

second international conference

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PACKED + COLUMN

Ultra High Performance/High Pressure Supercritical Fluid Chromatography On sub-2micron Particles Packed Columns

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2008
OCT 1-2

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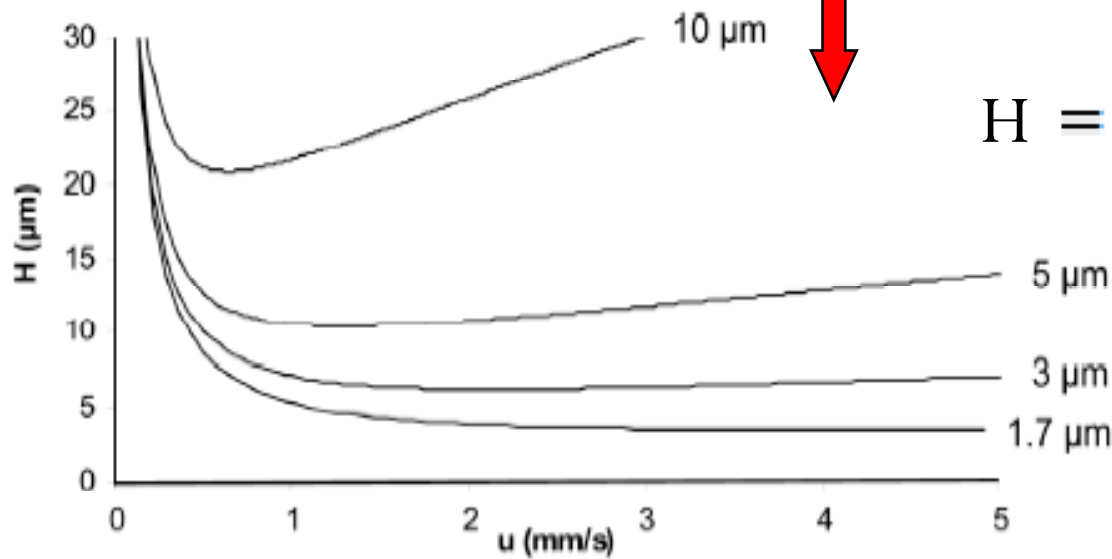
SMALL REMINDER

- **Carbon dioxide has a low viscosity**
 - **Fast separations** or extractions
 - **Low pressure drop in the column**
 - **Long packed columns**
- **Water free medium**
 - **Stability of stationary phases**
 - **Stability of analytes**
 - **Allows unusual conditions (**higher temperature**) vs LC or for extraction**



EFFICIENCY/SEPARATION SPEED vs DIAMETER OF PARTICLES **UHPSEC???**

$$N = \frac{L}{hd_p} \quad u = \frac{vD_m}{d_p} \quad u_{opt} = \frac{D_m}{d_p} \sqrt{\frac{B}{C}}$$



$$H = Ad_p + \frac{BD_m}{u} + \frac{Cd_p^2u}{D_m}$$



MAIN DRAWBACK: COLUMN PRESSURE DROP

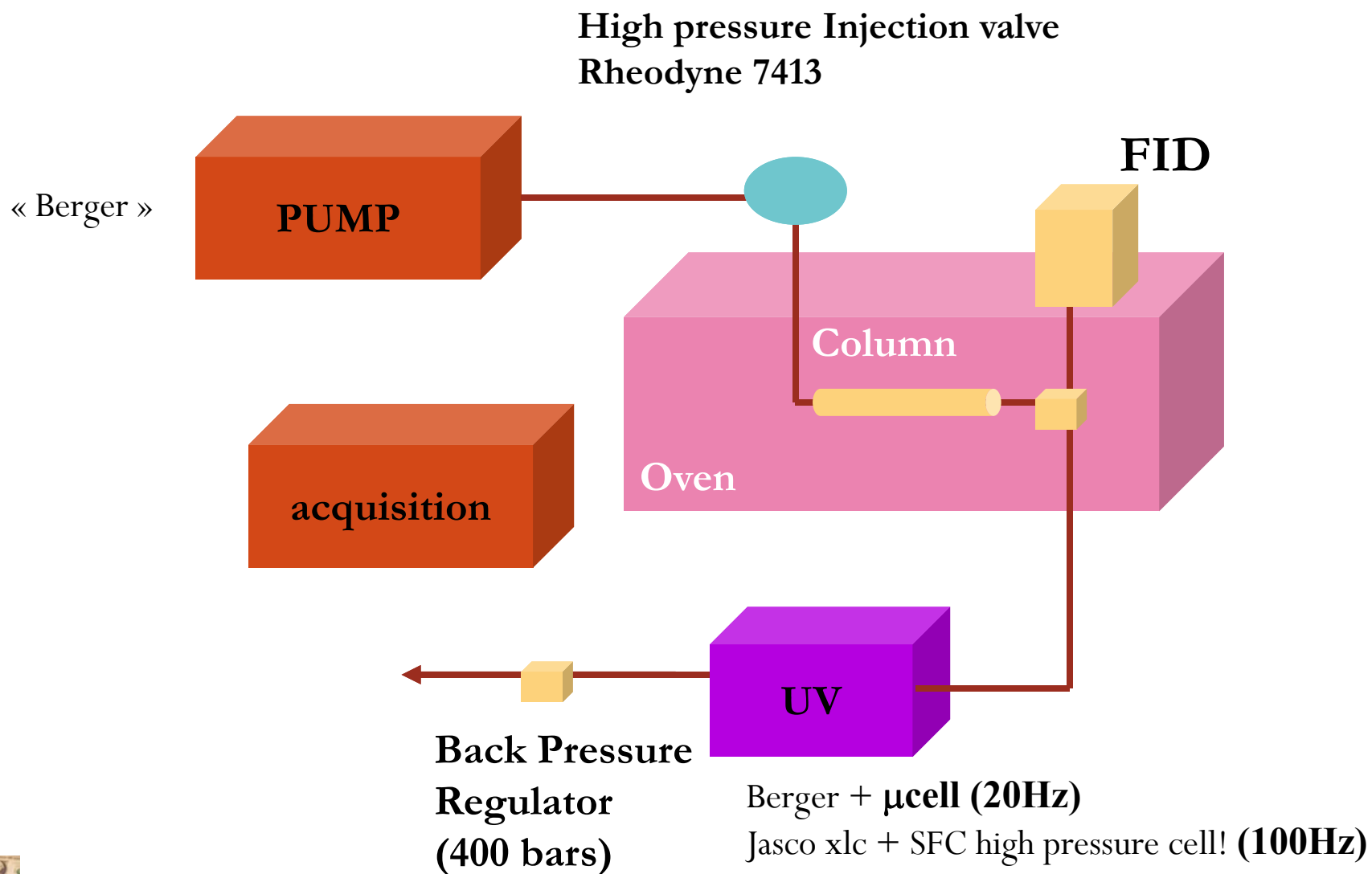
•Darcy' Law

$$\Delta P = \frac{uL\eta\phi}{d_p^2}$$

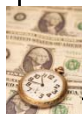
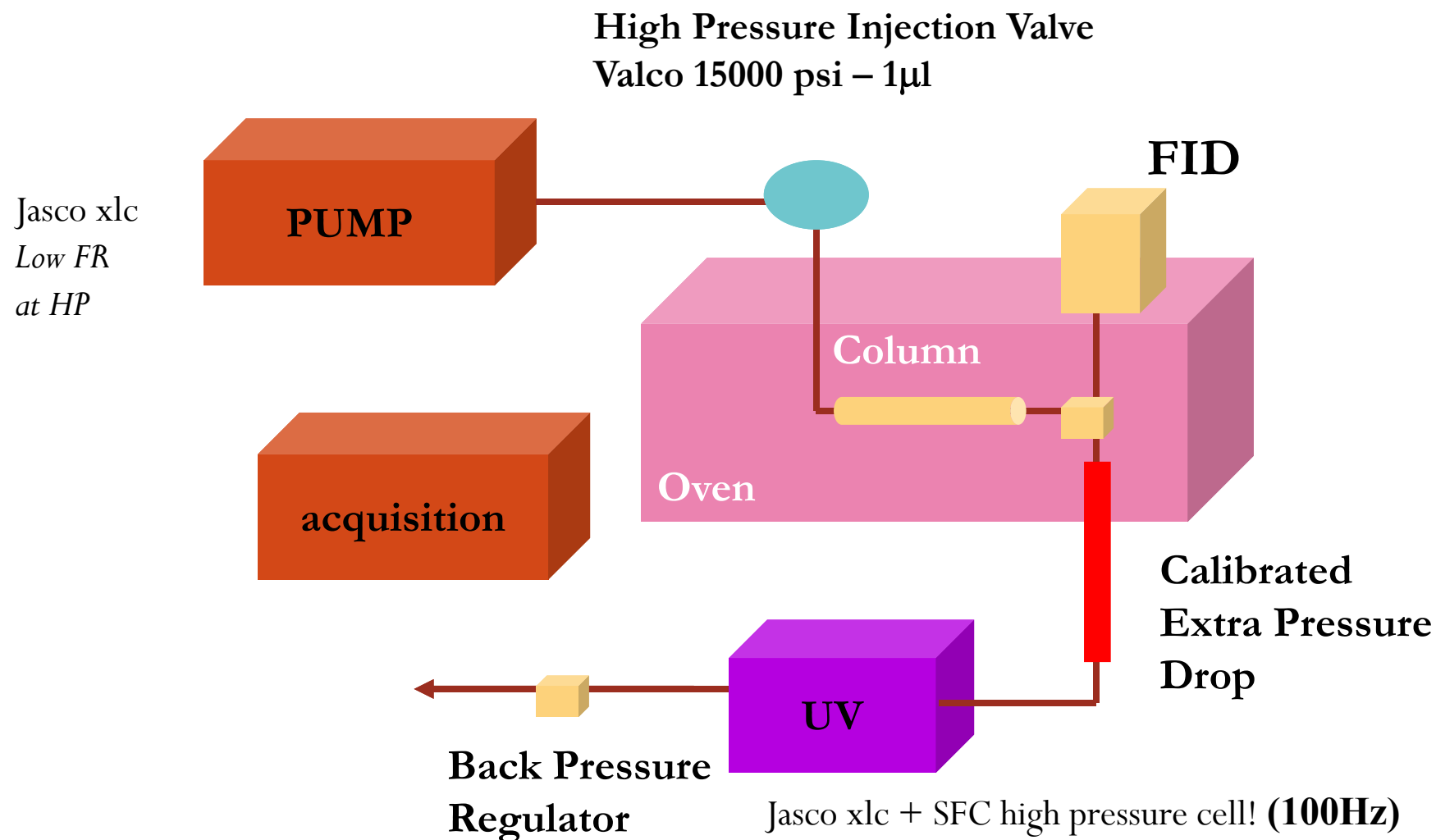
- Pressure drop in UHPSFC should be lower than in UHPLC
- Pressure drop in SFC = density gradient
- $\Delta\rho$ in the column must be lower than 0.1 g/cm^3



« REGULAR » APPARATUS

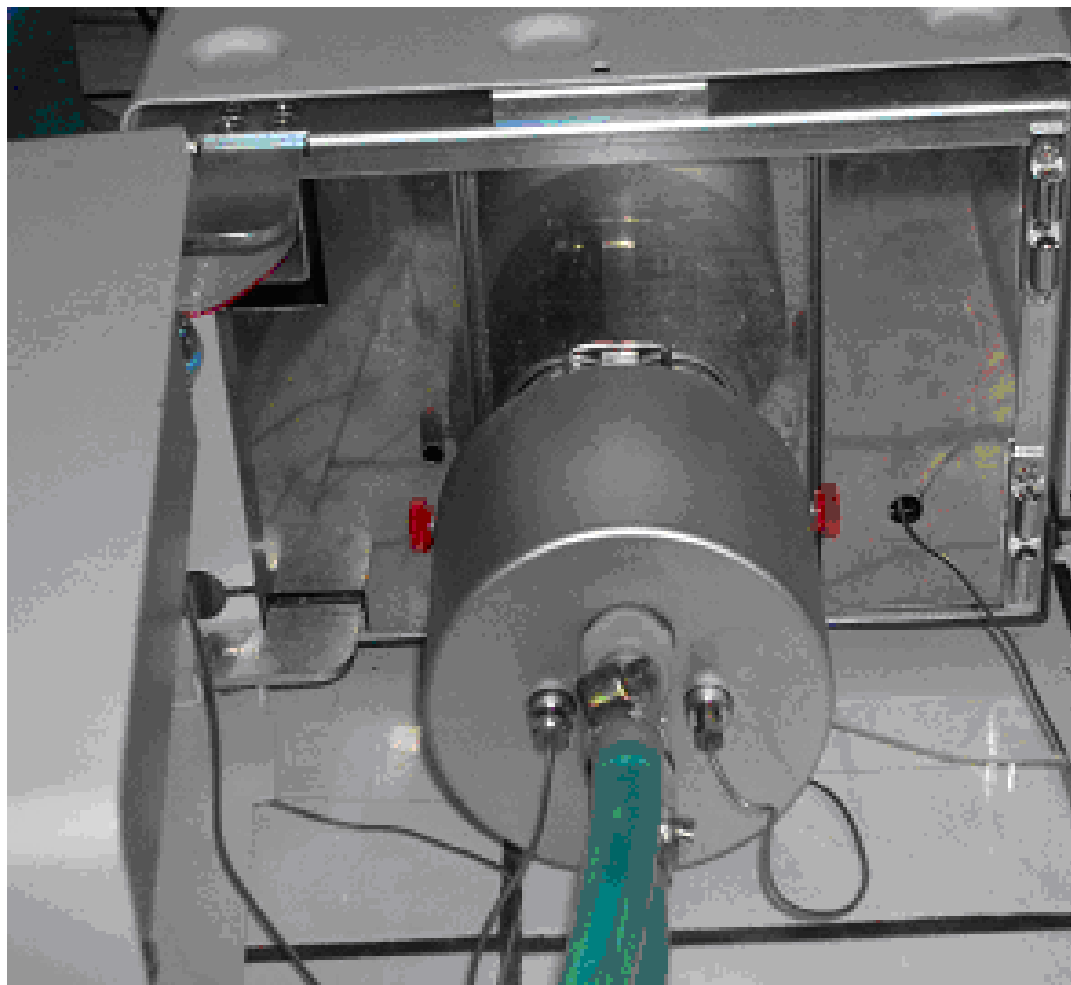


HIGH PRESSURE SFC APPARATUS

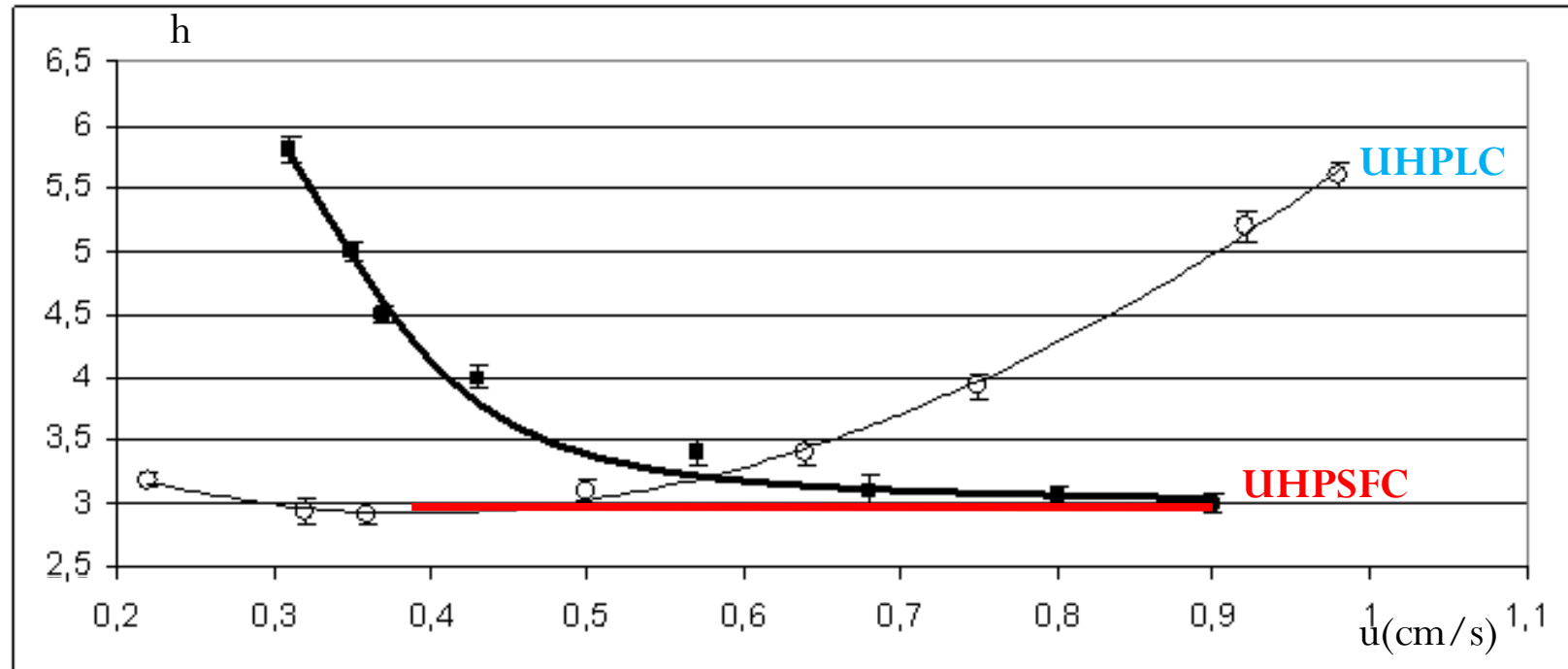


HIGH PRESSURE SFC PUMP

Jasco SFC cooling device was mounted on the xlc series pump head:
Piston seal and check valves were « adapted »



COMPARISON LIQUID/SUPERCritical

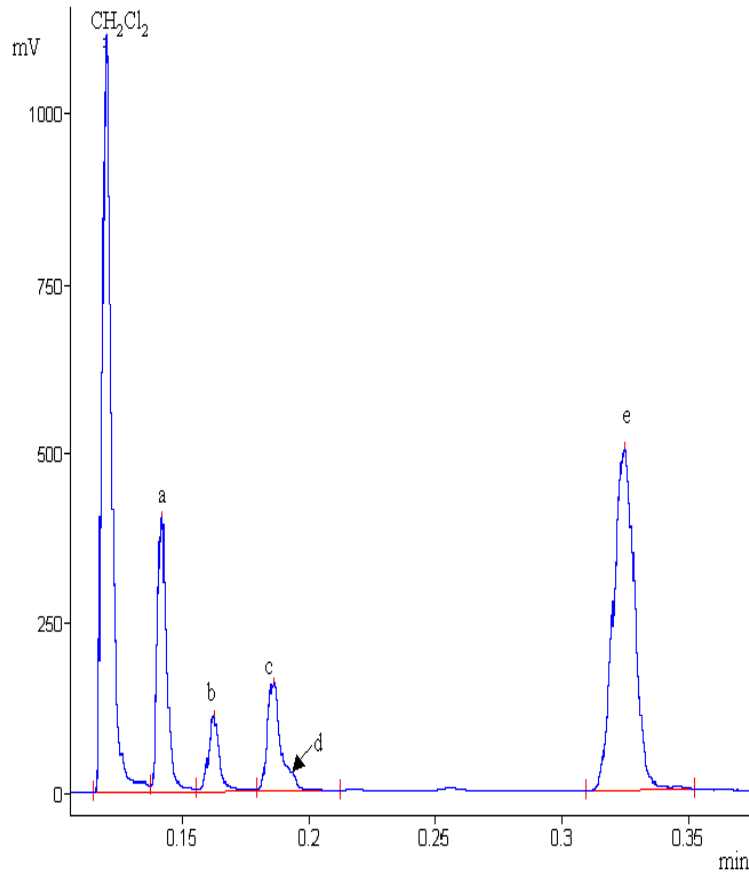


Nucleodur Gravity 10 cm x 0.3cm, 1.8 μ m LC : WATER/ACN 40/60 v/v, T=40°C λ =205nm;
SFC : P=200bars, T=50°C, anthracene

SAME h - DIFFERENT u_{opt}



VERY FAST SEPARATIONS



(a) naphthalene, (b) dodécylbenzene,
(c) octahydroanthracene, (d) anthracene
(e) benzantracene

D = 5mL/min ; P = 150bars, ΔP: 250 bars

column Nucleodur Gravity 5cm x 0.3cm, 1.8μm ; UV 205nm

D = 5mL/min

t₀ = 0.12 min ; u = 7mm/s

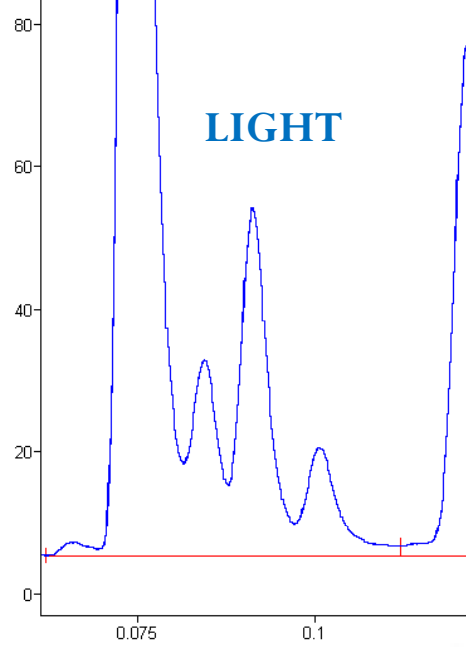
t_e = 0.32 min = 19 seconds

Pressure drop : 230 bars

peak Capacity : 22

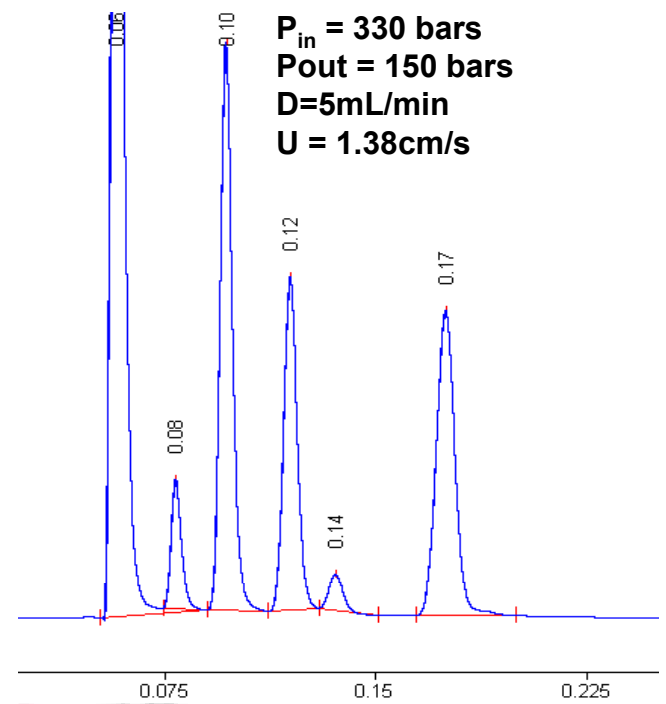
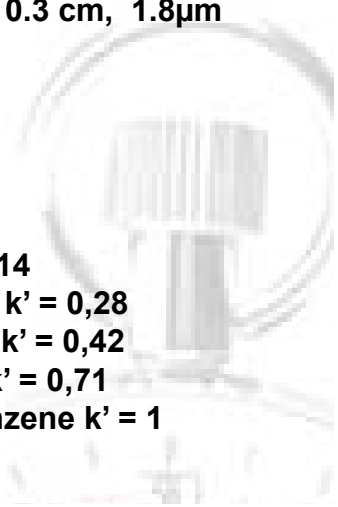
$$n_c = \frac{\sqrt{N}}{4} \ln(1 + k'_e) + 1$$





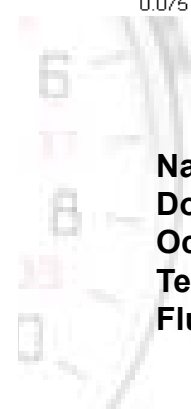
Nucleodur 5cm x 0.3 cm, 1.8 μ m
P_{in} = 215 bars
P_{out} = 80 bars
D=5mL/min
u= 1.19cm/s

Toluene k' = 0,14
Propylbenzene k' = 0,28
Pentylbenzene k' = 0,42
Octylbenzene k' = 0,71
Hexamethylbenzene k' = 1



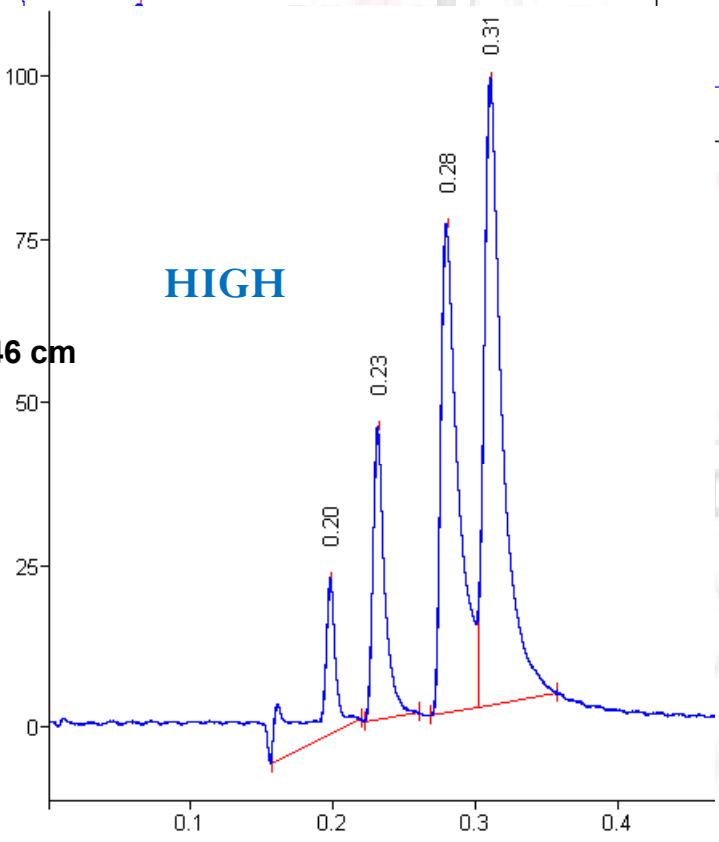
P_{in} = 330 bars
P_{out} = 150 bars
D=5mL/min
U = 1.38cm/s

Naphthalene k'=0.33
Dodecylbenzene k'=0.66
Octahydroanthracene k'=1
Tert Butyl-2 anthracene k'= 1.33
Fluoranthene k'= 1.83



Sepax C₄ 5cm x 0.46 cm
1.9 μ m
P_E = 230 bars
P_S = 150 bars
D=5mL/min
u = 0.52 cm/s

Chrysene k' = 0.25
Benzantracene k' = 0.43
Dibenzanthracene k' = 0.75
Benzo(ghi)perylene k' = 0.93



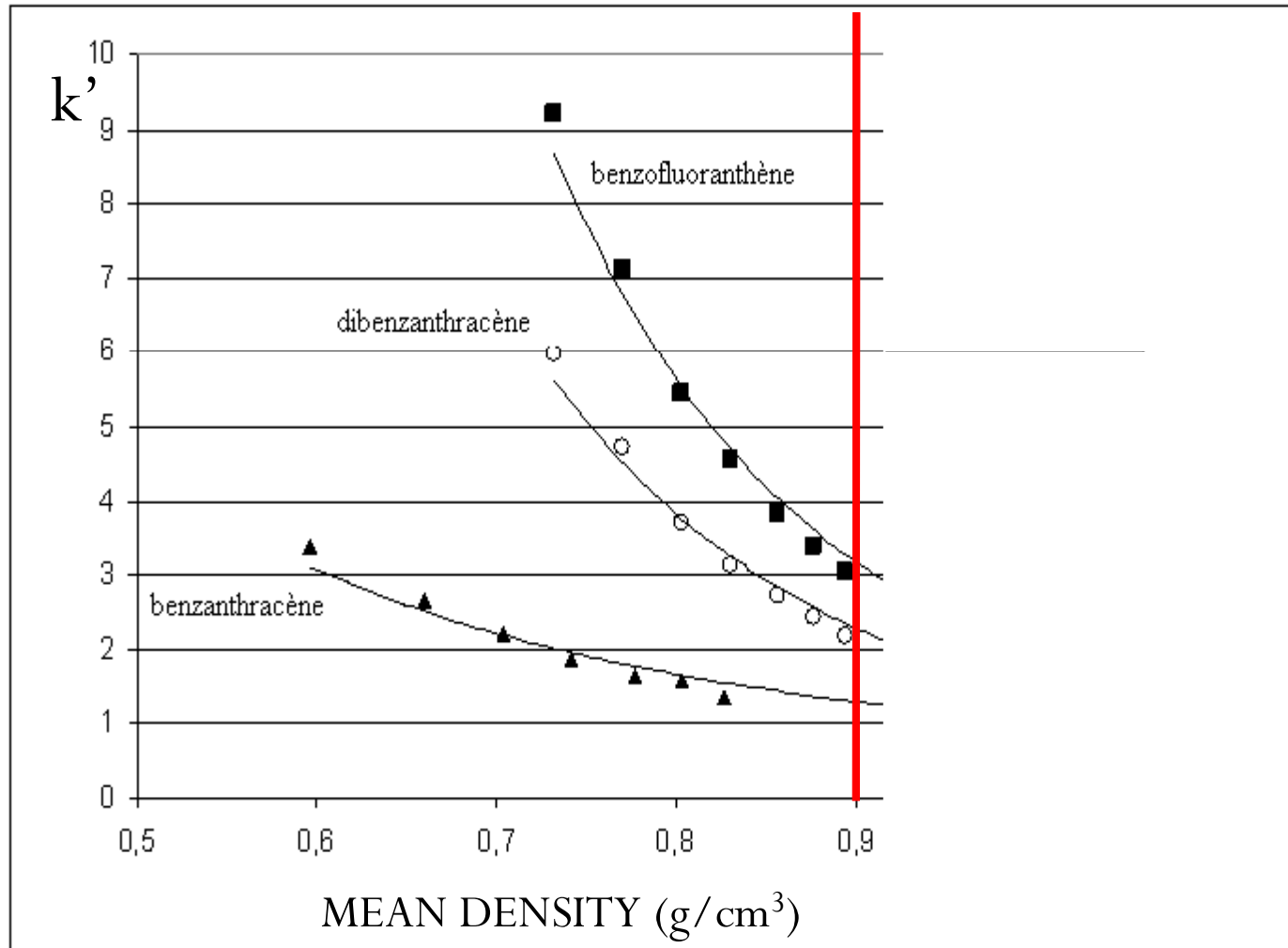
HIGH

MEDIUM

?? x UHPSFC
?: LC or SFC



HIGHER PRESSURES: WHAT FOR?

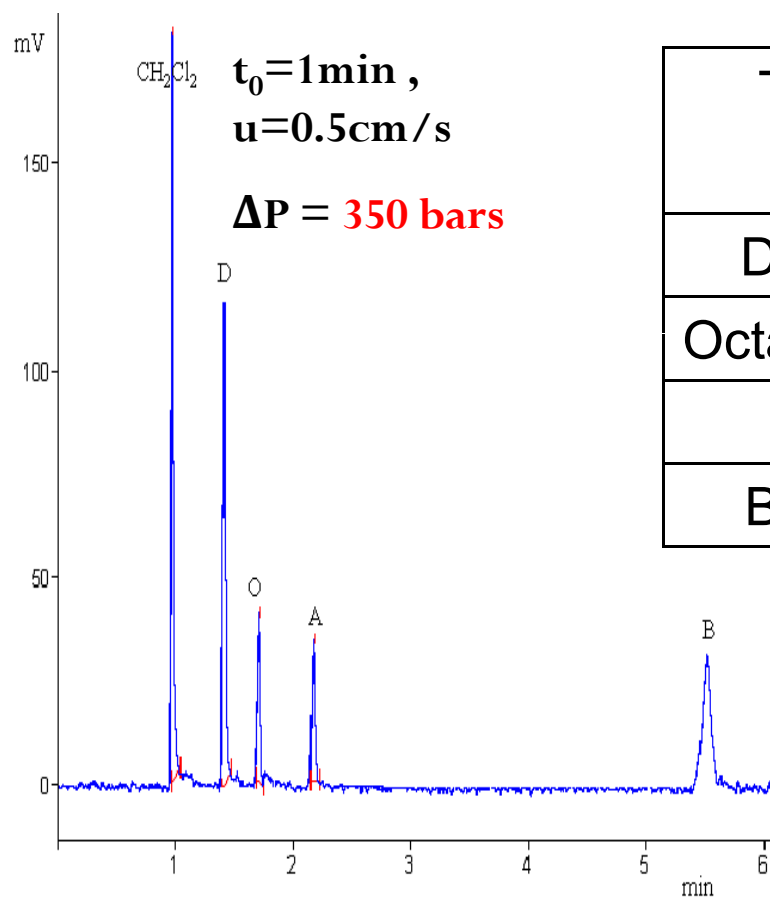


$\rho(\text{CO}_2) >$
 $\rho(\text{H}_2\text{O})!$

Nucleodur Gravity C_{18} 10cm x 0,3cm, 1,8 μm ; $D=1,3\text{mL/min}$; $T=100^\circ\text{C}$
Low ρ : restrictor= 50cm x 50 μm / high ρ : 15cmx25 μm



LONG COLUMNS: 3 x 10 cm



Test compound	tr (min)	k'	N	h
Dodecylbenzene	1,42	0,38	27662	6,1
Octahydroanthracene	1,72	0,8	22845	7,2
Anthracene	2,18	1,2	36038	4,6
Benzanthracene	5,54	4,5	33121	5,1

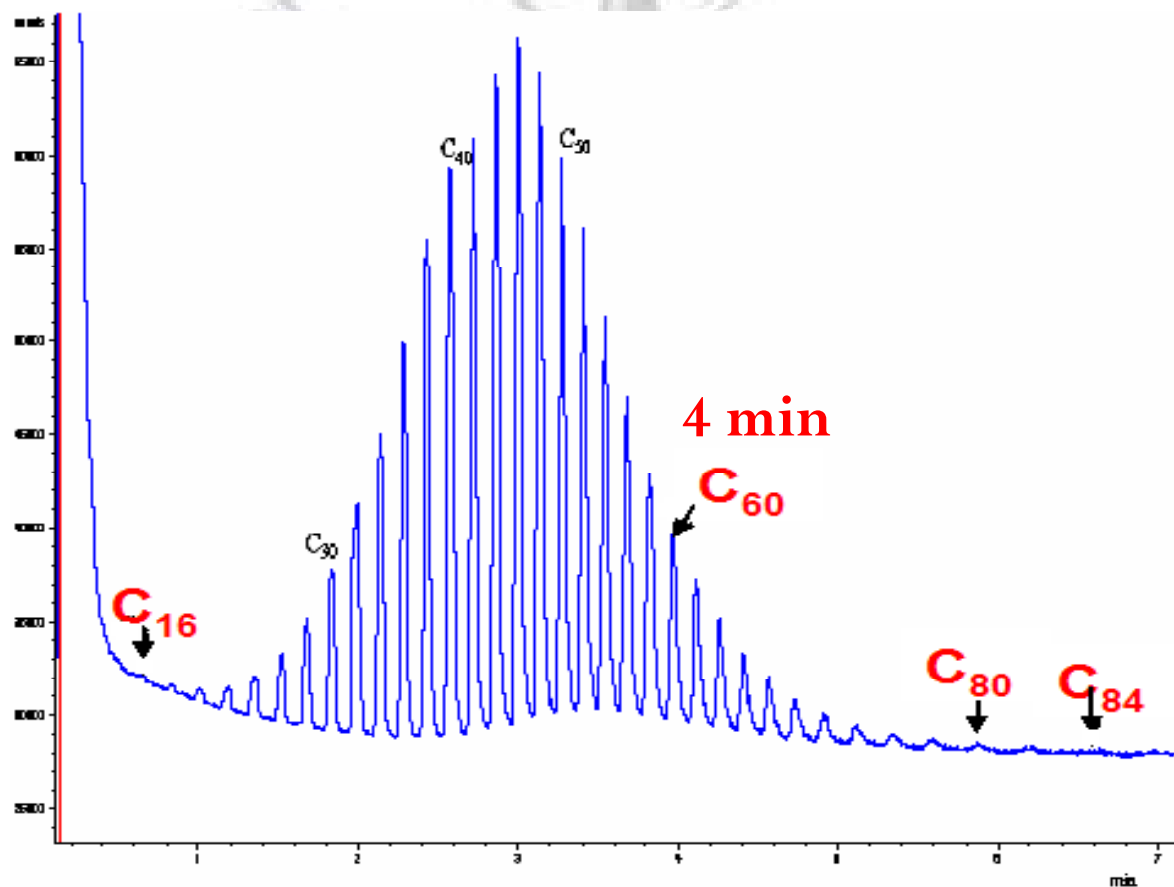


At least 12000 plates are missing
because each column could
deliver 16000 plates!



UHPSFC OF ALKANES

Polywax 655

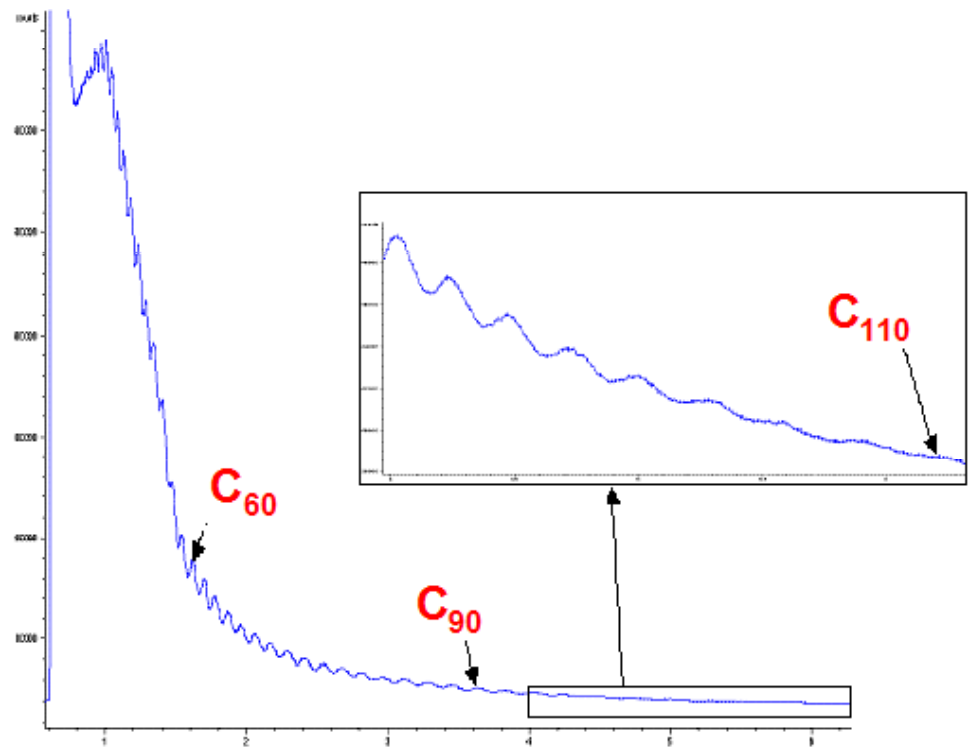
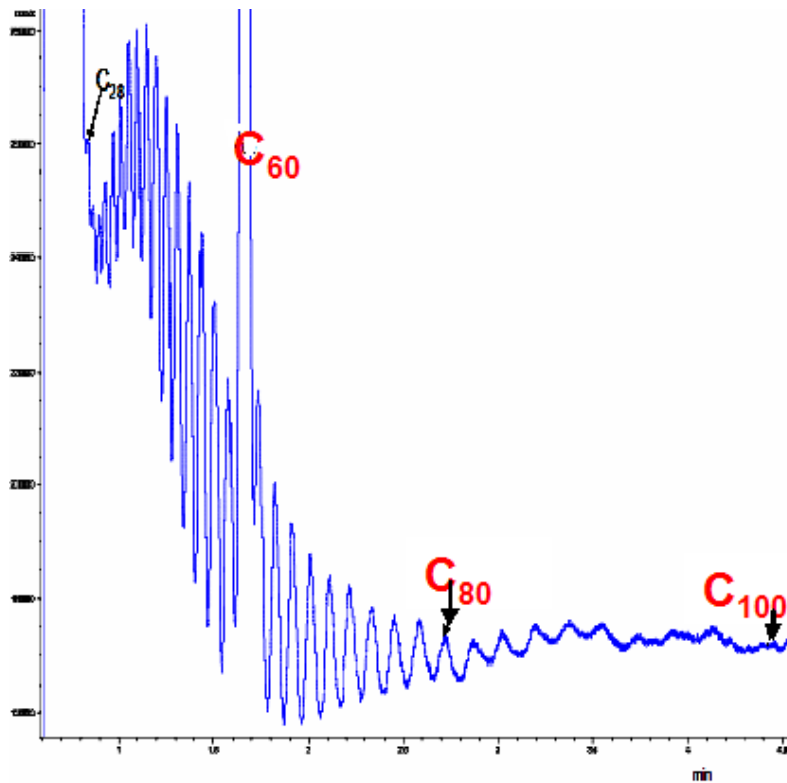


D = 2mL/min, T = 100°C ; pressure gradient from 80 bars to 300 bars at 99 bars/min
column Nucleodur Gravity 5cm x 0.3cm, 1.8µm ; FID



UHPRESSURESFC

POLYWAX 655+1000 → $P_{\max} = 750$ bars



D = 1,3mL/min, T_{oven} = 100°C – linear pressure gradient from 100 bars to 400 bars (100 bars per minute)

Nucleodur Gravity 5cm x 0.3cm, 1.8 μ m ; FID Restrictor : 10cm x 25 μ m



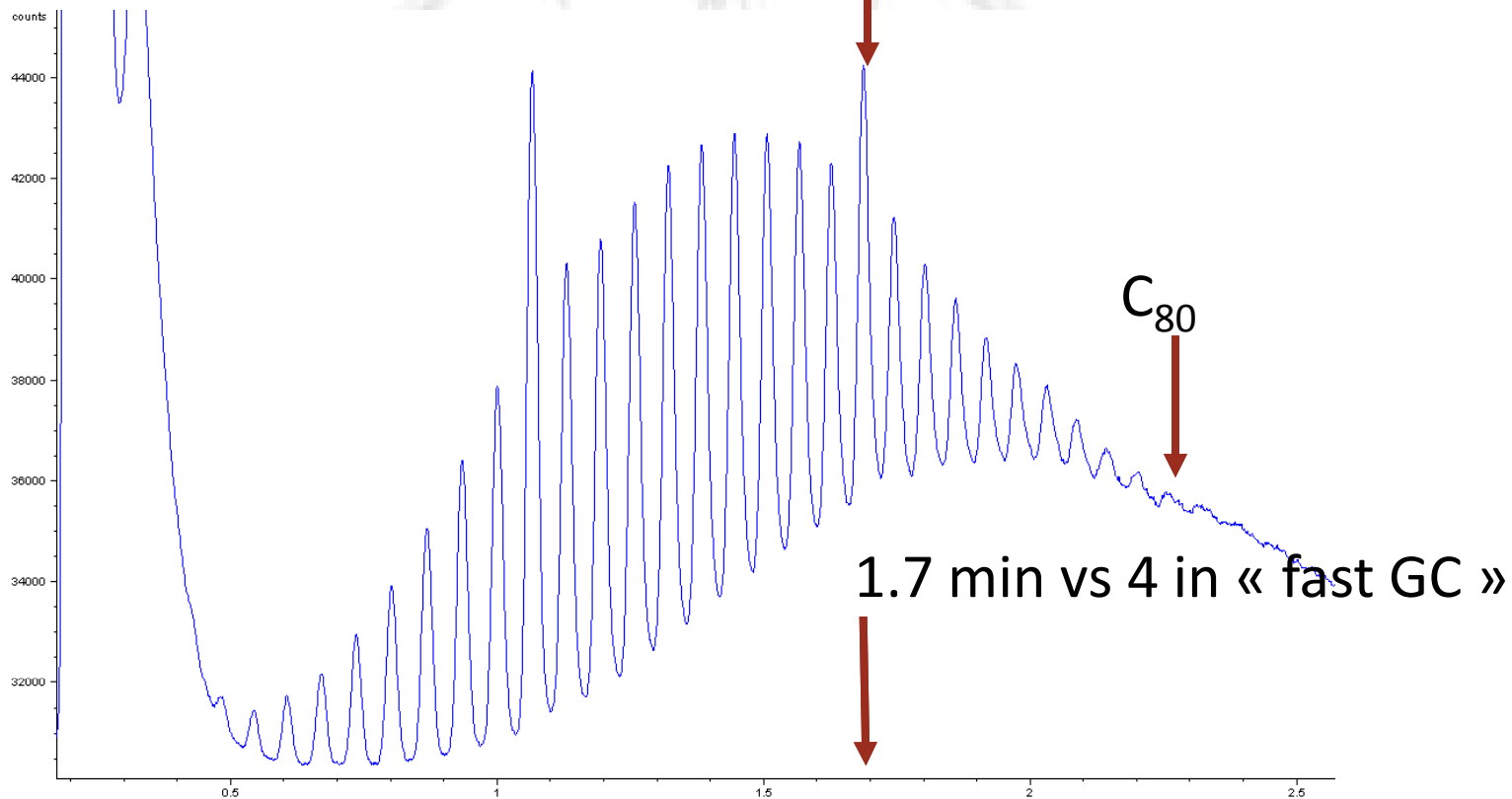
UHPSFC = ULTRAFAST SFC

$D = 2.5 \text{ mL/min}$,

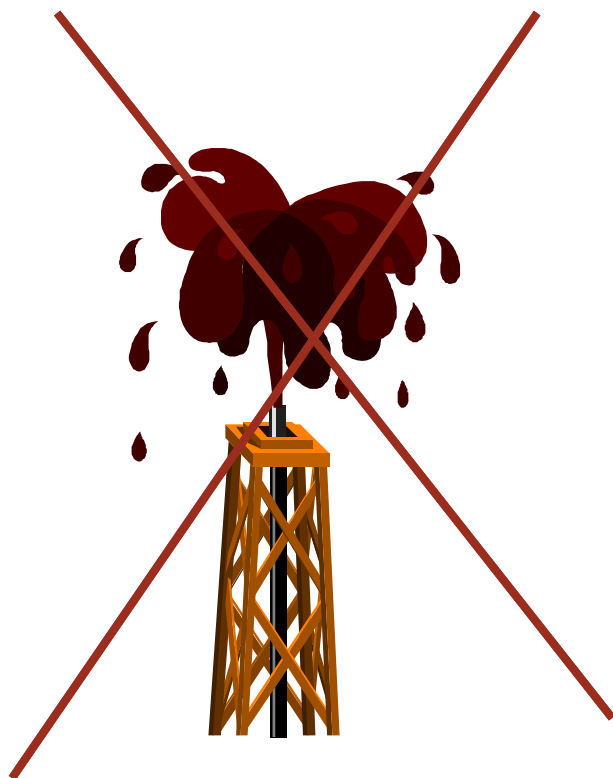
$T_{\text{oven}} = 100^\circ\text{C}$

Pressure gradient : 80 to 370 bars (99 bars/min) C_{60}

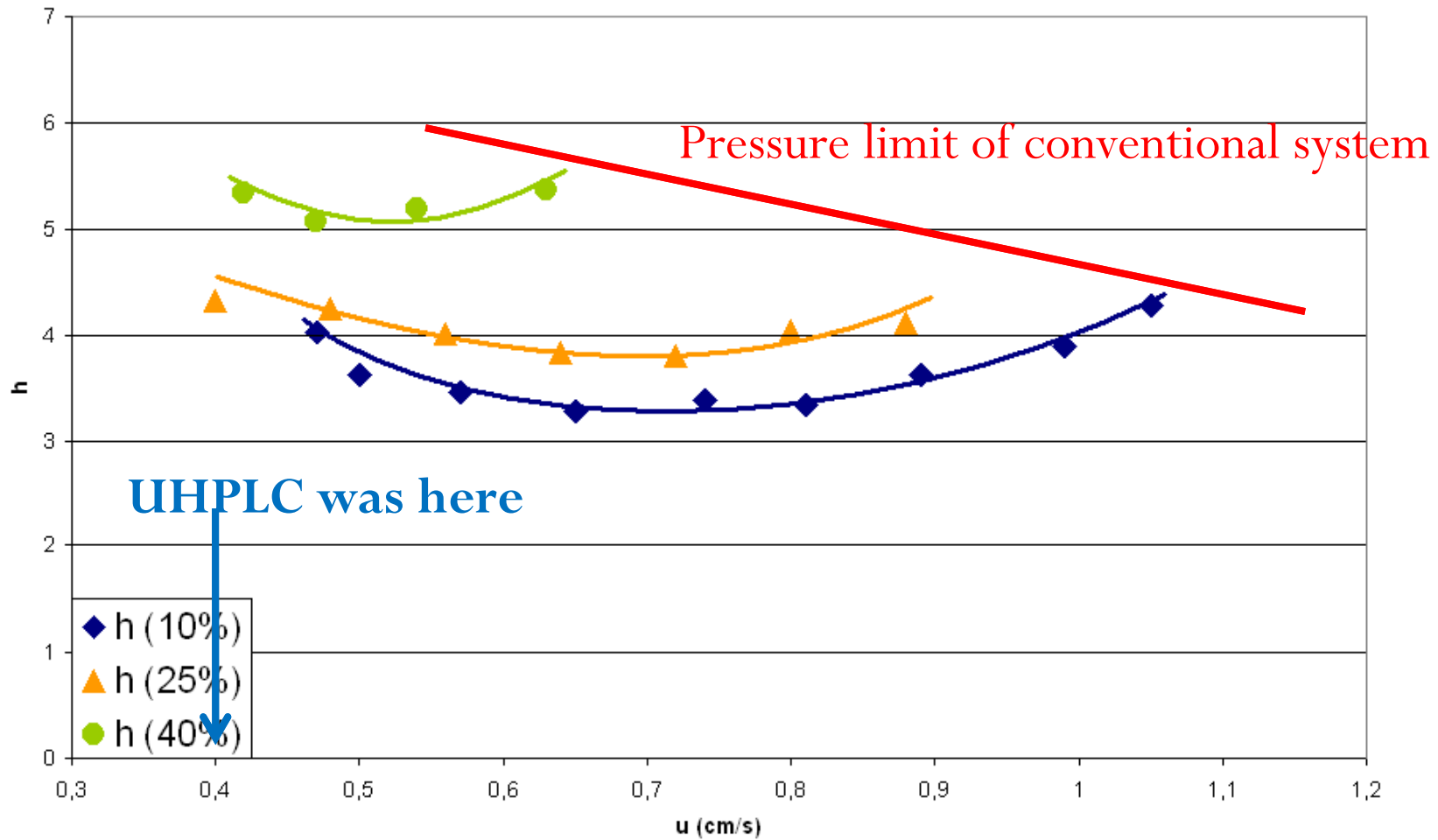
Column Sepax C_4 5cm x 0.46cm, $1.9\mu\text{m}$; FID



WHAT ABOUT MORE POLAR COMPOUNDS?



KNOX CURVES vs POLAR MODIFIERS



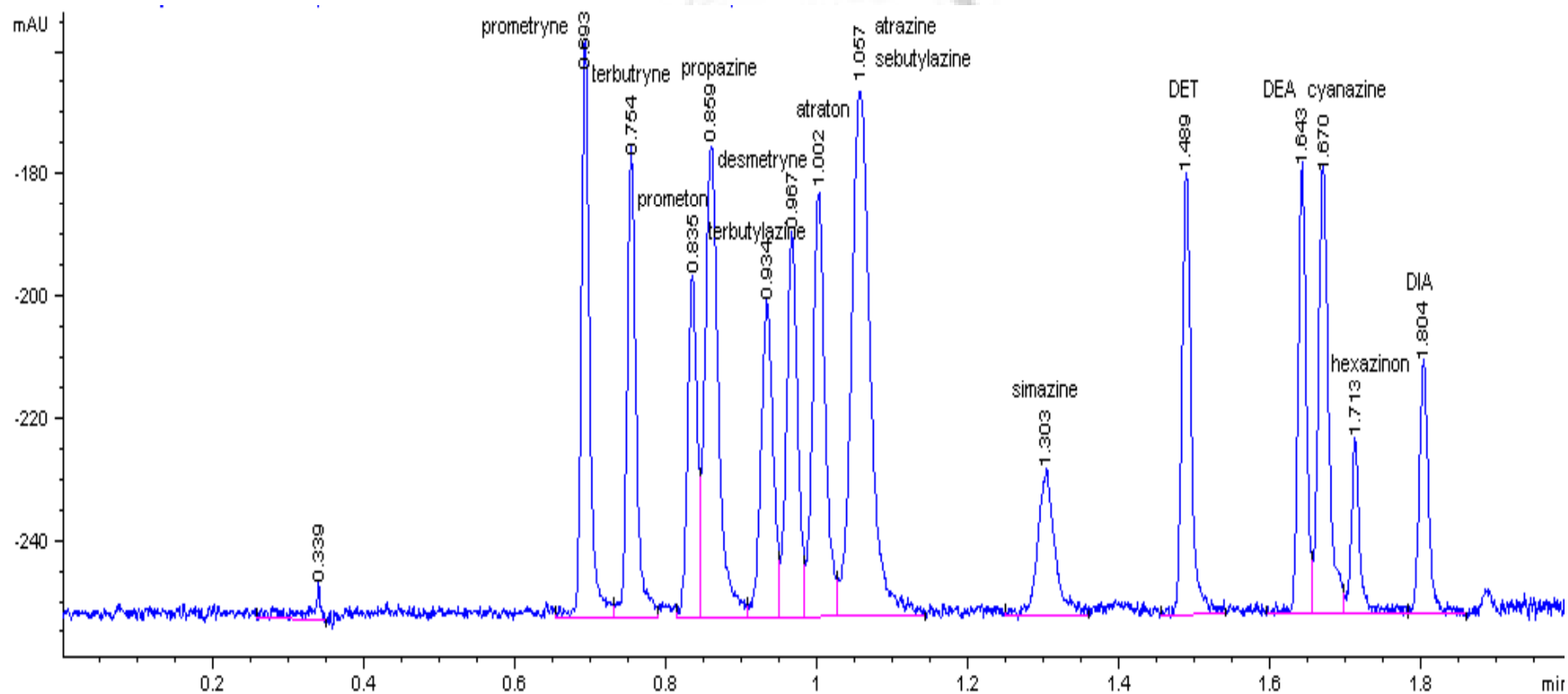
P=150bars, T=50°C

Column Nucleodur Gravity 100 x 3 mm, 1,8µm

Test Compound : dibenzanthracene



UHPSFC OF PESTICIDES

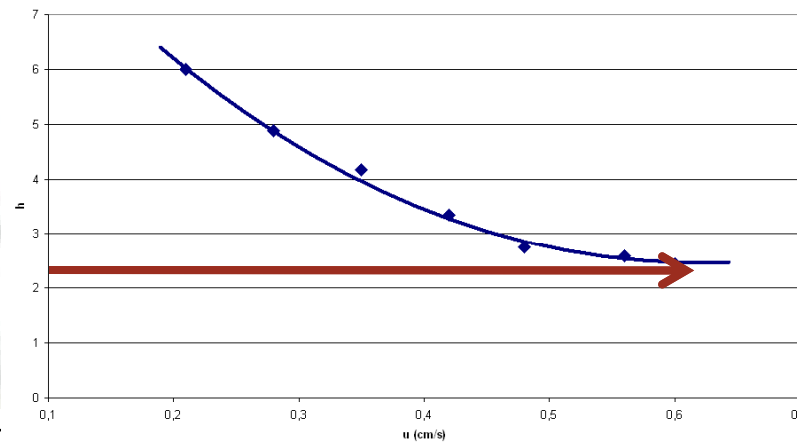


Column Sepax HP-Amino 100 x 4.6 mm 1.8 μ m

P = 150 bars, T = 50°C, D = 4 mL.min⁻¹

Methanol : 3% during 15 s then 10% per min to 15%

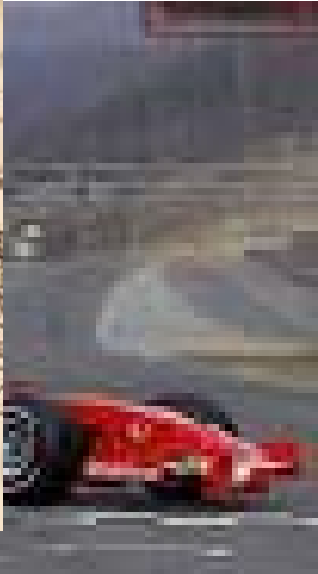
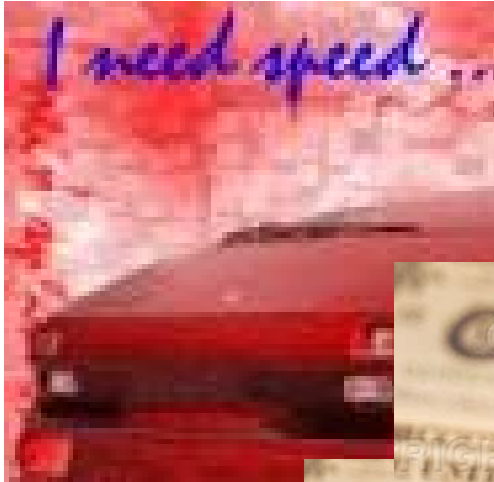
$h=2.3$



CONCLUSION

- UHPSFC IS DEMONSTRATED
- REGULAR SYSTEMS CAN BE USED
- POLAR MODIFIERS CAN BE USED
- UHPSFC SUITS FOR COMPREHENSIVE SYSTEMS
- HIGHER PRESSURES TO BE INVESTIGATED
- 3 mm ID COLUMNS BETTER SUIT FOR HIGH FLOW RATES
- LONG COLUMNS?
- CHIRAL PHASES?
- HIGH PRESSURE: MICROCELLS AND REGULATORS?





THANK YOU FOR YOUR ATTENTION



ACKNOWLEDGMENTS

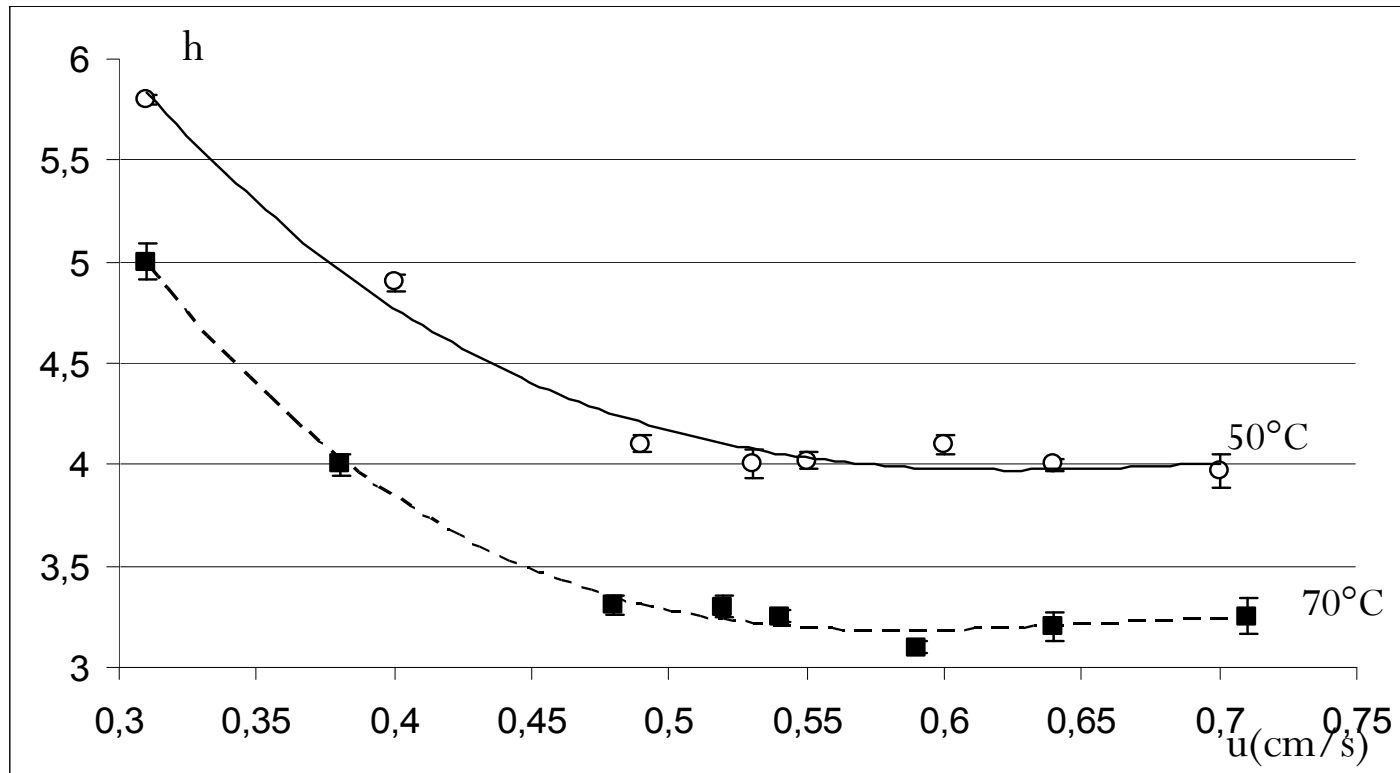
METTLER-TOLEDO

THAR

JASCO

MACHEREY-NAGEL

- Influence de la température sur N et sur u



P = 150 bars, colonne : Nucleodur Gravity 10cm x 0,3cm, 1,8 μ m sur le pic d'anthracène

Différence de h : présence d'un gradient de masse volumique, de vitesse linéaire, de viscosité interne à la colonne \rightarrow gradient de rétention

