4th International Conference on Packed-Column SFC
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Towards comprehensive techniques involving a supercritical fluid: SFC-xGCxGC and SFCxSFC

D. Thiébaut, S. Jenadi, J. Vial, P. Sassiat, T. Dutriez*, M. Courtiade*

Laboratoire Sciences Analytiques, Bioanalytiques et Miniaturisation
CNRS UMR 7195 PECSA - ESPCI-ParisTech 10 rue Vauquelin,
75 005 Paris – France

*IFP Energies nouvelles, Division Physique et Analyse
BP3, 69360 Solaize

PETROLEUM RELATED SAMPLES

- Hydrocarbons are soluble in the CO_2
  - SFE
  - SFC without modifiers
- Detection, the « forgotten advantage »
  - FID is used (restrictor required)
    - Almost universal trace
    - Similarity of response vs structure of analytes
    - Easy quantification vs RID or ELSD in LC
  - Specific detectors

PETROLEUM RELATED SAMPLES

- Complex samples
  - Similar families of hydrocarbons
  - Different families of hydrocarbons
  - New families coming from new processes
    - O, S, N…
- Heavy compounds to be transformed
- Treatments to remove unwanted compounds

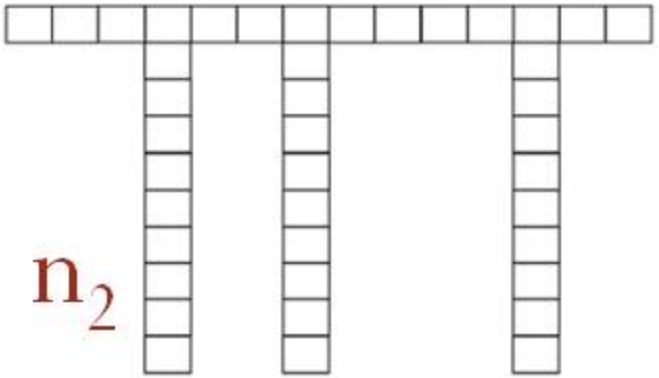
PETROLEUM RELATED SAMPLES

Increasing complexity with carbone atoms number

GC…SFC….(LC)…

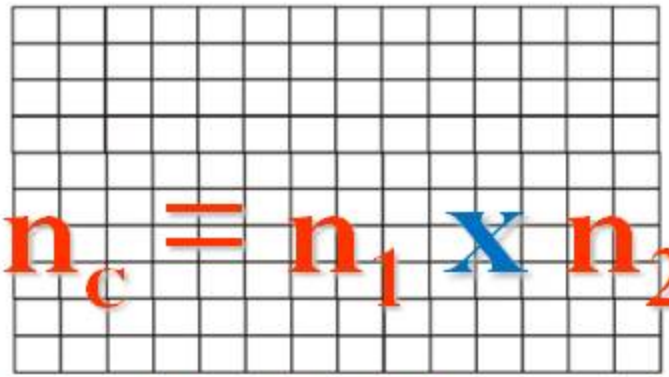
COMPREHENSIVE MULTI – DIMENSIONAL TECHNIQUES

n_1



n_2

$$n_c = n_1 + 3n_2$$



$$n_c = n_1 \times n_2$$

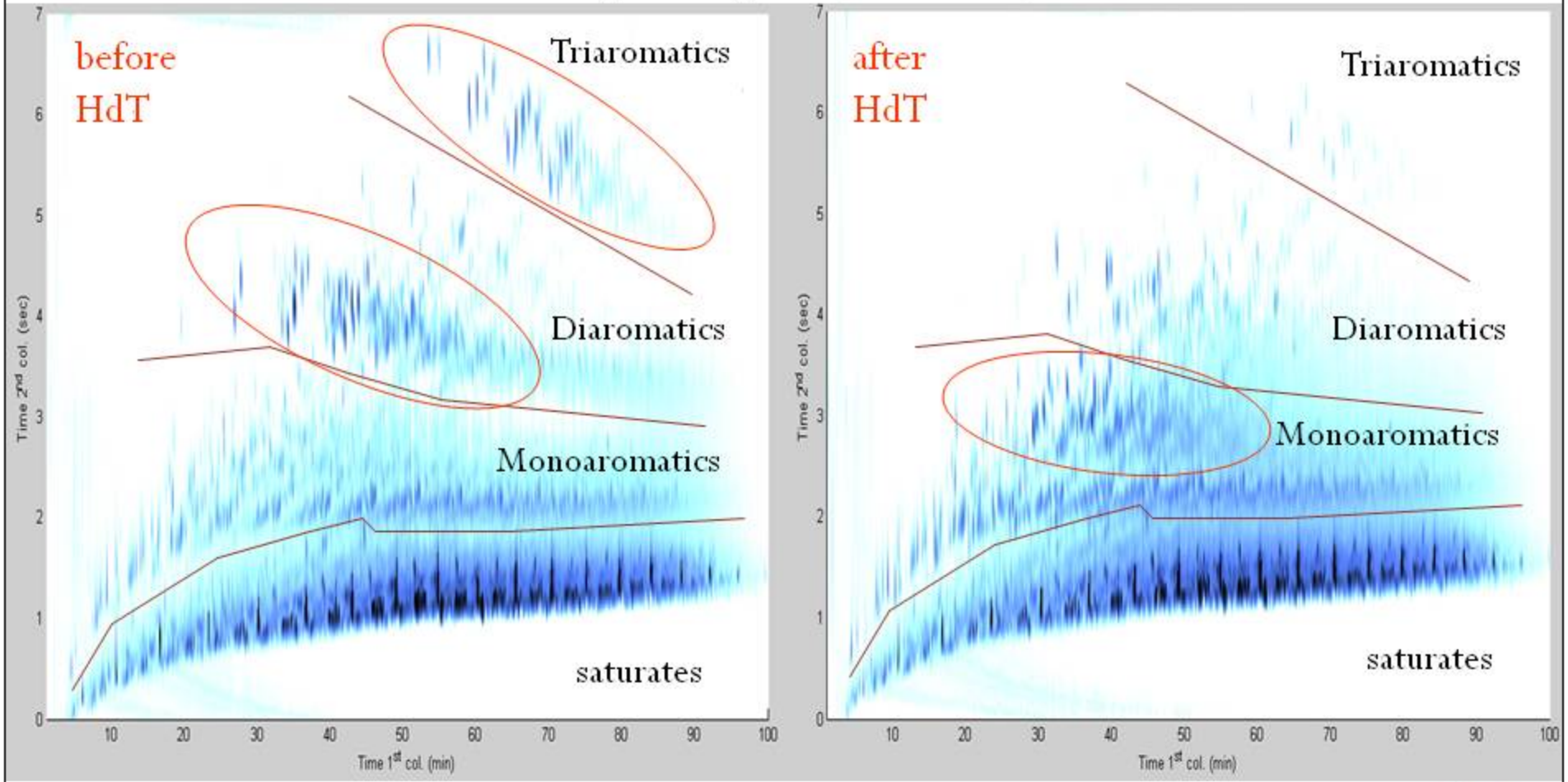
Comprehensive 2D separation

GAS-OIL: HYDROTREATMENT EFFECT

Reduction of S, N, aromatics in gasoils

Straight-run gasoil (224-404°C)

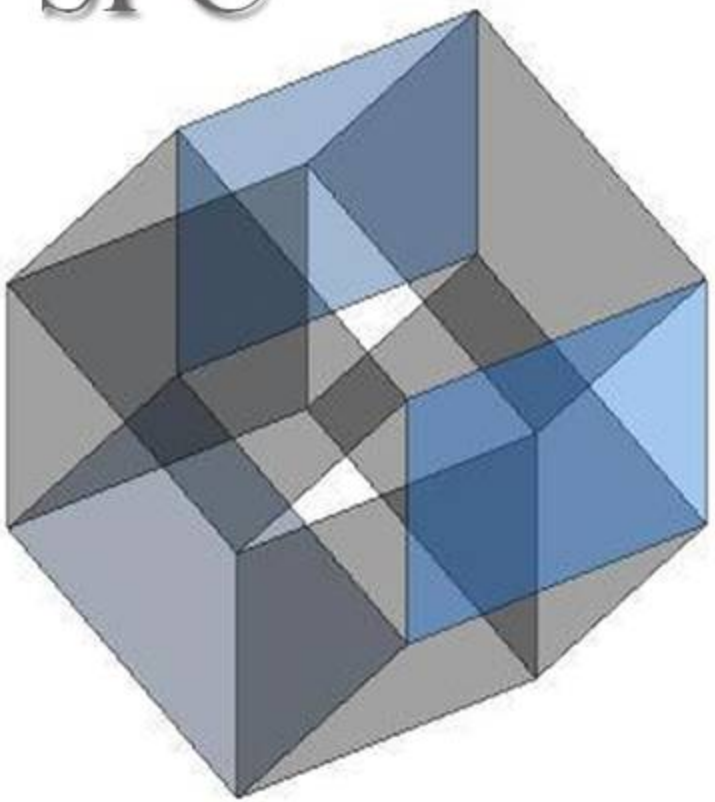
#C25…



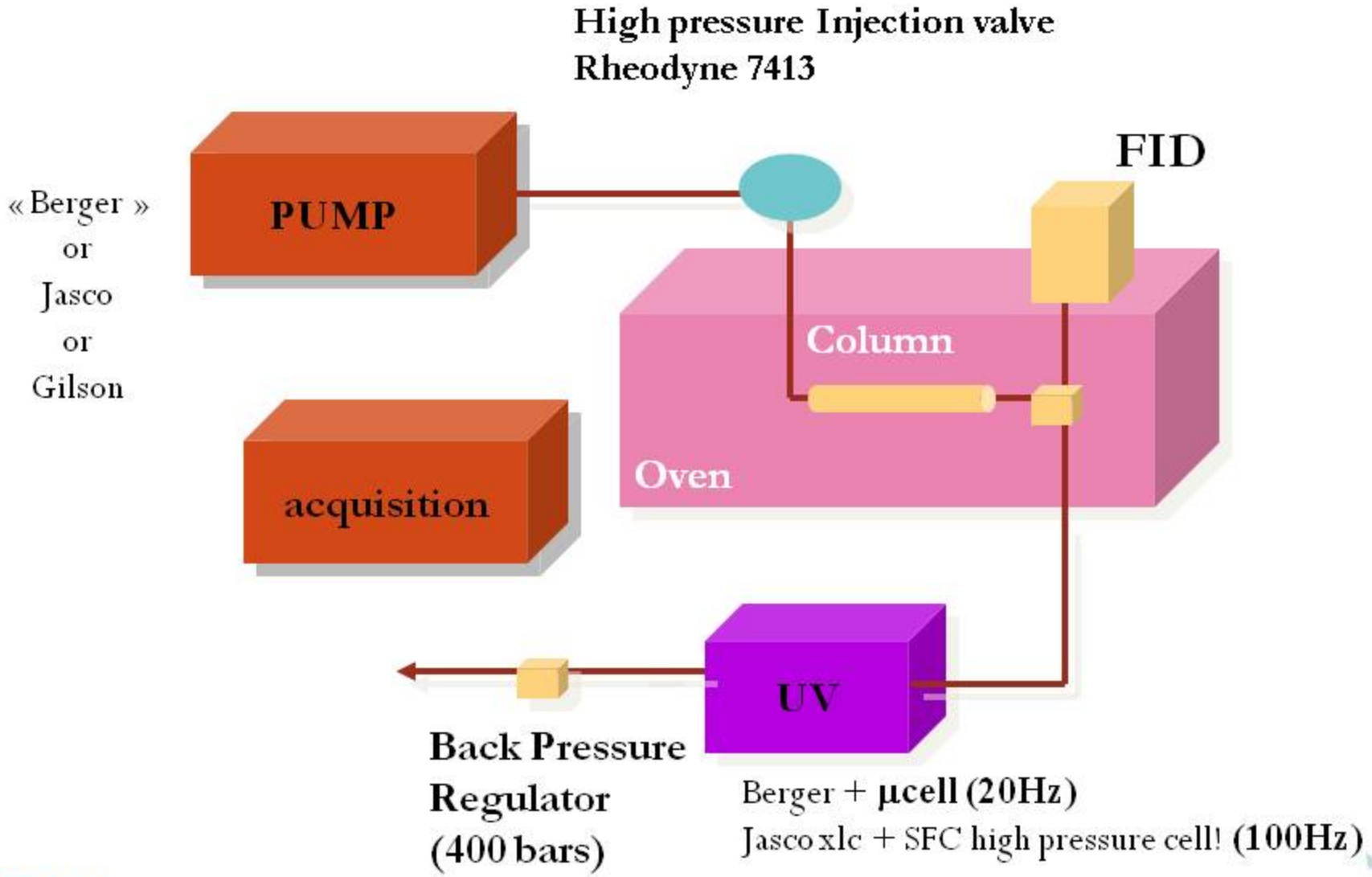
GCxGC MONITORING ("NORMAL PHASE" MODE)

NEED FOR THE 3RD OR 4TH DIMENSION: SCIENCE FICTION CHROMATOGRAPHY?

SFC

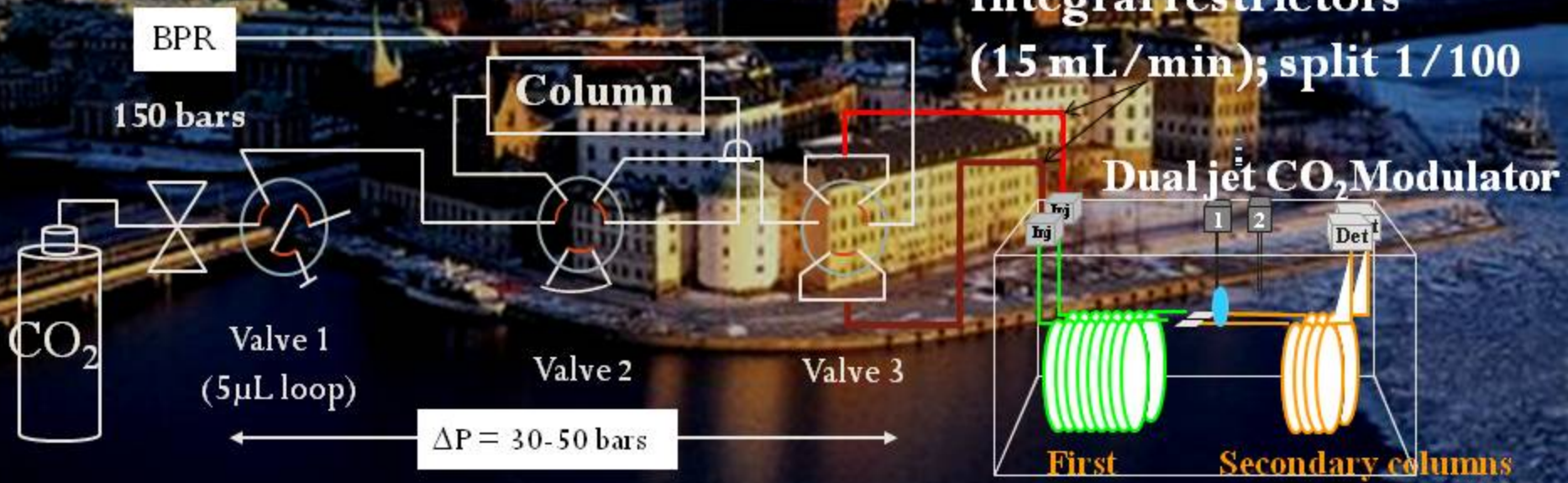


SFC « REGULAR » APPARATUS



ONLINE SFC - TWIN-GC×GC

- **Objectives:**
  - SFC : Hydrocarbon group separation into saturated and unsaturated
  - Simultaneous and subsequent 2D-GC analysis of each fraction



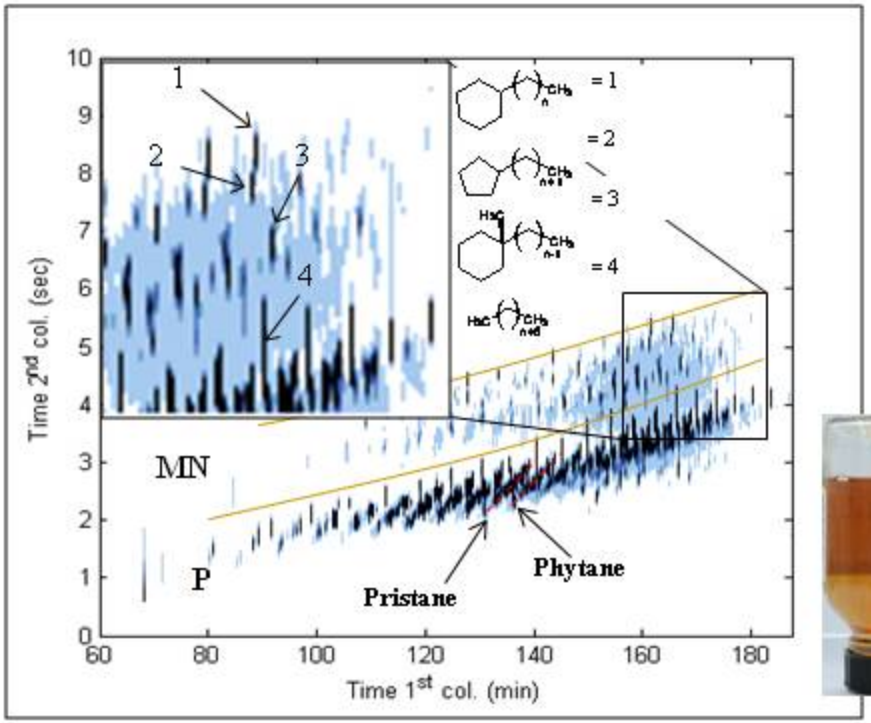
SFC columns: Silica gel (LiChrospher 600 m^2/g, VWR, 250 x 4.6 mm) or
Silver loaded cation exchange column (Chromsphere Lipids, Varian, 100 x 4.6 mm)

Pump (Model Gilson 306)

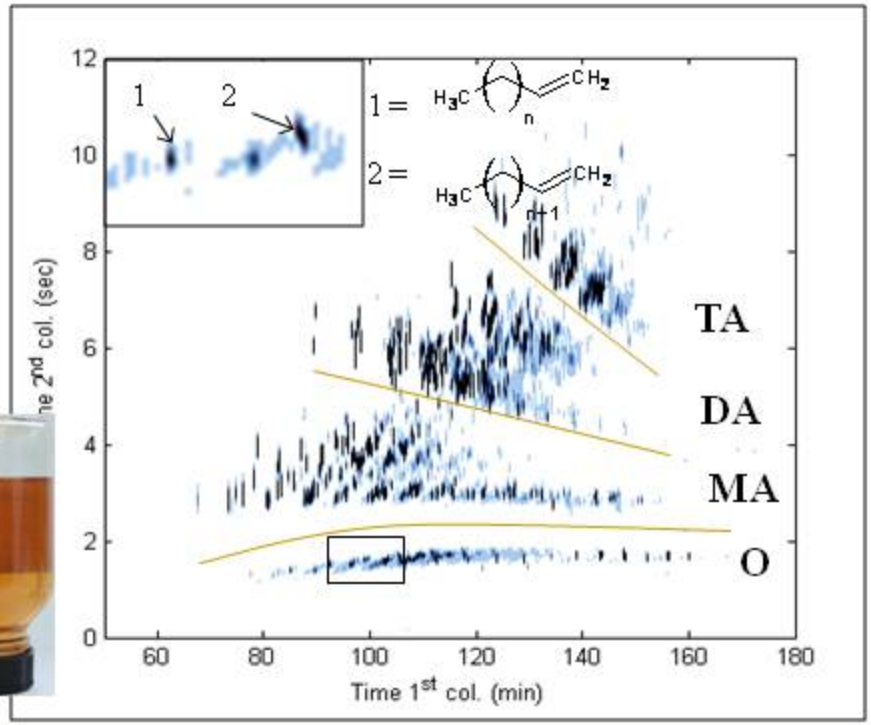
SFC-TWIN-GCxGC OF A LIGHT CYCLE OIL GASOIL

>C25

Saturated fraction



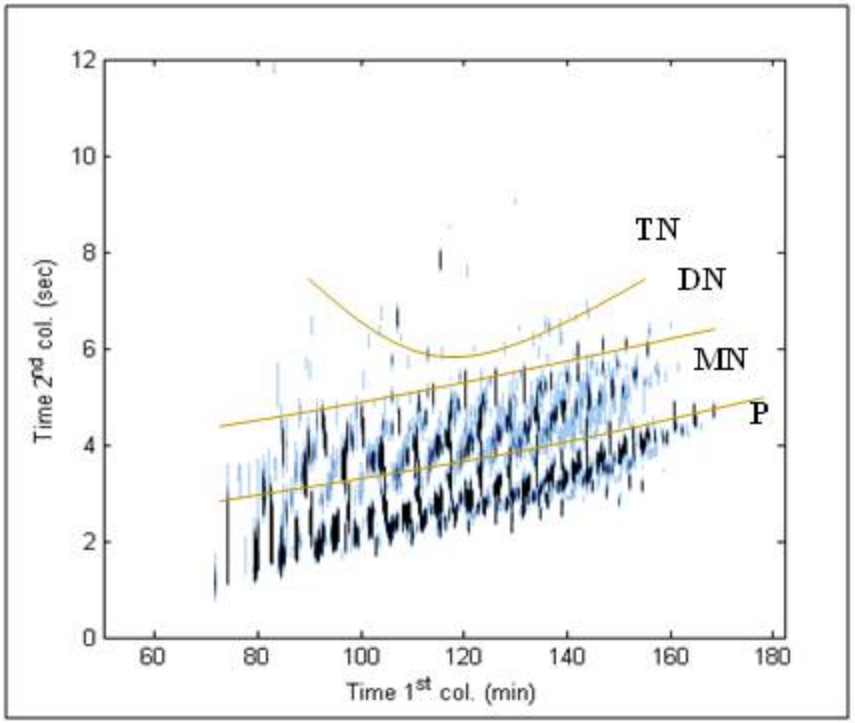
Unsaturated fraction



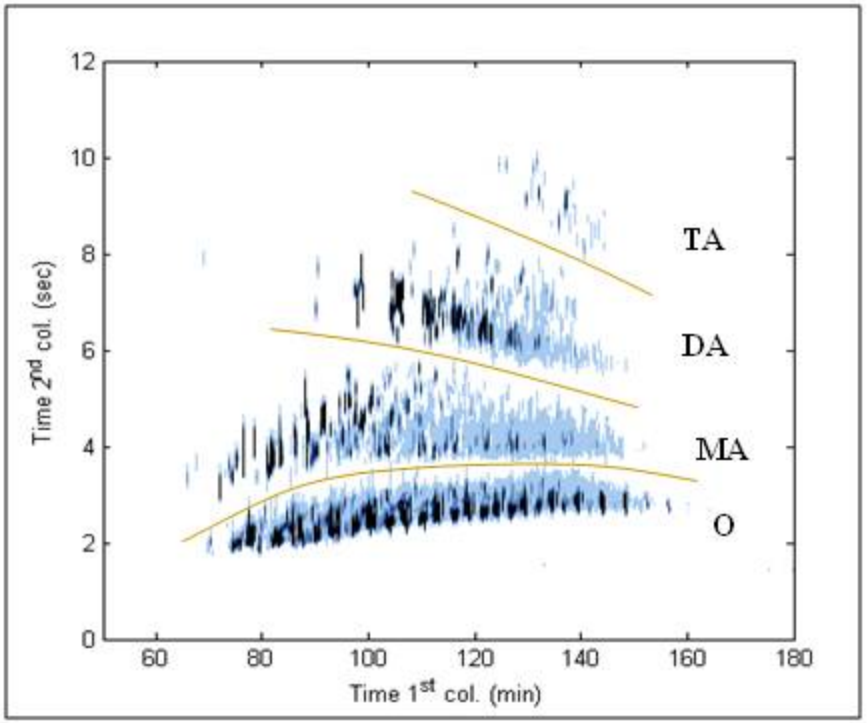
- Identification of each chemical group (Extended PIONA analysis)
- Subdivision of each chemical group by carbon number

SFC-TWIN-GC×GC OF A COKER GASOIL

Saturated fraction

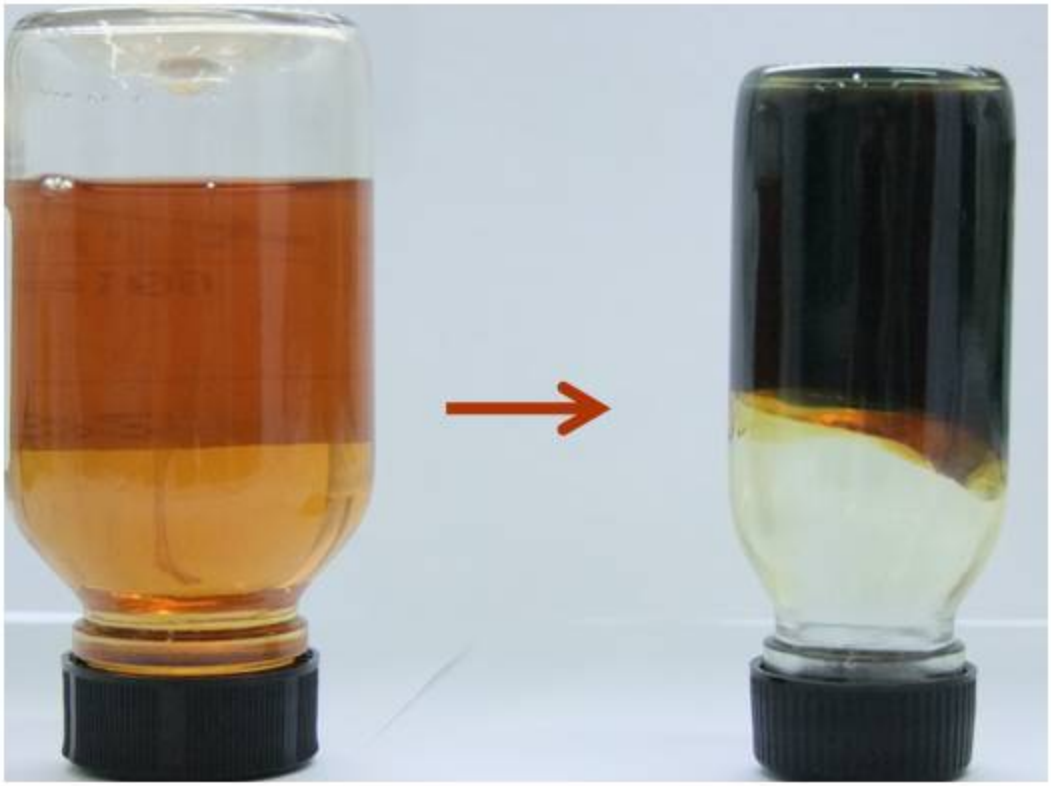


Unsaturated fraction



Used in routine analysis at IFP!

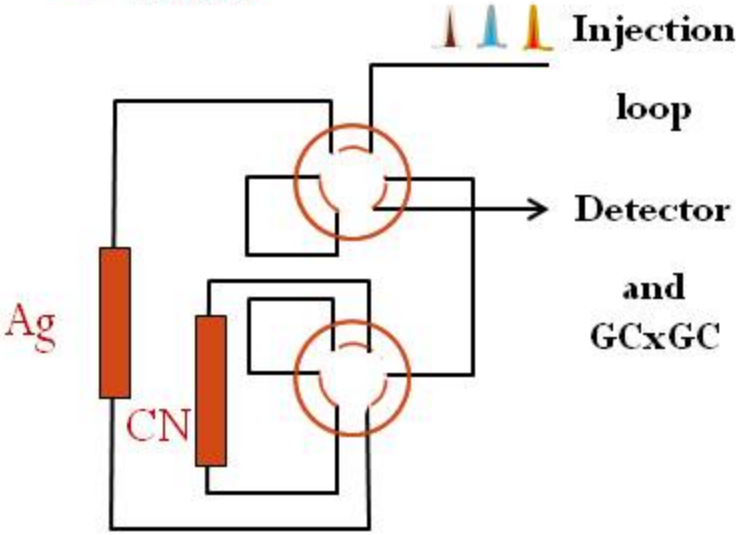
SFC - GCxGC OF VACUUM DISTILLATES?



2D-SFC-HTGCXGC OF VACUUM DISTILLATES.

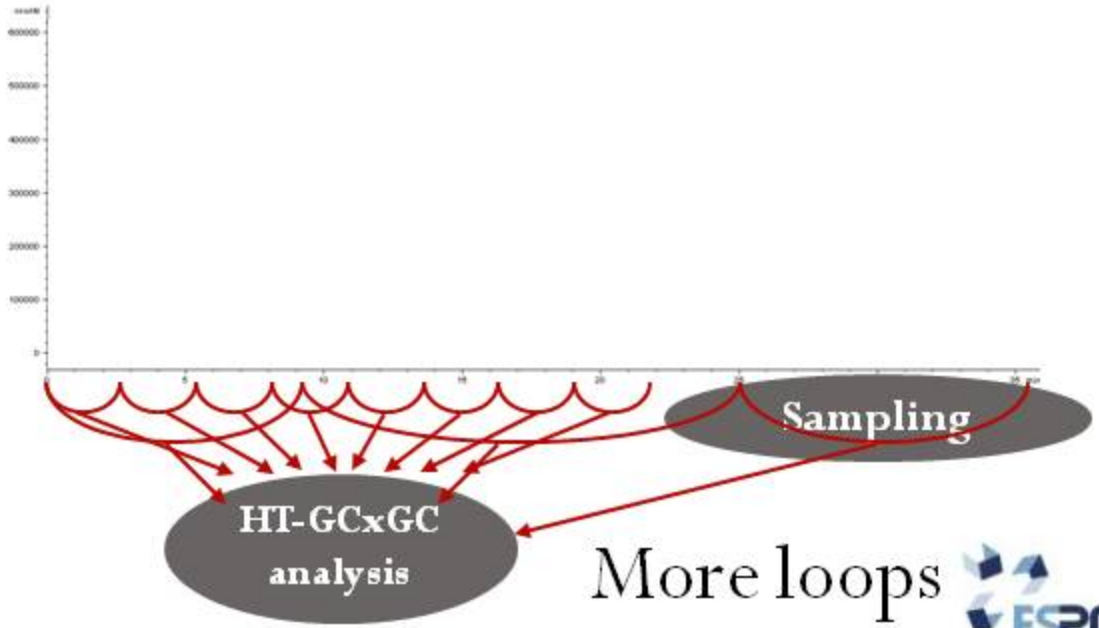
Normal phase chromatography (CN) / charge transfer (Ag)

Saturates
Aromatics
Resins



250 Bars, 65°C

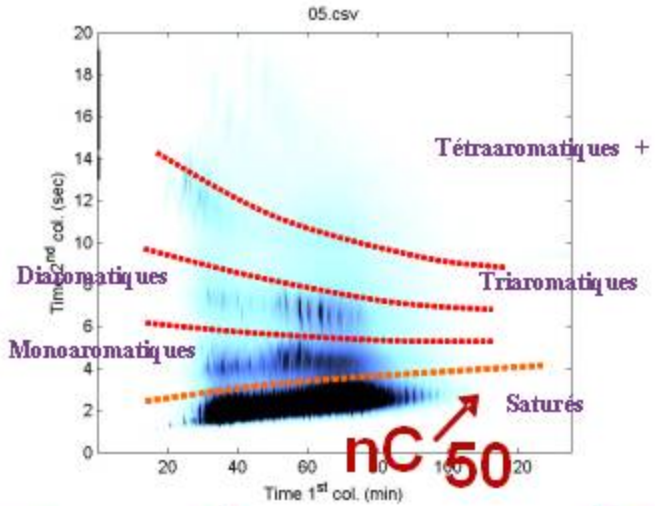
Position 1 => Trapping of resins (CN)
Position 2 => Isolation of resins (CN)
Position 3 => Backflush of aromatics
Position 4 => Backflush of resins



More loops

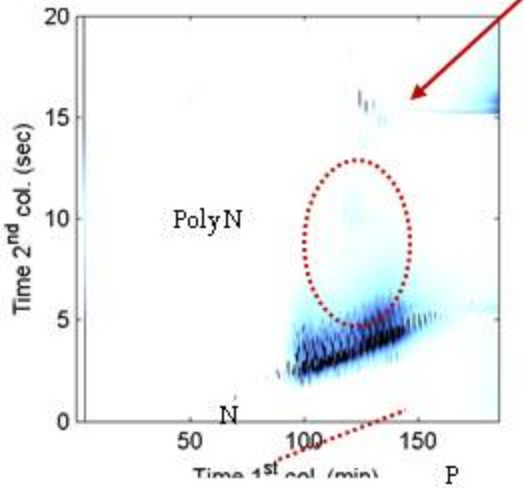
2D-SFCx-HTGCxGC OF VACUUM DISTILLATE

DB1-HT 10m x 0.32(0,2)mm x 0.1µm(/5)

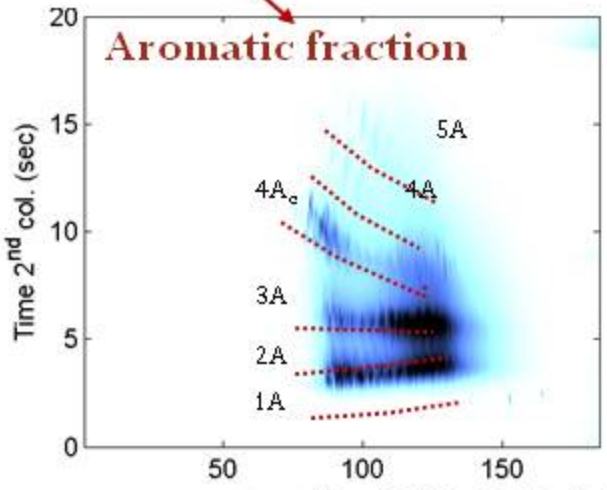


It's quite long!

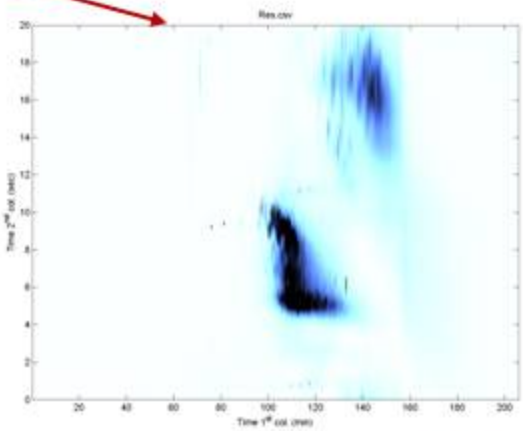
saturates fraction



Aromatic fraction

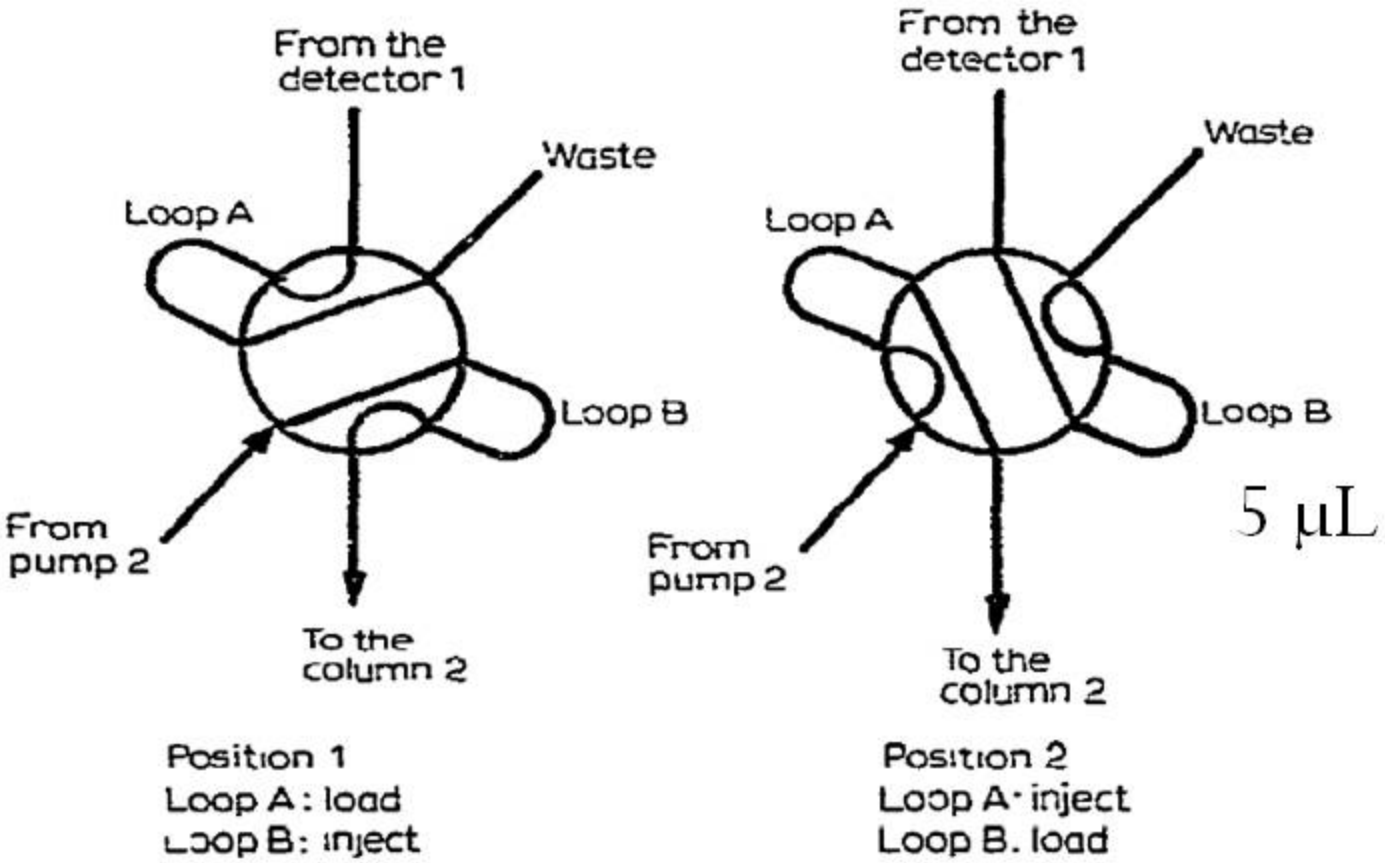


"resin" fraction



BPX-50 (0.5(1)m x 0.1mm x 0.1µm)

TOWARDS COMPREHENSIVE 2DSFC



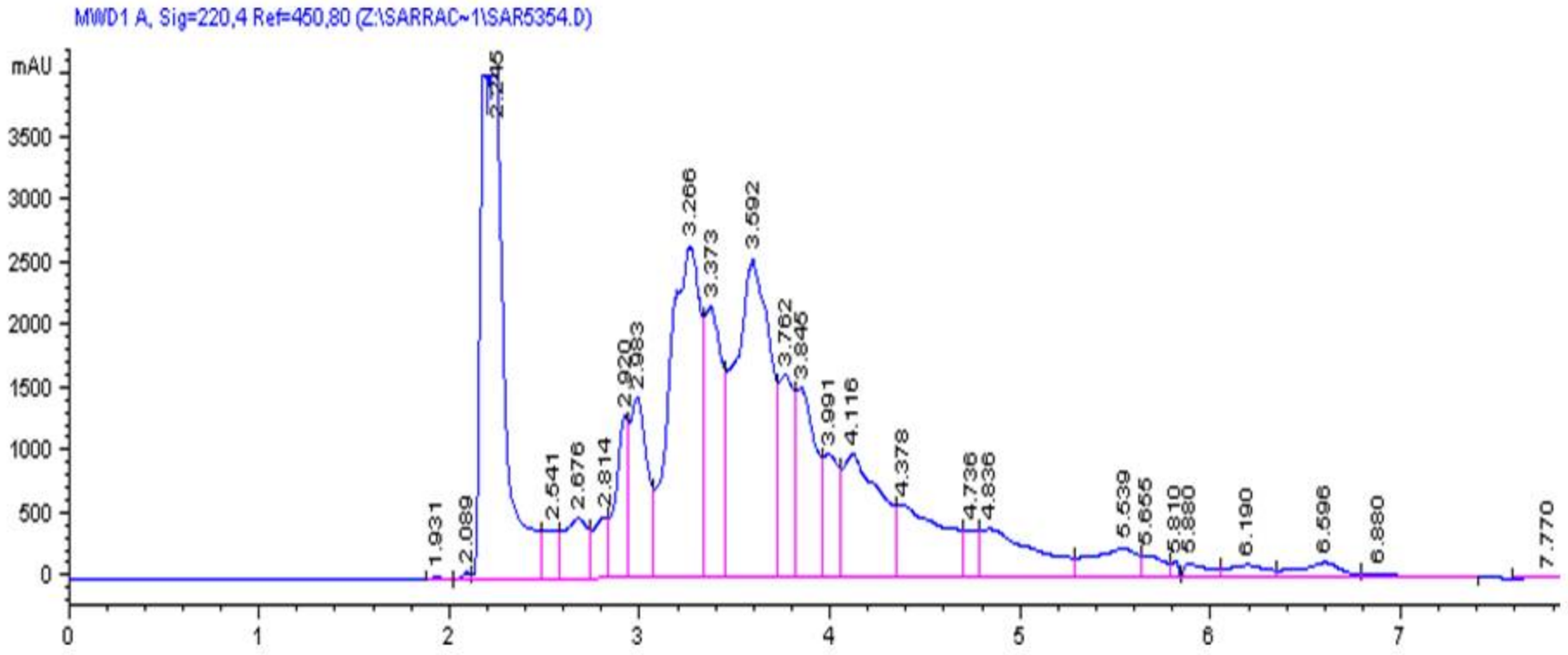
Journal of Chromatography, 149 (1978) 561–569

CHROM. 10,733

TWO-DIMENSIONAL COLUMN LIQUID CHROMATOGRAPHIC TECHNIQUE FOR RESOLUTION OF COMPLEX MIXTURES

F. ERNI and R. W. FREI*

TOWARDS COMPREHENSIVE 2DSFC



T1=2.983 min

T2=3.592 min

T3= 4.116 min

T1=3.329 min

T2=4.545 min

T3= 6.428 min

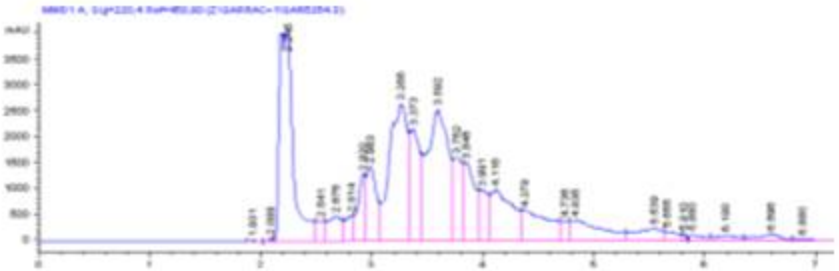
Gasoil sample 1 D : Column C18 15cm x 4.6mm / Supelco

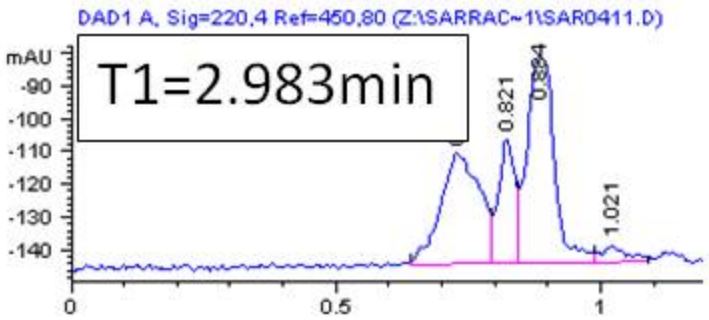
TOWARDS COMPREHENSIVE 2DSFC

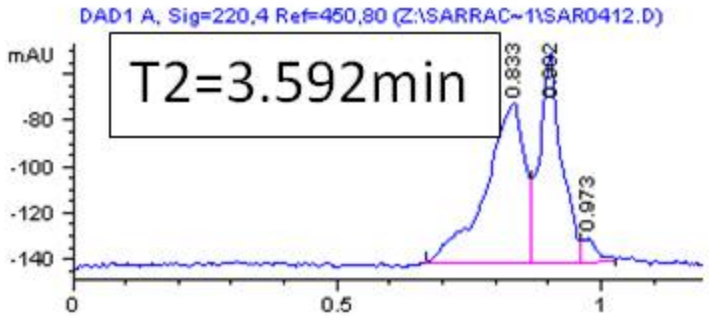
T1=2.983 min

T2=3.592 min

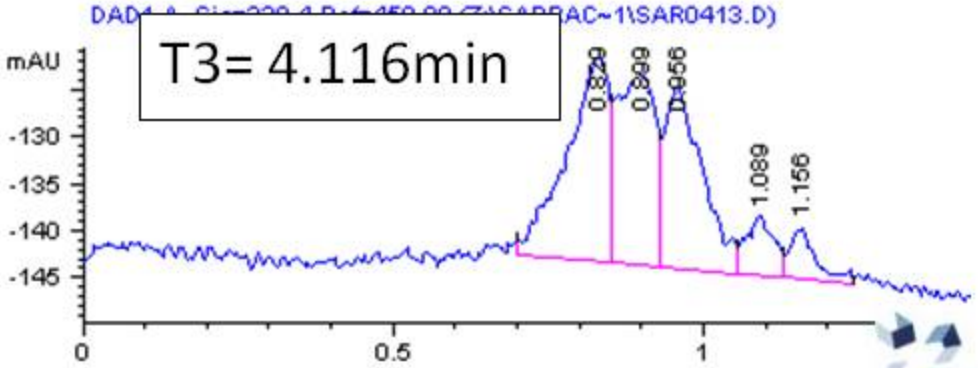
T3= 4.116 min







Machine 1 : P= 250 bars,
D= 1ml/min, T= 40 °C
Machine 2 : P= 150 bars,
D= 2 ml/min, T=30 °C
Column Sepax 1.8µm
Silica 100 mm x 4.6 mm



TOWARDS COMPREHENSIVE 2DSFC

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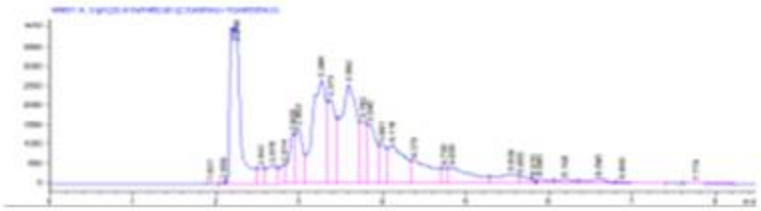

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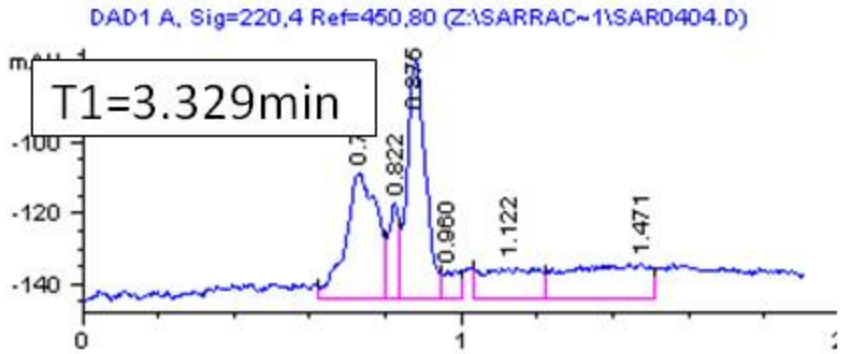

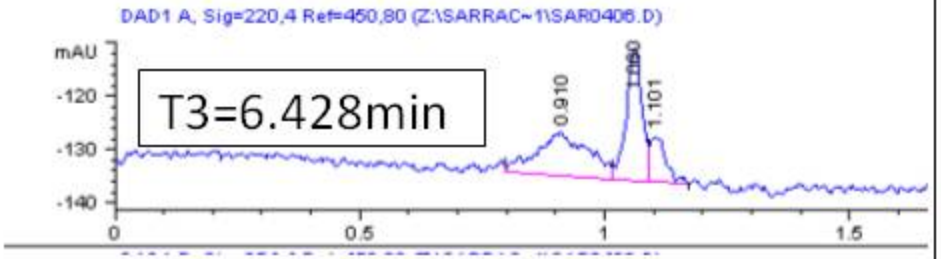

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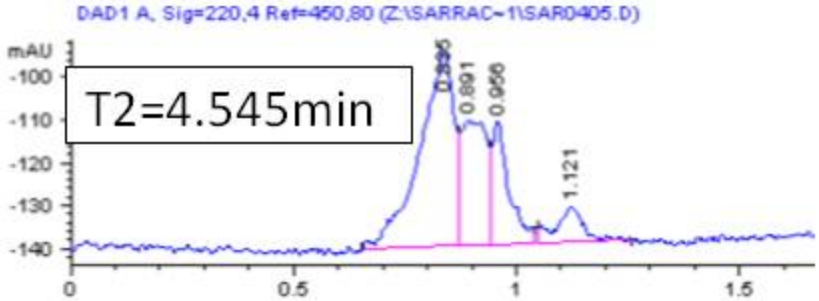
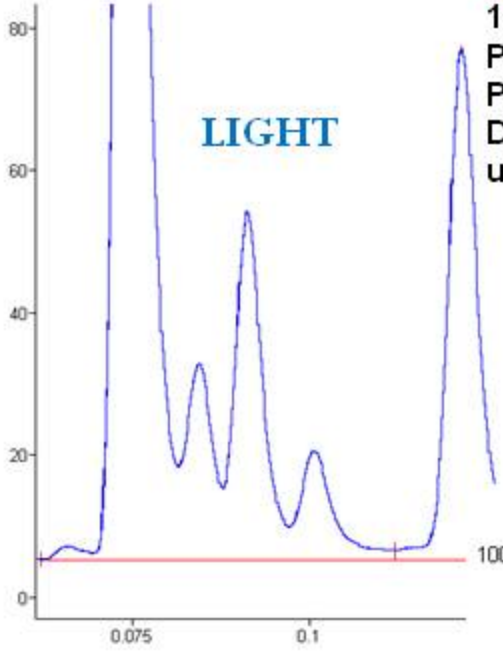
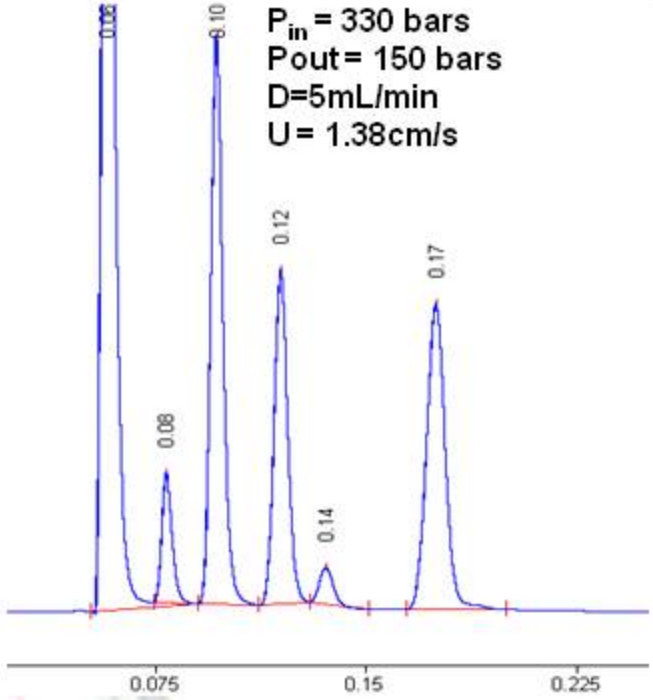


Nucleodur 5cm x 0.3 cm

1.8µm
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

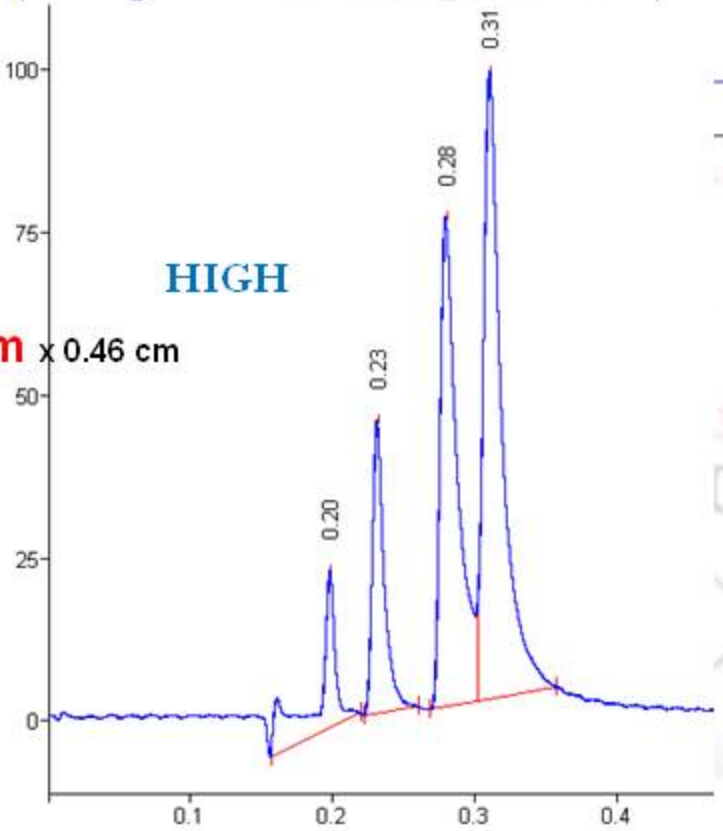


P_{in} = 330 bars
Pout = 150 bars
D=5mL/min
U = 1.38cm/s

Sepax C_4 5cm x 0.46 cm

1.9µm
P_E = 230 bars
P_S = 150 bars
D=5mL/min
u = 0.52 cm/s

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

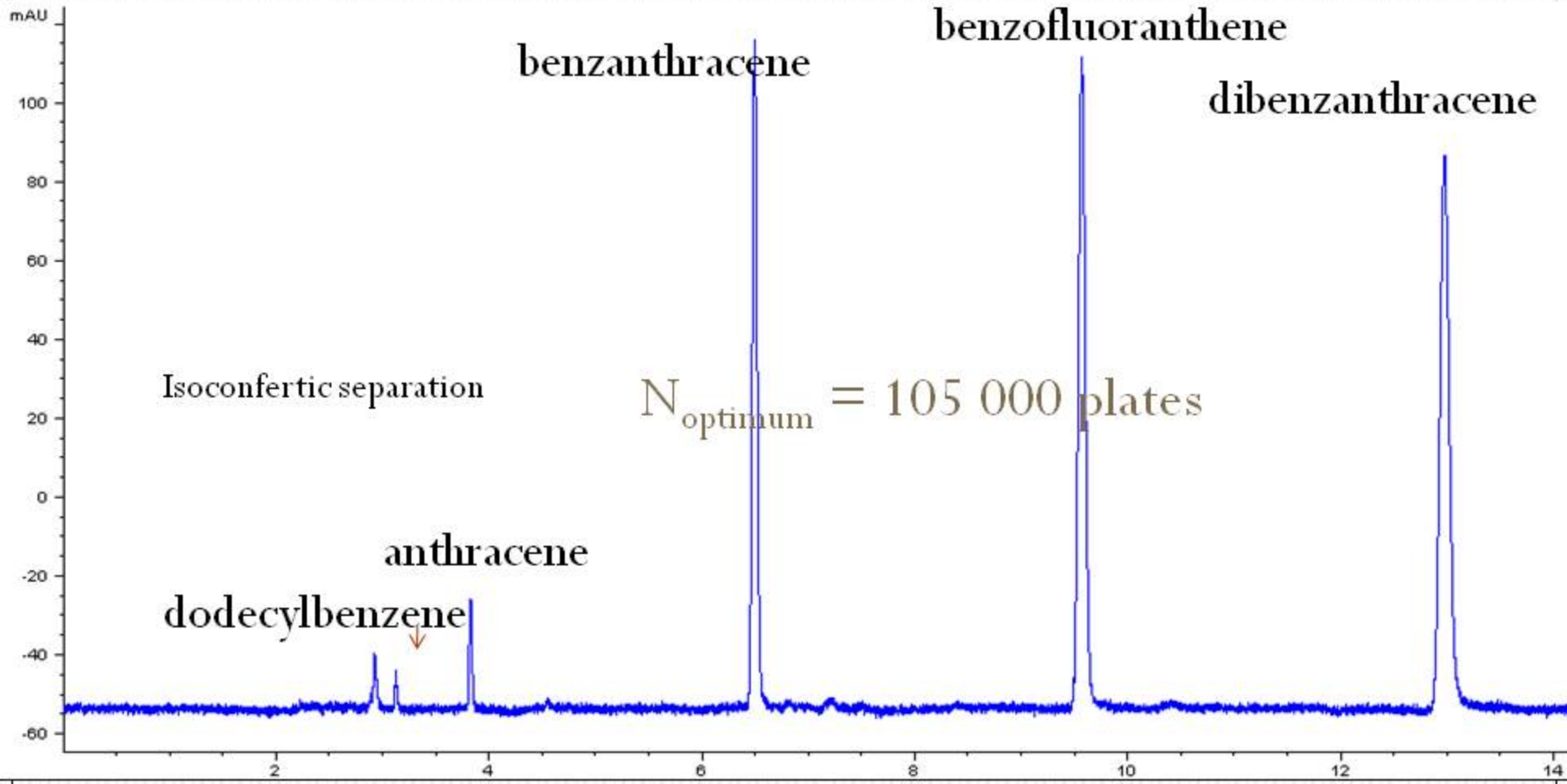


MEDIUM

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

12 to 20 s

UHPSFC: THE FOUR COLUMNS…



4 columns C18 150 x 4.6 mm, P_{out} = 150 bars, P_{in} = 530 bars, T = 60°C, D = 4.5 mL/

PECSA

ESPCI ParisTech

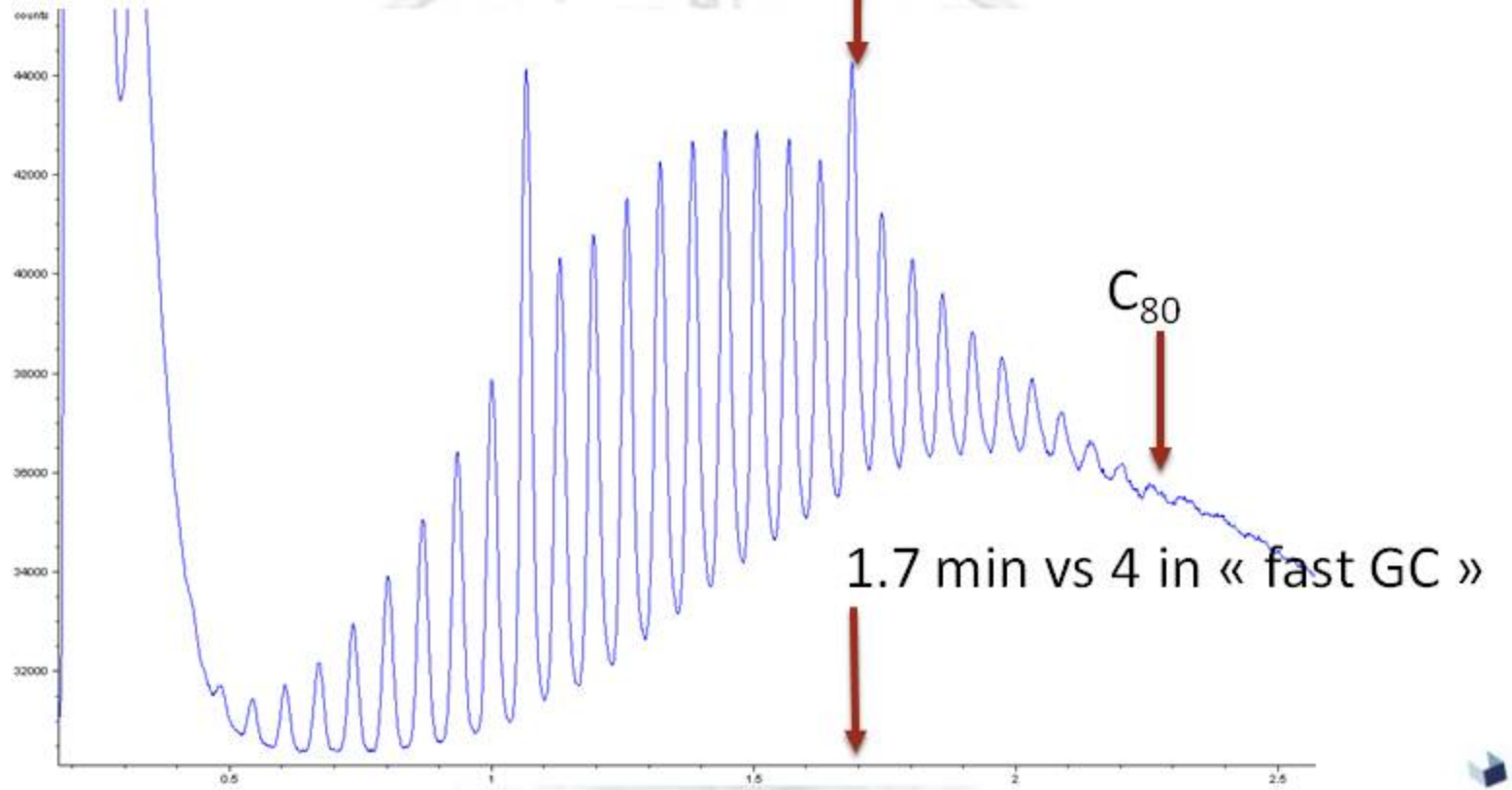
UHPSFC = ULTRAFAST SFC

D = 2.5 mL/min,

T_{oven} = 100°C

Pressure gradient: 80 to 370 bars (99 bars/min)

Column Sepax C_4 5cm x 0.46cm, 1.9µm ; FID



CONCLUSION

- 2DSFC-/xGC x GC is very powerful for middle distillates and more…
- SFC x SFC IS FEASIBLE AND DESIRABLE FOR HEAVIER SAMPLES: N/α/speed/transfer
- REGULAR SYSTEMS CAN BE USED
- UHPSFC SUITS FOR COMPREHENSIVE SYSTEMS
- LONG COLUMNS &
- VERY FAST SEPARATIONS REQUIRED!
- PRICE TO PAY: ANALYSIS TIME