International Symposium for Thin Layer Chromatography

INTEREST OF HPTLC FOR FOSSIL DERIVED PRODUCTS ANALYSIS : A SIMPLE APPROACH TO HYDROCARBON GROUP TYPE ANALYSIS

Muriel Matt[1,2], Vicente L. Cebolla[1], Luis Membrado[1], Eva M. Galvez[1], Jesus Vela[1], Robert Bacaud[3]

1 :Instituto de Carboquimica, CSIC, Zaragoza. Spain
2 : LTAC, Université de Metz. France
3 : Institut de Recherches sur la Catalyse, CNRS, Lyon. France

Acknowledgements to :

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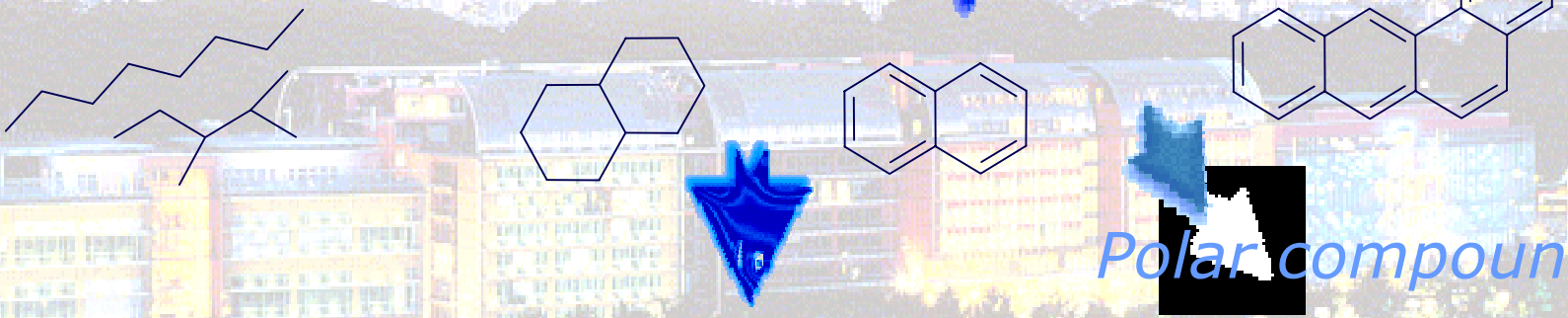
Aims

Hydrocarbon Type Analysis



planar chromatography

- HPTLC plates
- UV and Fluorescence scanning densitometry
- Horizontal developing chamber

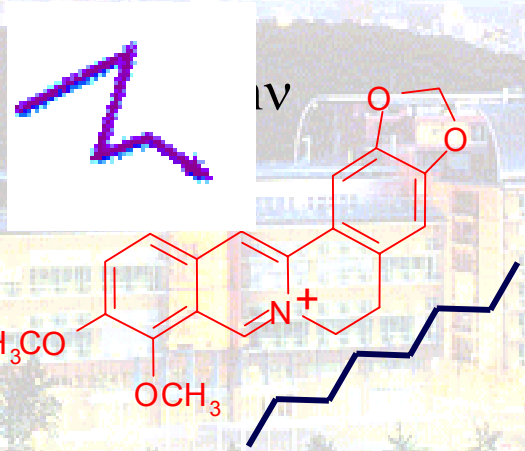
Interests

- Why HTA for fossil derived products ?
  - Fuel formulation
    - *Products of thermal pyrolysis*
    - *Coal conversion*
    - *Desulfurization of fuel*
  - To follow a process
  - Legislation
    - *PACs*
- Problem of standards
- Planar Chromatography
  - The whole sample is analyzed
  - Rapidity
  - Automation

Detection of Alkanes and Naphthenes

Saturated compounds are not detected in UV/Visible region

Have no fluorescent properties



Fluorescence emission

BERBERINE-INDUCED FLUORESCENCE

Analyte/Berberine interaction is responsible of fluorescence enhancement

ion-induced dipole interactions

Environment polarity modulates the fluorescence response

Which standards ?

- One molecule → Its commercial standard
- Complex mixtures → One molecule as standard ?

Detection method is chosen regarding to the structure of the molecules

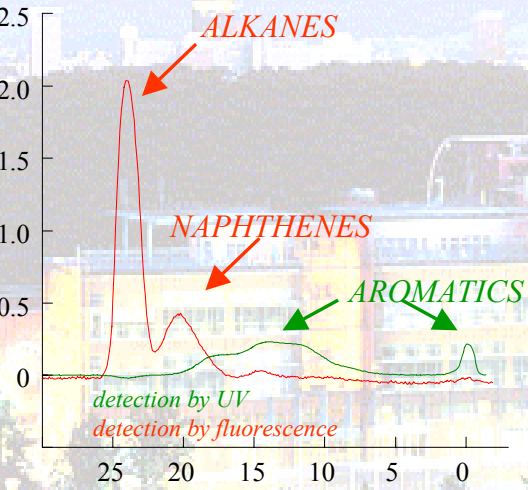
→ Response factor is generally structure dependent

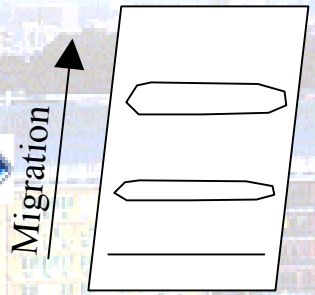
↓

Preparative step based on TLC

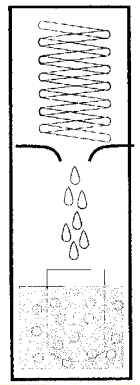
Standard Purification

Example for the Fuel





Preparative TLC



Soxtec extraction

Extract concentrated under N_2 until constant weight

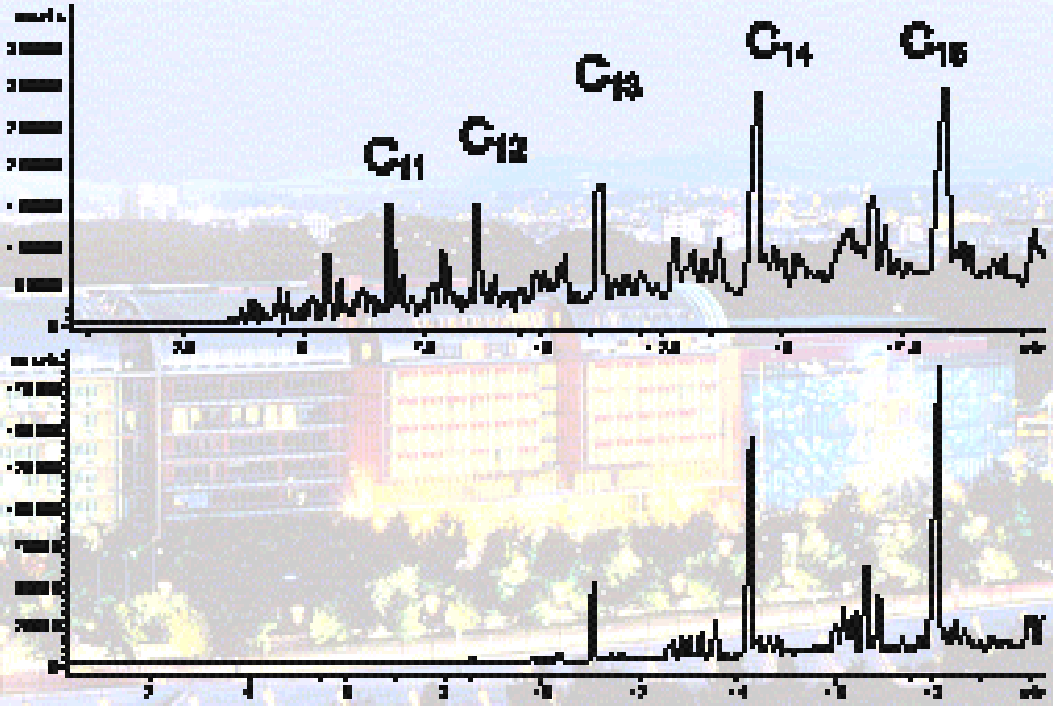
Purity checked

- GC-MS
- TLC
- NMR

Each fraction will be a standard

Evaluation of evaporation losses during standard purification

- GC-FID of gas oil
- GC-FID of alkanes fraction



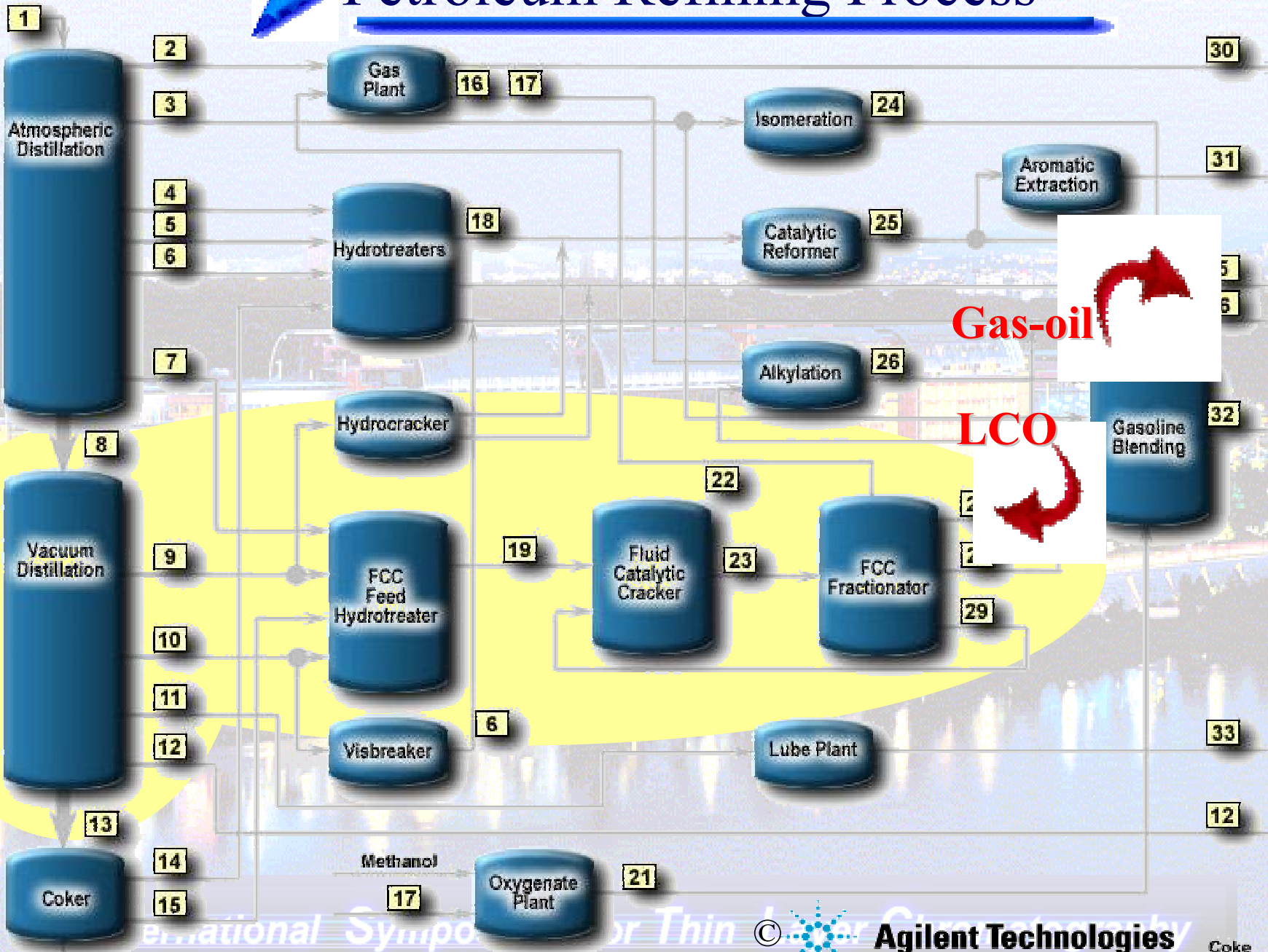
- *6 % for alkanes*
- *1 % for aromatics*

Samples

Middle Distillates

- Straight-run gas-oil (230-380°C)
  (Institut de Recherche sur la Catalyse, Lyon)
  - also submitted to hydrodesulfurization
- Light cycle oil (CEPSA, Madrid)

Petroleum Refining Process



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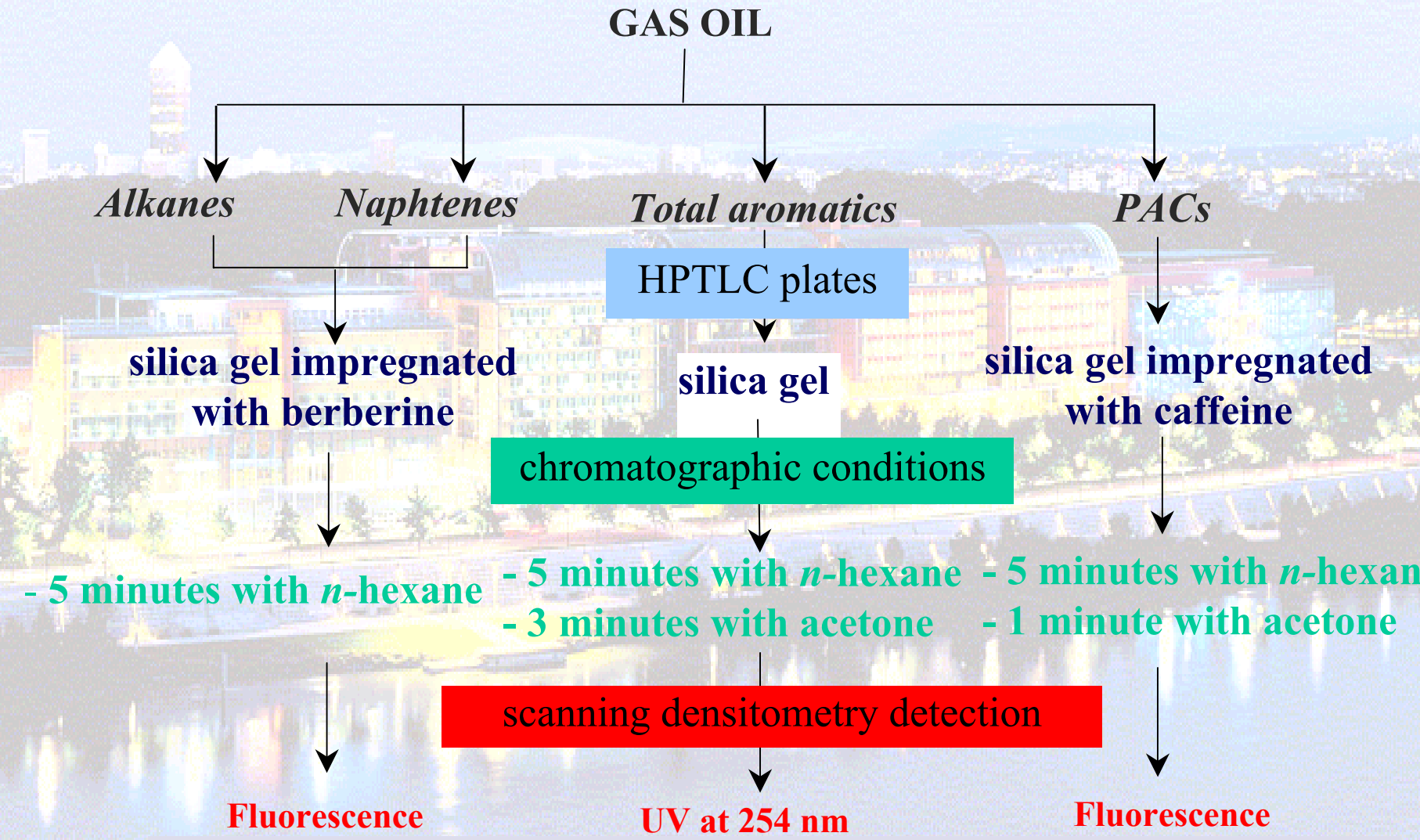
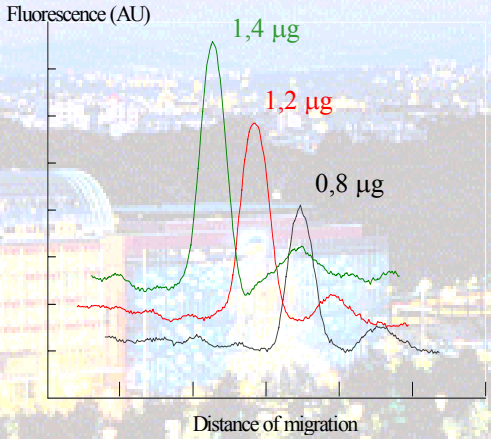
Chromatographic Parameters

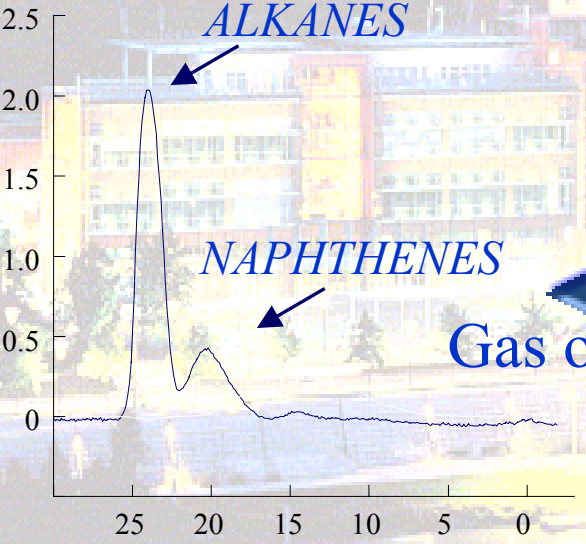


Analysis of the saturated compounds

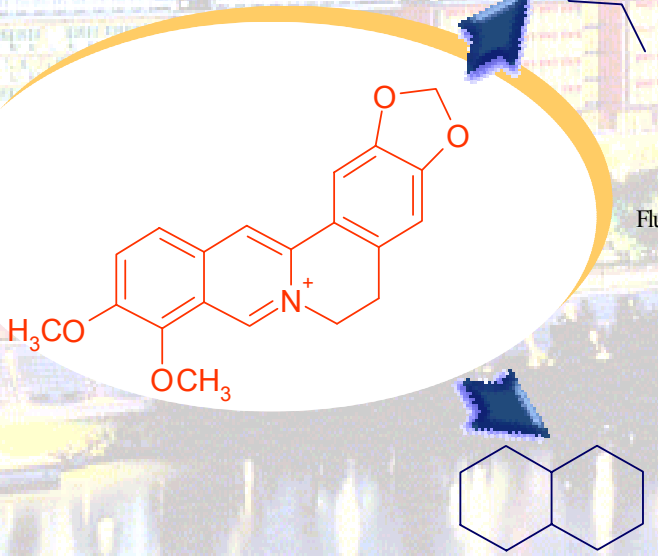
Fluorescence Scanning Densitometry

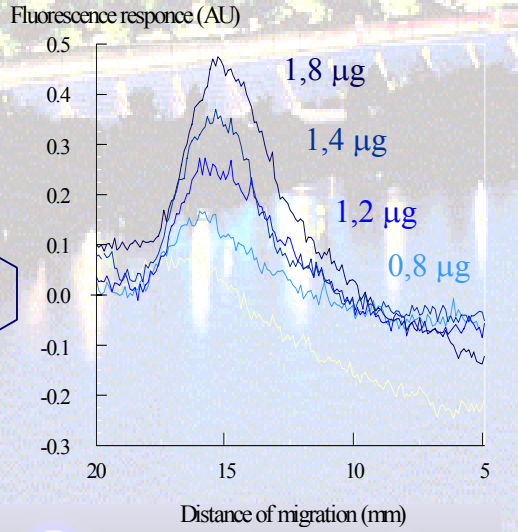
Calibration Range : 0.05 to 1.5 µg
y=1163x+744 R^2 = 0.9862
LOD = 0.05 µg LOQ = 0.15 µg





Gas oil



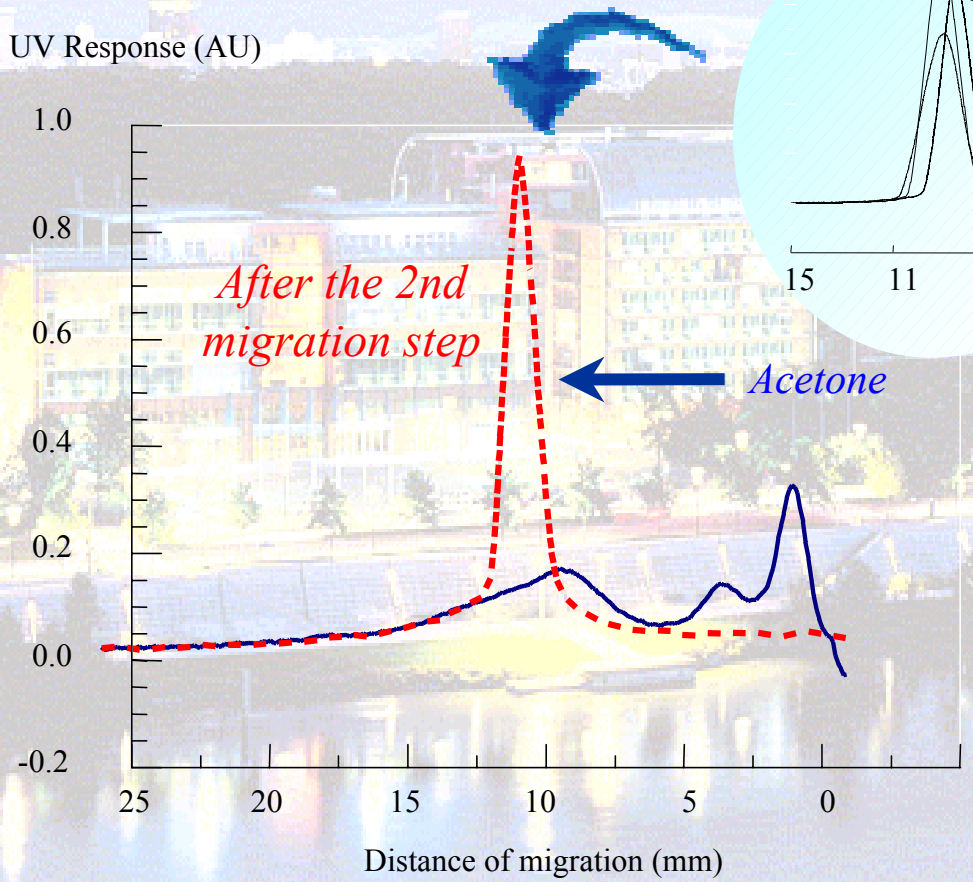


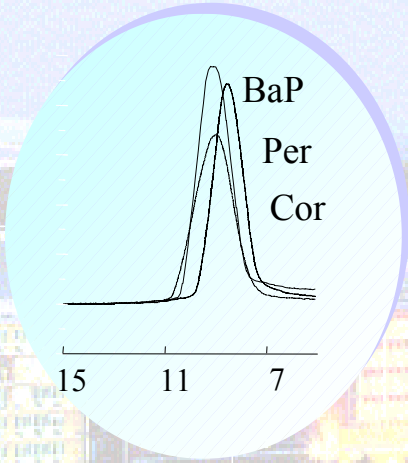
Calibration Range : 0.6 to 2.4 µg

y=655x-89 R^2 = 0.9097
LOD = 0.1 µg LOQ = 0.3 µg

Total aromatics

UV Scanning Densitometry





Calibration Range : 0.1 to 2.0 µg

$y=873x+89$ $R^2 = 0.9684$

LOD = 0.06 µg LOQ = 0.18 µg

Accuracy

Standard Addition

External Standard

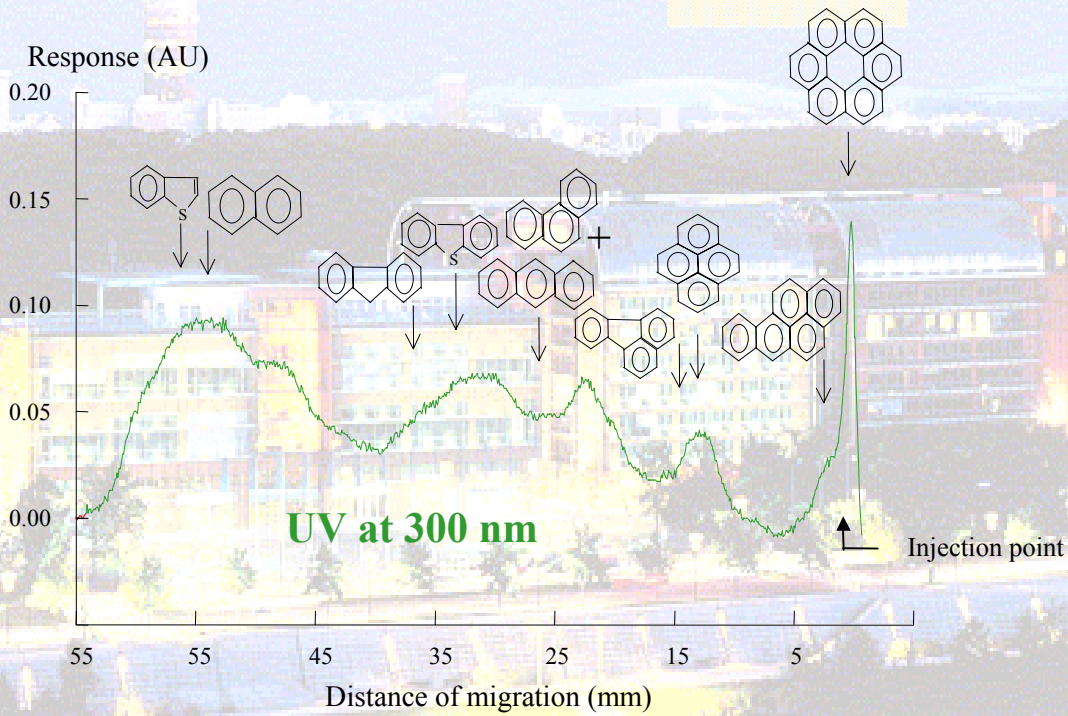
	Percentage (m/m) determined by standard addition	Percentage (m/m) determined by external standard (RSD%)
LCO	57.7 %	57.5 % (4.3)
GO	16.1 %	17.0 % (3.9)

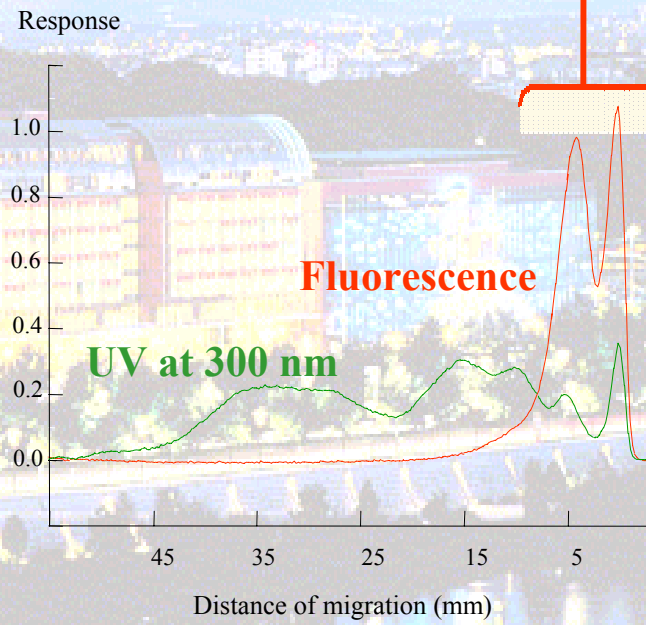
Preparation of Synthetic Fuel

Theoretical value (%)	Measured value (%) (RSD%)	Recovered value (%)
16.8	15.3 (6.5)	91.1
22.2	22.7 (20.0)	102 . 2
32.2	29.8 (10.0)	92.5
52.3	47.1 (4.1)	90.1

Heavy aromatics (PACs)

Plate impregnated with Caffeine : electron acceptor





- 2nd migration step to merge PACs
- Fluorescence scanning densitometry

➡ Selective detection and quantification of PACs

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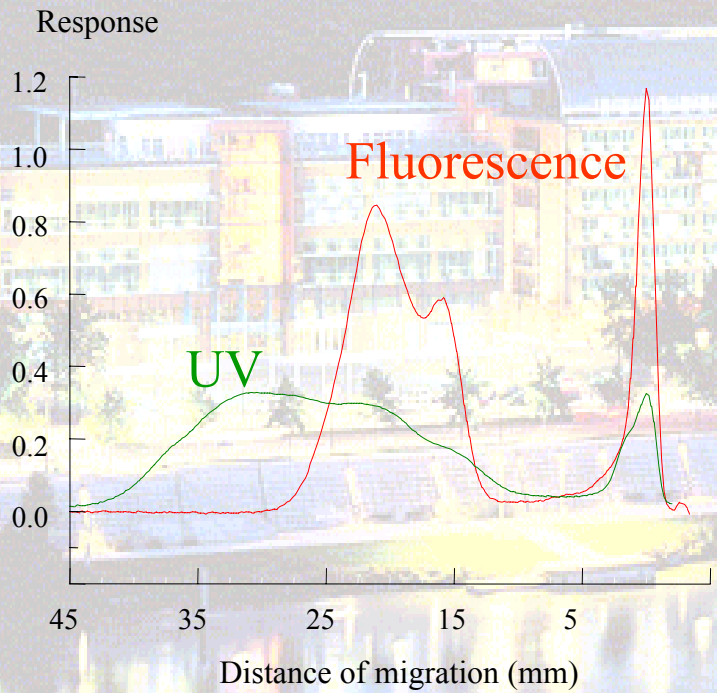
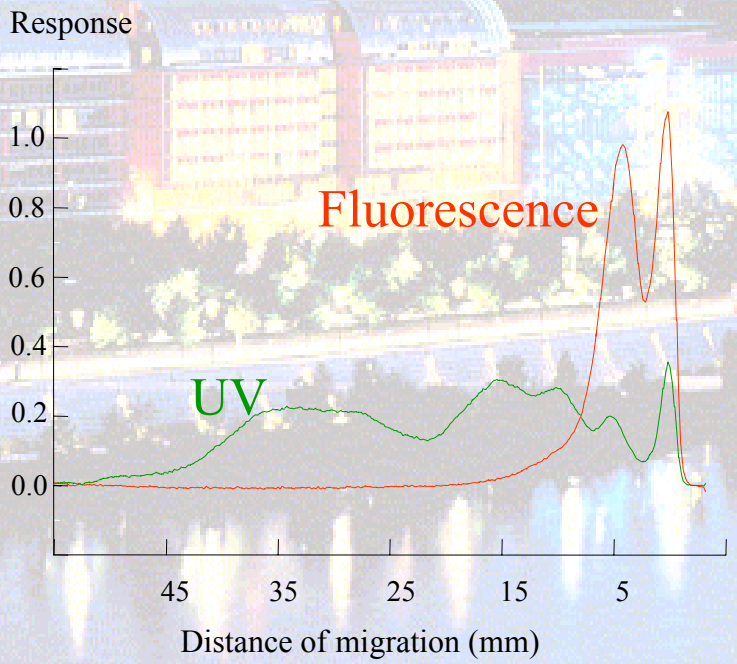
Influence of Caffeine in the separation of aromatic

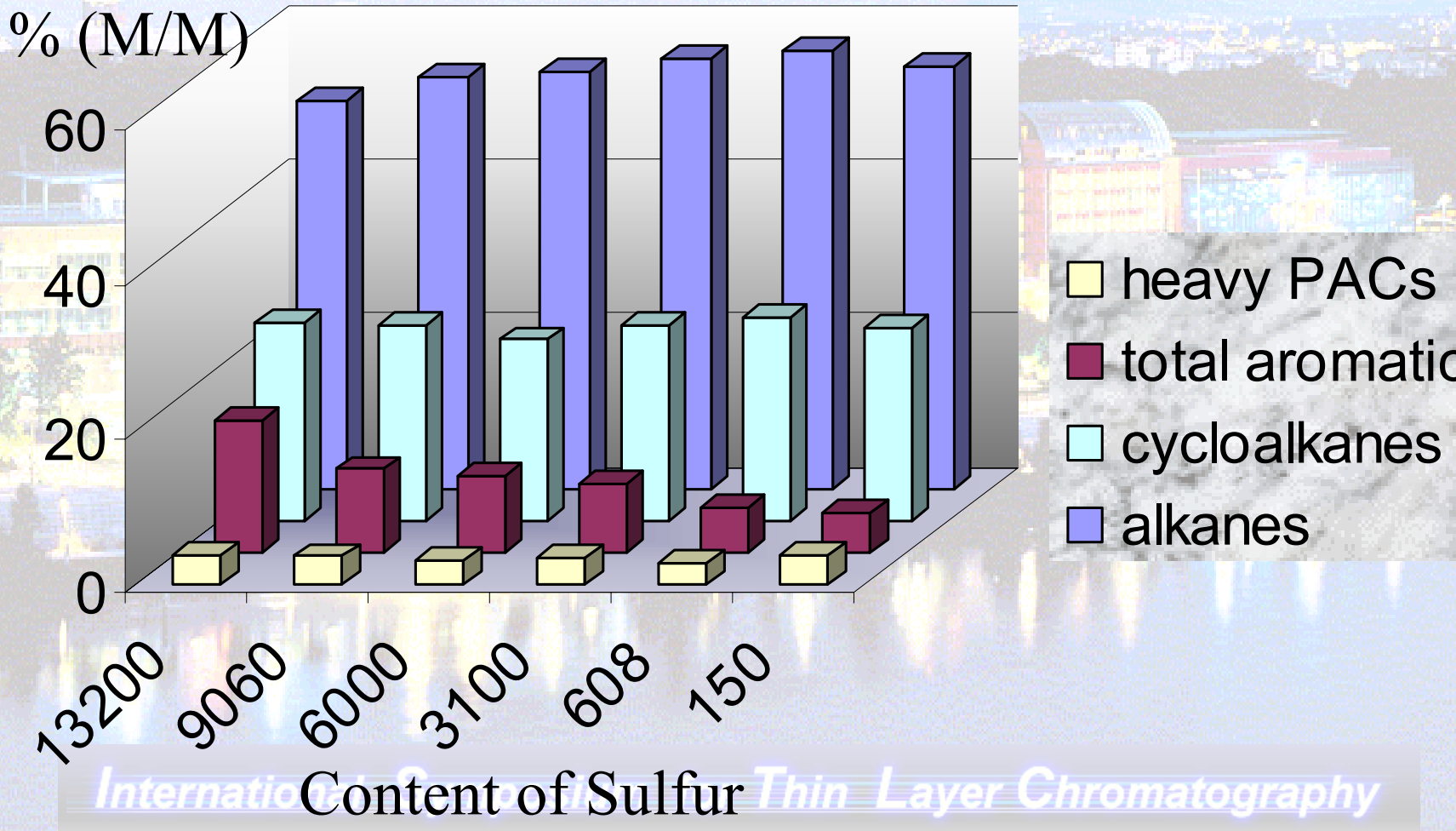
Silica gel



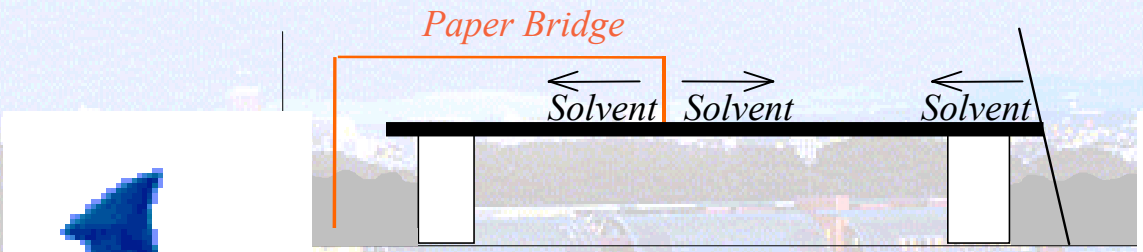
Caffeine stationary phase

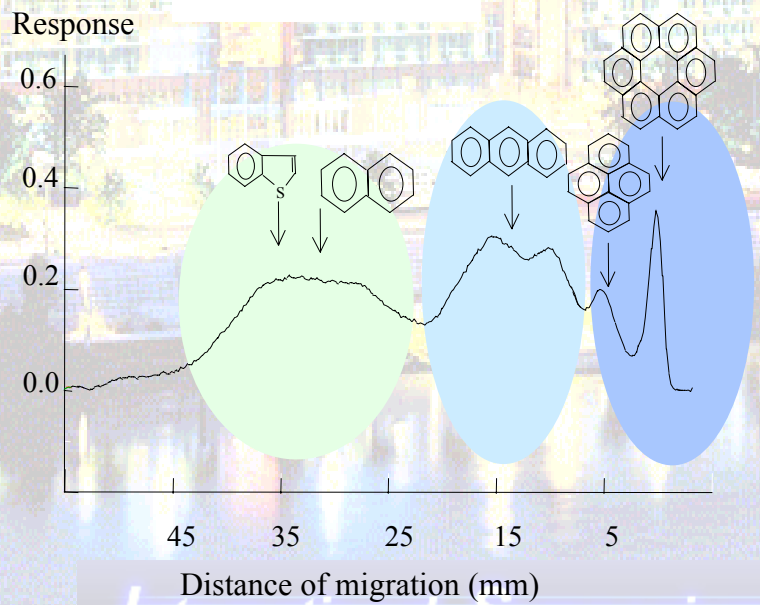


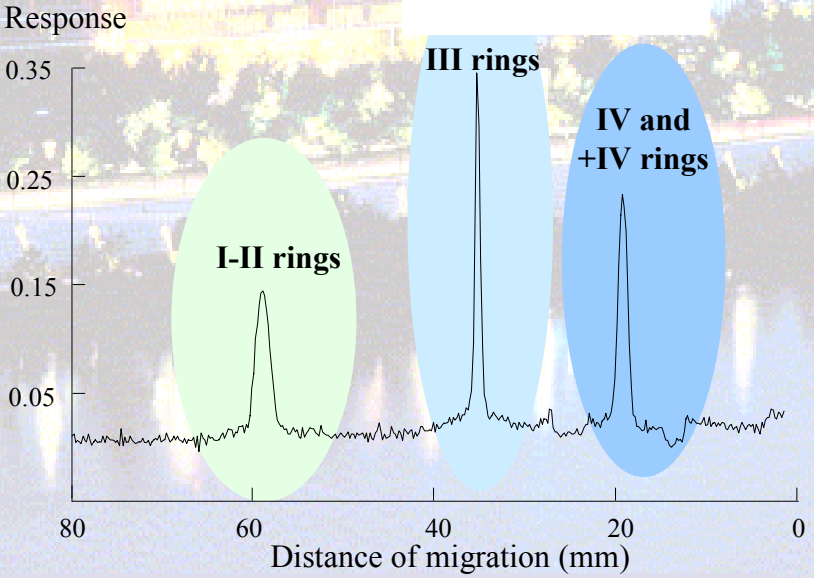
Complete analysis of a Gas oil submitted to desulfurization



Separation of Aromatics according to the number of rings







Conclusions

HPTLC is an interesting system for the analysis of complex samples

- **Low cost**
- **sensitive**
- **Accurate**
- **Rapidity**

HPTLC coupled to UV and fluorescence scanning densitometry is a powerful tool

- **Flexibility of development**
- **Applicable to a wide range of sample**

Suitable alternative to HPLC and other techniques utilized in HTA

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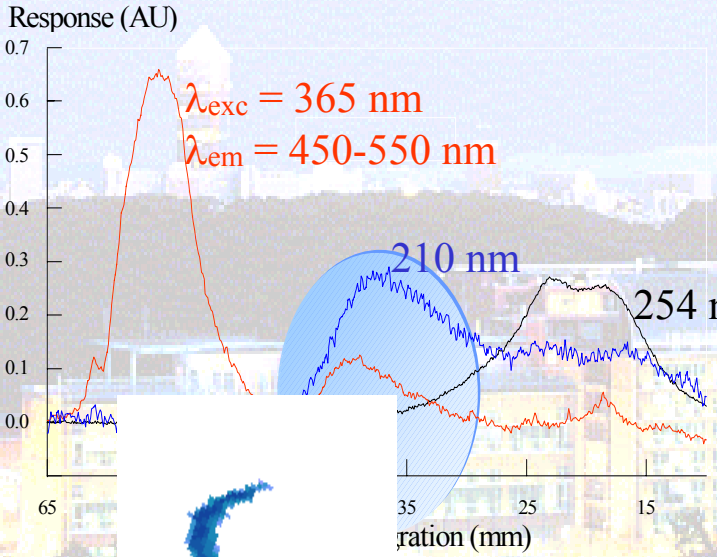
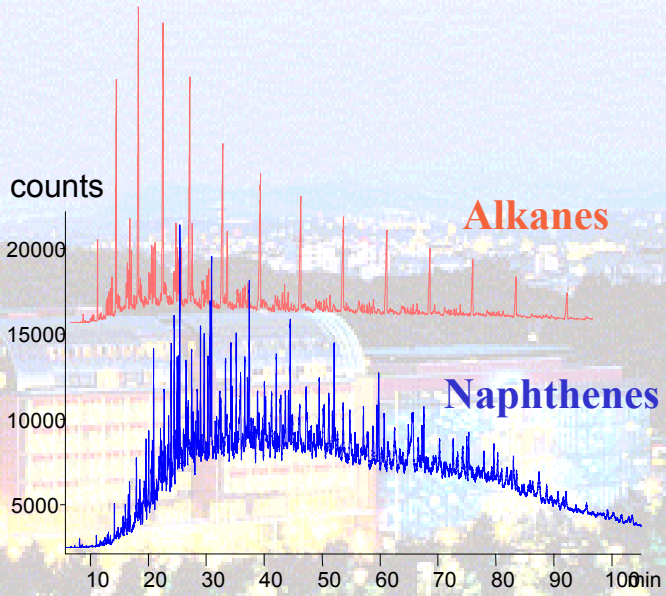
Identification of Naphthene fraction



GC-FID



aphthenes absorb at 210 nm

^{1}H-NMR

Chemical shifts and coupling constant typical of cyclic -CH_2-

ncreasing of the ratio CH_2/CH_3 (1459 cm^{-1} - 1380 cm^{-1})

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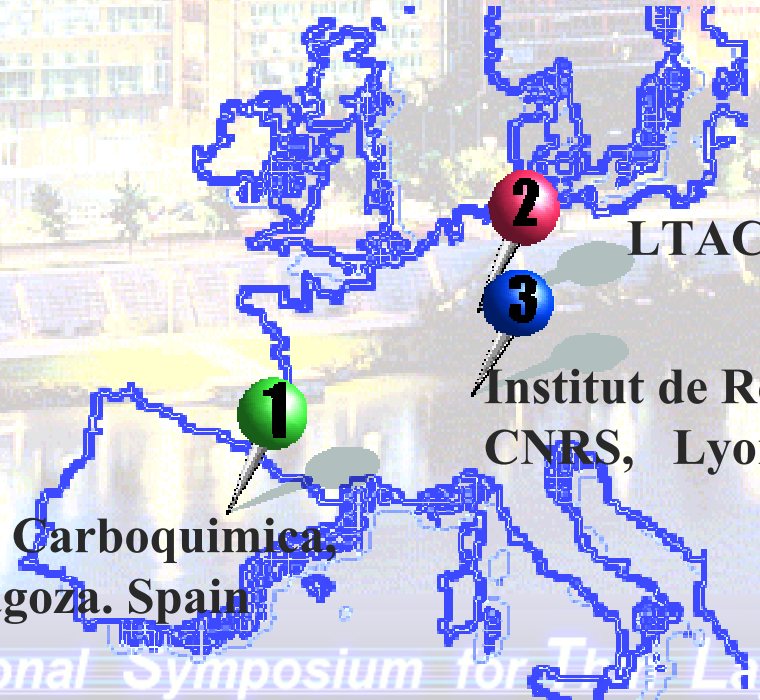

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