

Consideration of Effect of Frictional Heat Using UHPLC Column Packed with Sub 2 μm Particle



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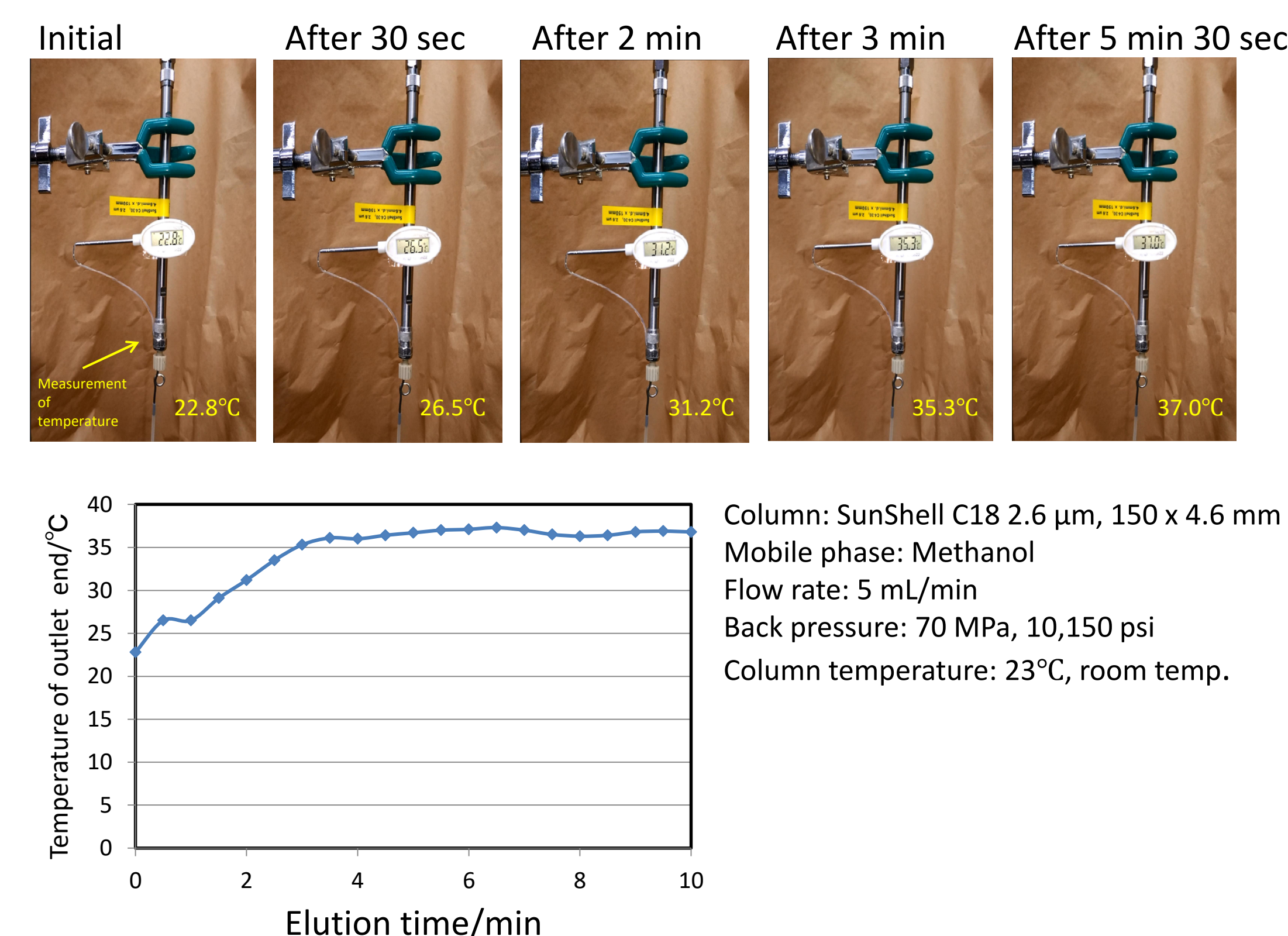
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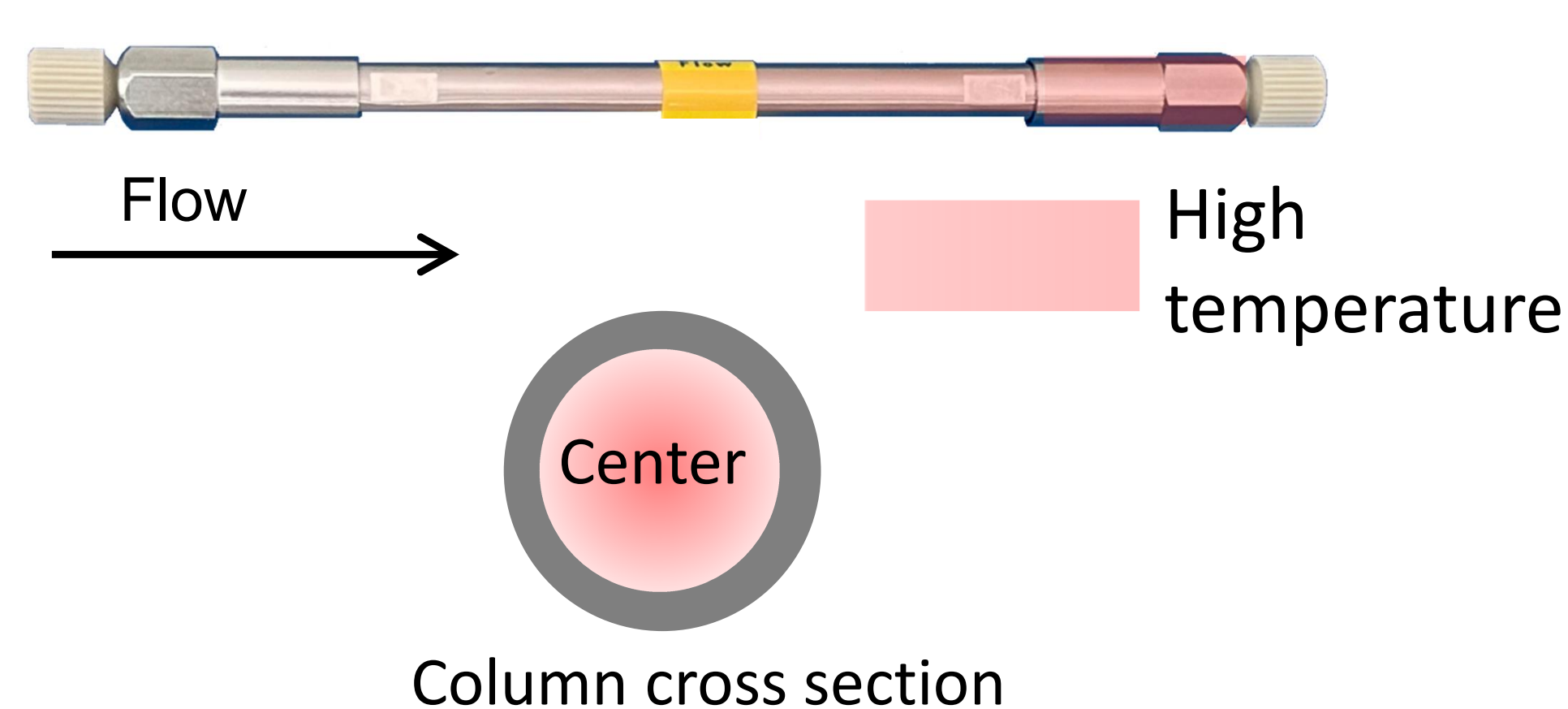
UHPLC columns packed with sub-2 μm particles have been in use since 2004, with the launch of UHPLC instruments. A typical sub-2 μm particle is a hybrid silica packing made in the United States, incorporating carbon within silica. Around 2006, reports began to emerge that this hybrid silica packed column's theoretical plate number suddenly decreased when the flow rate was increased. In 2009, Gritti et al. reported on the frictional heat generated between the mobile phase and packing material at high column backpressures. They concluded that hybrid silica has one-third the thermal conductivity of superficially porous silica, which significantly impacts the plate number due to the frictional heat, leading to a greater plate number loss for hybrid silica.

In this report, we evaluated the relationship between flow rate and theoretical plate number for two types of hybrid silica C18 columns, and found that the effect of frictional heat on theoretical plate number varied even for the same hybrid. This was considered to attribute to the different amounts of carbon present in the silica framework. Furthermore, with a 150mm column, the column backpressure becomes very high and is affected by frictional heat at even low flow rates. However, as the column oven temperature was increased from 25 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$, the maximum value of the theoretical plate number gradually shifted to the higher flow rate side, and even at high column back pressure, the rate of decrease in the theoretical plate number decreased, reducing the effect of frictional heat.

Temperature rise of the column tube due to frictional heat



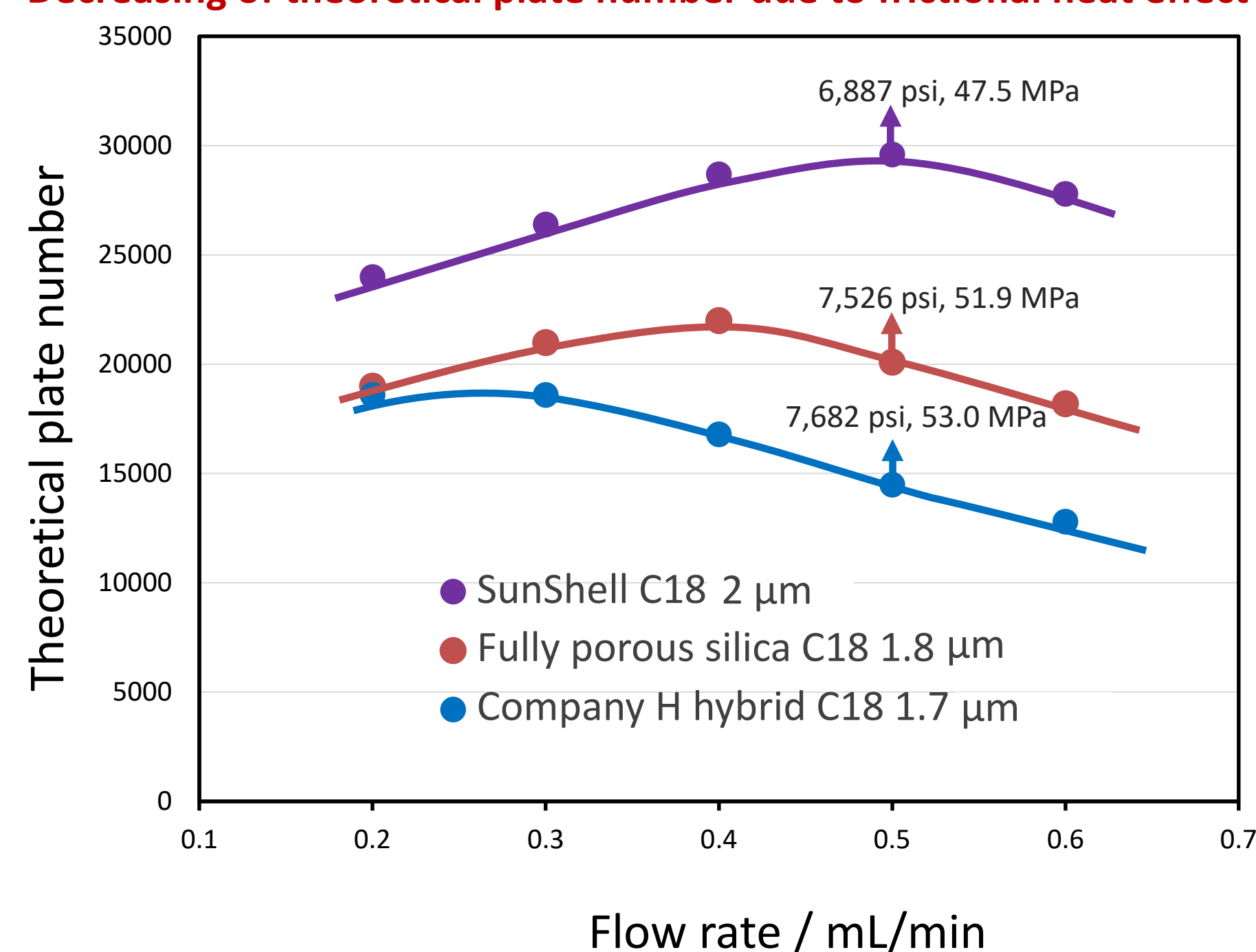
Reduction in the number of theoretical plates caused by column temperature rise due to frictional heat



Due to frictional heating, the column temperature increases as it approaches the column outlet. When attempting to maintain a constant column temperature in a column oven, the temperature on the outside of the column tube becomes lower than the temperature inside the column. As a result, the mobile phase flows faster in the center of the column than on the outside, resulting in broader peaks and a lower theoretical plate number.

Relationship between flow rate and theoretical plate number 1

Decreasing of theoretical plate number due to frictional heat effect



Column: shown in figure
Column dimension: 100 x 2.1 mm ID
Mobile phase: $\text{CH}_3\text{CN}/\text{H}_2\text{O}=60/40$
Temperature: 40 $^{\circ}\text{C}$
Sample: Acenaphthene,

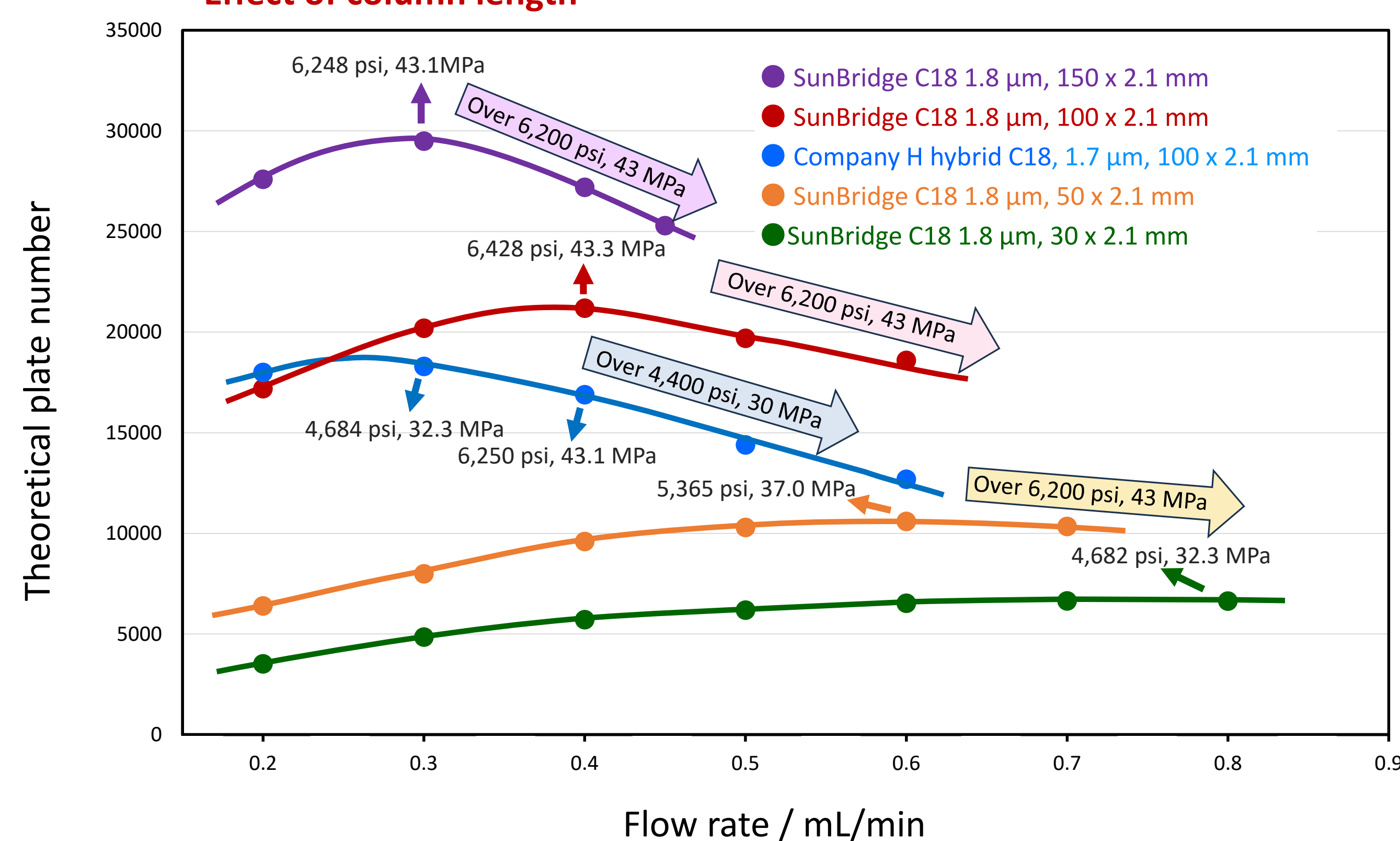
Regarding totally porous hybrid silica, not only totally porous structure but also including ethylene groups make thermal conductivity be low in the column. It is considered that frictional heat deflects thermal distribution in the column and theoretical plate number decreases. Core shell (SunShell) silica has core made by silica, so that the total volume of silica is large. As a result, core shell silica has a high thermal conductivity, so that the effect of frictional heat be low.

* Fabrice Gritti, Georges Guiochon, *J. Chromatogr. A* 1217 (2010) 5069.

A part of abstract
This unexpected result is accounted for by the three times smaller heat conductivity of the BEH bed (BEH 0.25 W/m/K) than that of the Kinetex (core shell) bed (Kinetex 0.75 W/m/K).

Relationship between flow rate and theoretical plate number 2

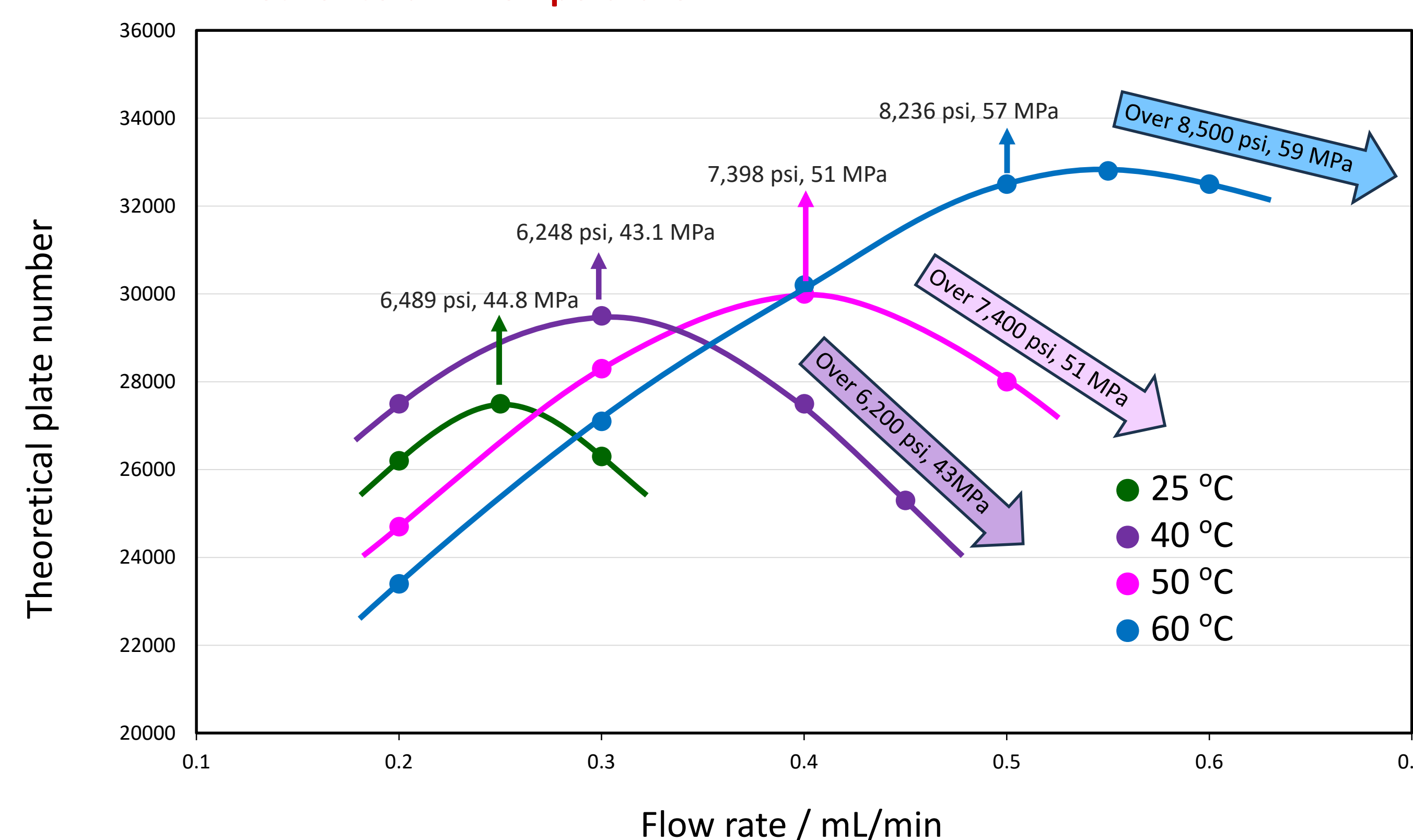
Effect of column length



Column: SunBridge (Fully hybrid) C18 1.8 μm
Company H hybrid C18 1.7 μm
Column dimension: 150, 100, 50, 30 mm x 2.1 mm ID
Mobile phase: $\text{CH}_3\text{CN}/\text{H}_2\text{O}=60/40$
Temperature: 40 $^{\circ}\text{C}$
Sample: Acenaphthene for 150, 100 mm length,
Butylbenzene for 50, 30 mm length

The theoretical plate number of SunBridge C18 decreases at back pressures above 6200 psi due to the effect of frictional heat, while the theoretical plate number of Company H hybrid C18 decreases at back pressures above 4400 psi due to the large effect of frictional heat.

Effect of column temperature



Column dimension: 150 x 2.1 mm
Mobile phase: $\text{CH}_3\text{CN}/\text{H}_2\text{O}=60/40$
Temperature: Room temp. (25 $^{\circ}\text{C}$), 40 $^{\circ}\text{C}$, 50 $^{\circ}\text{C}$, 60 $^{\circ}\text{C}$
Sample: Acenaphthene
Pre-heat system between Injector and column: No

The relationship between flow rate and theoretical plate number for a 150 mm column at different column temperatures is shown in this figure. At 25 $^{\circ}\text{C}$, the theoretical plate number was maximum at a flow rate of 0.25 mL/min, and the degree of decrease in the theoretical plate number was also large when the flow rate was increased, making separation at high speed and with a high theoretical plate number difficult. However, as the column temperature was increased, the theoretical plate number gradually increased, and the maximum theoretical plate number was achieved at higher flow rates. Furthermore, the rate of decrease in the theoretical plate number with increasing flow rate also decreased the higher the column temperature. This indicated that frictional heat has less effect on the theoretical plate number when the column temperature is high. It was shown that high-speed, high-theoretical-plate-number separation is possible even with a column with a column length of 150 mm, when operated at a column temperature of 60 $^{\circ}\text{C}$.

Conclusions

- ✓ The effect of frictional heat varies depending on the base material of the packing material, and base materials with high thermal conductivity are less affected by frictional heat.
- ✓ Frictional heat is generated in a column packed with Sub 2 μm particle, resulting in a temperature difference between the center and outside of the column, reducing efficiency.
- ✓ The longer the column length, the greater the frictional heat effect, while the higher the column temperature, the less frictional heat effect there is.