SOLUTES

Temperatures and Pressures



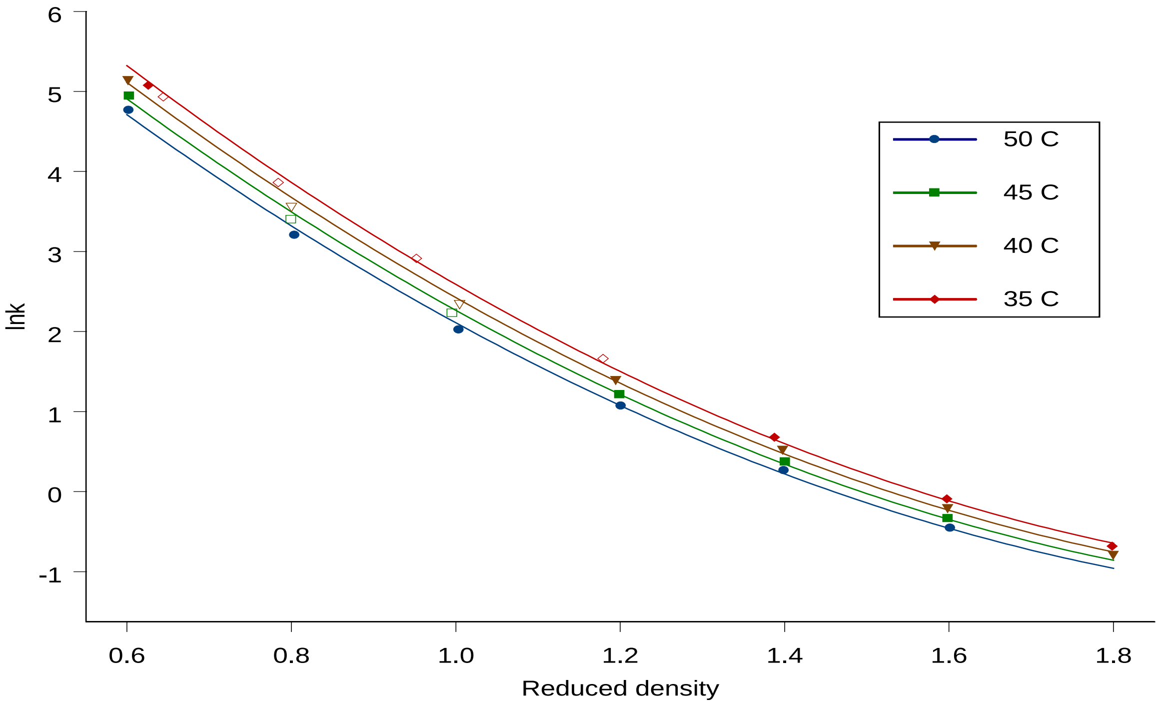
Distance x [m]	Flow rate mL/min (at pump), RD=1.0				Flow rate mL/min (at pump), RD=1.5			
	0.638		1.478		0.5		1.5	
	T_{exp} [K]	T_{calc} [K]	T_{exp} [K]	T_{calc} [K]	T_{exp} [K]	T_{calc} [K]	T_{exp} [K]	T_{calc} [K]
0.025	322.80	322.75	322.21	322.08	323.02	322.98	322.73	322.66
0.05	322.50	322.48	321.41	321.30	322.98	322.95	322.45	322.42
0.075	322.26	322.27	320.79	320.50	322.95	322.94	322.25	322.22
0.1	321.92	322.08	319.48	319.64	322.89	322.93	321.9	322.05
0.125	321.83	321.92	318.65	318.69	322.9	322.92	321.77	321.89
x [m]	P_{exp} [bar]	P_{calc} [bar]	P_{exp} [bar]	P_{calc} [bar]	P_{exp} [bar]	P_{calc} [bar]	P_{exp} [bar]	P_{calc} [bar]
0.0	112.8	112.8*	120.3	120.3*	156.0	156.0*	168.7	168.7*
0.15	100.4	100.3	91.0	91.0	145.0	145.0	134.9	135.2

* assumed values

- Temperature data from multiple RTDs, ±0.01 K
- Pressure data ±0.1 bar

The agreement between experimental and simulated data is excellent.

Distribution Isotherms



Retention factor for n-octadecane on 5-µm Spherisorb-C8.

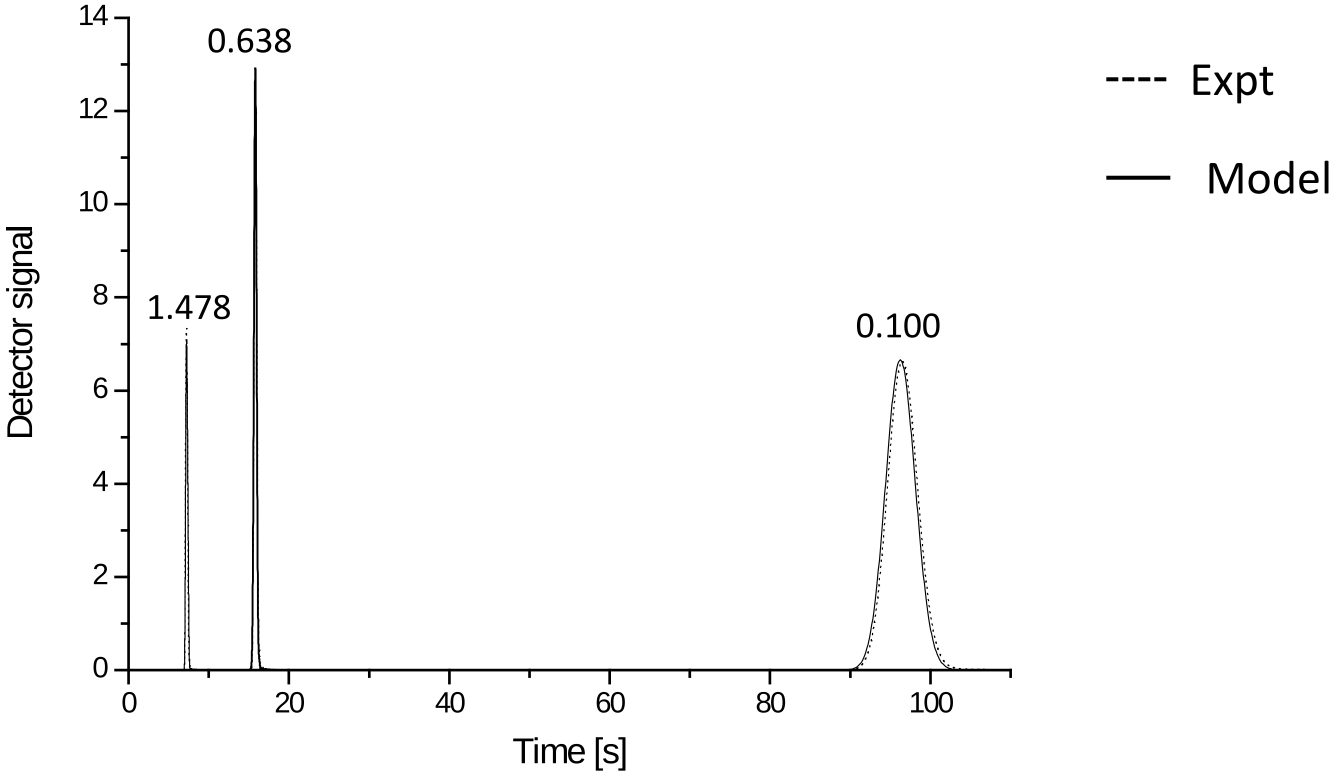
Retention factors measured on 1.50 x 2.0-mm column at 0.100 mL/min and $<\rho>_t$

$$\ln k = c_0 + c_1 T_R + c_2 \rho_R + c_3 \frac{\rho_R}{T_R} + c_4 \frac{\rho_R{}^2}{T_R}$$

(Martire and Boehm, J. Phys. Chem., 1987)

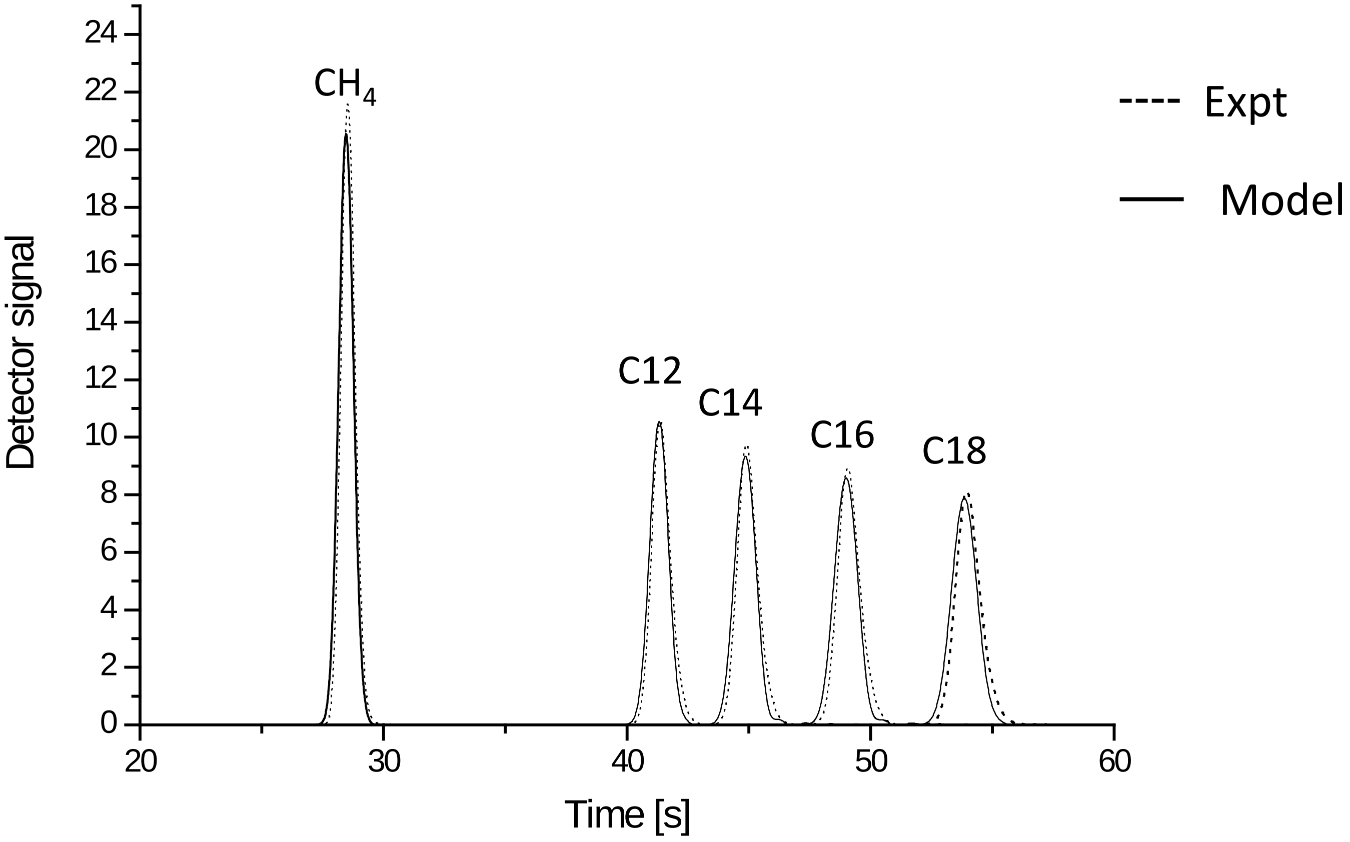
Elution of Methane at Three Flow Rates

Column: 150 x 2.0 mm, 5-μm Spherisorb-C8. 50 ^{o}C, RD = 1.0.
Flow rates in mL/min.



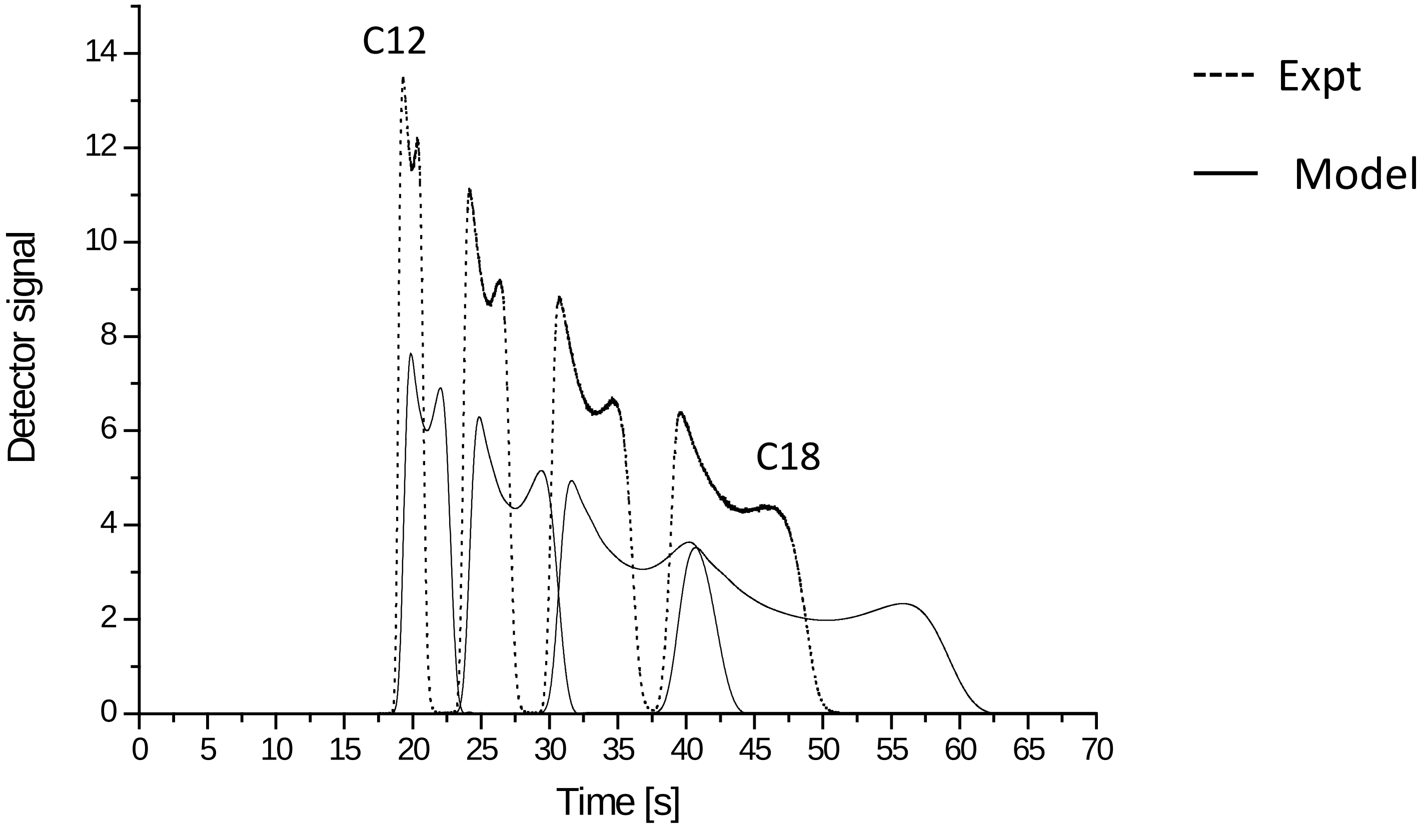
Elution of n-Alkanes at RD 1.5

Column: 150 x 2.0 mm, 5-µm Spherisorb-C8. 50 °C, RD = 1.5.
Flow rate: 0.500 mL/min.



n-Alkanes at Low Density and High Flow

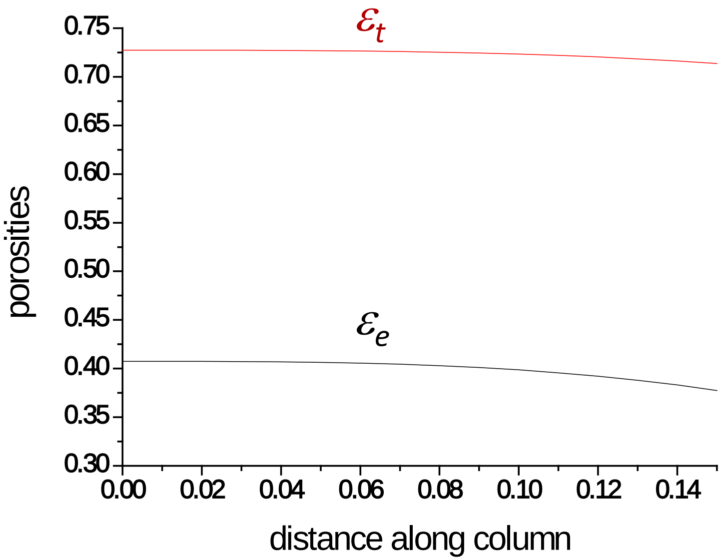
Column: 150 x 2.0 mm, 5-μm Spherisorb-C8. 50 ^{o}C, RD = 1.0.
Flow rate: 1.478 mL/min.

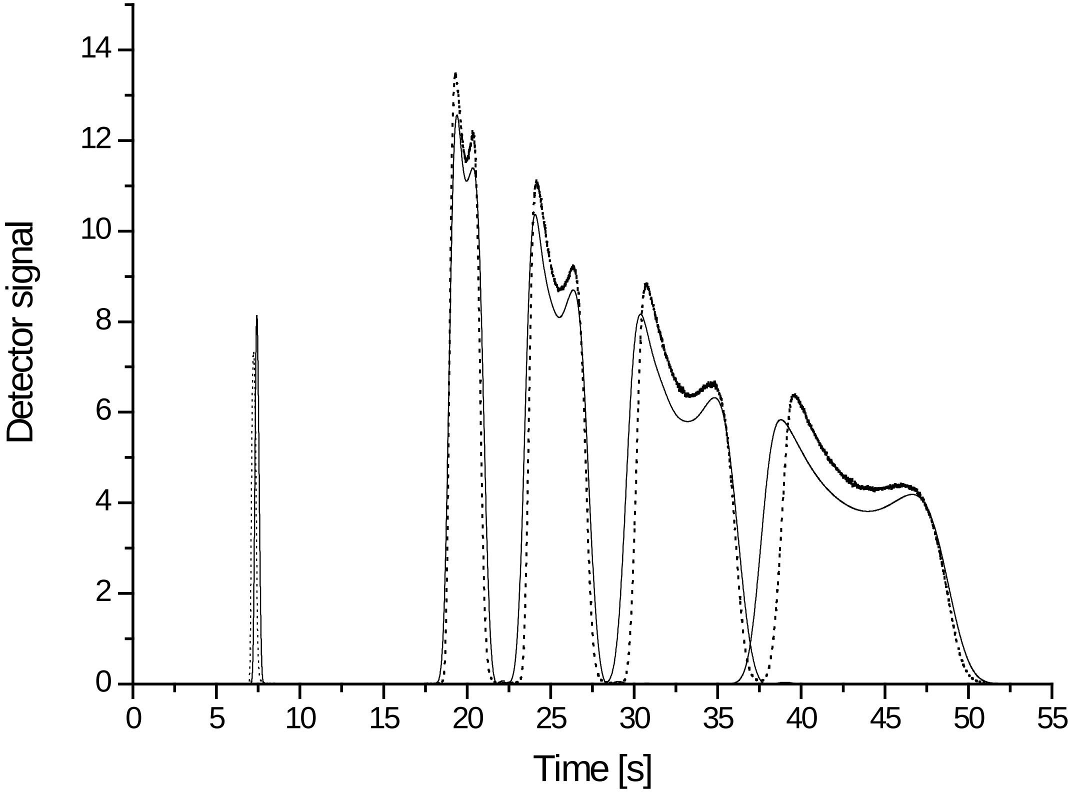


Impact of Packing Heterogeneity

Column: 150 x 2.0 mm, 5-μm Spherisorb-C8. 50 ^oC, RD = 1.0.
Flow rate: 1.478 mL/min.

ε_t total porosity
ε_e external porosity





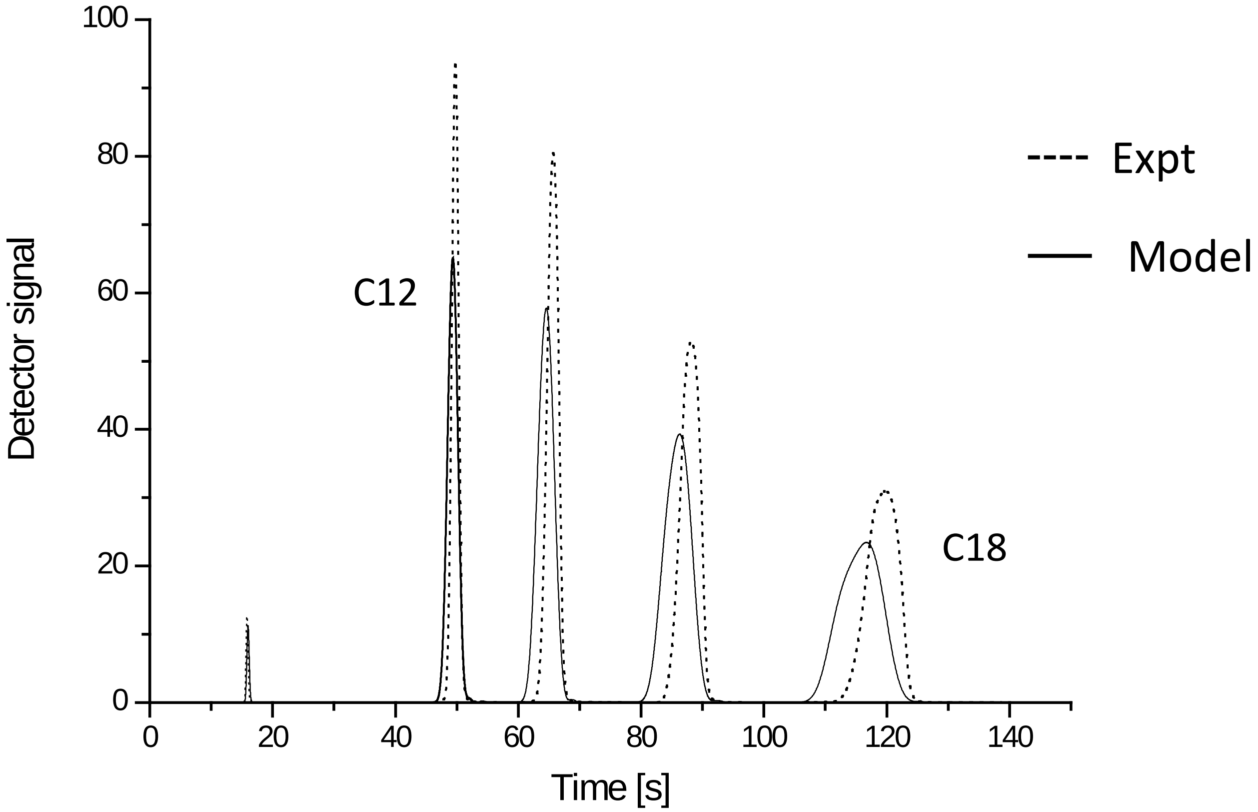
Typical HPLC columns show increase in packing density near outlet.

Simulations with axial porosity distribution.

V. Wong, R. A. Shalliker, and G. Guiochon, Anal. Chem. **76** (2004) 2601

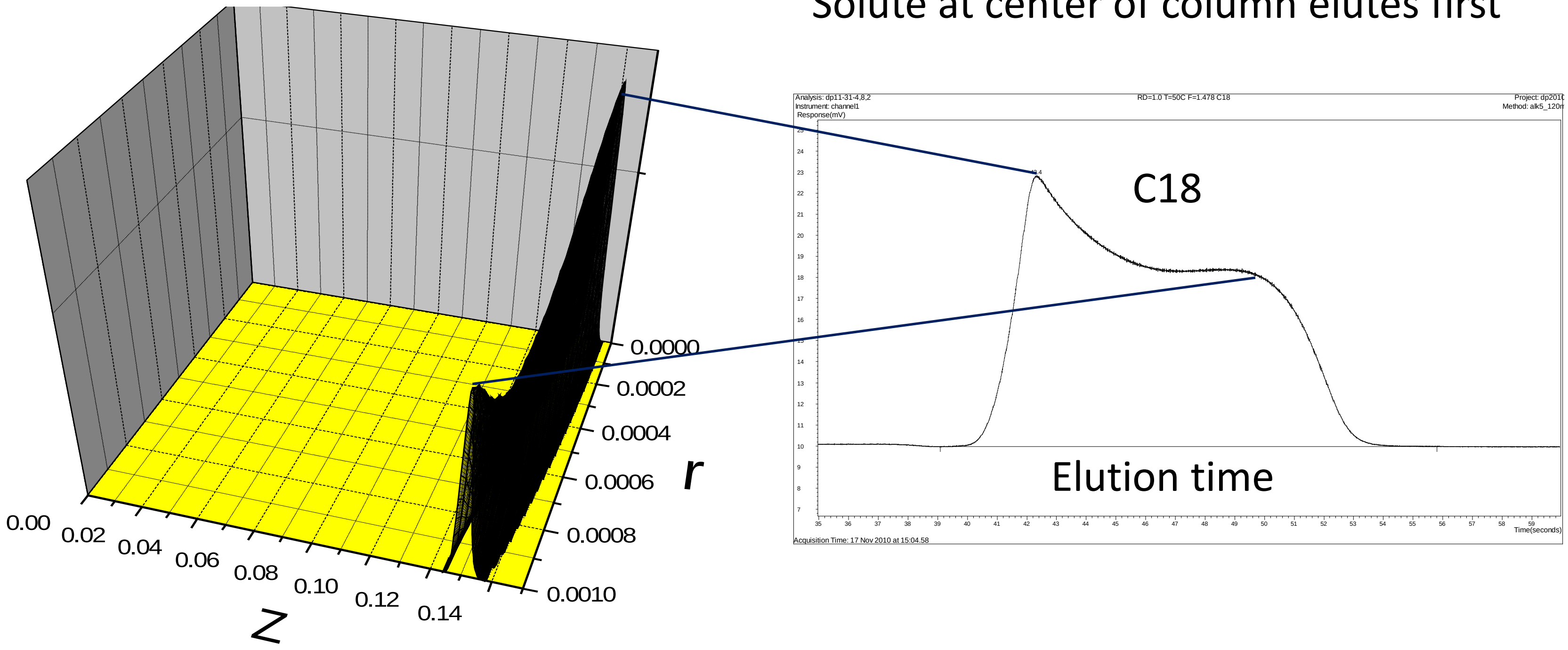
n-Alkanes at Low Density and Moderate Flow

Column: 150 x 2.0 mm, 5-µm Spherisorb-C8. 50 °C, RD = 1.0.
Flow rate: 0.638 mL/min.



Concentration Band Profile

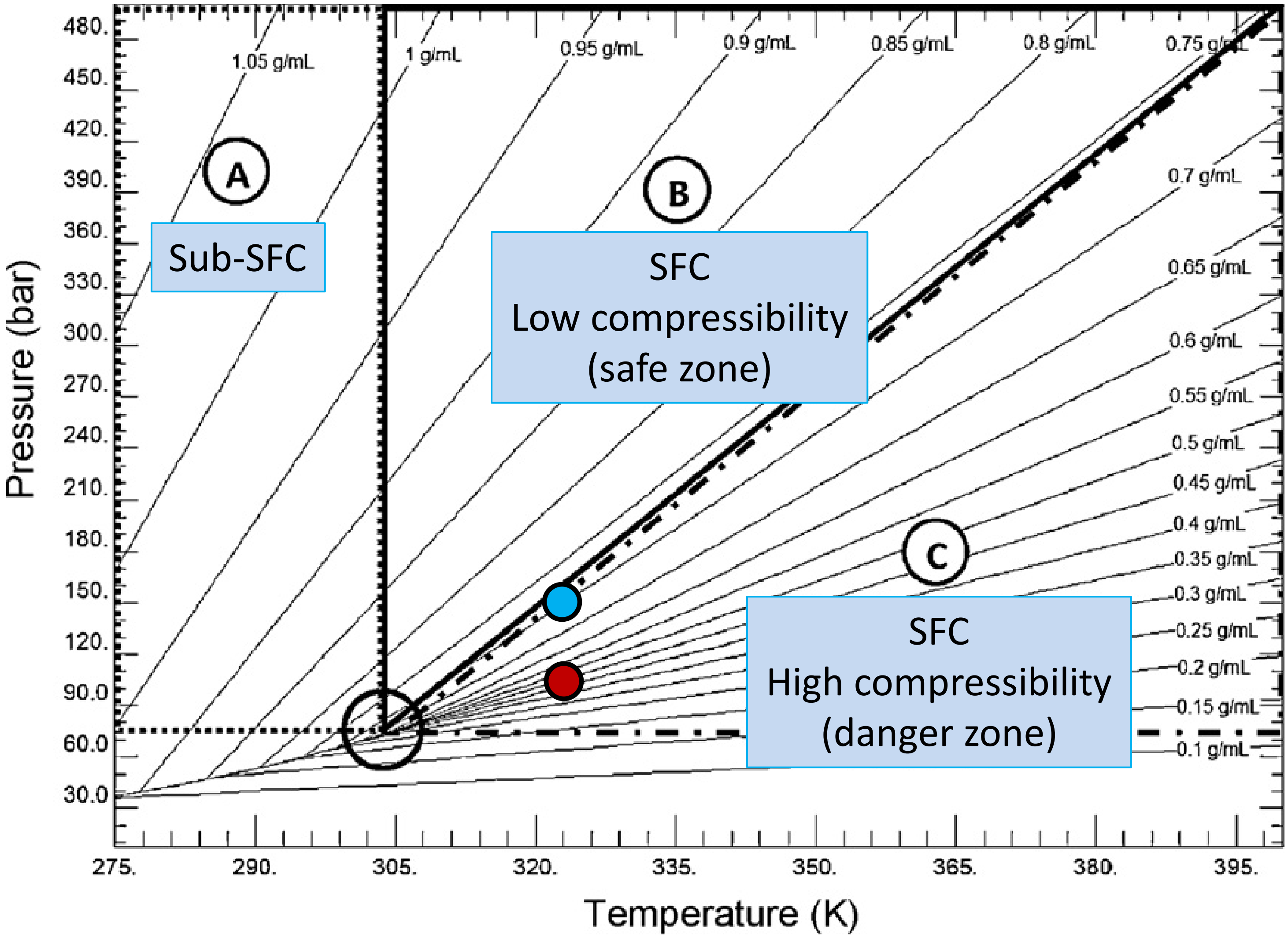
Solute at center of column elutes first



Column: 150 x 2.0 mm, 5-μm Spherisorb-C8. 50 °C, RD = 1.0.
Flow rate: 1.478 mL/min
Solute: n-octadecane

TEMPERATURE GRADIENTS, ISOPYCNIC PLOTS, AND ZERO HEAT BALANCE CONDITION.

Isopycnic Plot for Carbon Dioxide in Supercritical Region



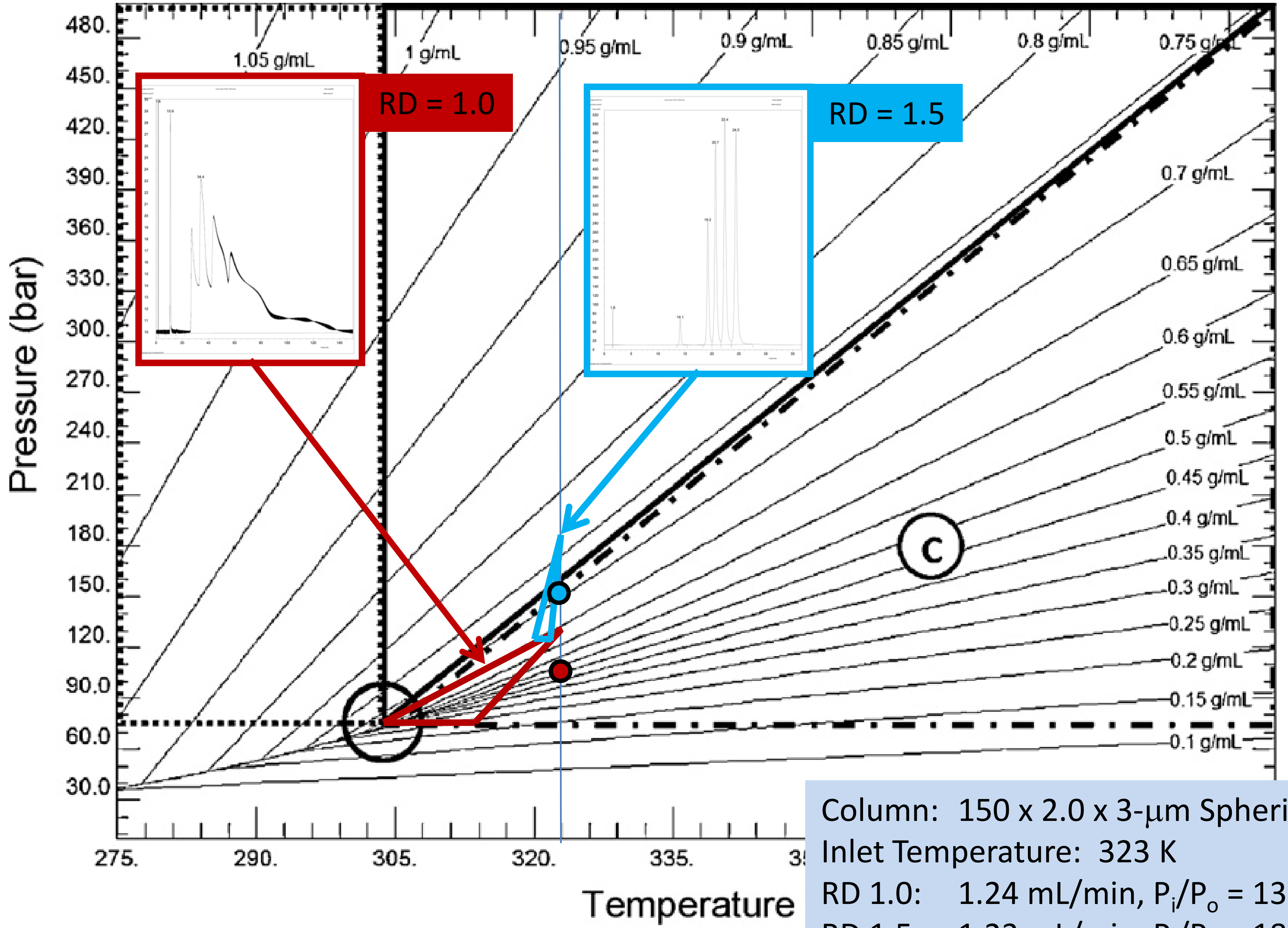
Sub-SFC

SFC
Low compressibility
(safe zone)

SFC
High compressibility
(danger zone)

A. Tarafder and G. Guiochon, J. Chromatogr. A, 1218 (2011) 4578-4585)

Pressure, Temperature and Density on an Isopycnic Plot



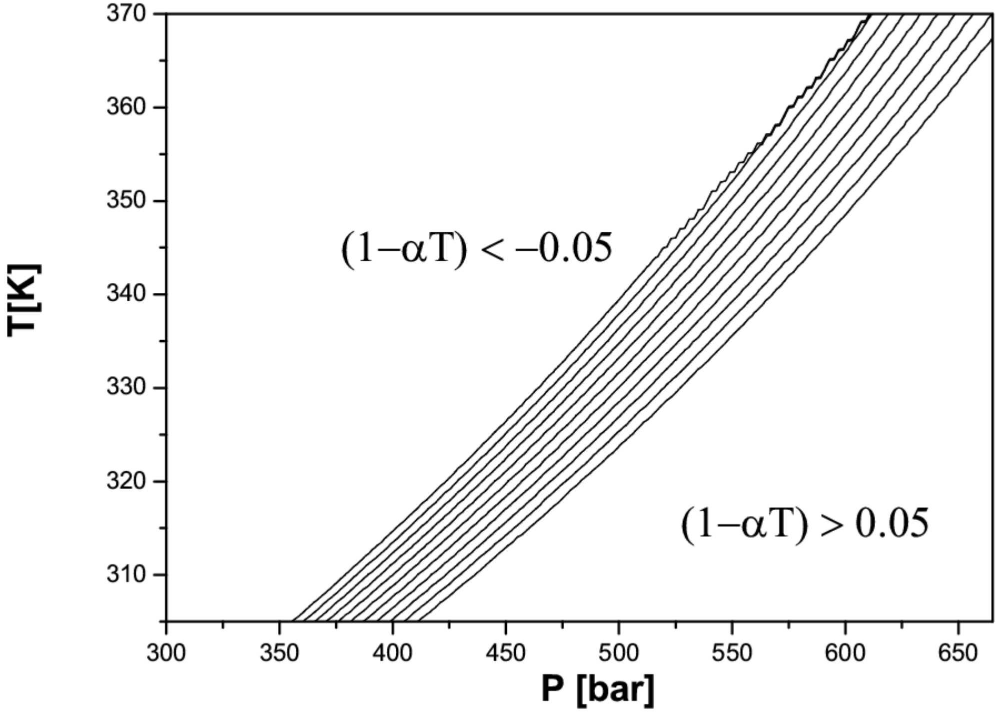
Column: 150 x 2.0 x 3-μm Spherisorb-C8

Inlet Temperature: 323 K

RD 1.0: 1.24 mL/min, P_i/P_o = 130/74

RD 1.5: 1.23 mL/min, P_i/P_o = 183/122

Zero Heat Balance Condition



Temperature and pressure conditions for

$q_{viscous\ heating} = q_{enthalpic\ expansion}$

K. Kaczmarski, D. Poe, G. Guiochon, J Chromatogr. A, 1217 (2010) 6578.

SUMMARY AND CONCLUSIONS

Implications for Analytical and Preparative SFC

- Analytical SFC
  - Complete, precise model supports rational design of optimized separation conditions.
  - Operating at higher outlet pressures may eliminate temperature gradients and provide significant performance gains.

- Preparative SFC
  - Complete, precise model supports rational design of optimized separation conditions.
  - May be especially relevant to prep SFC, where use of low to moderate pressures is desirable.

Summary and Conclusions

- Efficiency loss near the critical condition is largely due to radial temperature gradients.

- A new numerical model for SFC accurately predicts, over a wide range of operating conditions,
  - mobile phase properties (T, ρ, η, u)
  - peak profiles

- Peak profiles at low P, T are sensitive to porosity distribution.

- Operating at higher outlet pressures
  - effectively eliminate temperature gradients
  - may provide a route to increased performance

Acknowledgments

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- University of Tennessee and Oak Ridge National Laboratory
- University of Minnesota Grant-In-Aid