VRIJE UNIVERSITEIT BRUSSEL
Department of Chemical Engineering

Shear Driven Chromatography as a Potential Alternative to HPTLC

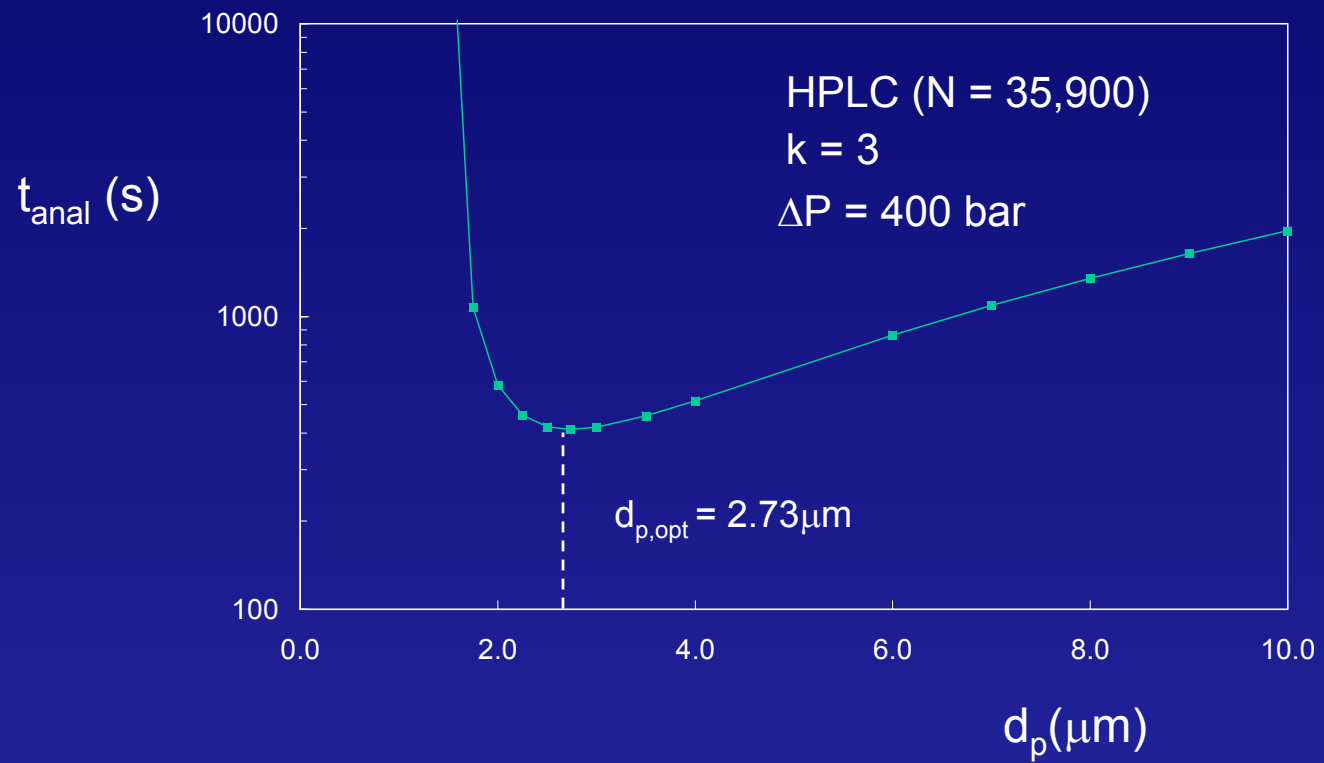
Vervoort N., Clicq D., Baron G. and Desmet. G

Structure of Talk

1. Shear-Driven Flows
2. Tracer Flow Experiments
3. Separation Experiments
4. Conclusions

Effect of Pressure Drop Limitation

$$t_{anal} \sim \frac{N.d_p^2}{D_{mol}} \quad \text{(when } u = u_{opt}\text{)}, \quad \underline{\textbf{but:}} \quad u_{opt} \sim \frac{1}{d_p} \quad \text{and} \quad \Delta P \sim \frac{u.L}{d_p^2}$$

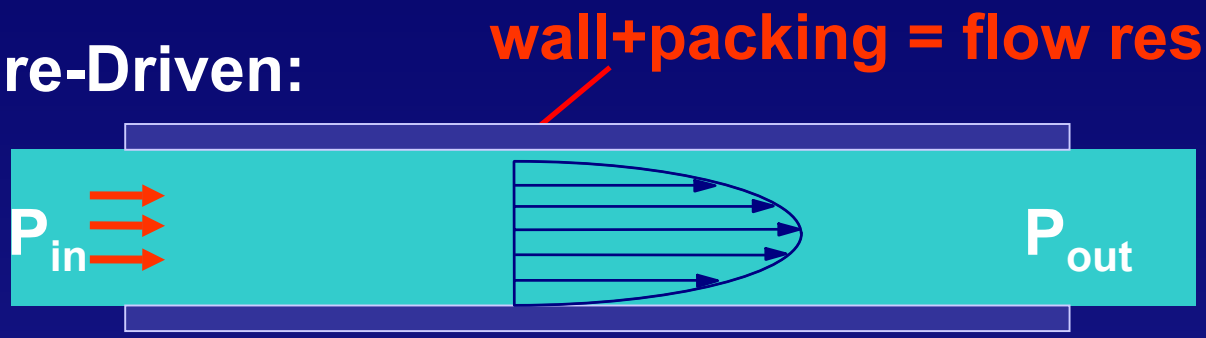


⇒ **optimal d-value for minimal t_{anal}**

⇒ **lower-limit for d**

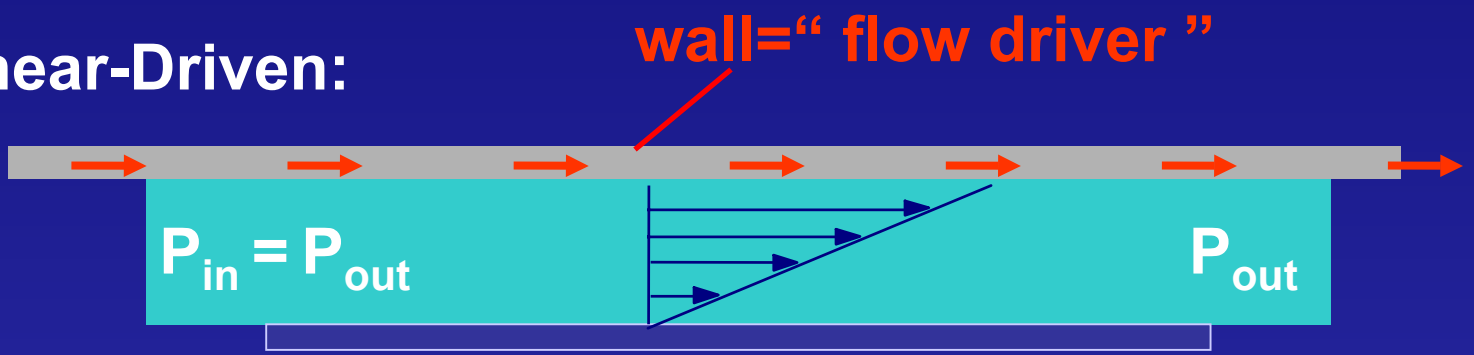
Getting Round Pressure Drop Limitation

Pressure-Driven:



Flow Driving Force at Channel Inlet

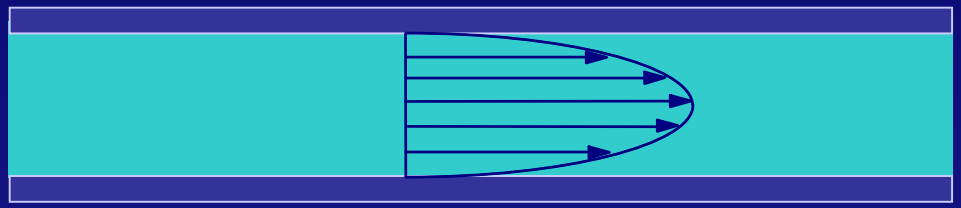
Shear-Driven:



Flow Driving Force along Mantle Surface

Comparison with OT-LC

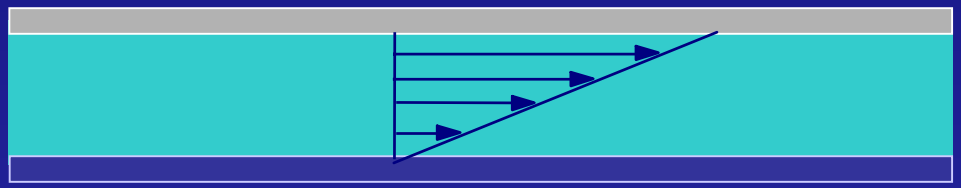
Pressure-Driven:



$$u \sim \frac{\Delta P.d^{2}}{L}$$

reduction of d restricted by ΔP-limitation

Shear-Driven:

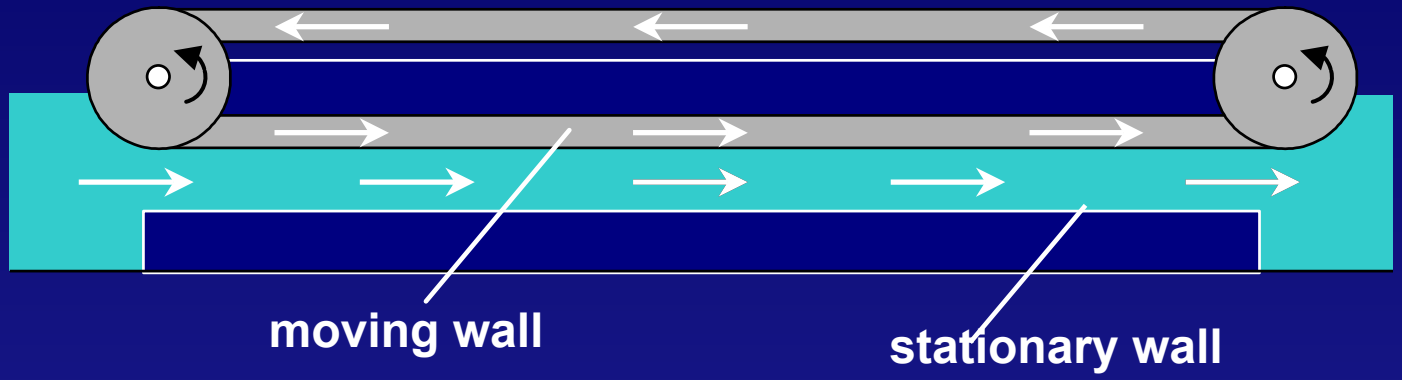


$$u_{avg} = \tfrac{1}{2}.u_{moving\ wall}$$

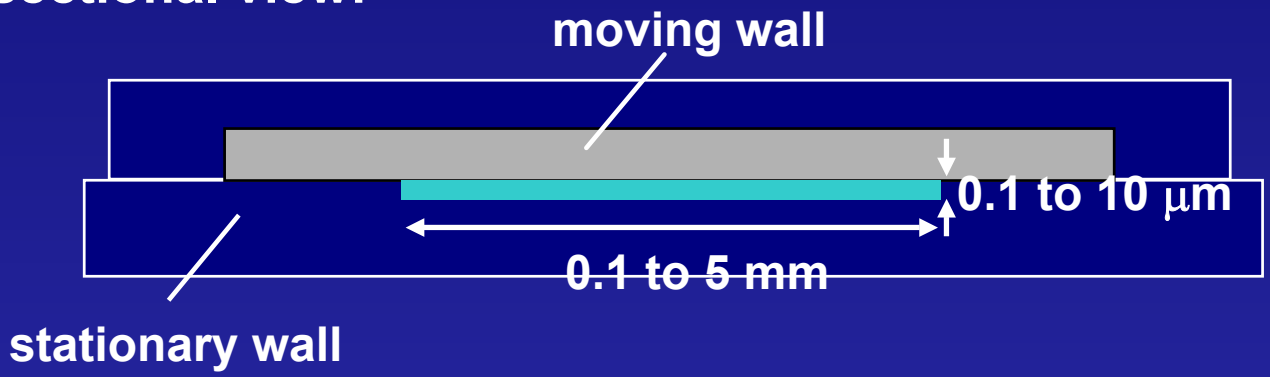
u and d can be selected independently

Shear-driven Flow Module

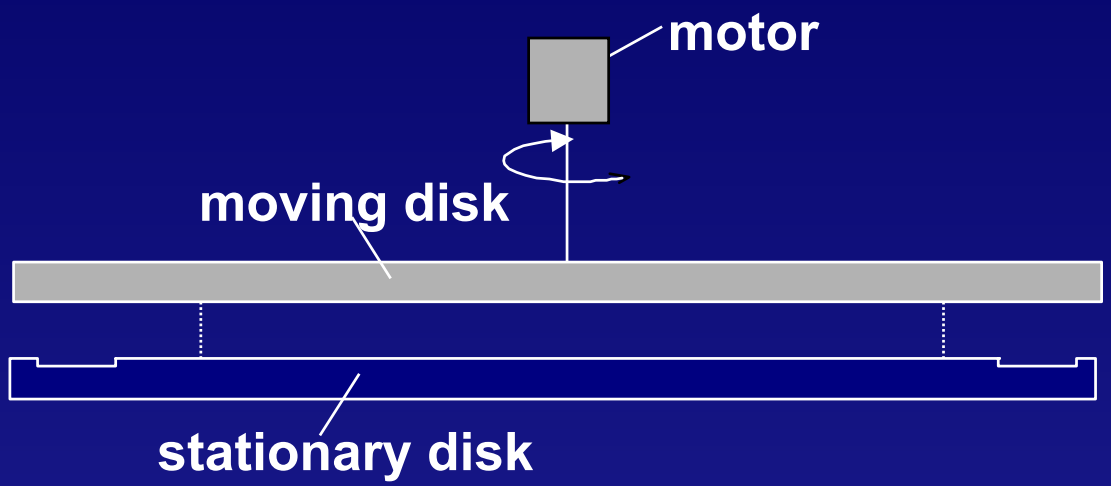
Longitudinal view:



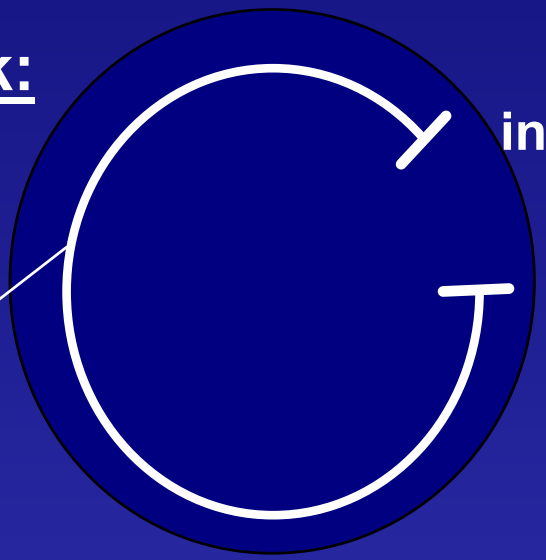
Cross-sectional view:



SD Flow Module (Rotating Disk)

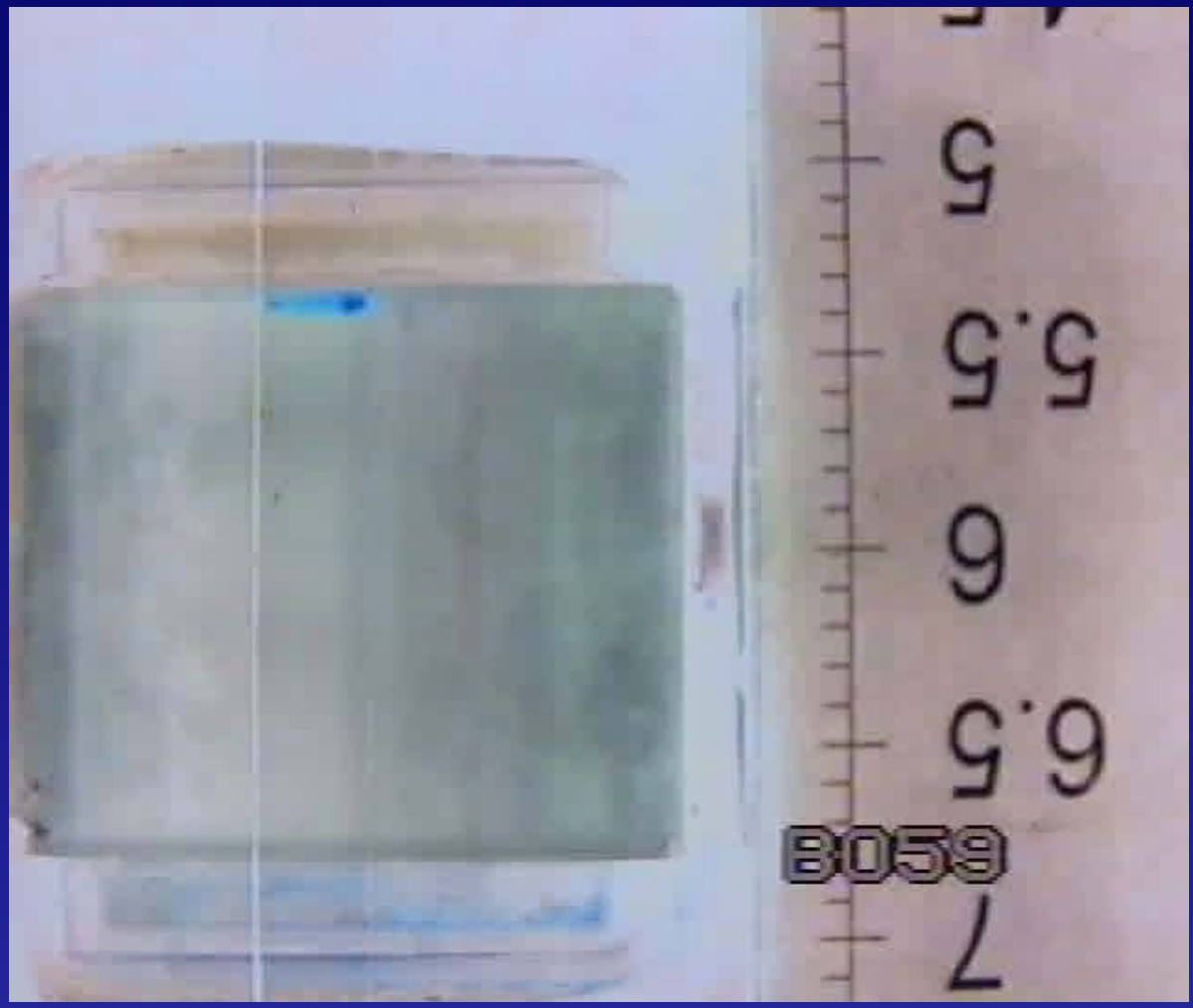


top view stationary disk:



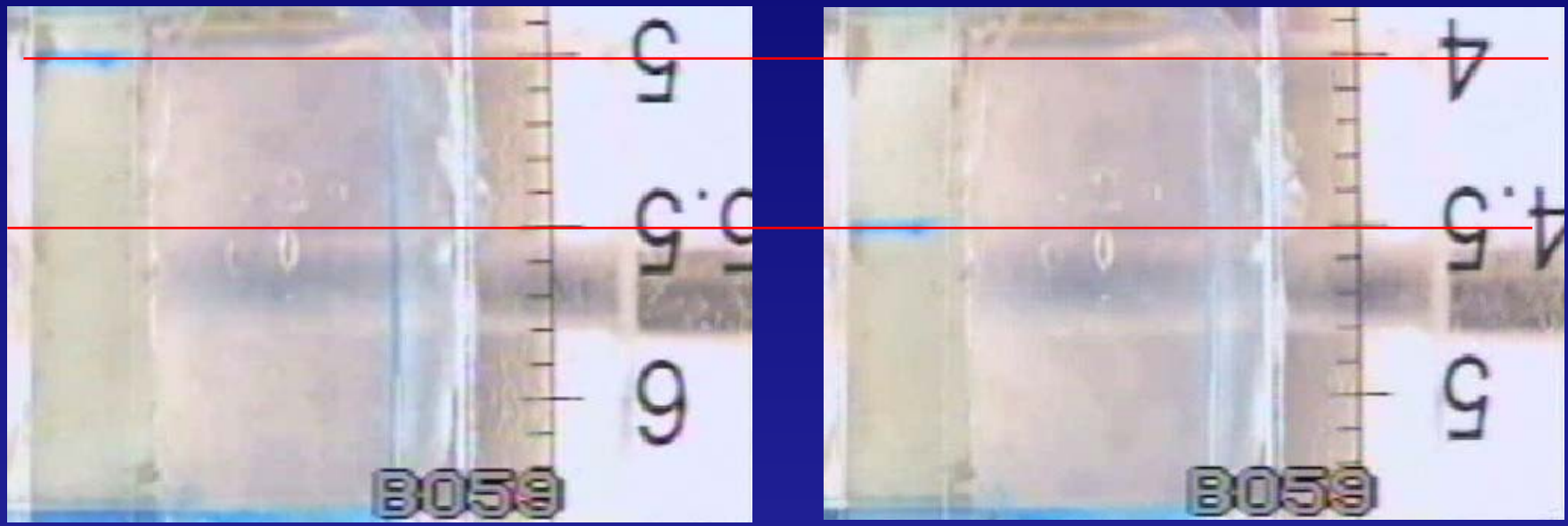
Tracer flow experiment

L = 15 mm
w = 4 mm
d = 400 nm
u_{mean} = 3 mm/s



Determination of Mean Velocity

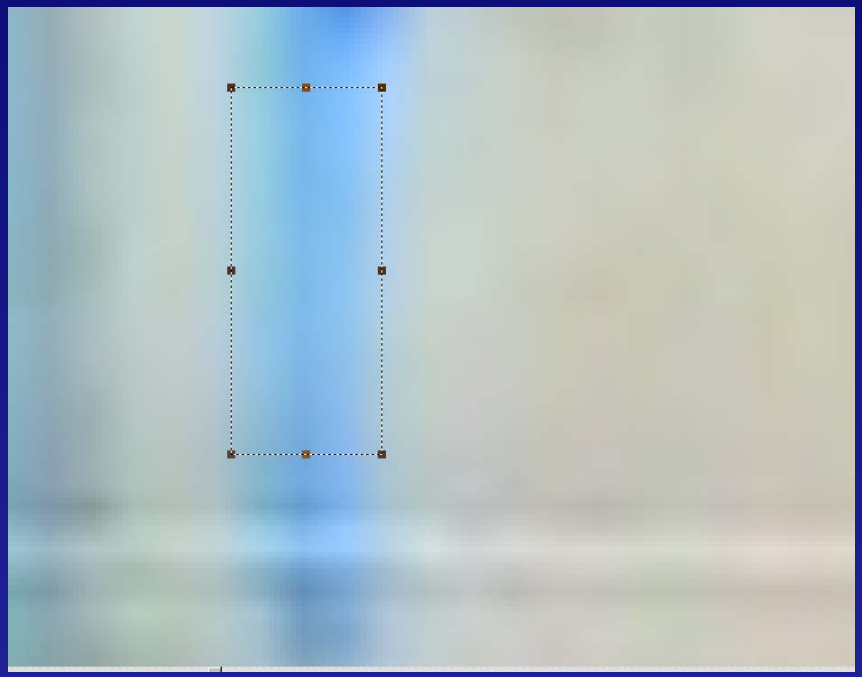
d = 400 nanometer, u_{wall} = 6 mm/s

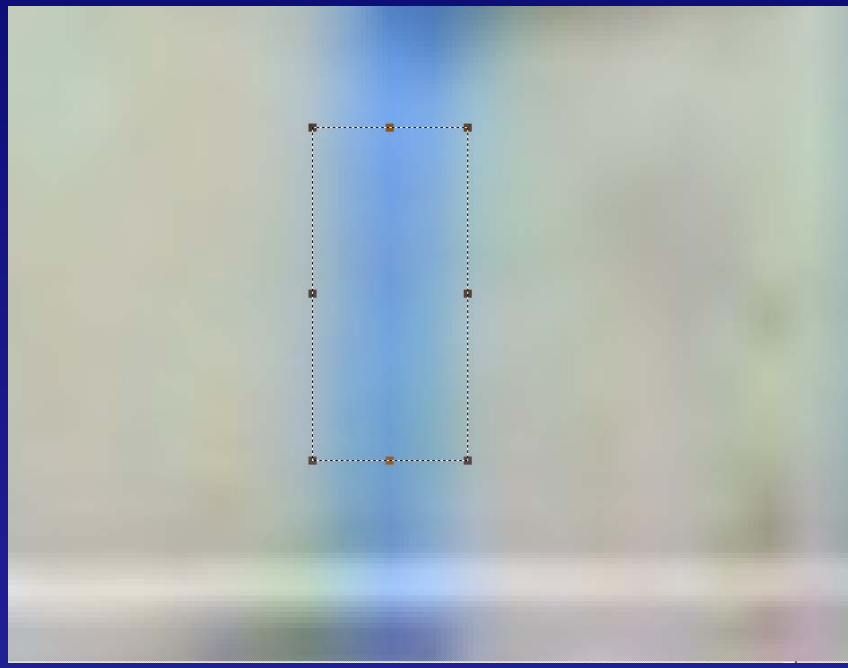


$u_{avg} = ½.u_{moving\ wall}$

Still Image Analysis

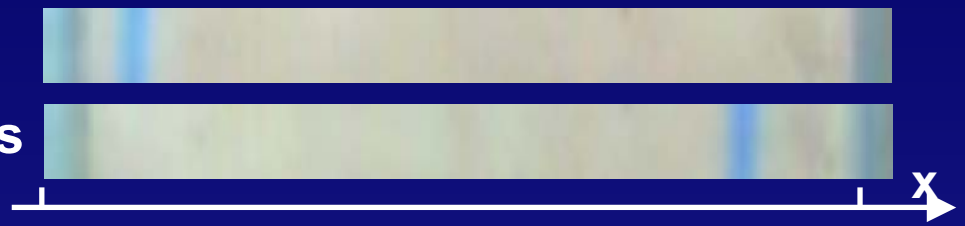
d = 100 nanometer, u_{mean} = 1.4 cm/s



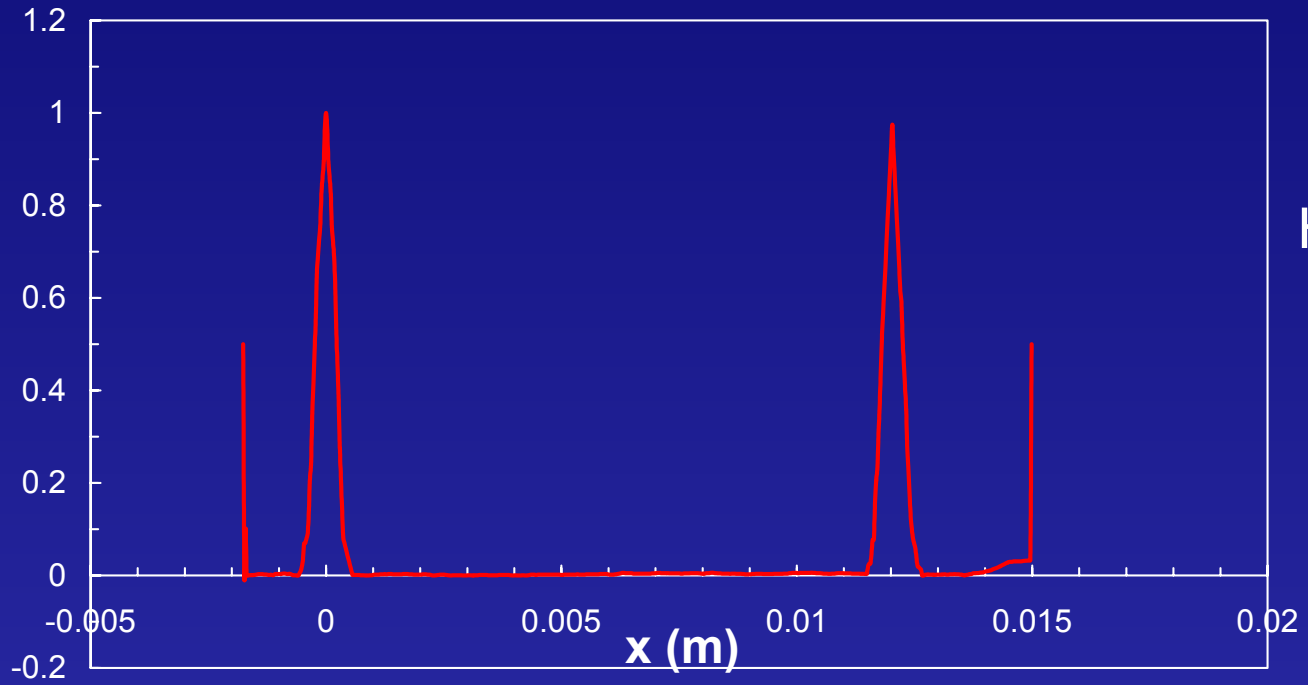


t = 0 zoom = 800% t = 0.92s

Colour Intensity Plot



Plot of Colour Intensity Foto 1 + Foto 2 :



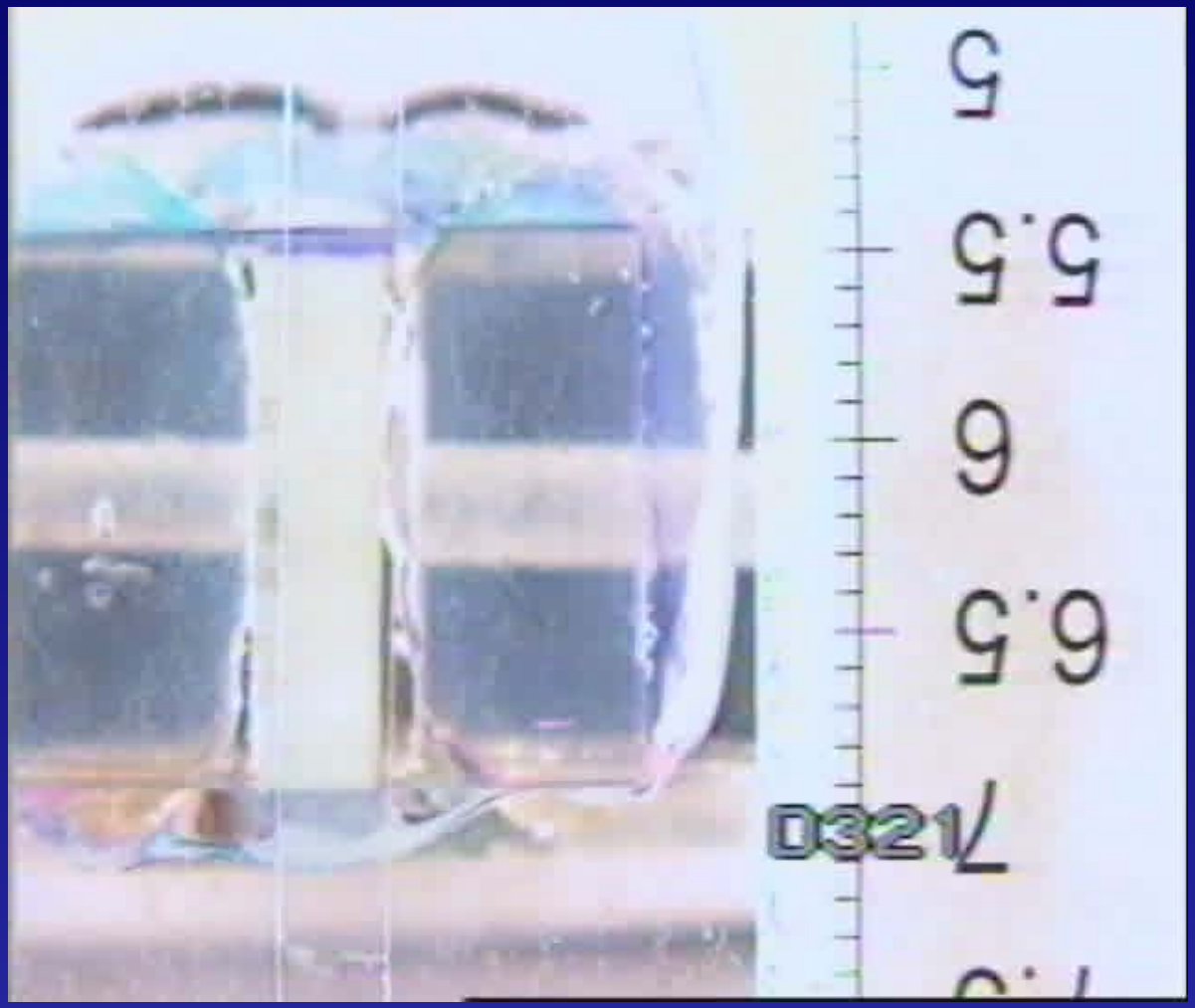
$$HETP = \frac{\sigma^2_{out} - \sigma^2_{in}}{L}$$

$$= 0.13\,\mu m$$

Experimental Run

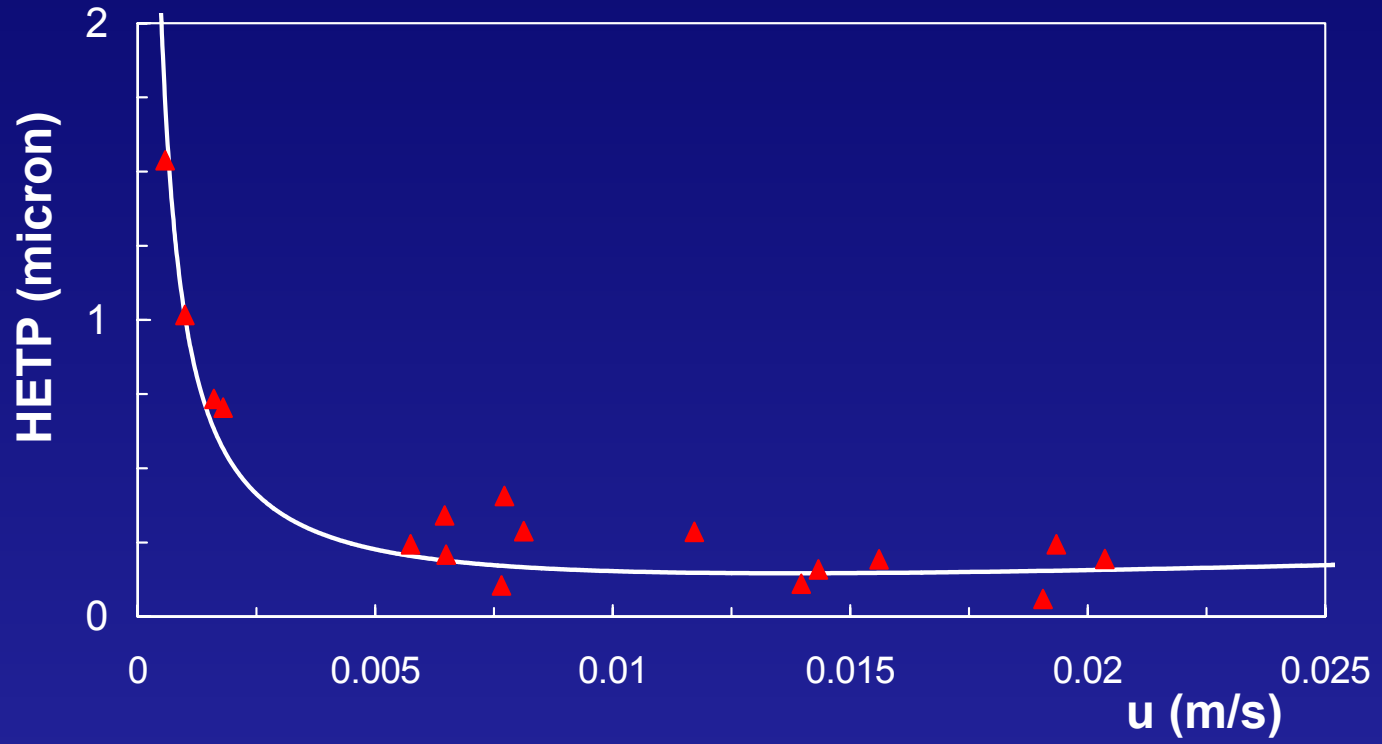
d = 100 nm,
u_{mean} = 1.4 cm/s

ΔP = 3400 bar !!



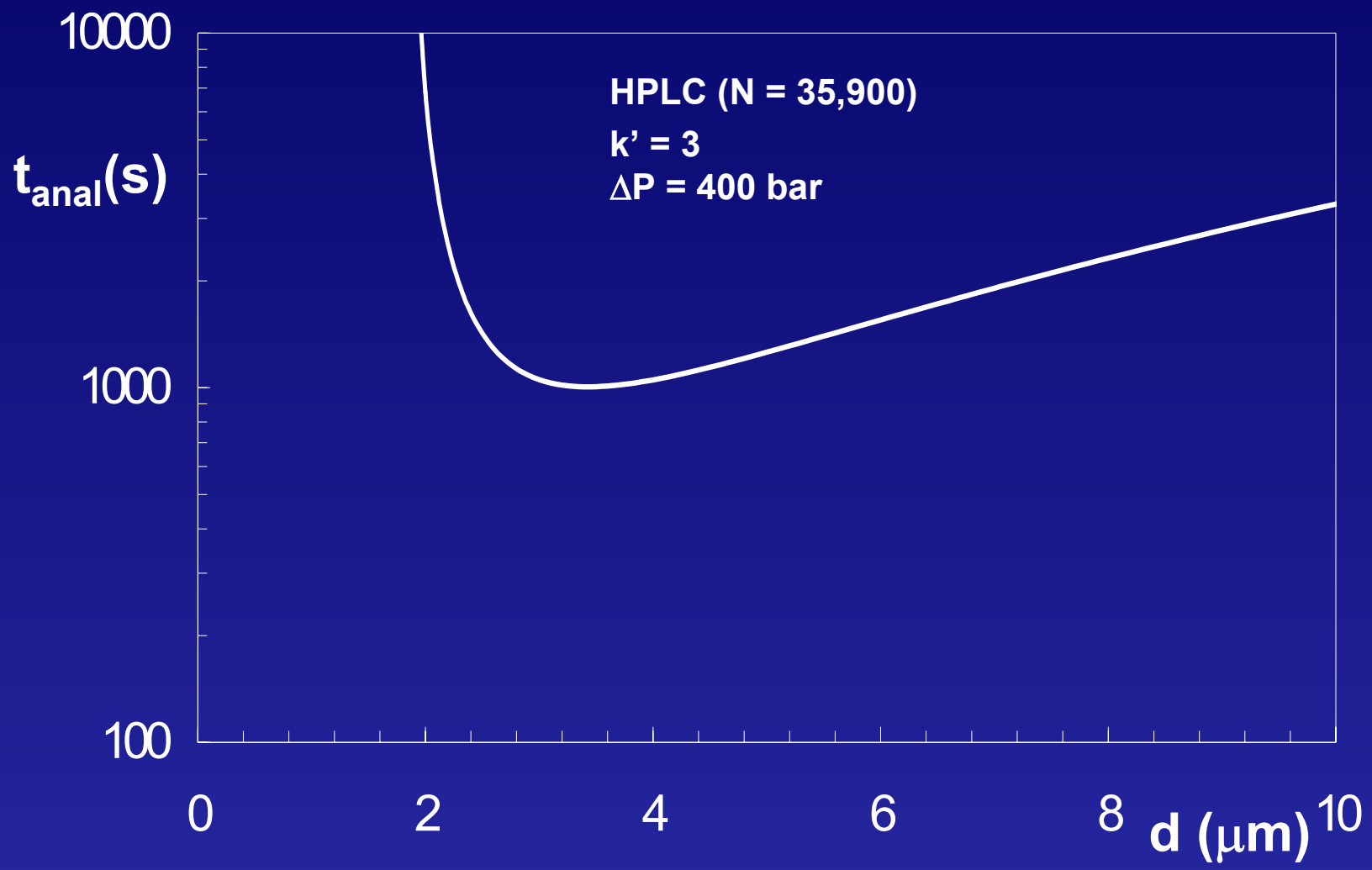
Peak Broadening-van Deemter Plot

$d = 100$ nanometer, $D_m = 6.10^{-10}$ m^2/s

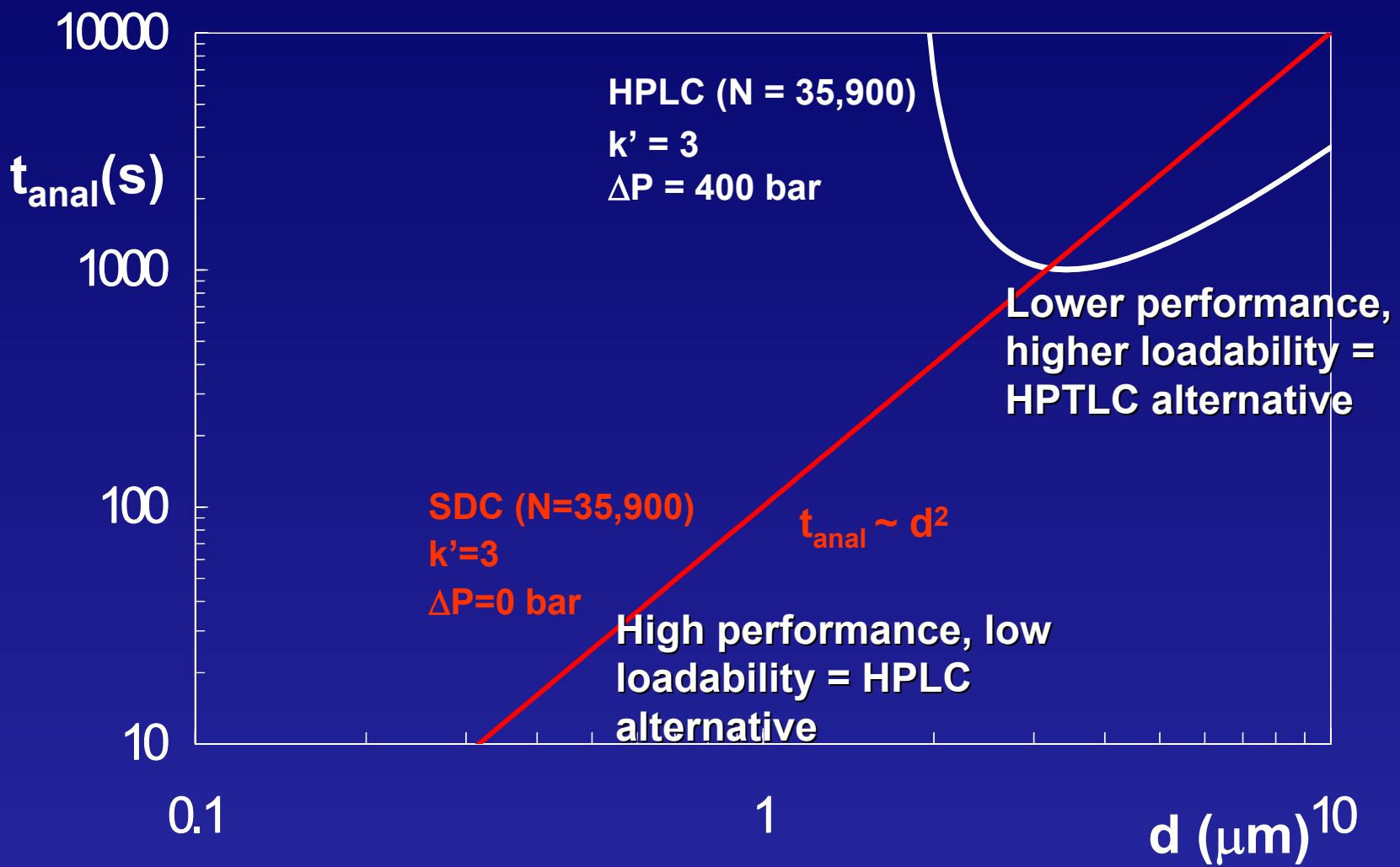


Theoretical: $$HETP = \frac{2}{u}.D_m + \frac{2}{30}.\frac{u.d^2}{D_m}$$

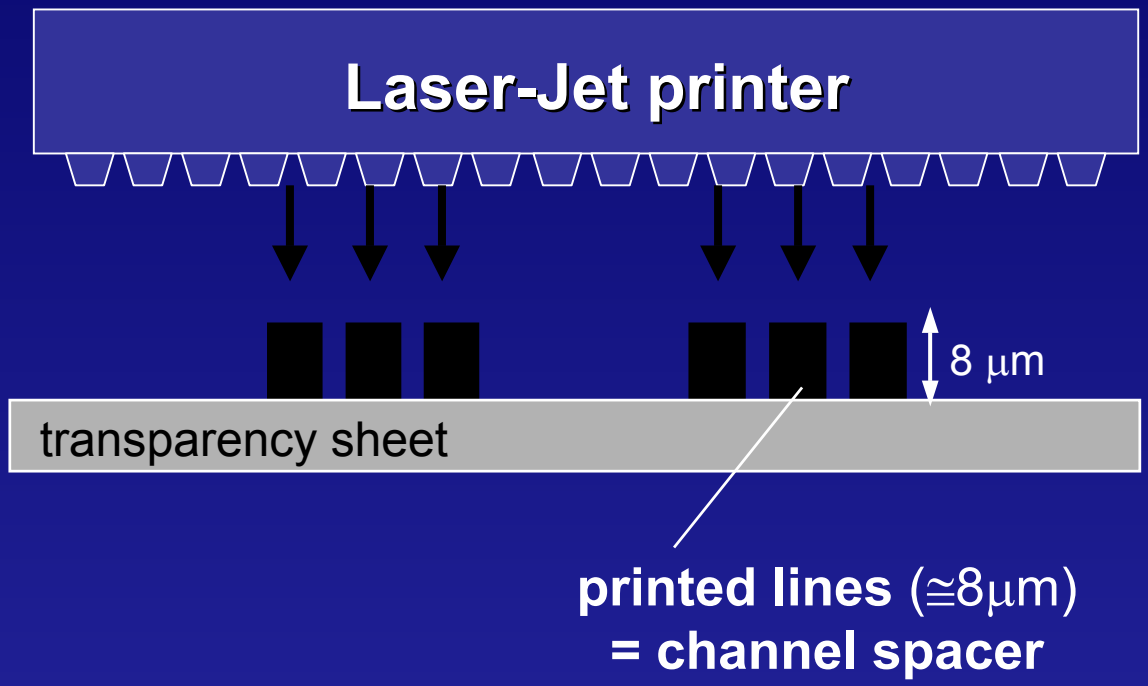
Time Gain with respect to HPLC



Time Gain with respect to HPLC

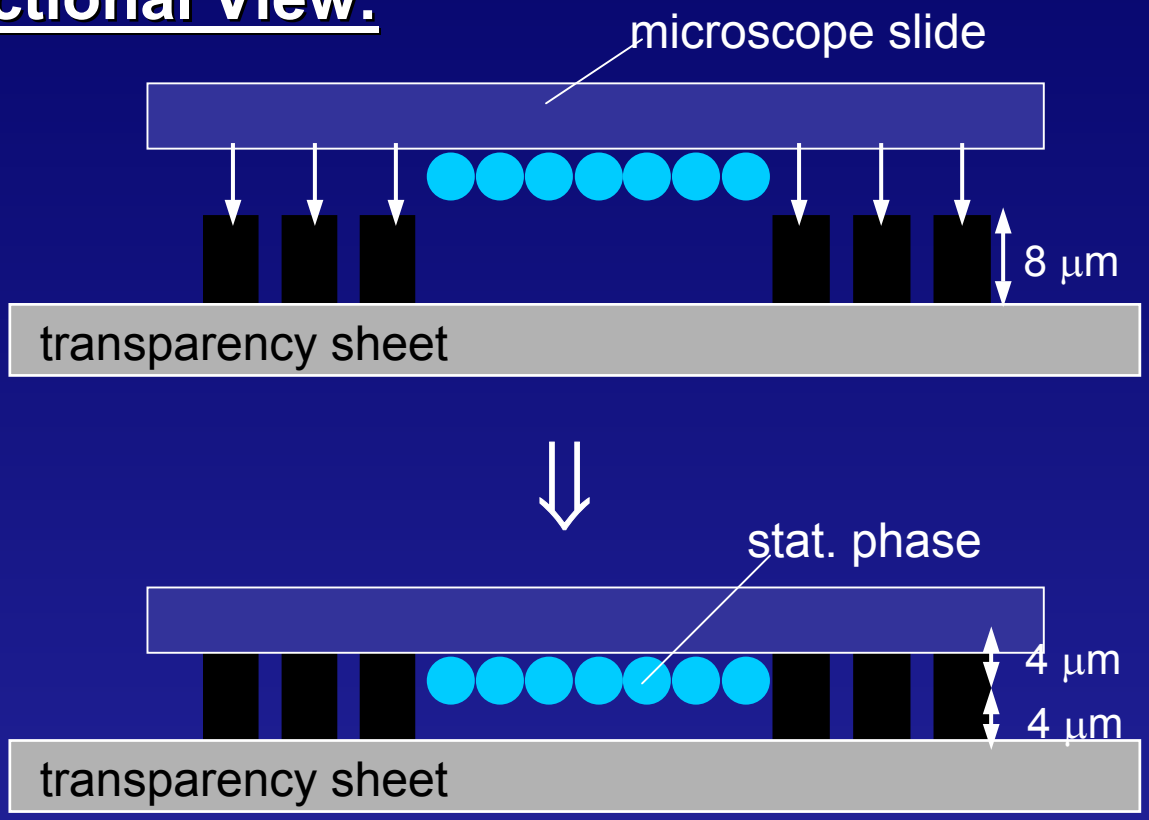


Experimental : Channel fabrication



Experimental: Channel Assembly

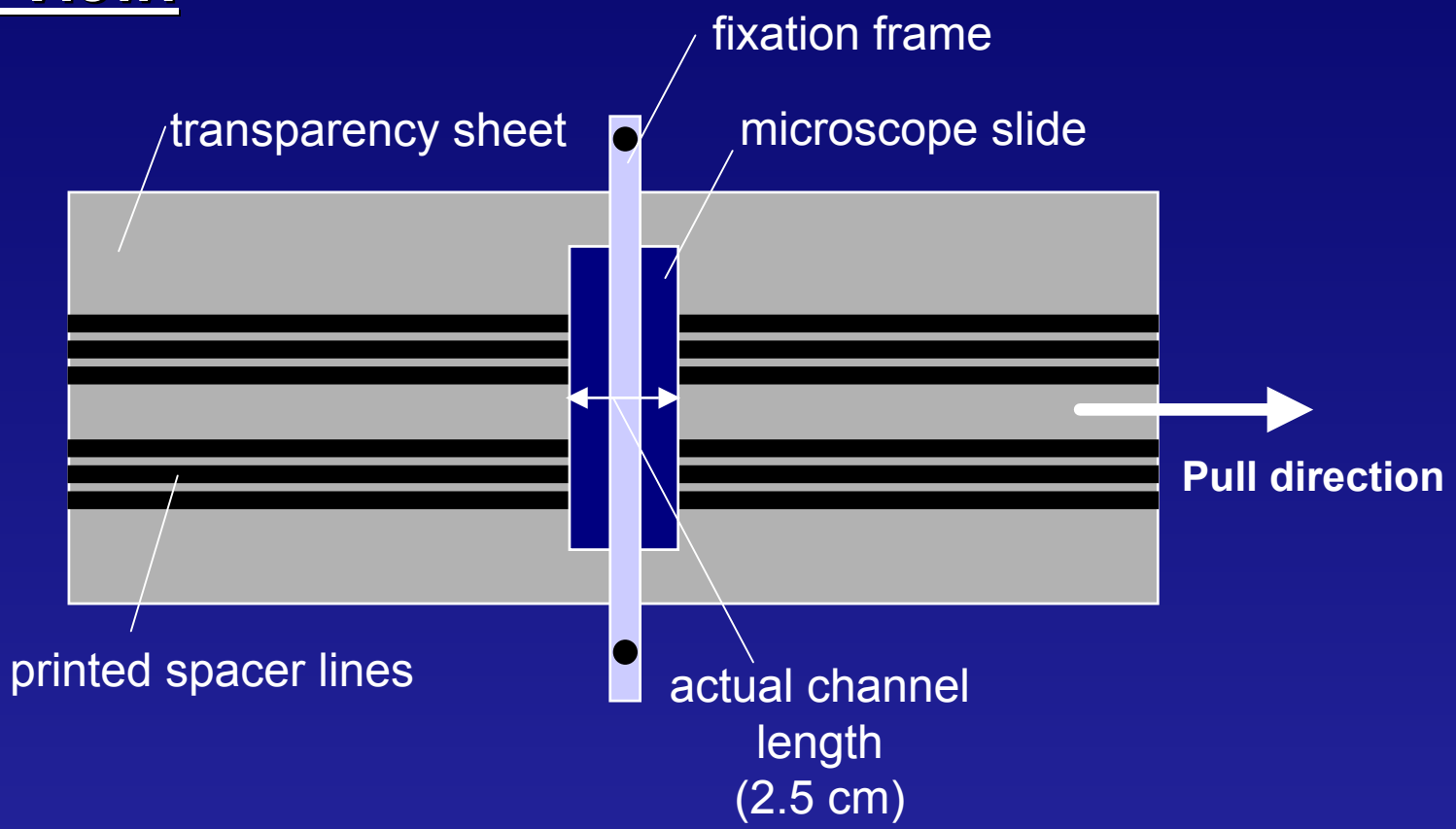
Cross-sectional View:



Unsealed channel parts = no problem

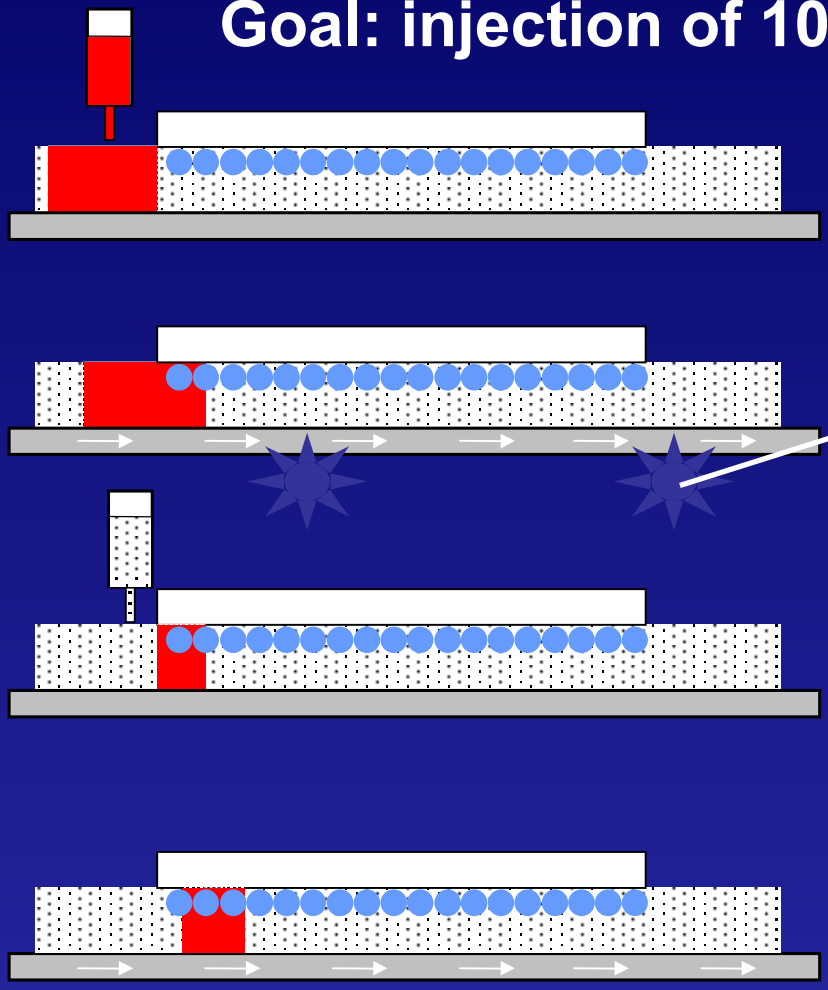
Experimental set-up I

Top View:



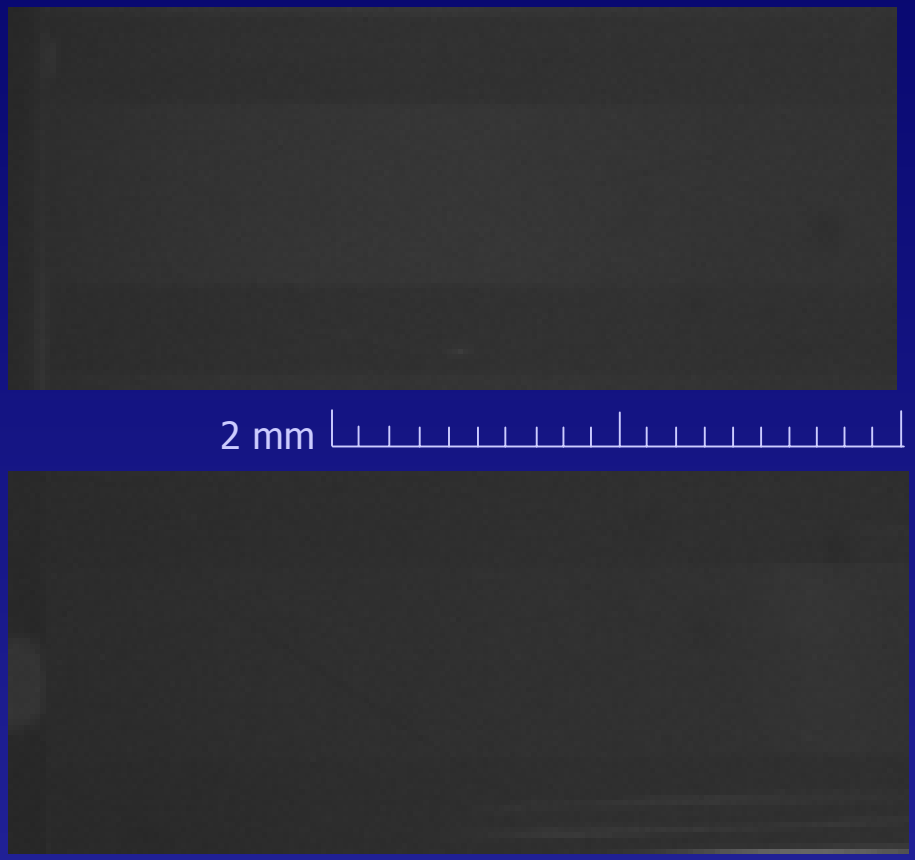
Injection Method

Goal: injection of 100 μm bands within 0.5 s



Method: micro-positioner and automatic displacement system (accuracy of 0.5 micron = >99% accuracy)

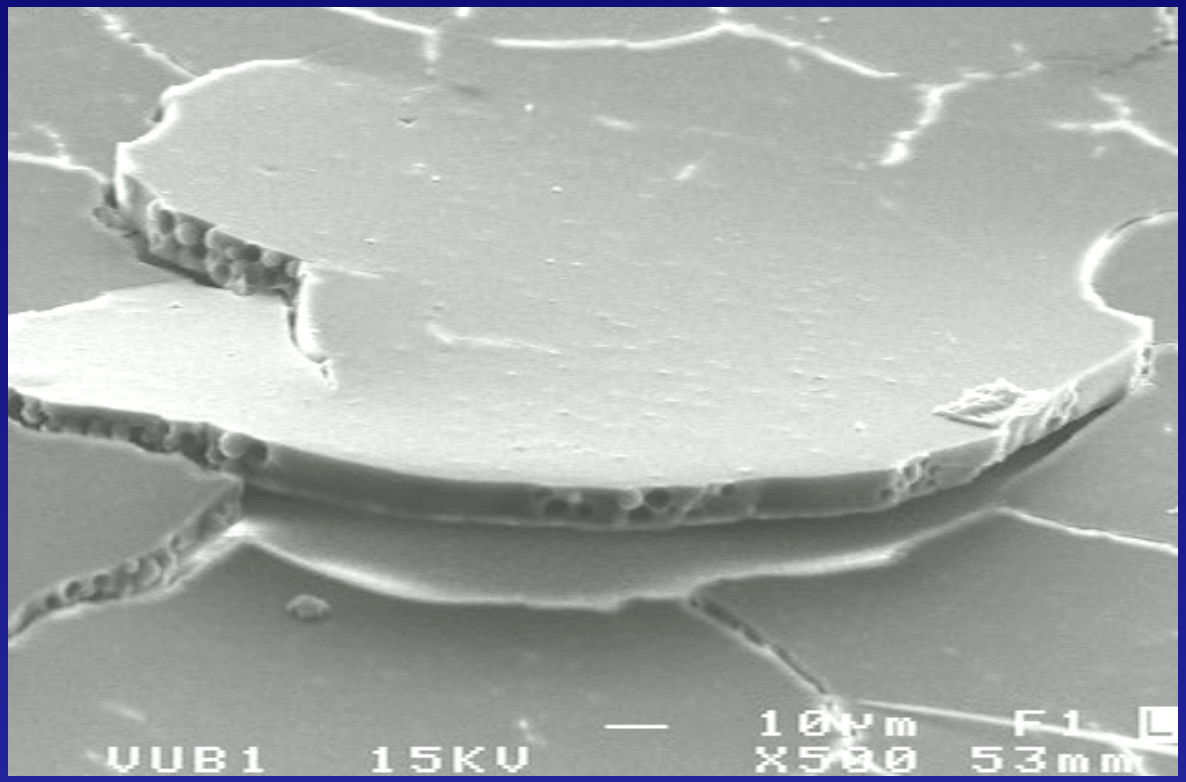
Injection Example



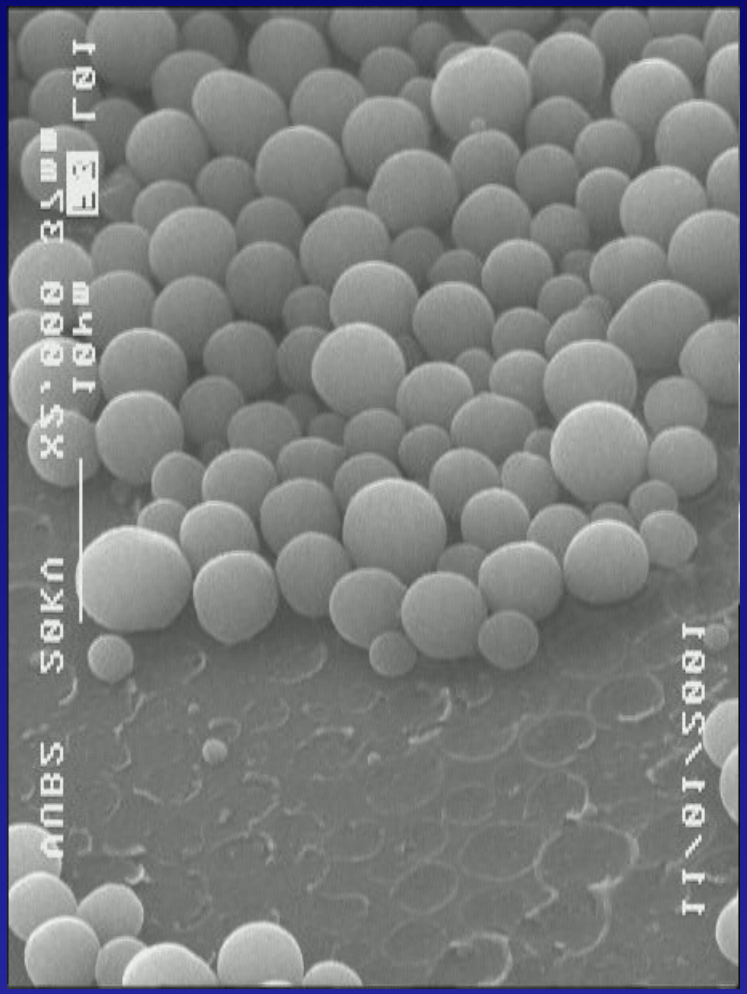
Channel depth = 200nm

Stationary Phase Layer-Ia

Preparation of layer: 4 μm RP-HPLC beads contained within a poly-acrylic polymer matrix

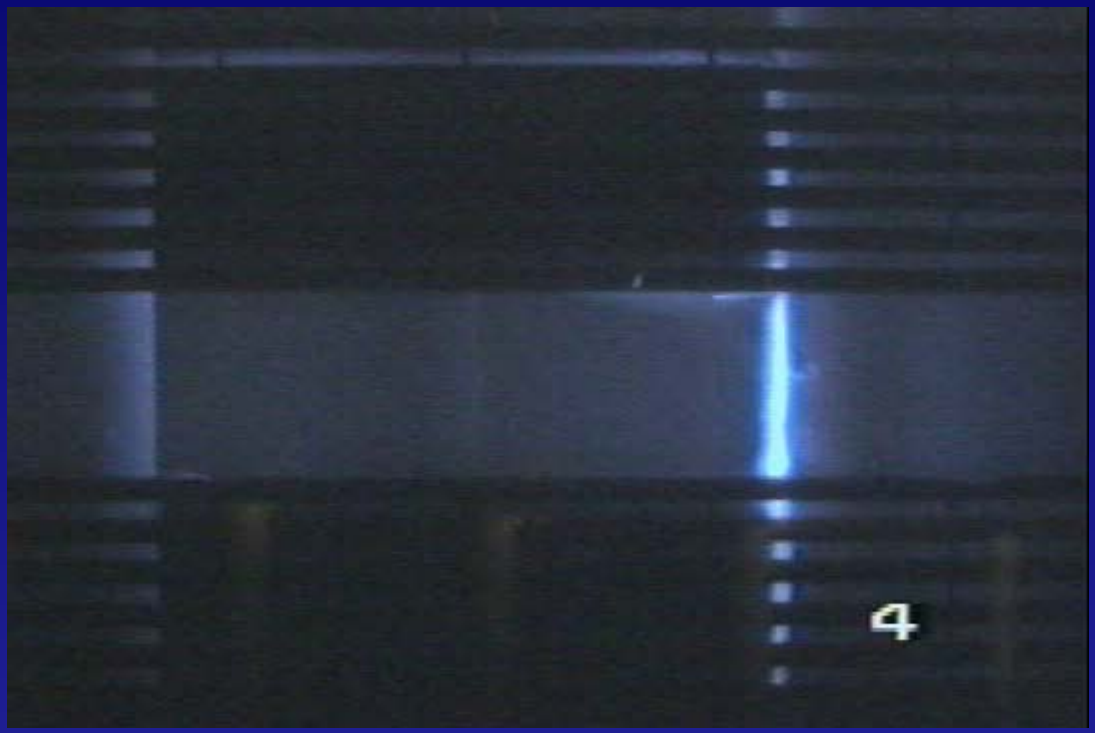


Stationary Phase Layer-Ib



Monolayer of commercial 4 μm HPLC-beads immobilised with Polyethoxysilane layer

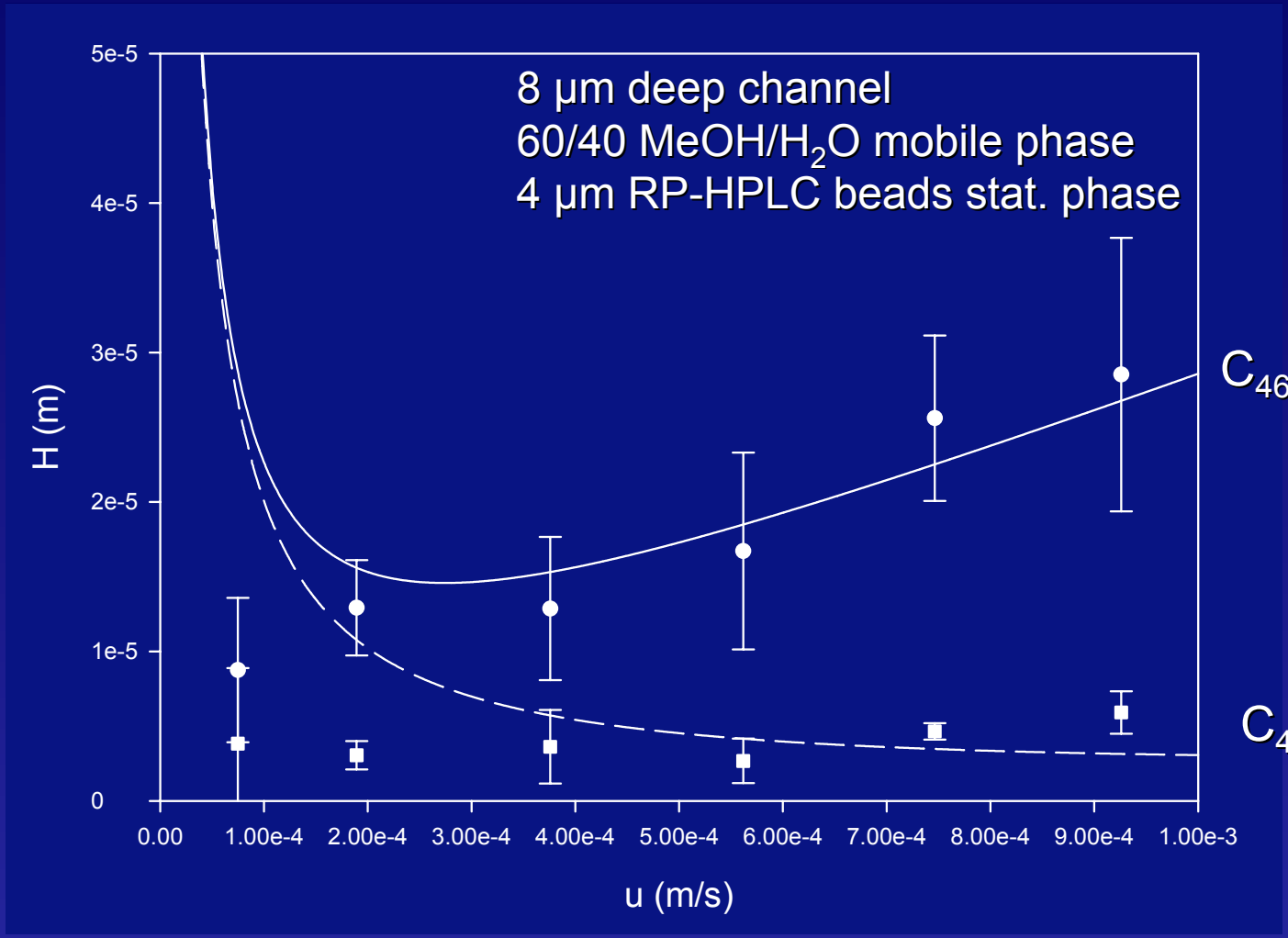
Separations in 8 μm channel



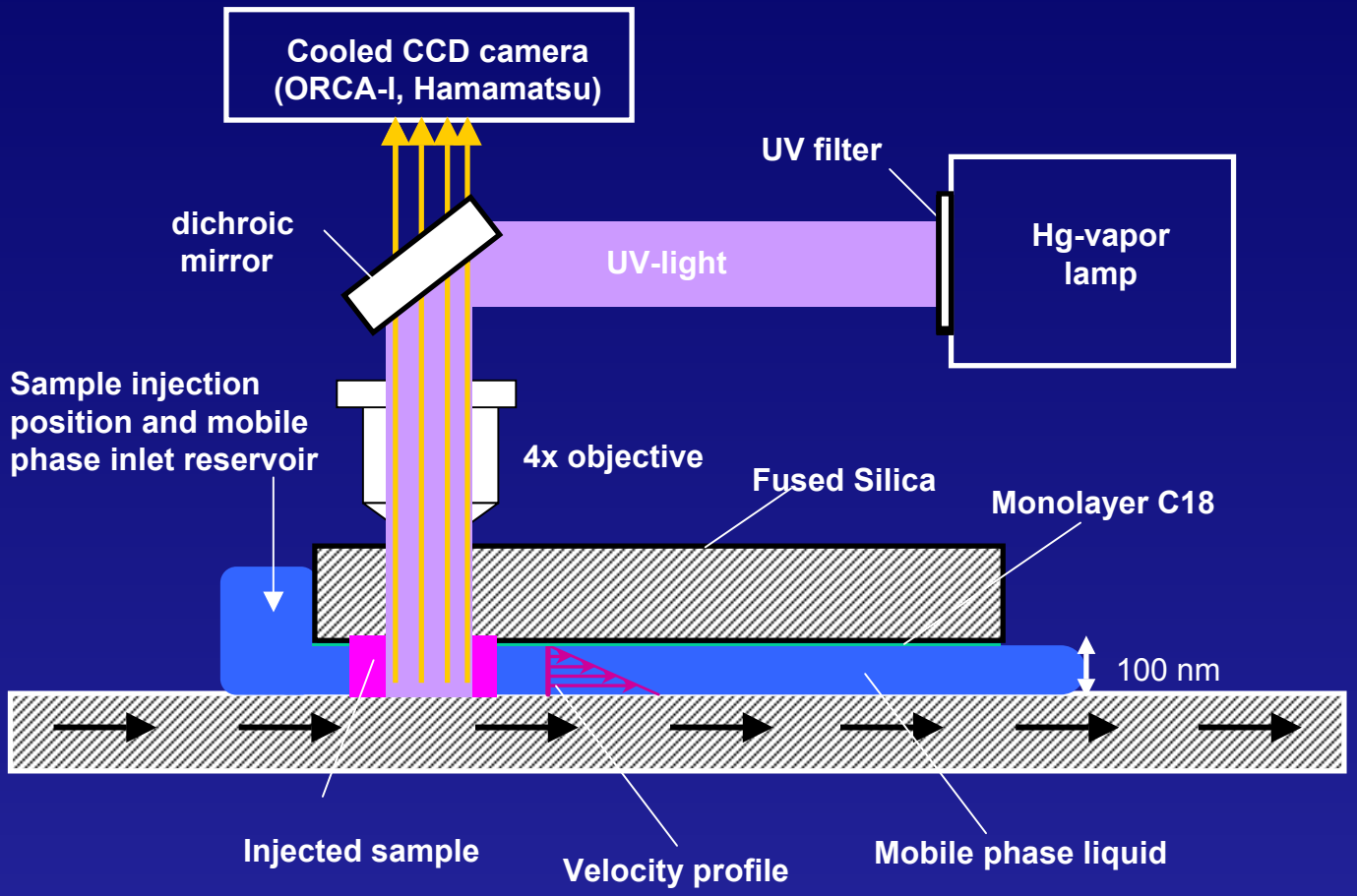
Mobile phase = 60%/40% water-methanol

u = 1.25 mm/s

Experiment *vs.* Theory



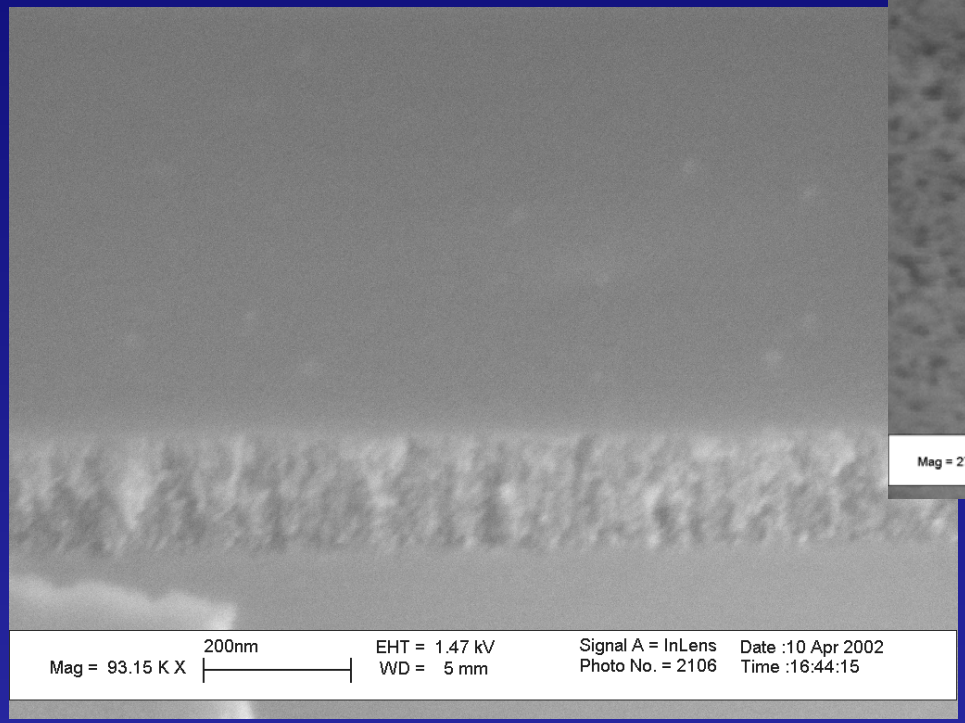
Experimental Setup II

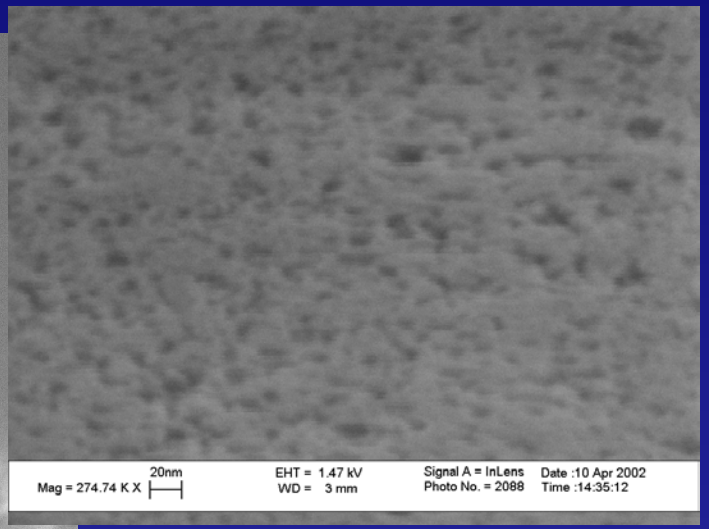


Stationary Phase

- Electrochemical etching of Si wafer
- Oxidizing Si $\rightarrow$ SiO_2
- Surface modification with C8/C18

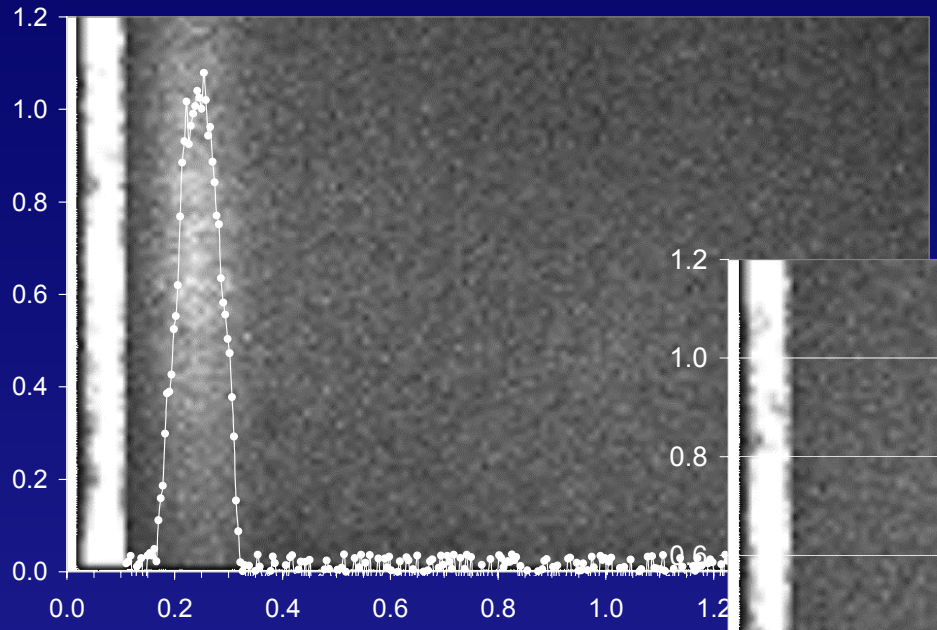
$\Rightarrow$ 100-200 nm thin Porous Silica layer



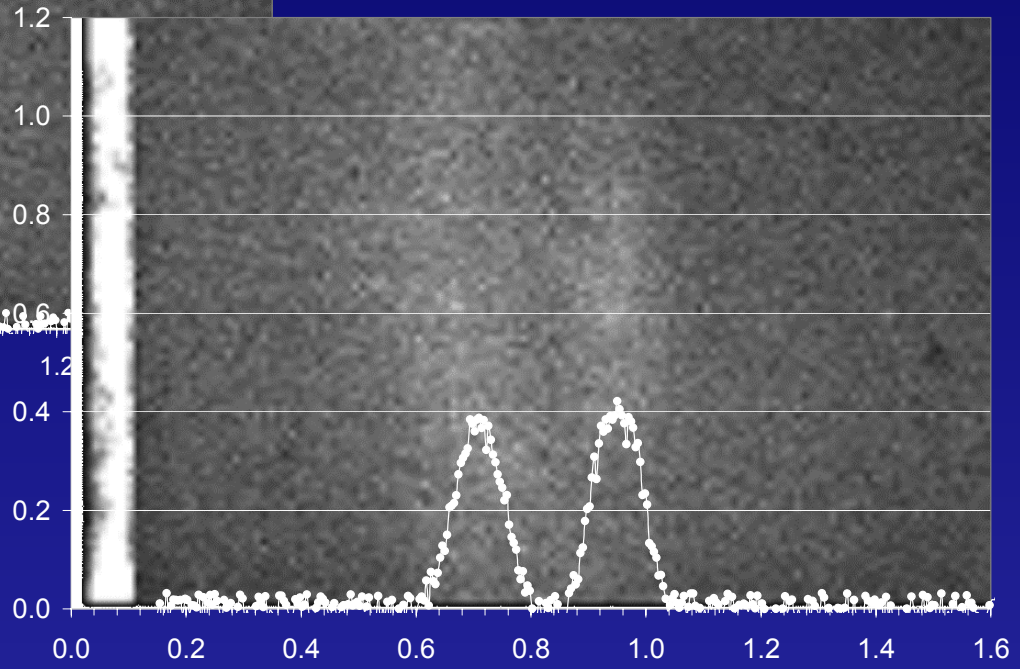


Separations in 300 nm channel

Stationary phase = porous silicon



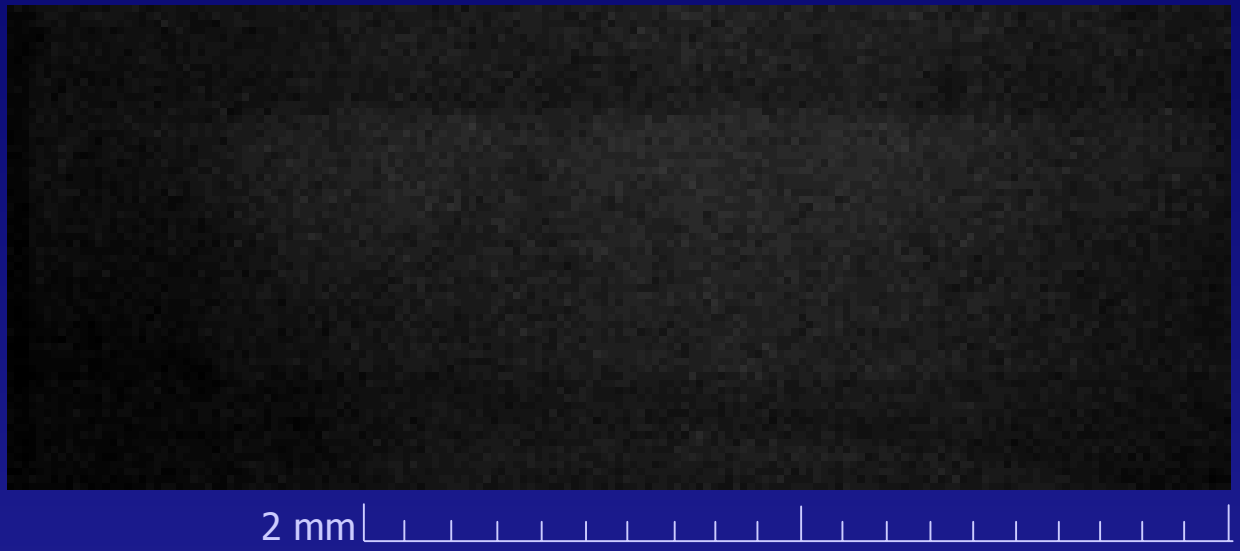
t = 0 sec



t = 0.05 sec

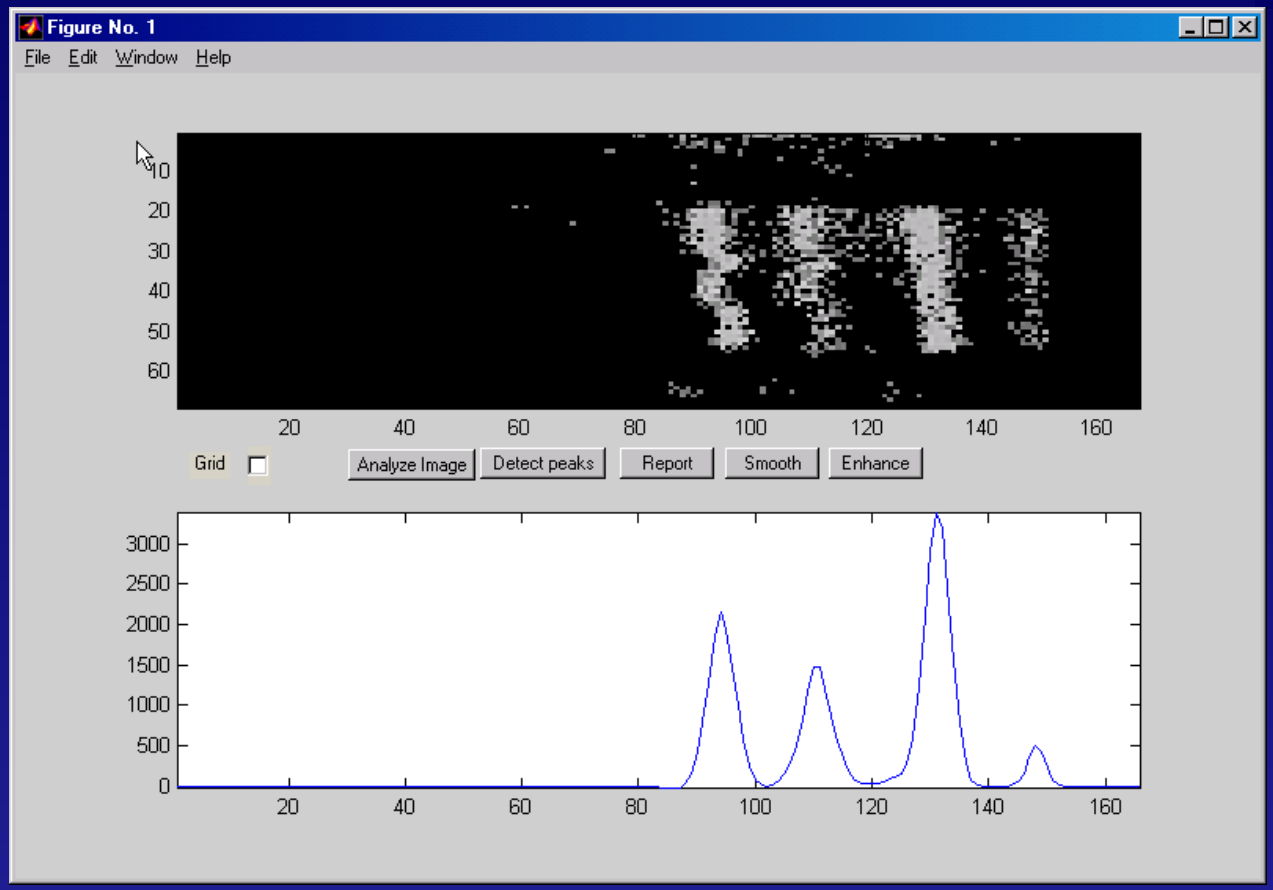
Separations in 200 nm channel

Separation of four Coumarin dyes on monolayer C8



- u = 2 mm/s
- Mobile Phase = 45/55 % MeOH/H_2O
- t = 3 seconds

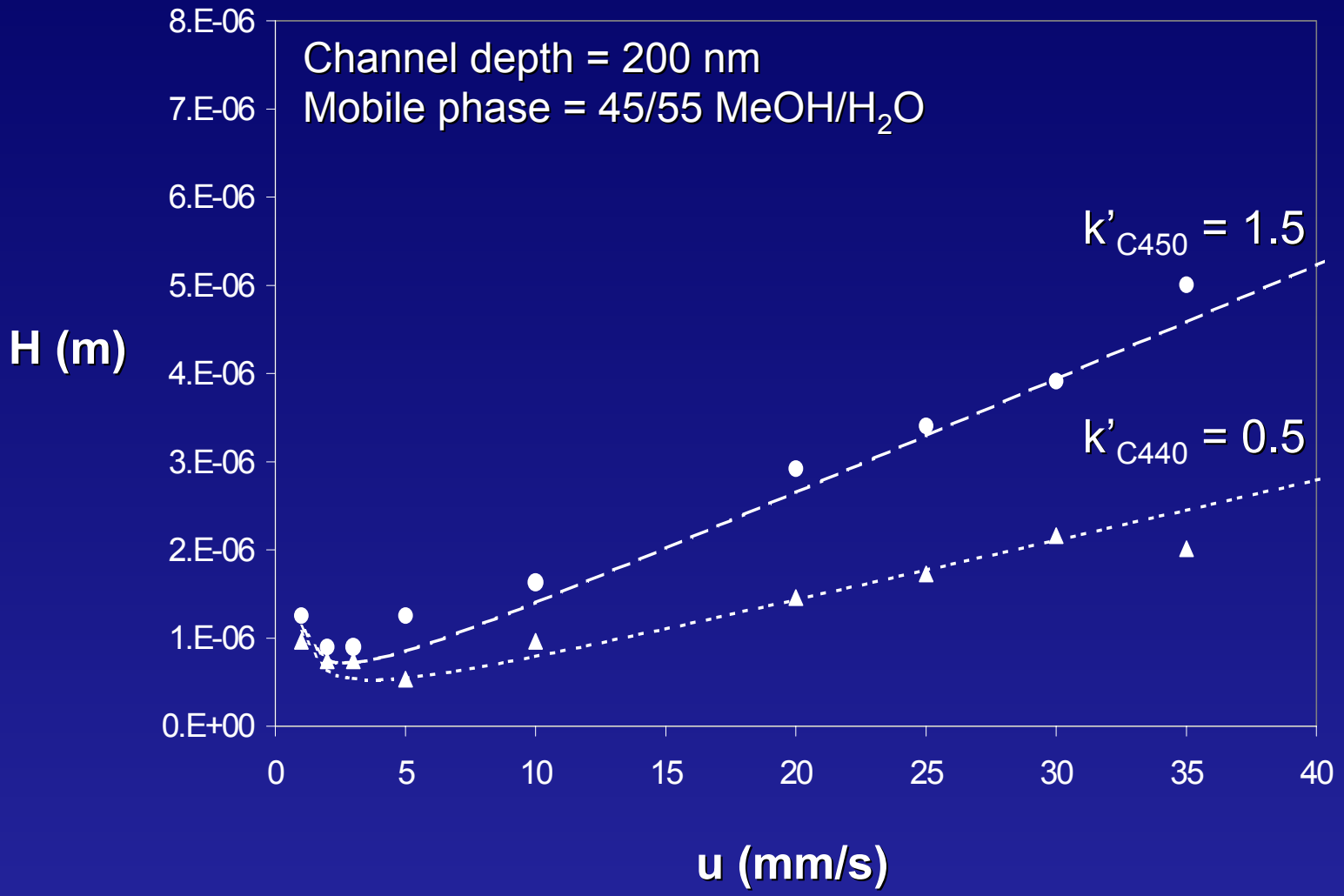
Separations in 200 nm channel



Baseline resolution of 4 compounds in 3 seconds

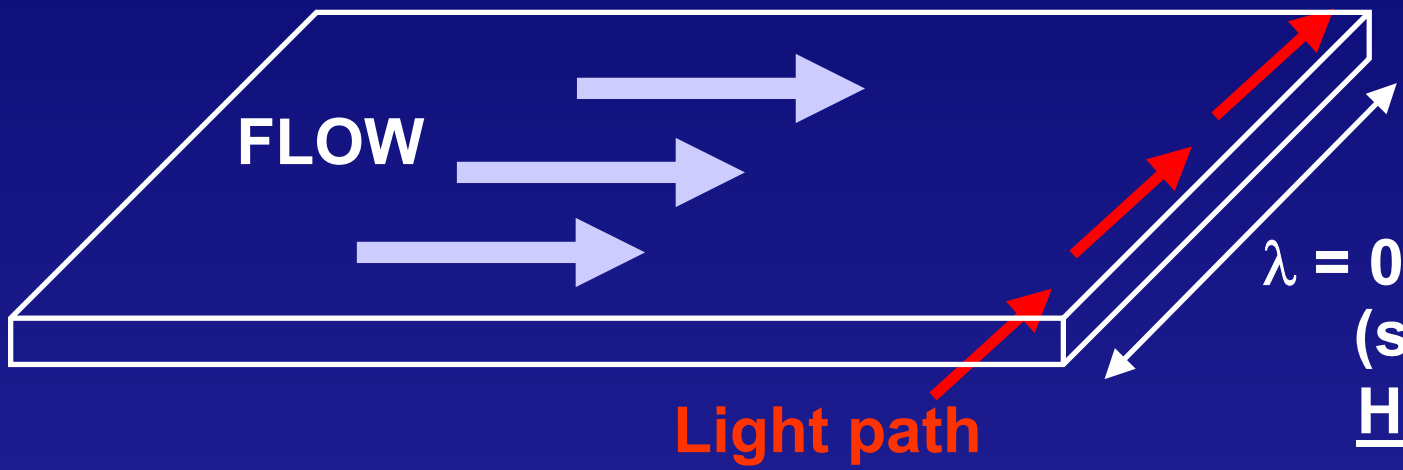
H ≈ 0.5 µm ⟶ ~ 2,000,000 plates/m

van Deemter-plot



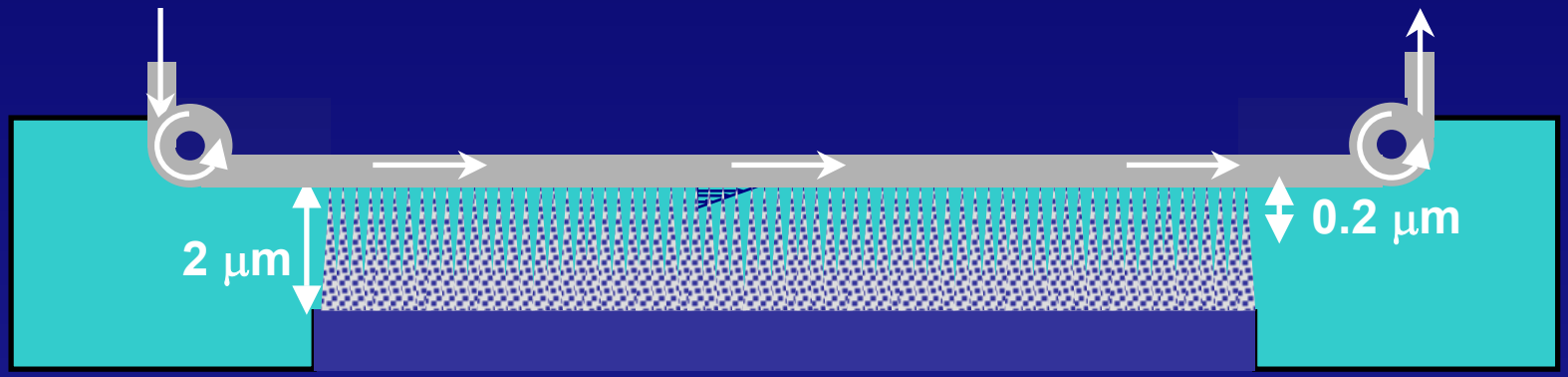
Detectability in SDC

Take advantage of rectangular channel format to benefit maximally from Beer-Lamberts' law: Log $I_0/I \sim C_{max}.\lambda$



λ = 0.1 to 5 mm (similar to HPLC !!!!)

Use of Thick Stationary Phase



e.g. use of HPTLC plate only few microns thick which can be processed in a conventional way after separation.

Conclusions

- Continuous, chromatography enabling flows in channels as thin as 100 nanometer are possible
- Perfect predictability of flow rate
- Flow system without ΔP or ΔE-limitation
- Large potential gain in analysis time or resolution
- Offers larger separation window than TLC (all compounds can be eluted at the end of the column)

The End