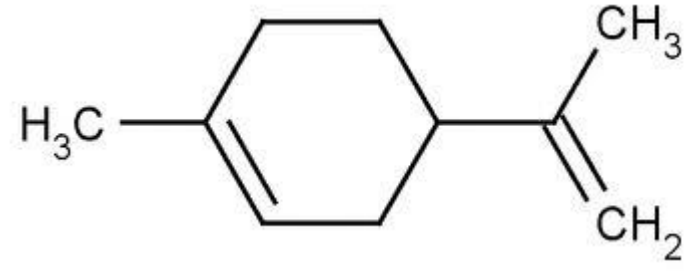


### Goal : Biorenewable solvents instead of petroleum-based solvents

#### LIMONENE



terpene family  
density 0.837 (density methanol = 0.79)  
viscosity 0.25  
 $\log P_{oct/eau} = 4.2$  ( $\log P_{oct/eau}$  heptane = 4.66)  
UV transparency

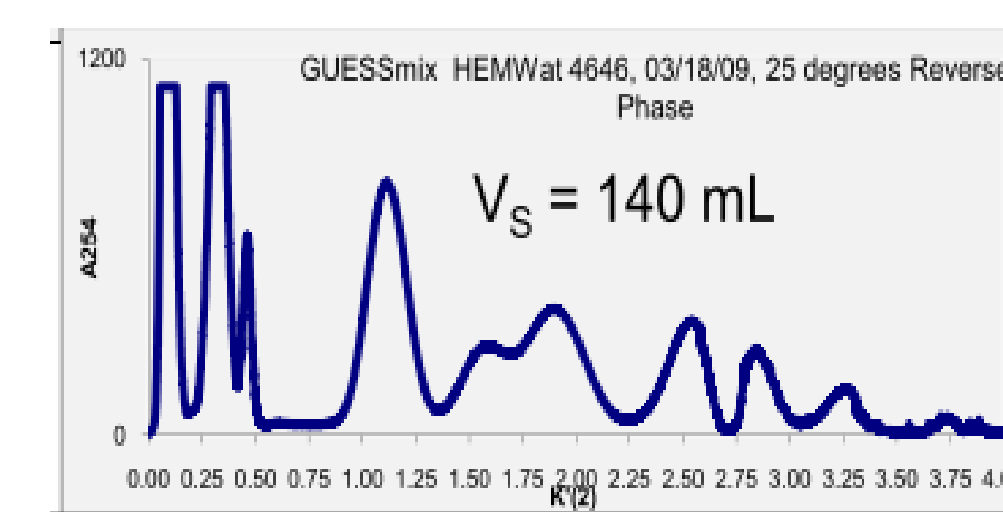
91% of orange essential oil  
non toxic (food flavouring)  
from food waste (70 000 tons per year)

CCC friendly

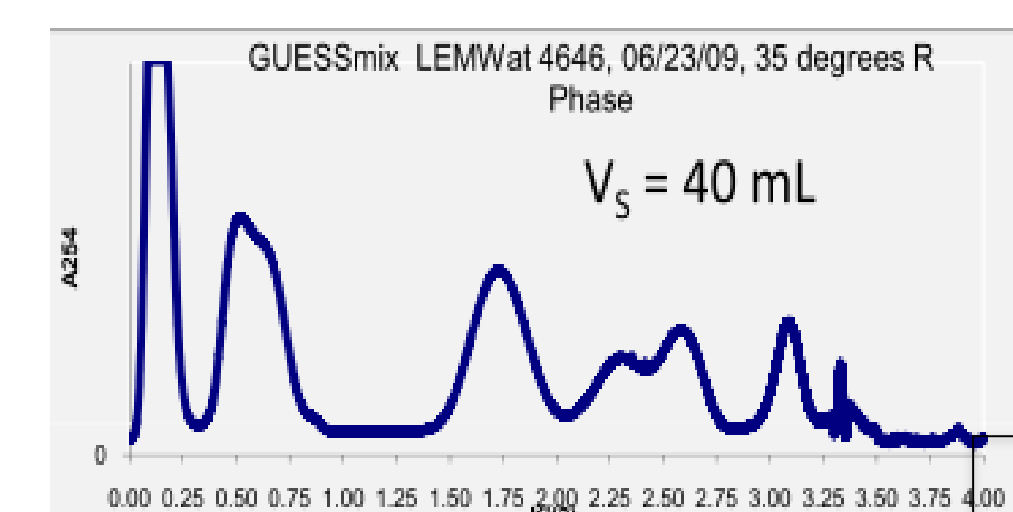
economic/environment friendly

### Preliminary results from Friesen

➤ N. Thompson and J. B. Friesen, Use of renewable solvents in the formulation of CCC separation systems, Communication 4-5, CCC 2010, Lyon, France



Heptane



Limonene

Vs is too low to allow separation

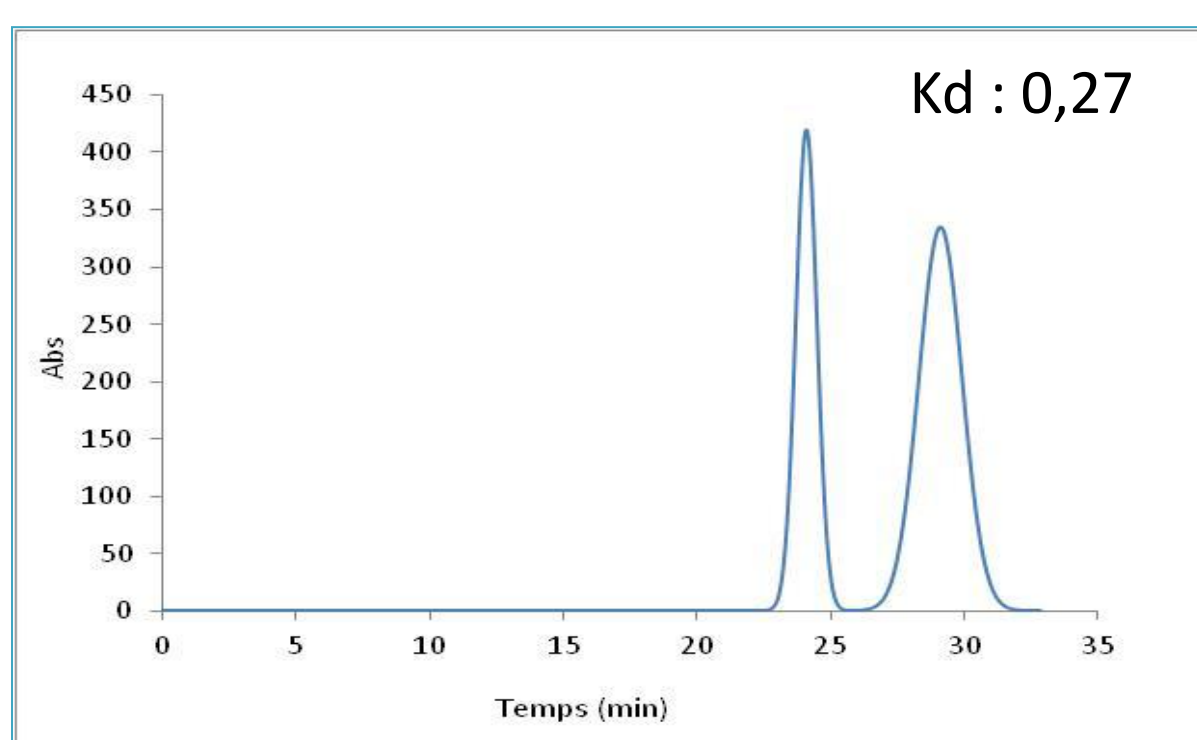
### Hydrostatic instruments

Total substitution: possible !!!

#### Heptane

Mode descendant  
2500 rpm 2ml.min-1

Sf : 69%

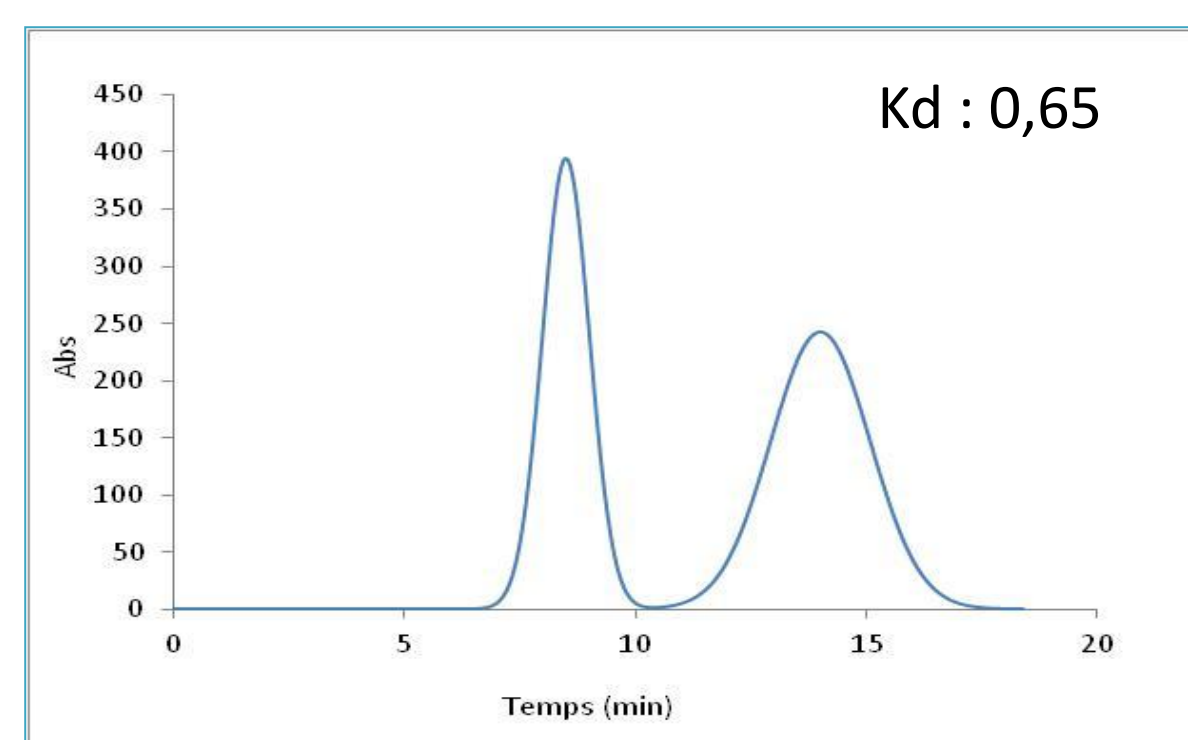


Rs : 1,72 P = 65 bars

#### Limonene

Mode ascendant  
2500 rpm 2ml.min-1

Sf=52%



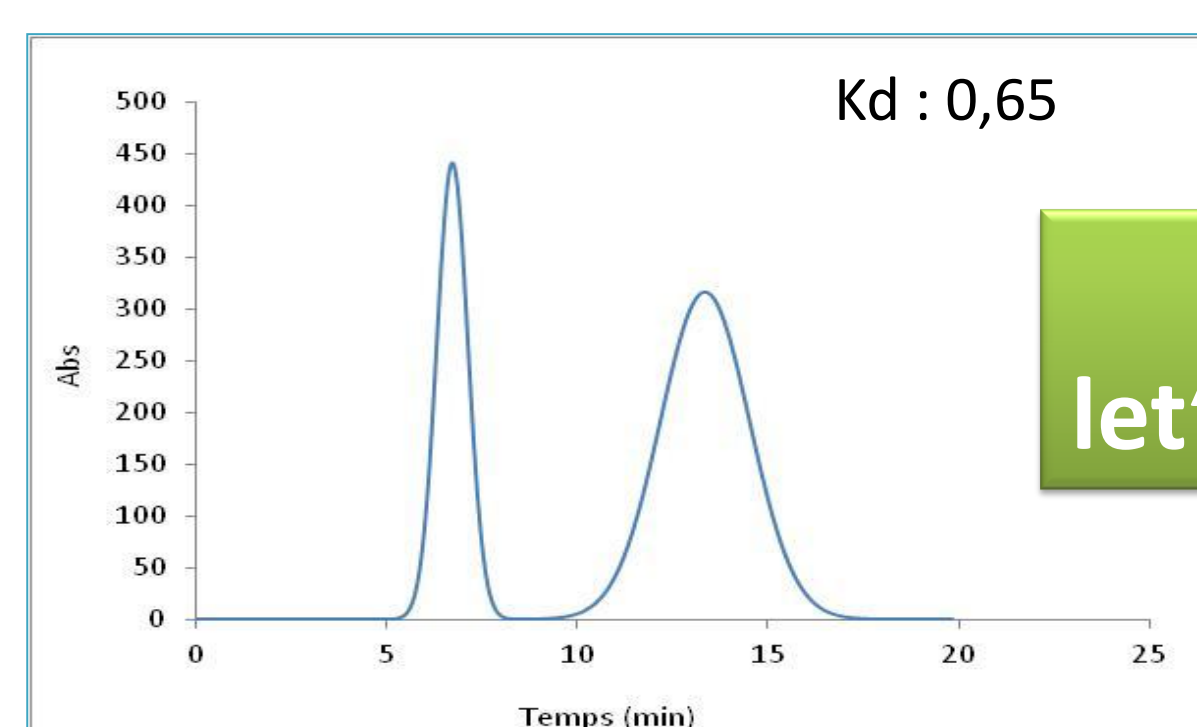
Rs : 1,84 P = 15 bars

better resolution because higher Kd

#### Limonene

Mode ascendant  
3000 rpm 2ml.min-1

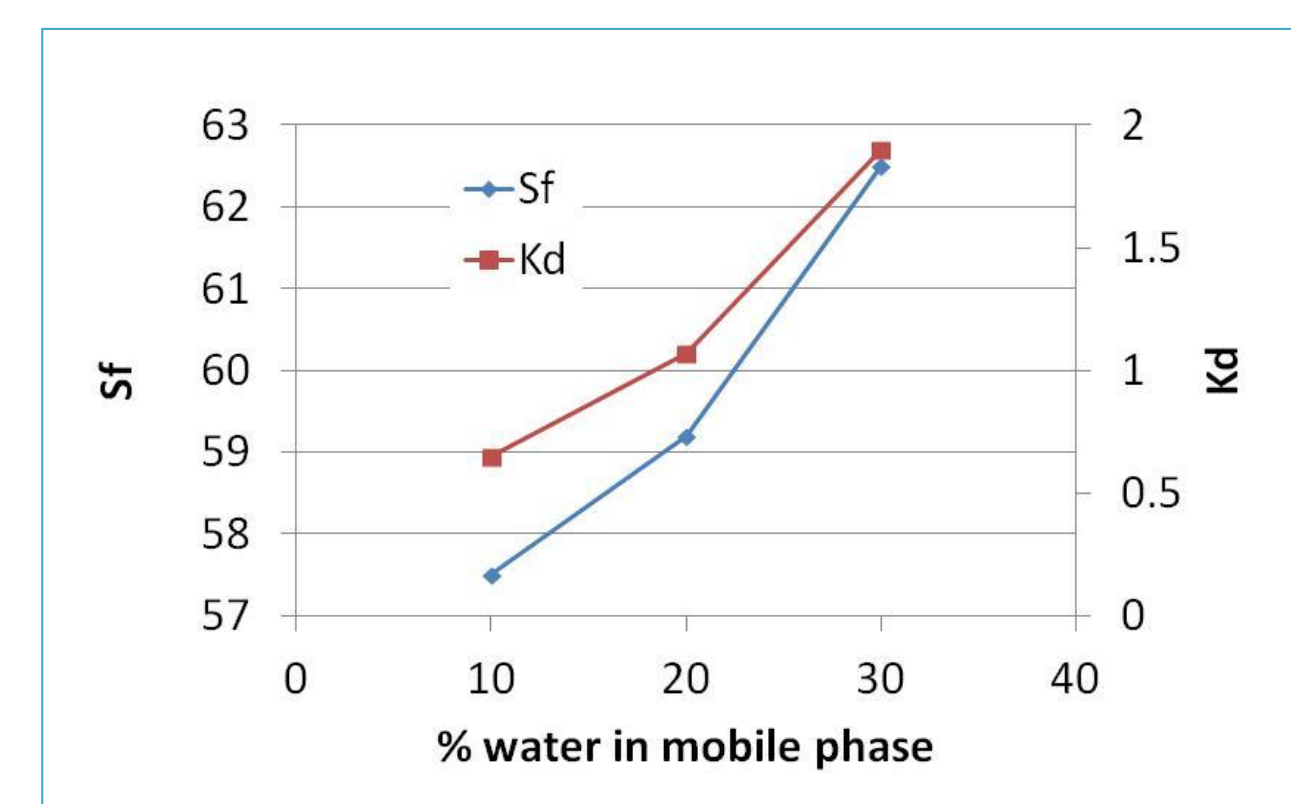
Sf=57%



Rs : 2.44 P = 17 bars

better resolution because higher Sf

modification of mobile phase (MeOH/water) ;  
100% limonene



no pressure:  
let's increase rpm !!!

not an issue  
in hydrostatic instruments

no pressure:  
we can modulate  
the retention !!!

better resolution because  
higher Kd and higher Sf

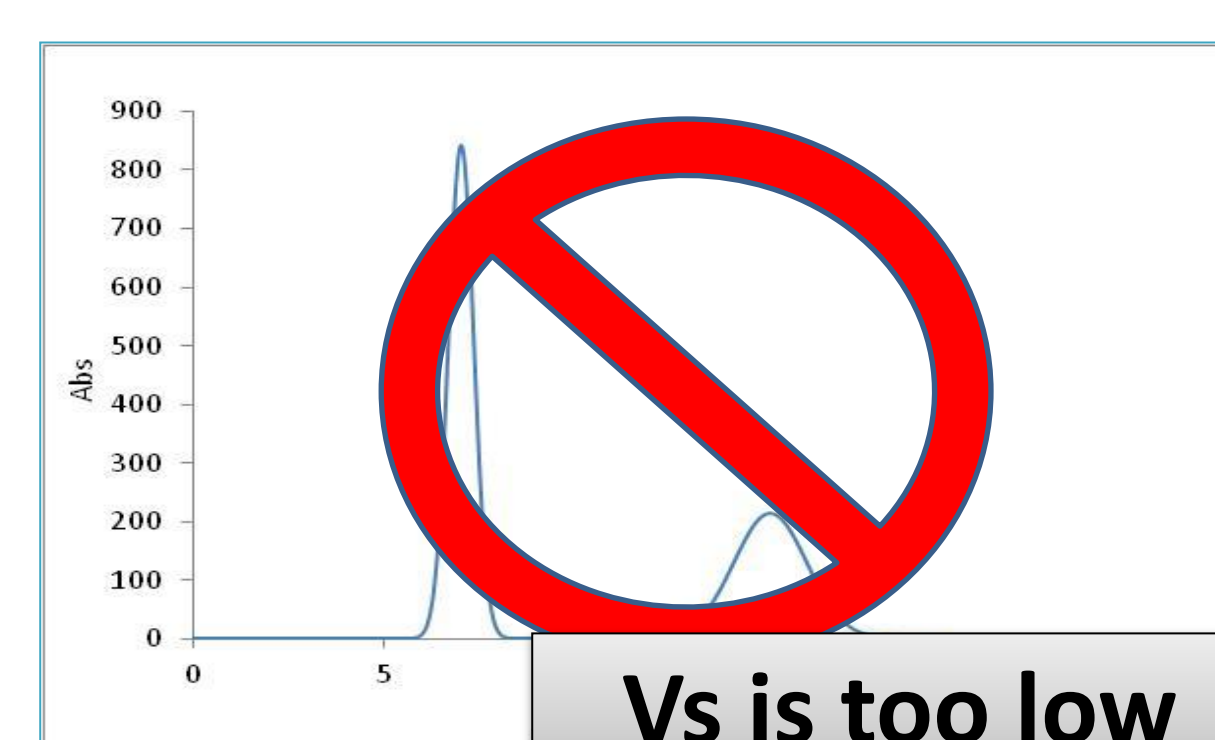
### Hydrodynamic instruments

Direct substitution  
not possible

#### Limonene

Mode ascendant  
1200 rpm 1ml.min-1

Sf=20%

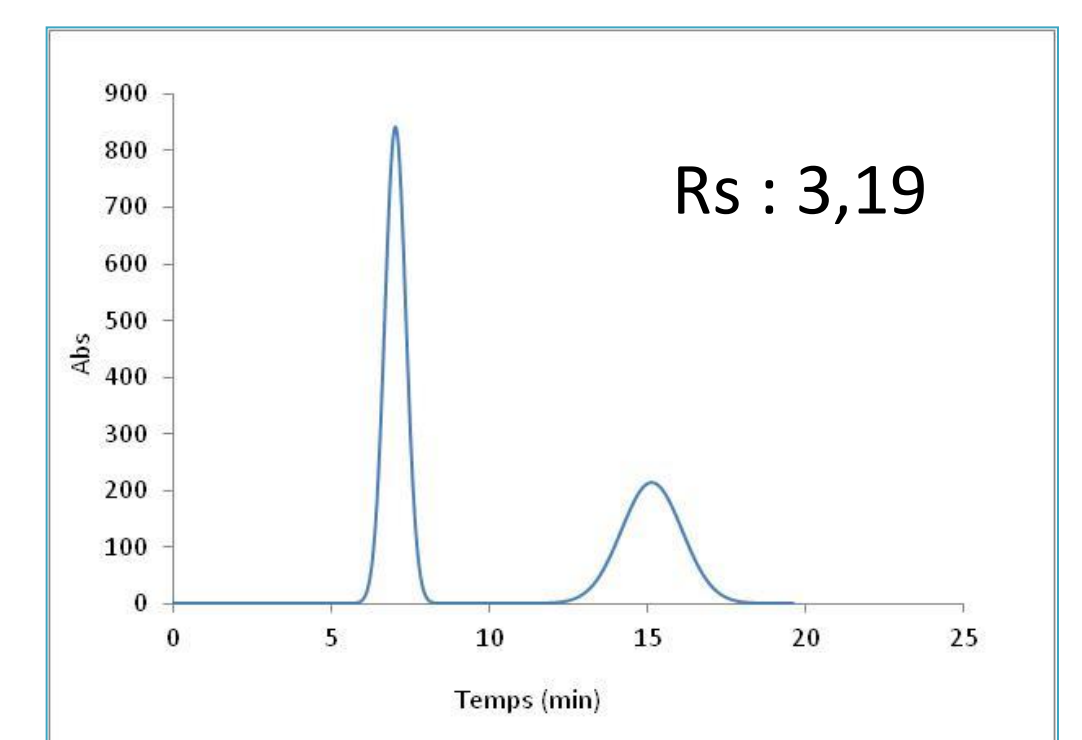


Vs is too low

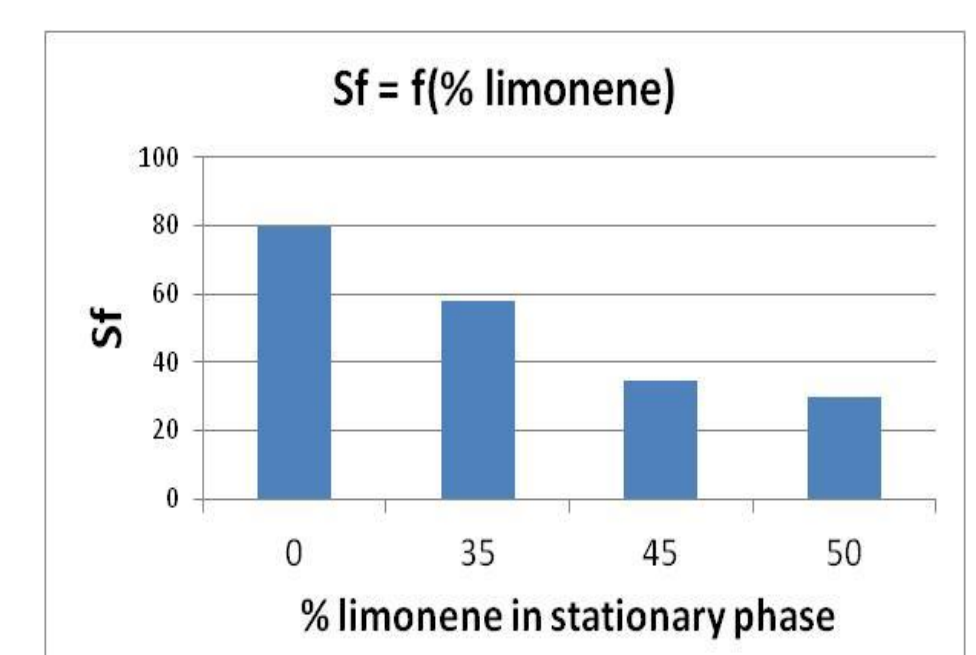
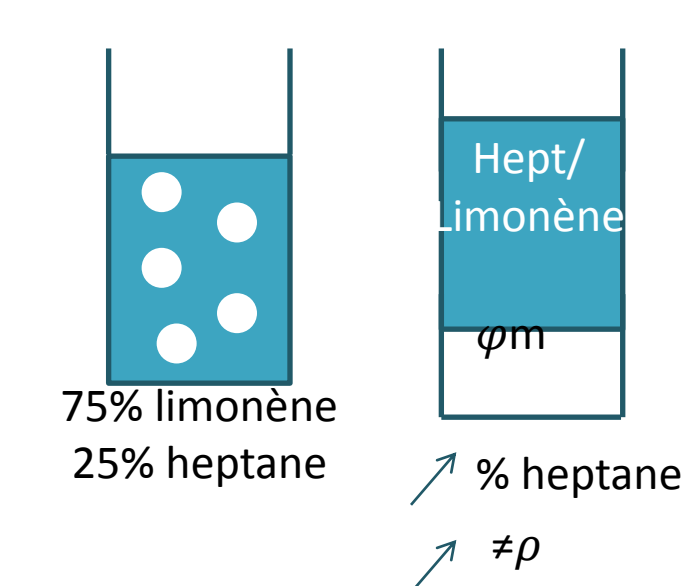
#### Heptane

Mode descendant  
1200 rpm 2ml.min-1

Sf : 80%



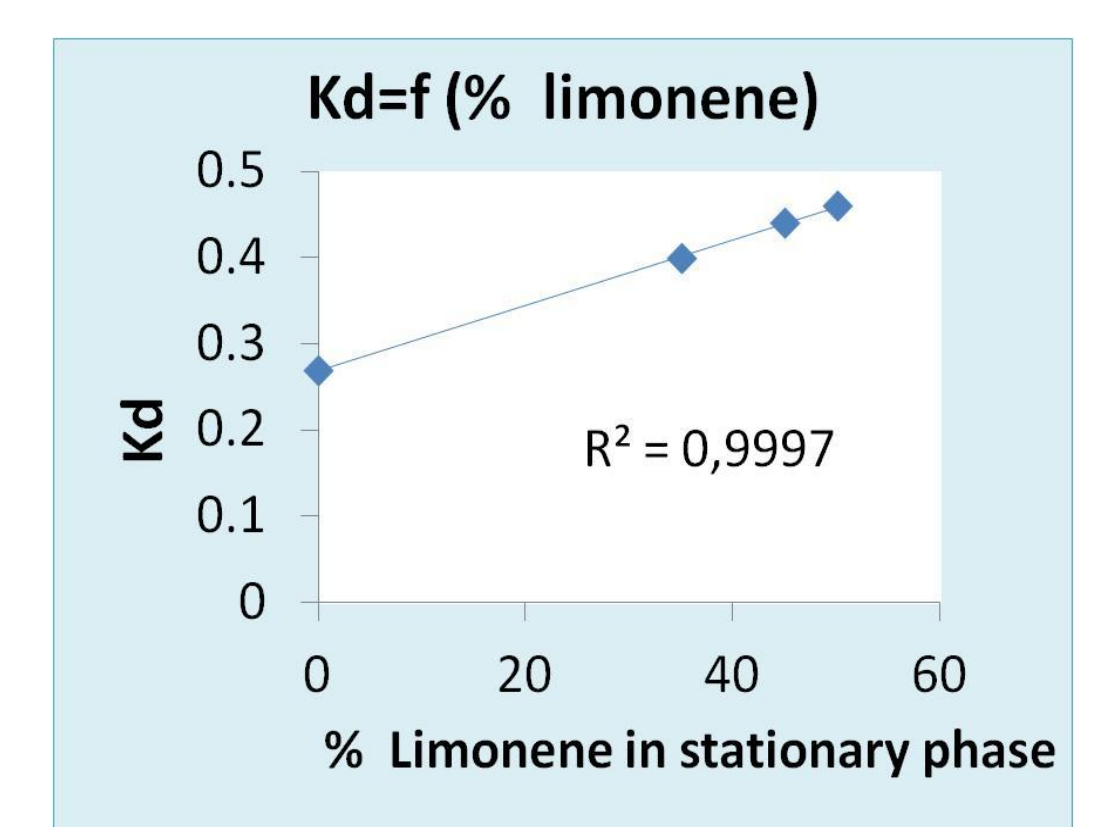
### Limonene as an adjuvant in heptane solvent



adding limonene  
= lower Sf

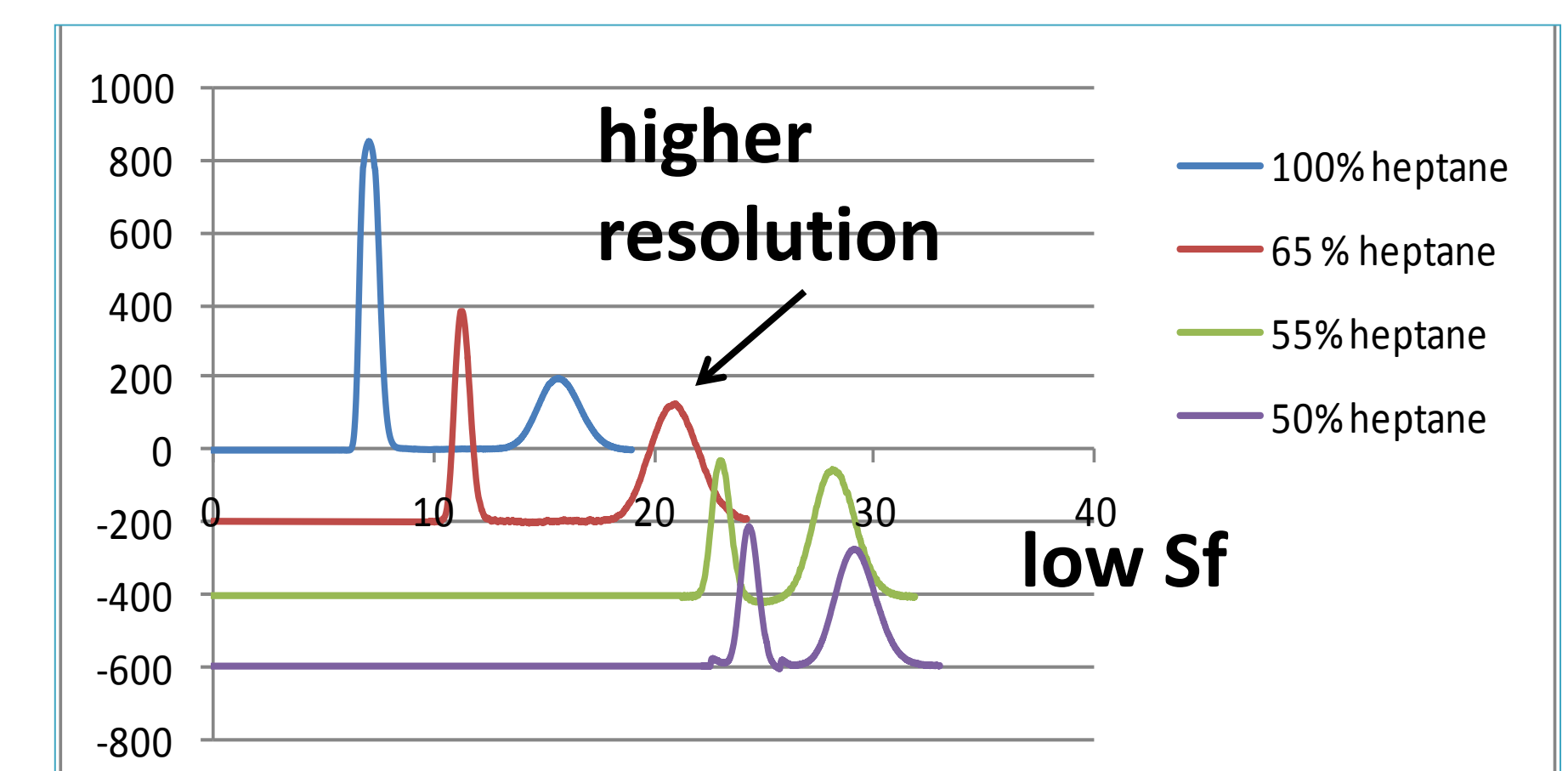
BUT

adding limonene  
= higher K



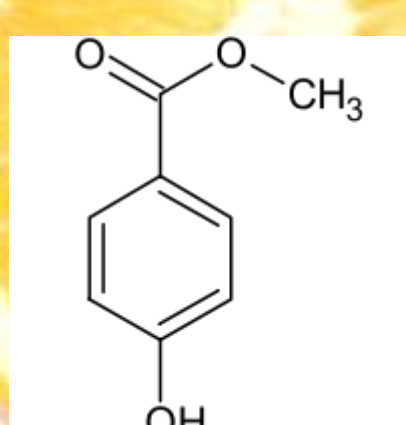
Density  
modification

optimal resolution  
when higher Kd  
and not too low Sf



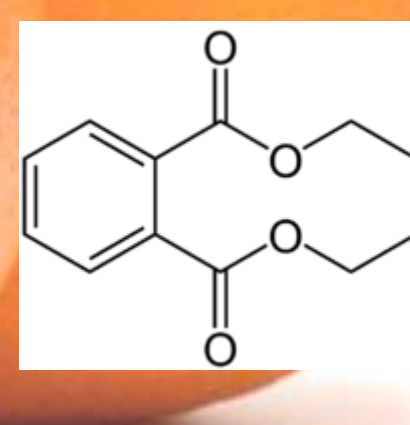
### Test description

Solutes : methylparaben (unretained) et diethylphthalate



Stationary Phase  $\phi_s$ : Heptane or limonene

Mobile Phase  $\phi_m$  : MeOH/water (90/10)



### Conclusion

- ❑ Limonene is much denser than heptane (lower apolar phase)
- ❑ Isodensity can be an issue with hydrodynamic columns
- ❑ Hydrostatic CCC columns are recommended
- ❑ Limonene can efficiently substitute heptane in some cases