

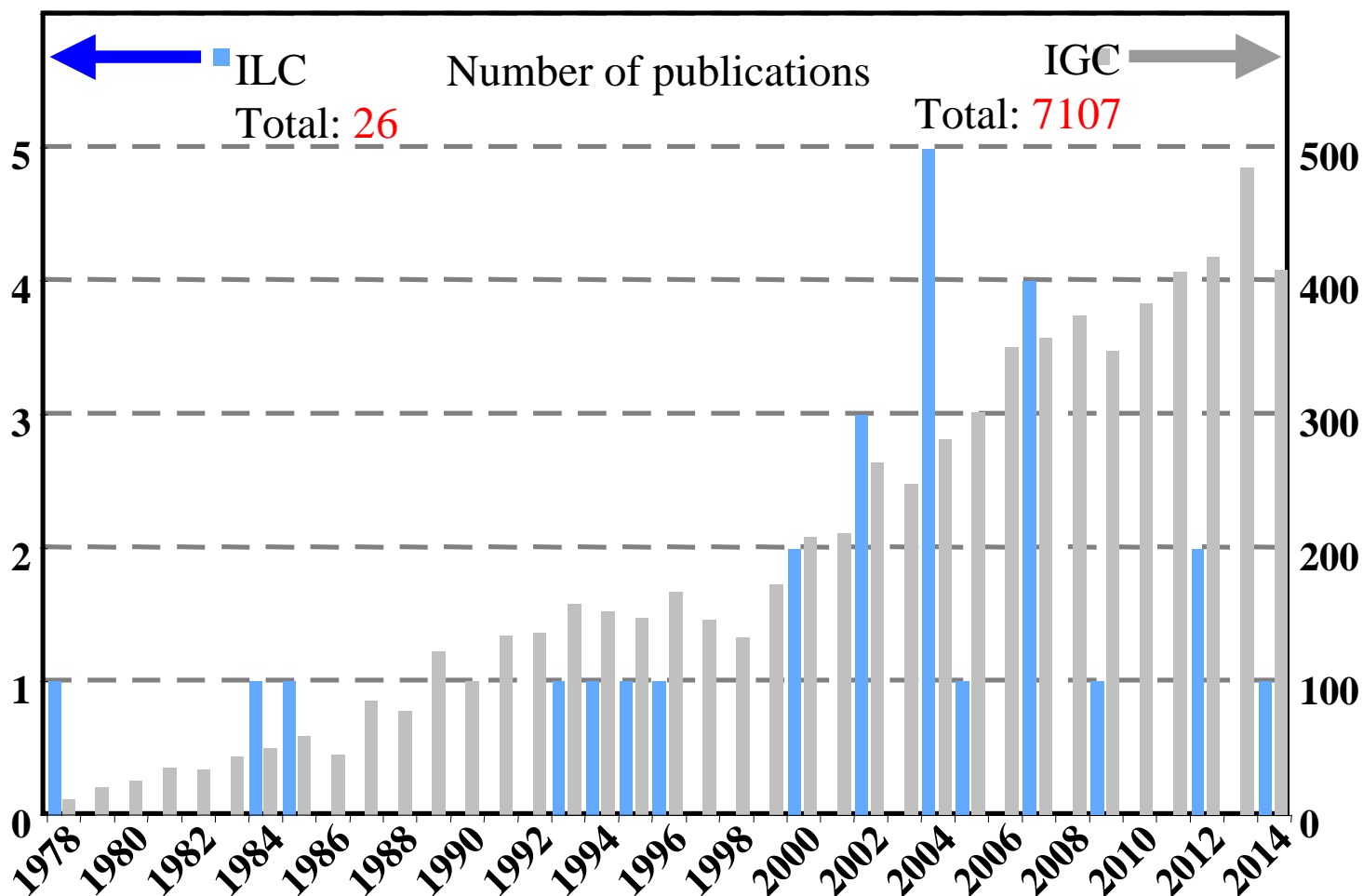
Adscientis

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On the underestimated potential of Inverse Liquid Chromatography

Dr Henri BALARD
Scientific Manager

Comparison of the reference number for ILC and IGC



*From Google Scholar seeking at the keywords
- Inverse gas chromatography and Inverse Liquid Chromatography -
-in the title of the publications*

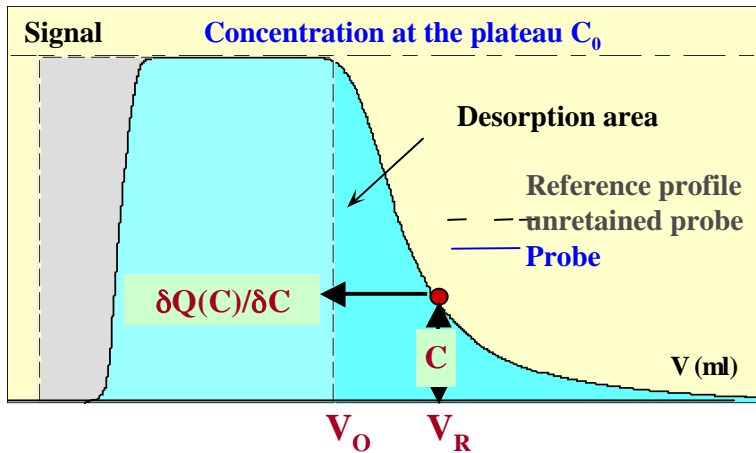
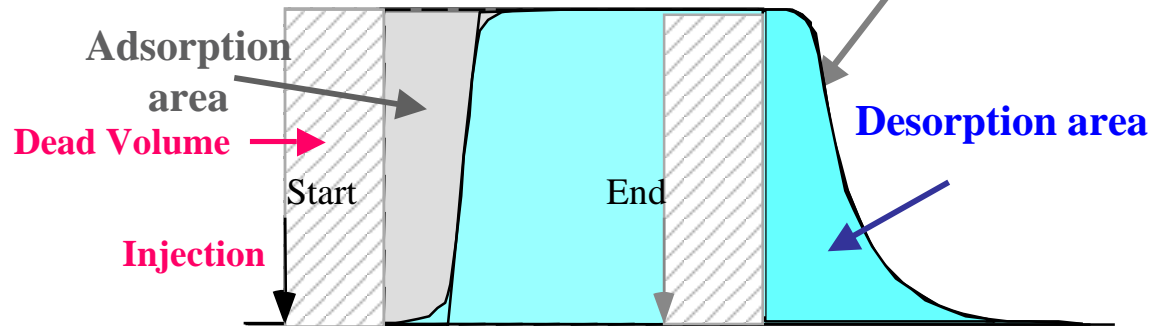
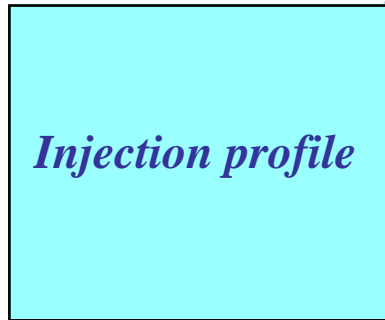
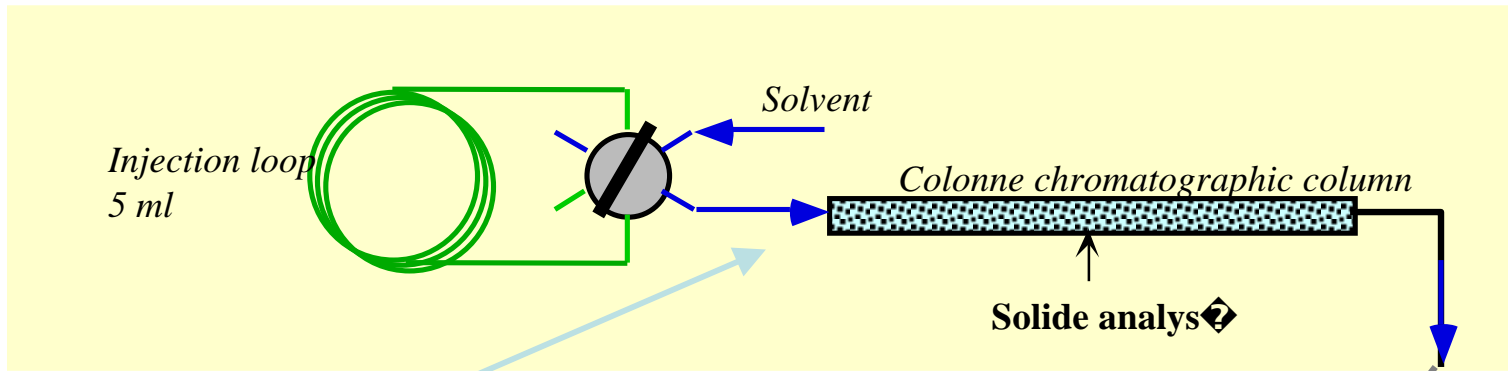
WHY?

FOR A LACK OF INTEREST ?

FOR SOME HISTORICAL REASONS ?

FOR SOME EXPERIMENTAL DIFFICULTIES ?

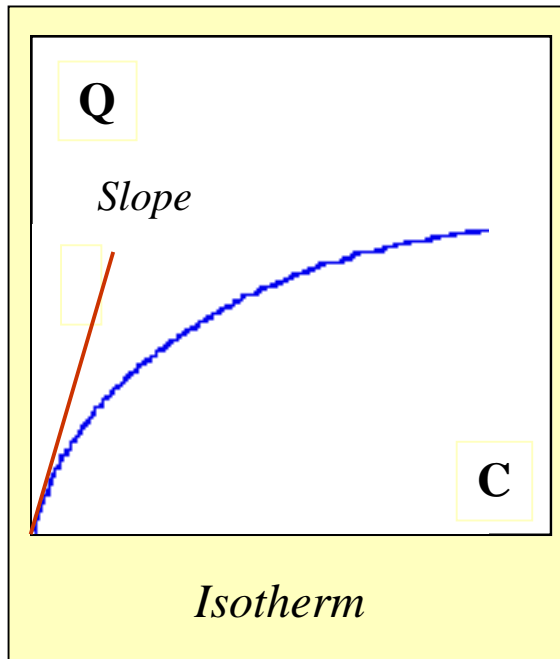
Practice of Inverse Liquid Chromatography (ILC) Frontal Analysis



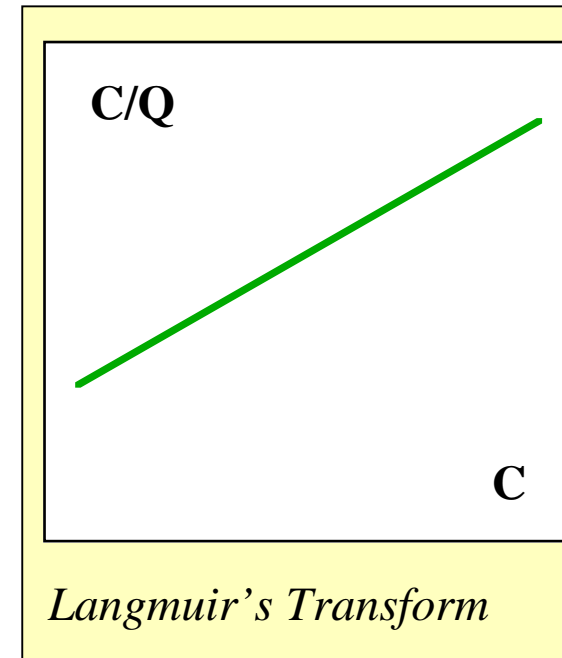
By integration we have access
To the desorption isotherm

$$\frac{\partial Q(c)}{\partial C} = \frac{V_R - V_0}{m_s} \quad \longrightarrow \quad Q(c) = \frac{1}{m_s} \int_{C_{\min}}^{C_{\max}} V_R' dC$$

Main Characteristics of the Adsorption Isotherm



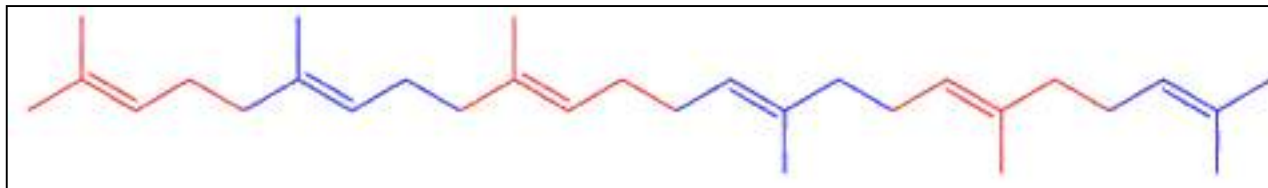
Henry's Constant
Interaction capacity
At low coverage ratio



Monolayer Capacity Q_0
Langmuir's Constant B_{Lang}

$$\frac{C}{Q(C)} = \frac{1}{Q_0 \cdot B_{Lang}} + \frac{C}{Q_0}$$

ILC of Squalene on Trimethylsilylated Silicas



Squalene : a model molecule of natural rubber

Solid: pyrogenic silica modified by controlled silylation

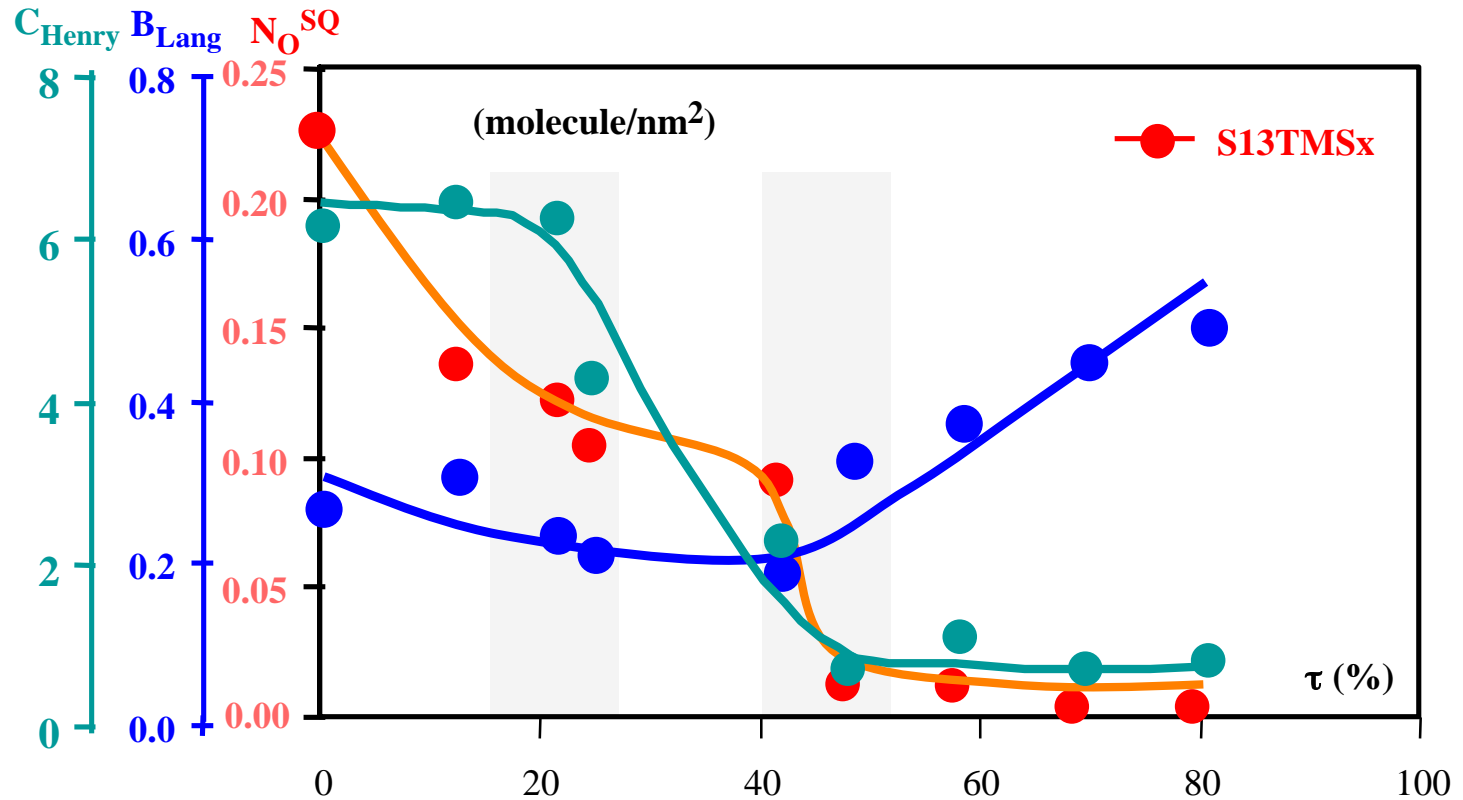


Grafting ratio from 0 to 1,7 TMS/nm²

Coverage ratio from 0 à 80 % of the surface by the TMS groups

TMS molecular area = 42 Å² (Maciel et al. 1985)

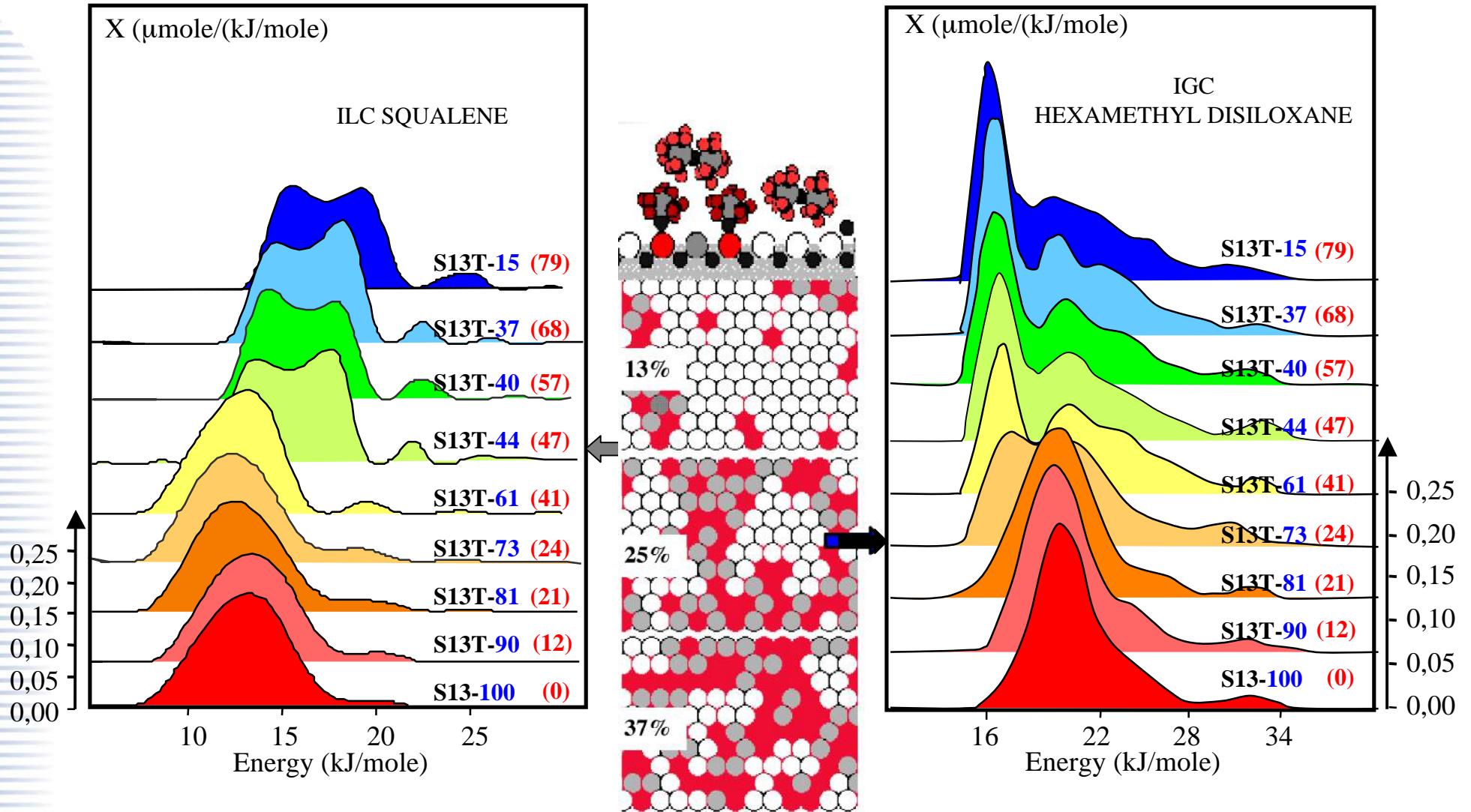
Main characteristic values of the squalene adsorption isotherms with increasing TMS coverage ratio



Evolution of the monolayer coverage (N_0^{SQ}), of the Langmuir's constant (B_{Lang}) and of the Henry's constant (C_{Henry}) of Squalene with the TMS coverage ration (τ).

Assessment of surface heterogeneity of silylated silicas

Distribution functions of adsorption energies according to the approach of DABROWSKI, PODKOSCIELNY P. BÜLOW M. (2002)

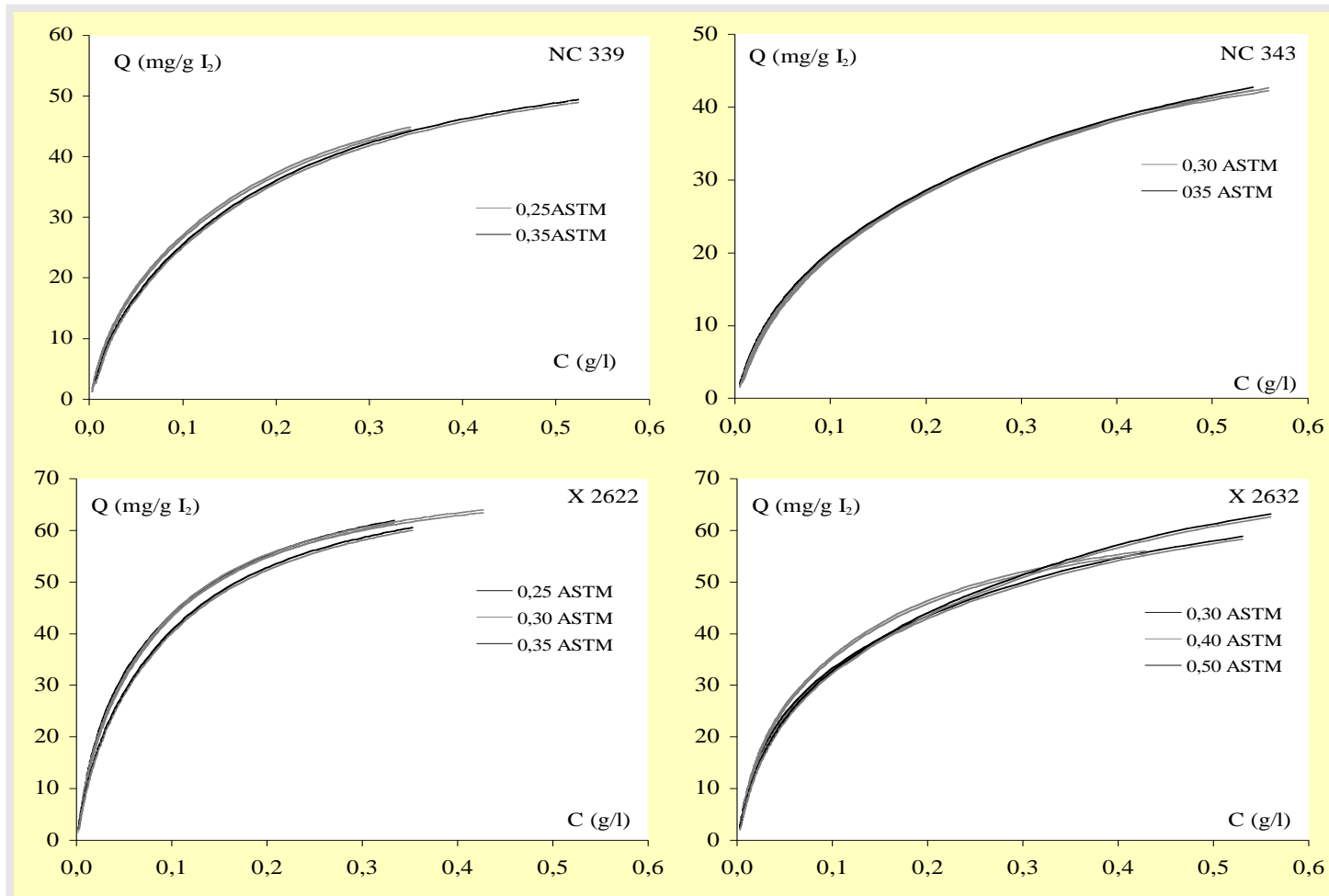


SQUALENE: FLEXIBLE PROBE

HEXAMETHYL DISILOXANE : BULKY PROBE

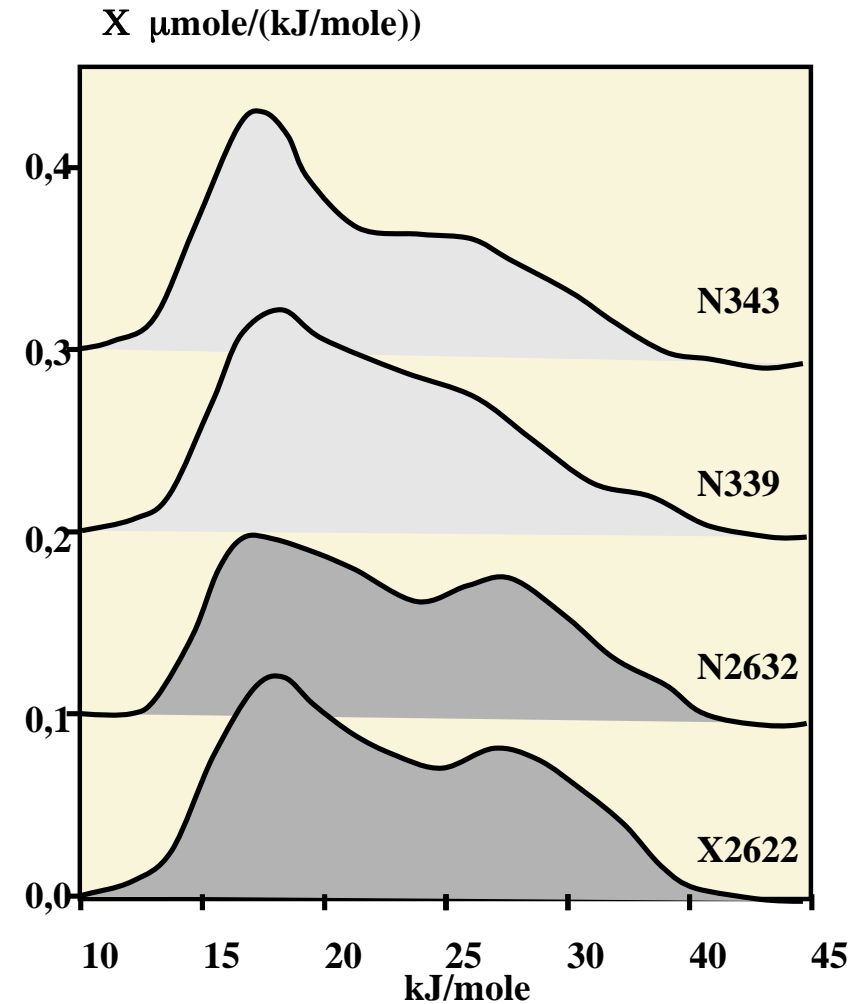
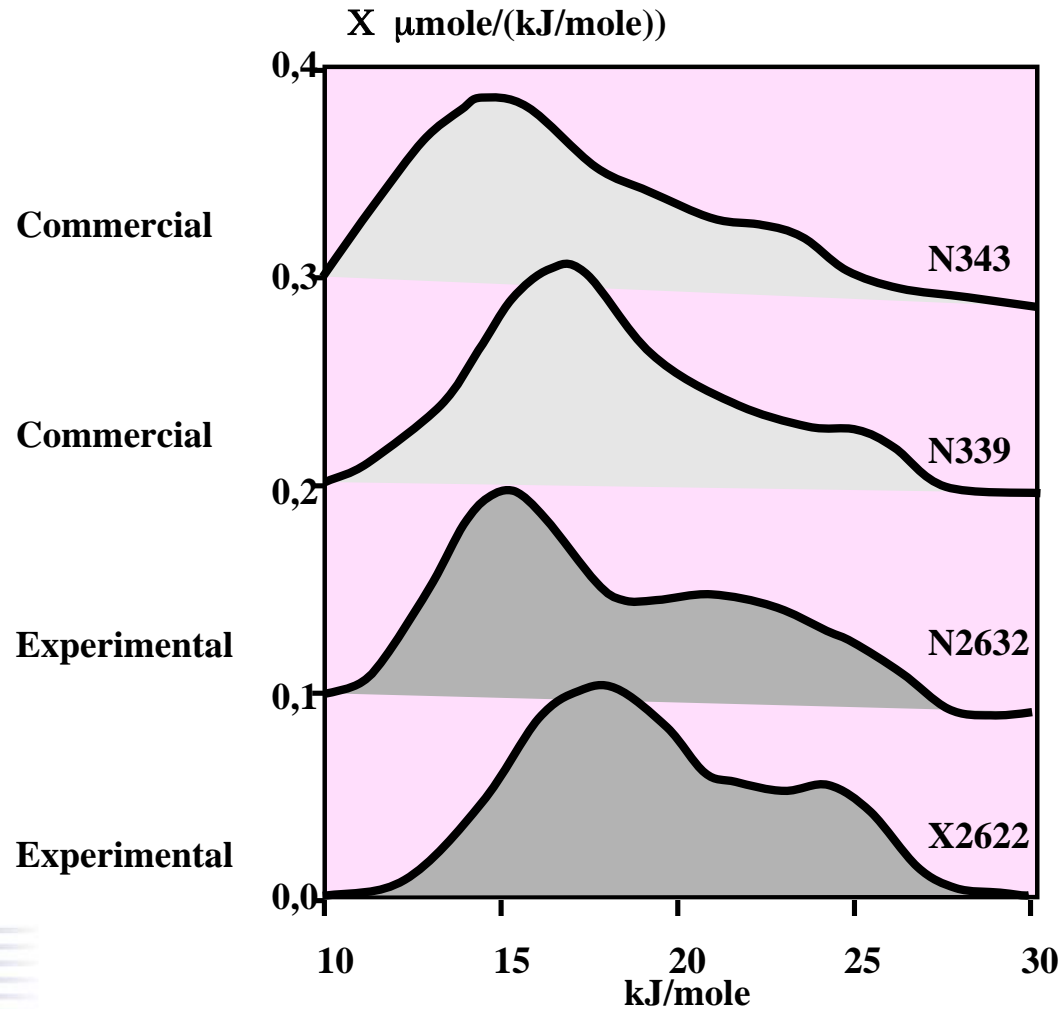
Isotherms of adsorption of Iodine on Carbon Blacks

ASTM Iodine number: measurement of the specific surface areas of carbon blacks



Adsorption Isotherms of Iodine dissolved in a Potassium Iodide solution on industrial N339, N343 and experimental X2622 et X2632 Carbon Blacks, for different ASTM concentrations .

Surface Heterogeneity of some carbon blacks



Distribution functions of adsorption energies measured on
4 commercial and experimental carbon blacks samples

For IODINE in KI solution

For HEPTANE by IGC-FC

Inverse Liquid Chromatography by Frontal Elution (ILC-FA) permits:

To characterize the surface properties just as IGC-FC

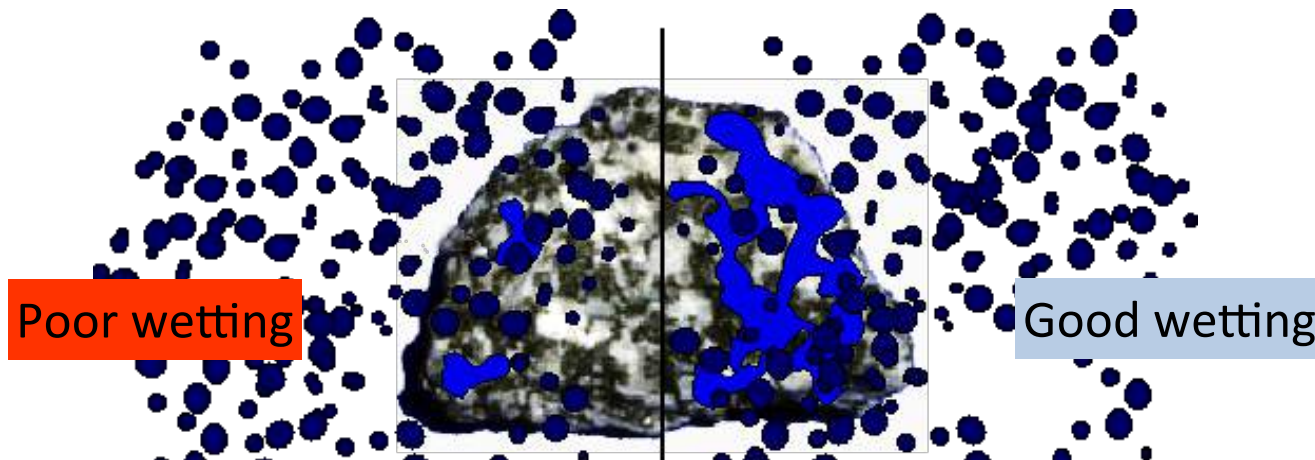
Extend IGC-FC analysis to non-volatile probe in a liquid mobile phase

Provides similar information concerning the surface heterogeneity as IGC-FC do

To lead studies in conditions more connected to the industrial problems

IGC probes are generally unrealistic models, e.g. of macromolecules

Application of ILC-FA to Road Technology



Solid

DIORITE granitoid road building material

Size particles: millimetric

Specific surface: 2 m²/g

Dispersive Surface energy, γ_s^d : 140 mJ/m²

Strong specific acidic and basic interactions

Very heterogeneous surface energy (IGC-FC)

Surfactants

DINORAM S

Linear N-alkyl propylene diamine

REDICOATE EN1009

Tallowamphopolycarboxyglycinate

Amphoteric and flexile fatty chains

SMAX 4000

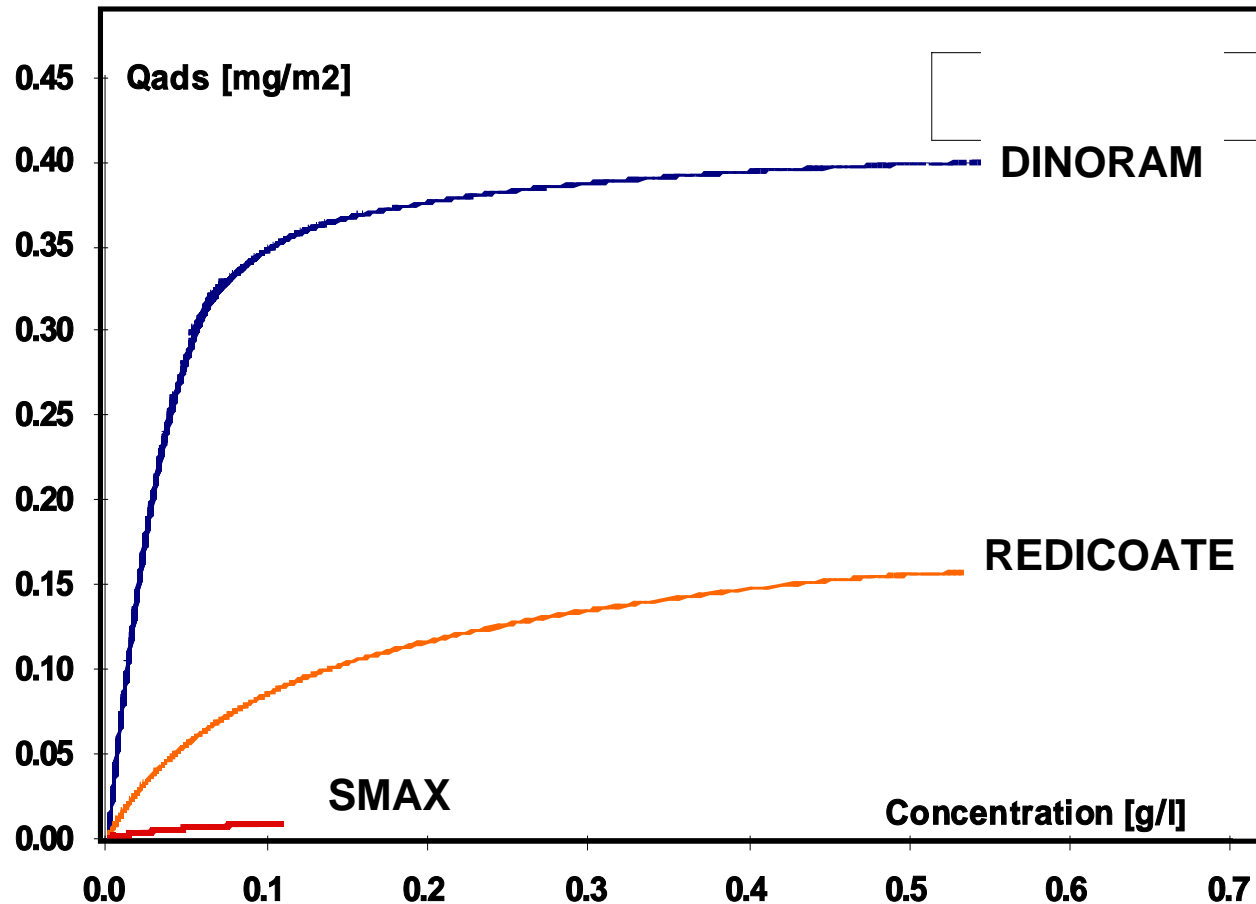
Copolymer styrene-malein-imide (4/1)

Strongly branched

ILC-FA: Mobile Phase Water

Probes: Surfactants

ILC Surfactant isotherms



$$Q_{ads} = \frac{a.C}{1 + b.C}$$

- ▲ *Isotherms are of Langmuir's type*
- ▲ *The 3 surfactants behave very differently*
- ▲ *These difference are related to the surface roughness evidenced by IGC*
- ▲ ***And DINORAM the most flexible one is the most efficient for the hydrophobation***

Conclusion about ILC Experiments

- ✦ **Quick Obtention of the adsorption isotherms in a solvent**
 - ✦ Amount adsorbed at the monolayer
 - ✦ Assesement of the surface heterogeneity
- ✦ **Possibility to operate in conditions close to the industrial application**
 - ✦ Using a convenient Solvent as mobile phase
 - ✦ Using probes directly related to the application

✦ **WHY ILC ANALYSIS IS SO SELTEN USED ?**

✦ **FOR HISTORICAL REASONS ?**

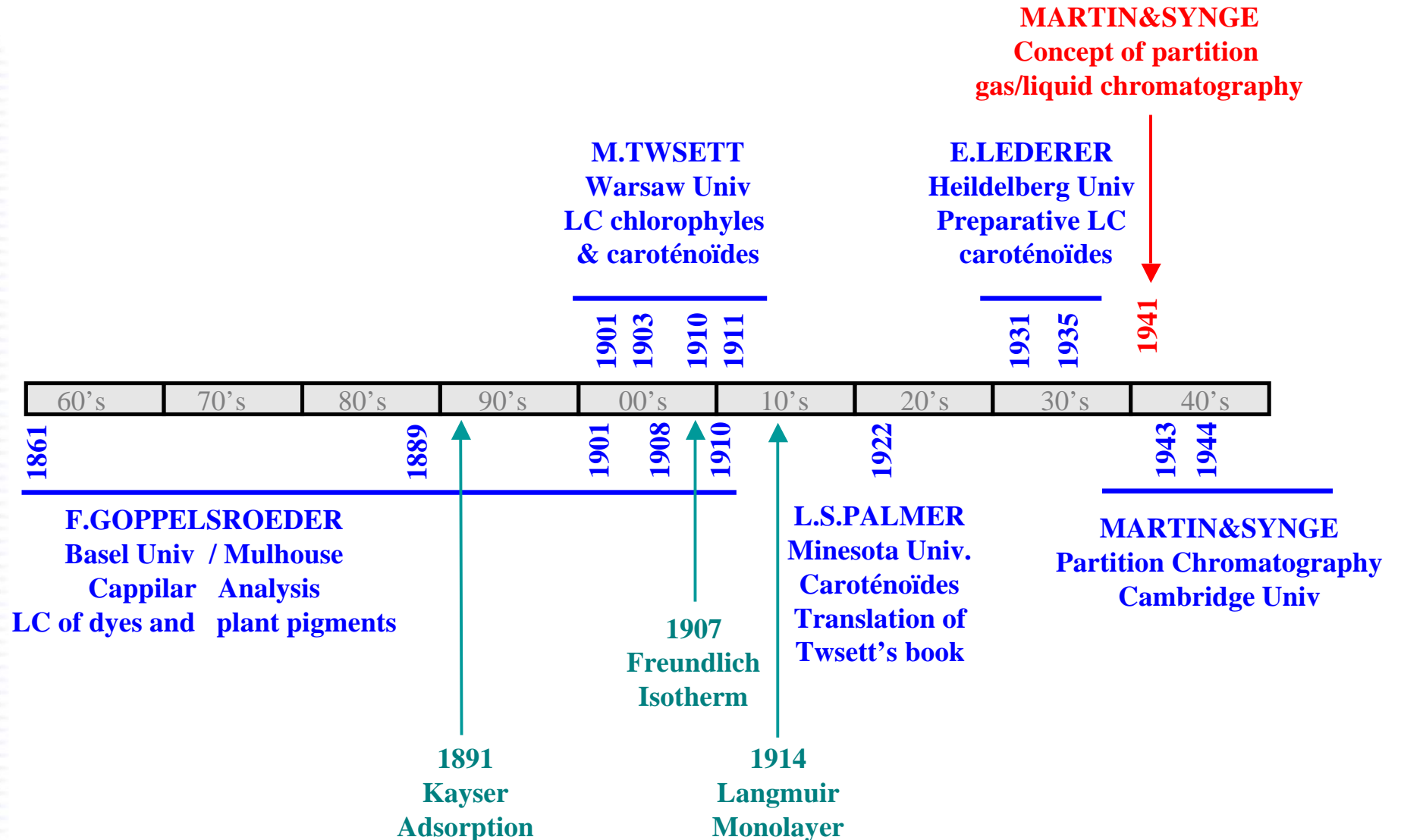
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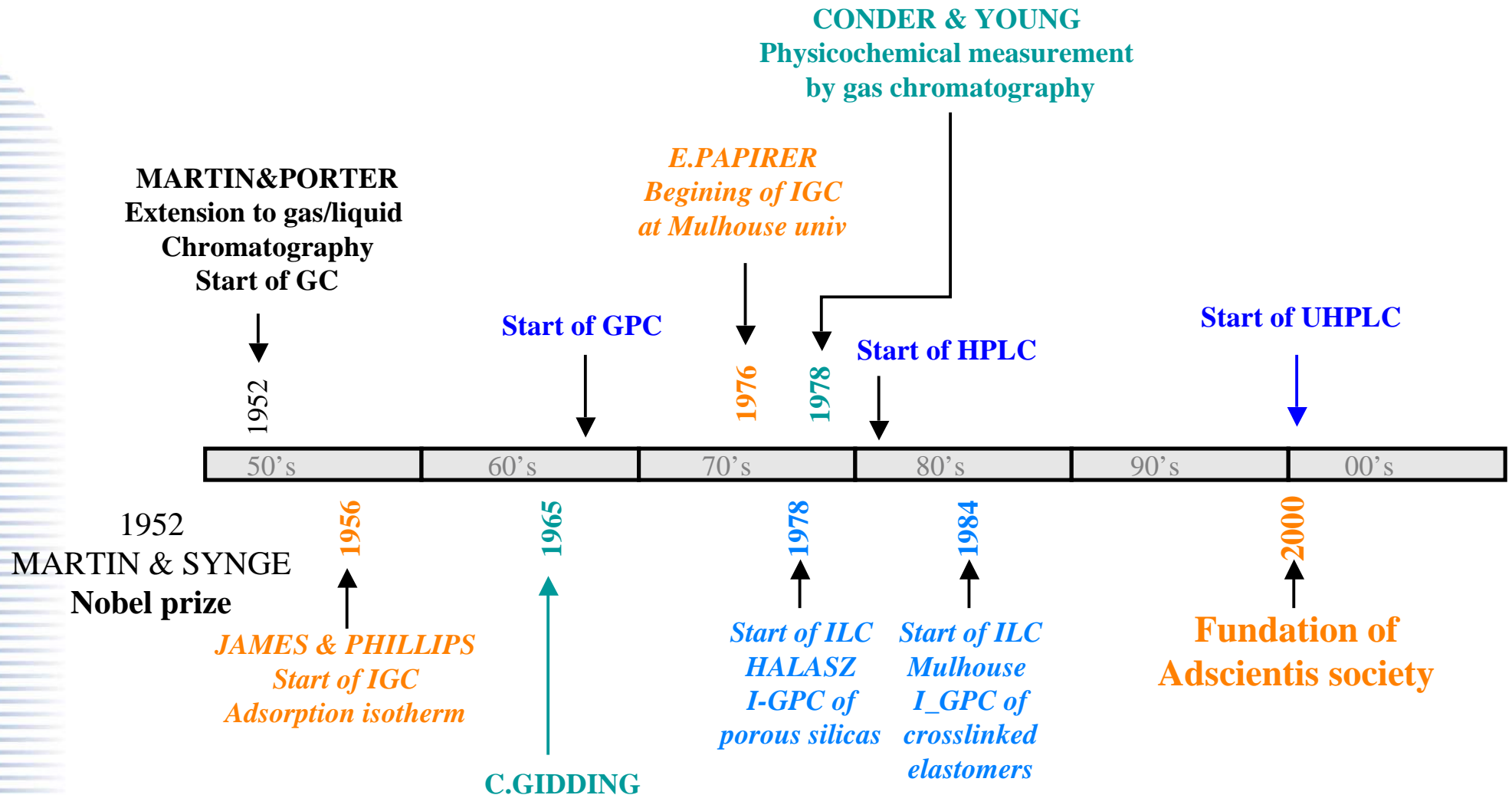
FOR SOME HISTORICAL REASONS ?

FOR SOME EXPERIMENTAL DIFFICULTIES ?

Beginning of Chromatography analysis before 1950



Evolution of Chromatography analysis after 1950



The delay in development of HPLC in comparison with GC was linked to difficulties encountered in the development of instrumentation: high pressure pumps, micrometric chromatographic phases, detectors of low dead volume

WHY?

FOR A LACK OF INTEREST ?

FOR SOME HISTORICAL REASONS ?

FOR MANY EXPERIMENTAL DIFFICULTIES ?

Pumping devices: no particular difficulties

Detectors: No difficulties so long properties of probe and mobile phase are enough different, but they are generally less sensitive than those used for IGC especially FID

Chromatographic phases:

In comparison with analytical chromatography, for ILC, **we have not the choice of the particle size**, which depends of the studied solid.

So long the permeability and stability of the chromatographic is good, no problem is encountered particles size from some microns up to millimeter

Problems of column plugging are encountered in case of:

- **sub-micrometric particles**
- **disaggregation of the particles by the probe e.g. tensides**

Professor Jean Baptiste DONNET
died on 30th November 2014



***He promoted actively physico-chemistry of solid surfaces
and in particular the inverse chromatography development***