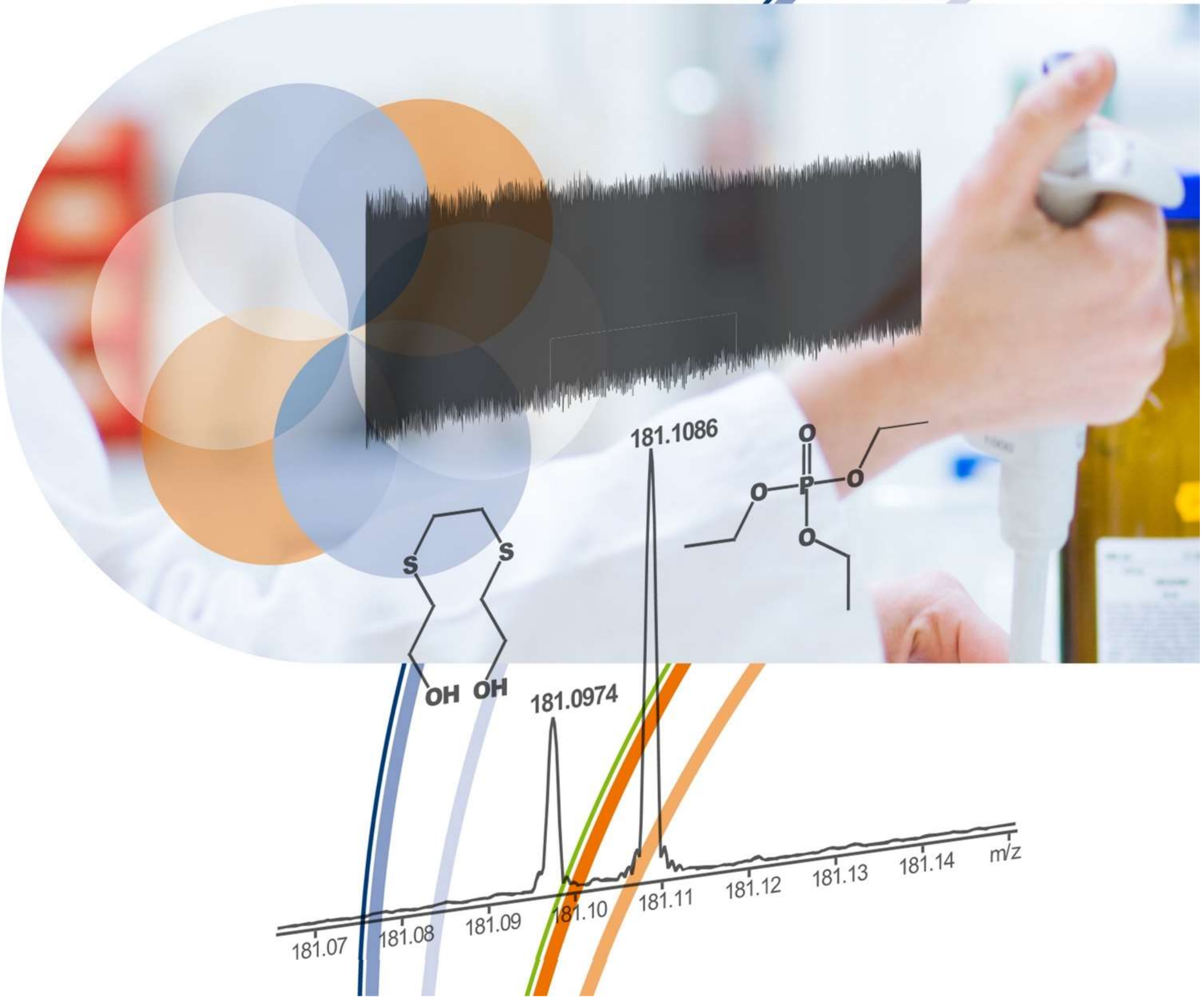
Highly complex analysis from petroleum to polymers

Carlos Afonso

Laboratoire Cobra



CNRS INSA UNIVERSITÉ DE ROUEN

Laboratoire COBRA

FR FT-ICR

FR 3624

Infrastructure de recherche nationale CNRS

Spectrométrie de masse FTICR à très haut champs

Responsable Guillaume Van der Rest

Paris - UPMC
SolariX 7T

Rouen
Univ. Rouen
SolariX XR 12 T

Paris
ESPCI ParisTech
LTQ FT 7T

Orsay
Uni. Paris Sud
APEX Q 7T

Lille – ULille 1
APEX Q 9.4T

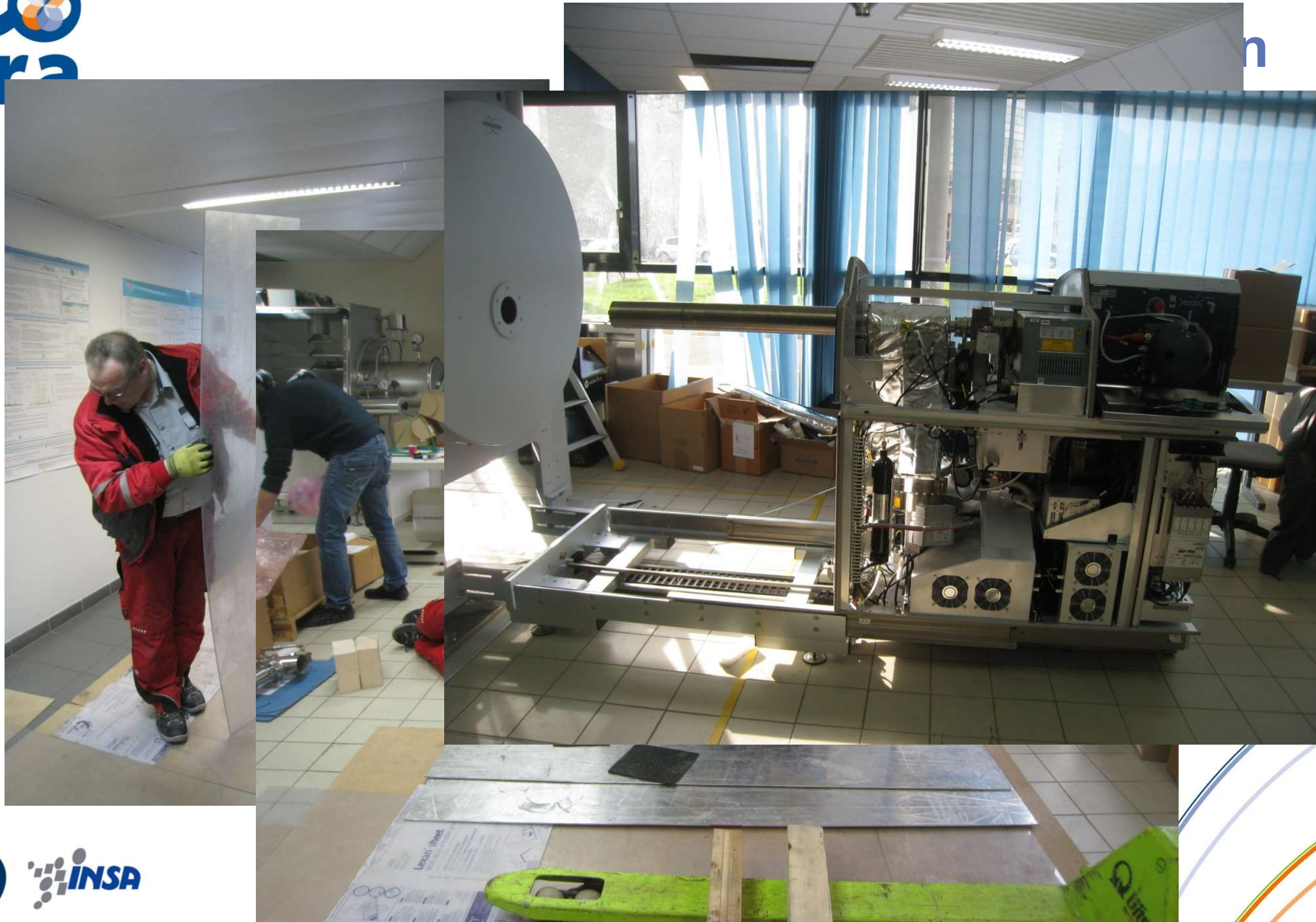
Metz
Uni. de Lorraine
Ion Spec 9.4T

Palaiseau
Ecole Polytechnique
SolariX XR 9.4 T

www.fticr.org

Hélène Lavanant : Responsable scientifique
Isabelle Schmitz : Responsable d'acceuil

Laboratoire Cobra



CNRS INSA

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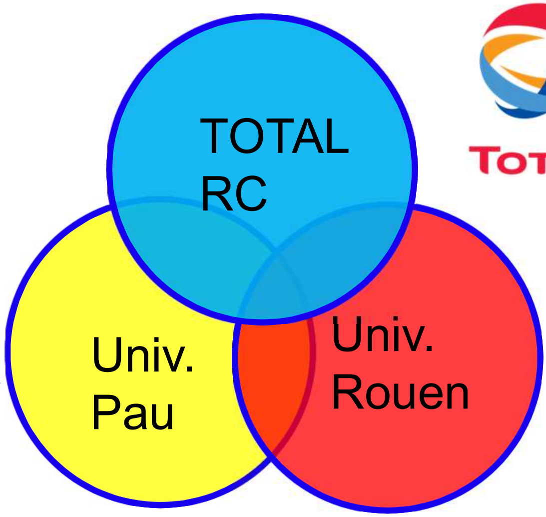
Laboratoire

UNIVERSITE DE ROUEN

C2MC joint lab

Complex Matrices Molecular Characterization

- Complementary expertise
  - Industrial applications
  - MS
  - ICP-MS



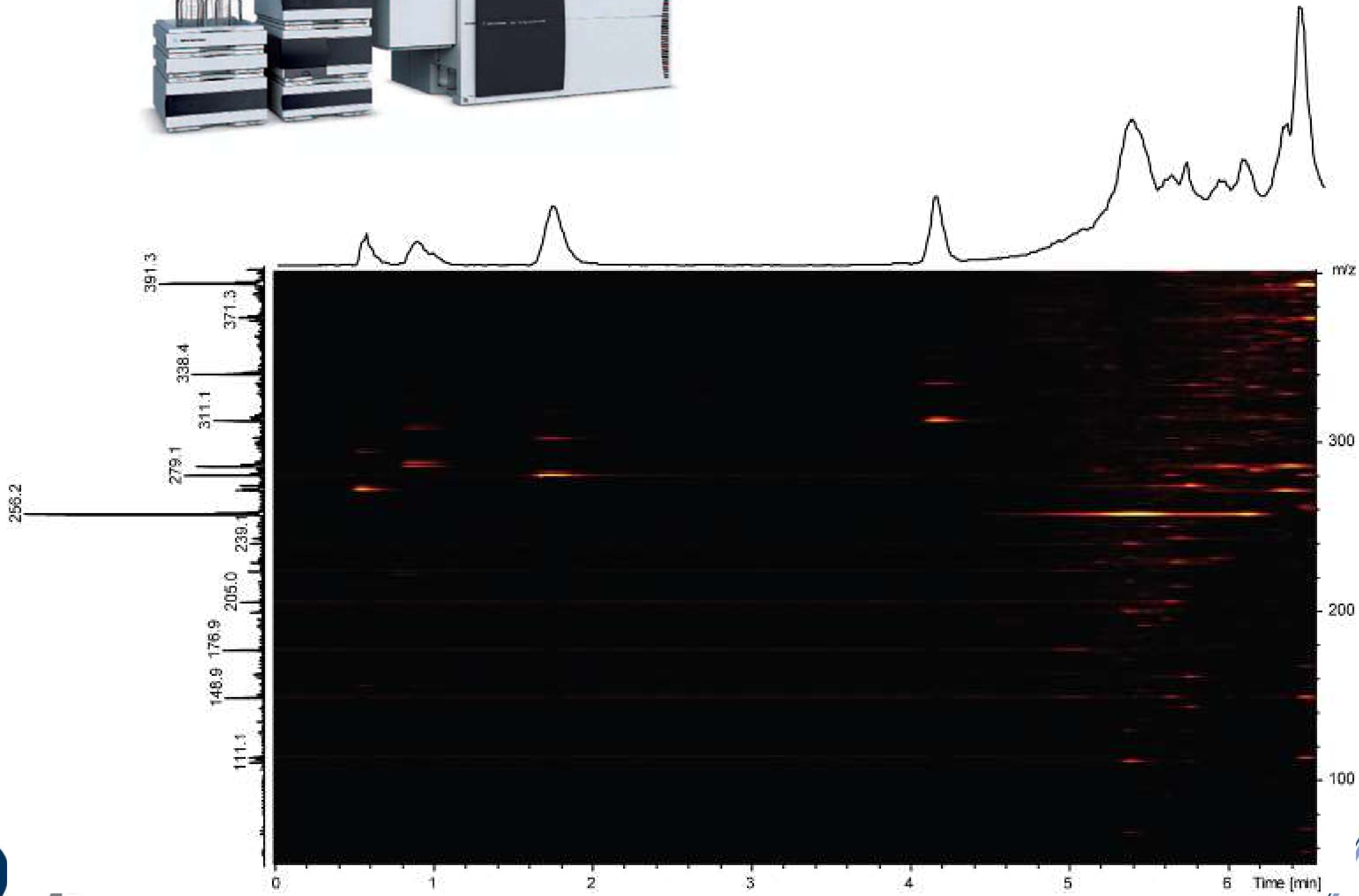
Pierre Giusti

Brice Bouyssière

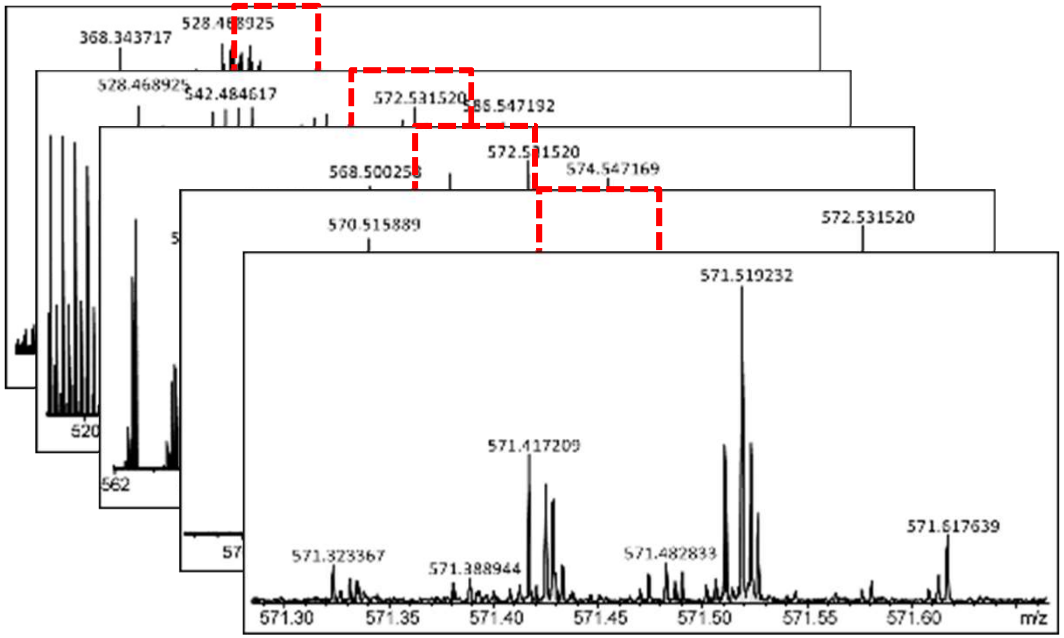
23 octobre 2015

Complex mixtures

LC/MS a 2D separation



Analysis of heavy petroleum product



Post ionization separation

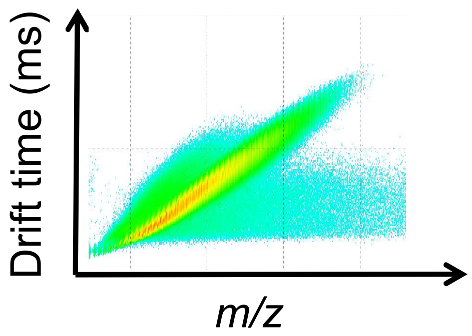
1D separation

Ultra high resolution

FT-MS

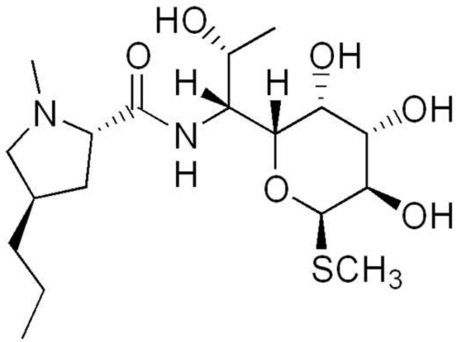
2D separation

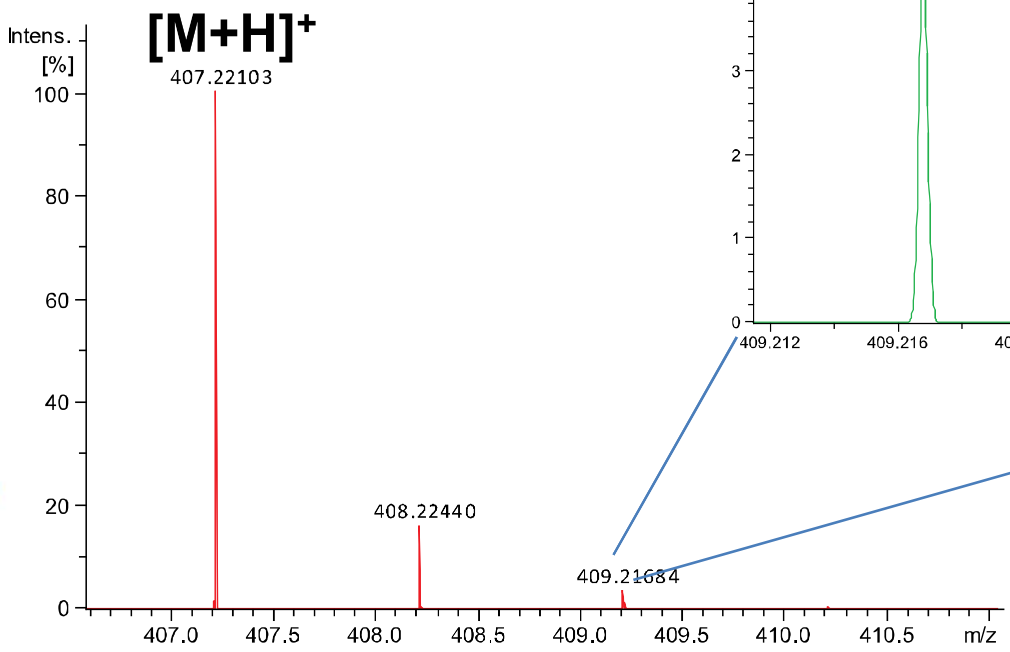
Ion mobility – mass spectrometry

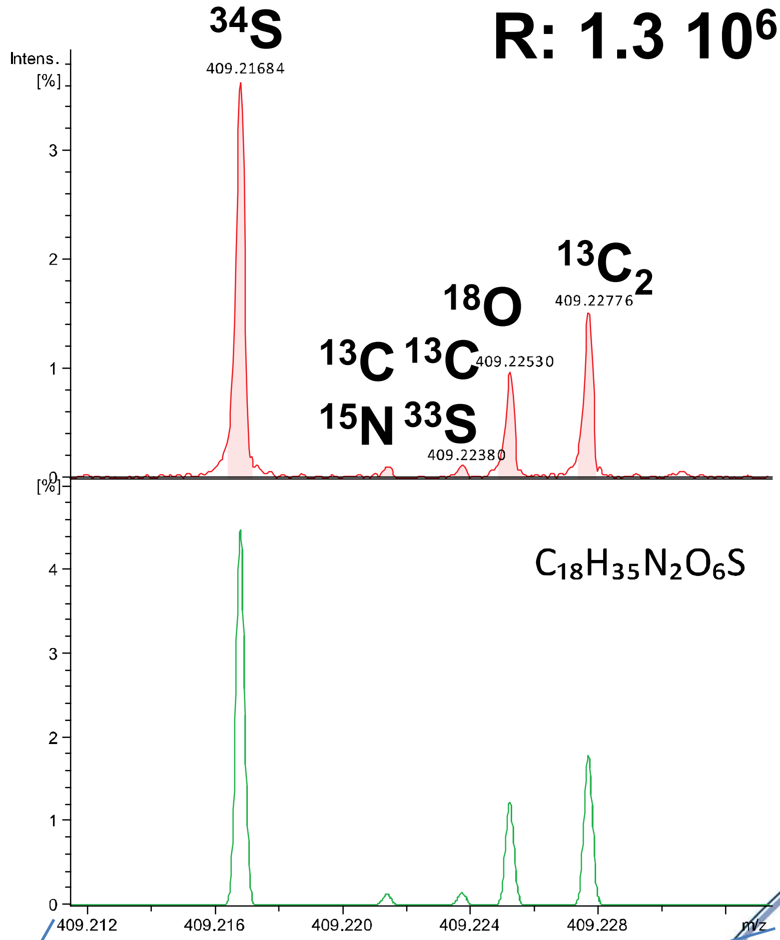


Isotopic Fine Structure

- Lincomycin ($C_{18}H_{34}N_2OS$)

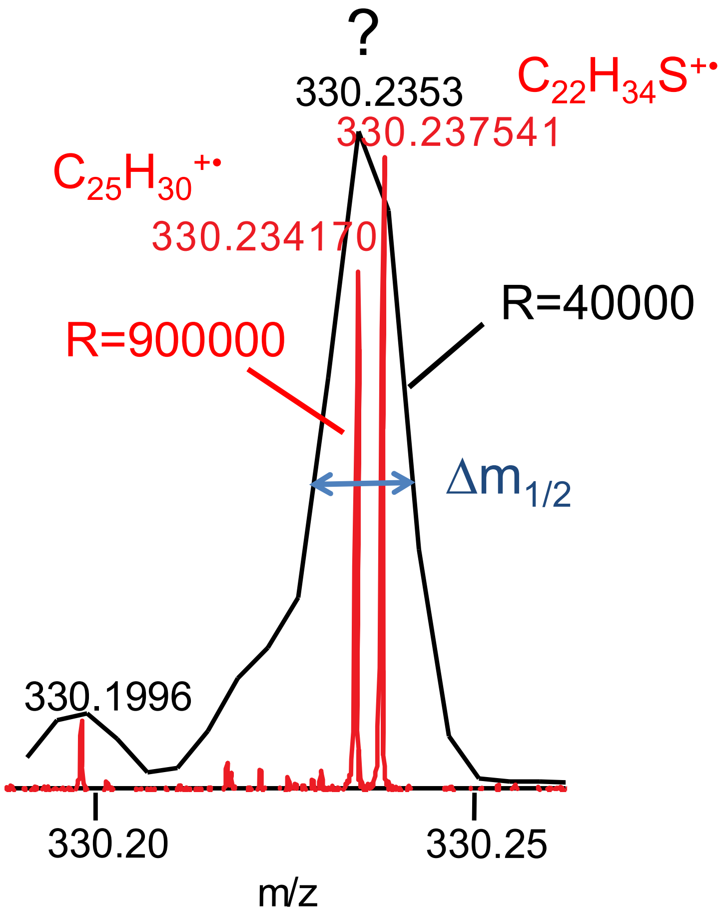






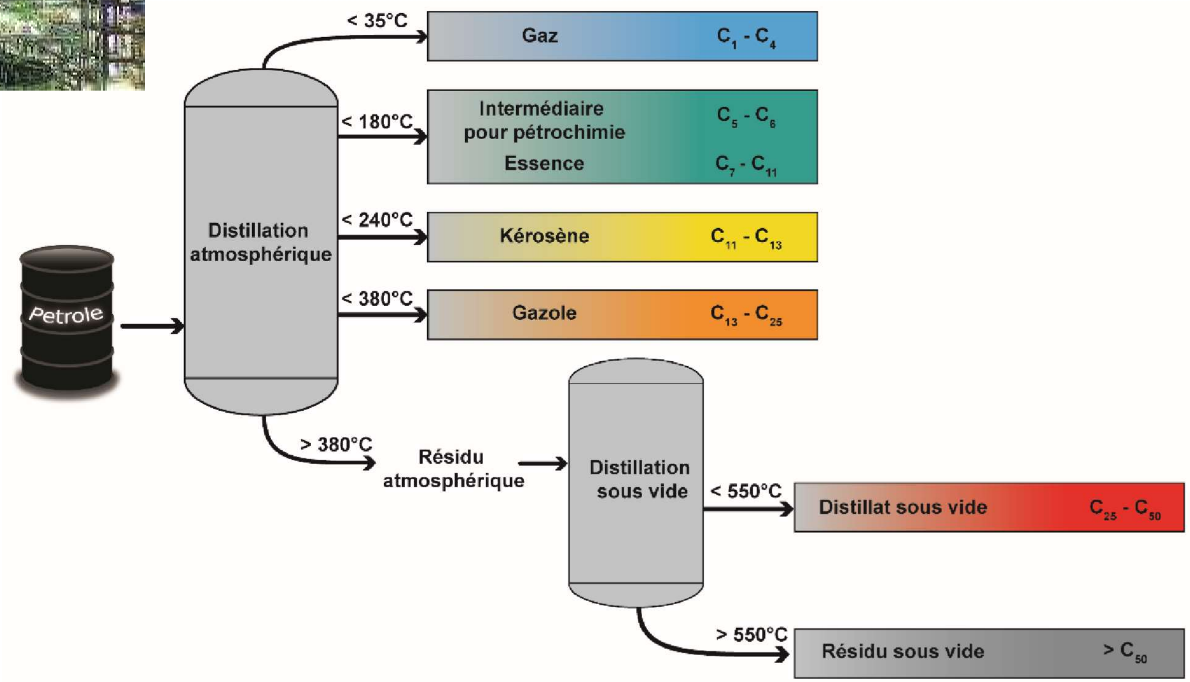
Petroleum complexity

- C_3 *vs* SH_4
  - 3.4 mDa

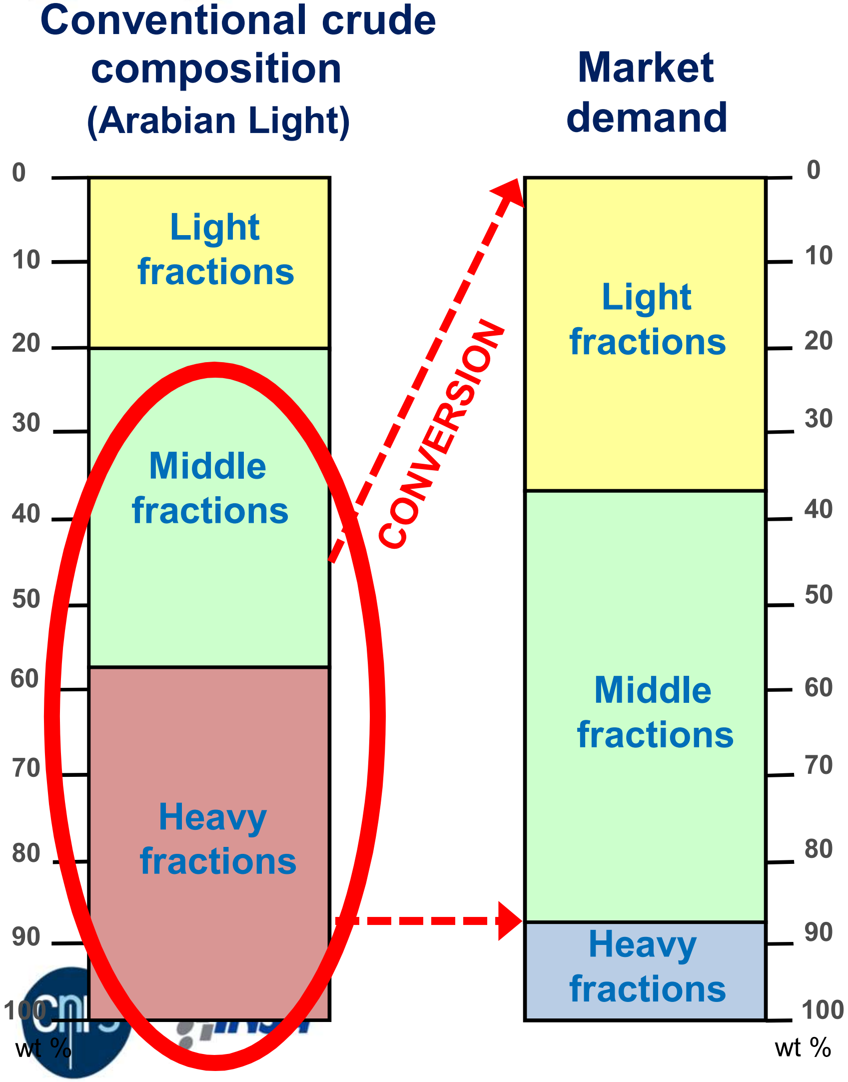


$R=m/\Delta m_{1/2}$

Petroleum refining processes



Context



Increase of light and middle fractions cuts (diesel) demand: conversion units

Need for hydrodemetallation, hydrodesulfuration, hydrodenitrogenation and hydrocracking process understanding at the molecular level :

Rationalization and prediction of processes at the molecular level

Why molecular characterization

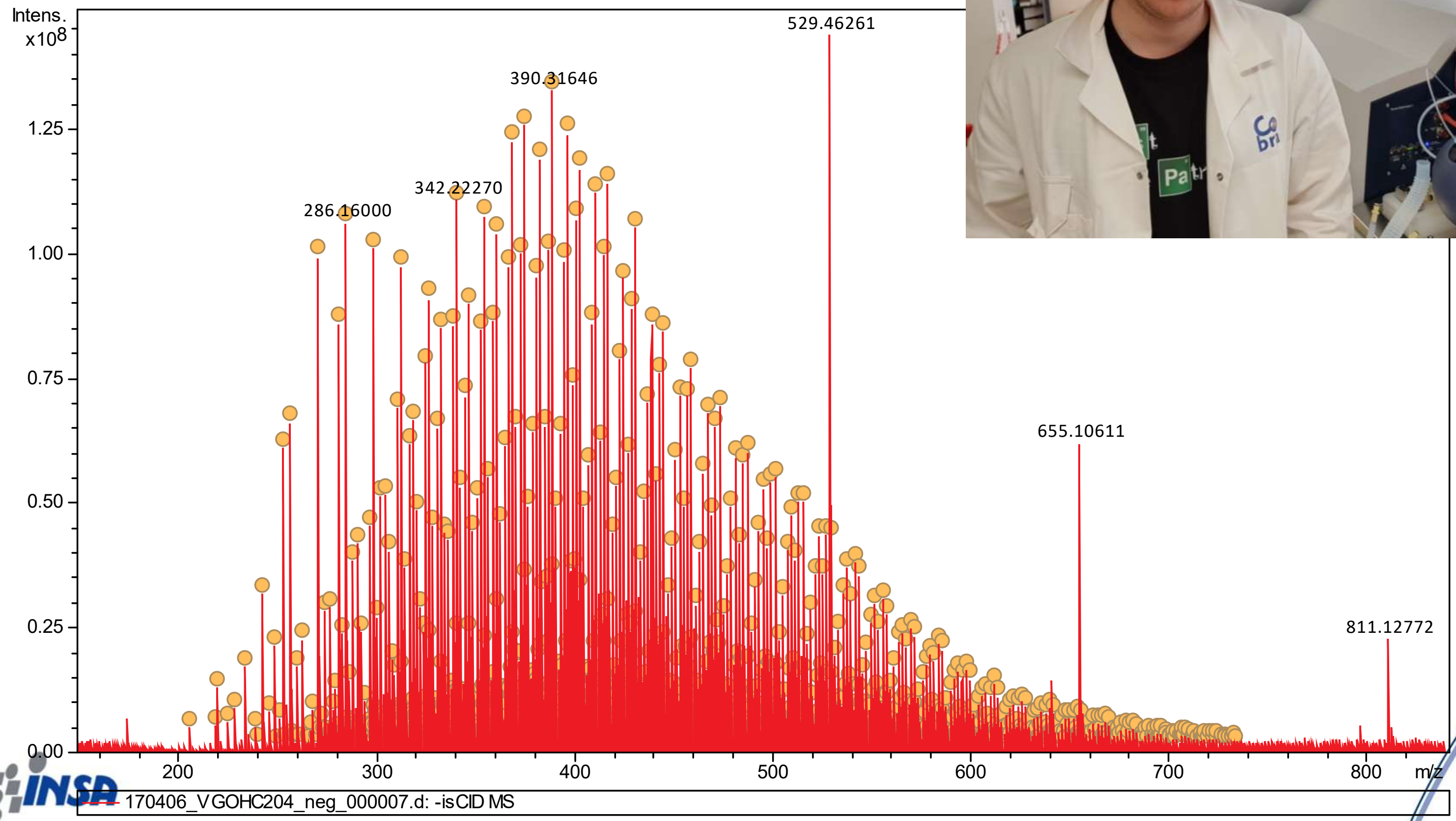
- Petroluem valued based on macroscopic descriptors
  - American petroleum institute (API) Gravity
  - Sulfur content
  - Total acidity number (TAN)
  - Metal content (V, Ni)…
- Understand macroscopic properties at the molecular level
  - Corrosion
  - Fouling
  - Emulsion…
- Petroleums with similar macroscopic descriptors may have different properties

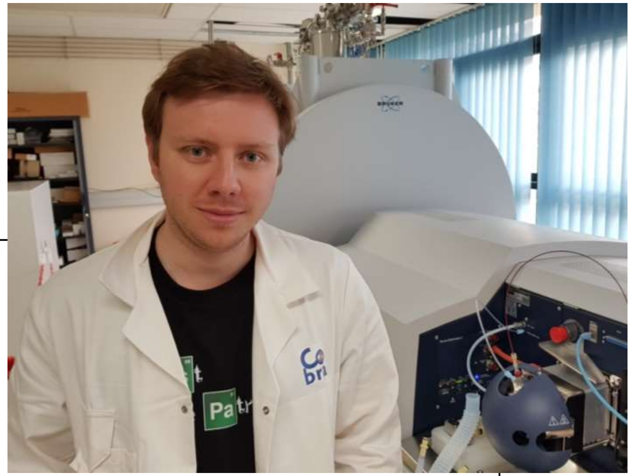
Crude Oil	Country of Origin	Crude Oil Class	Properties		Price USD (2018/03)
			Gravity °API	Sulfur (wt.%)	
Brent	UK	Light Sweet	40.0	0.5	69.0
West Texas Intermediate	USA		39.8	0.3	64.8
Arabian Extra Lt. Export	Saudi Arabia	Light Sour	38.1	1.1	68.9
Daqing	China	Medium Medium Sour	33.0	0.1	63.1
Arabian Light Expor	Saudi Arabia	Medium Sour	34.0	1.9	64.0
Kuwait Export Blend	Kuwait		30.9	2.5	62.1
Oriente Export	Ecuador	Heavy Sour	25.0	1.4	60.3
Maya Heavy Export	Mexico		21.3	3.4	57.0

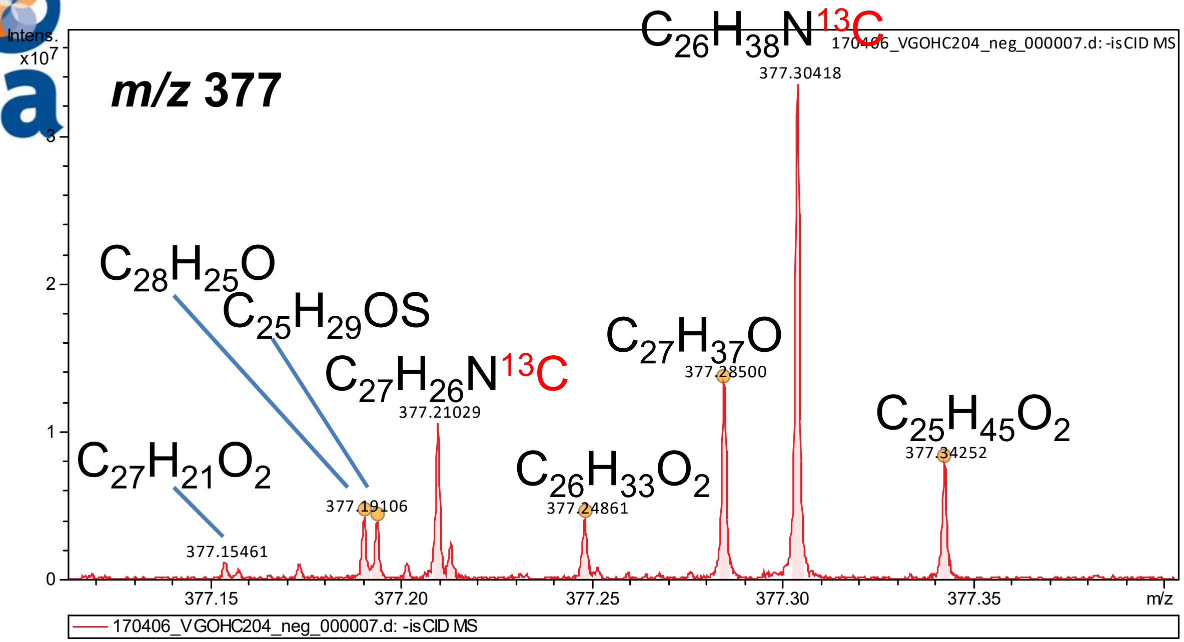
Thèse de Johann Le Maitre

Vacuum Gasoil ESI(−)

VGO 0.5 mg/mL toluene/MeOH 3% NH_4OH





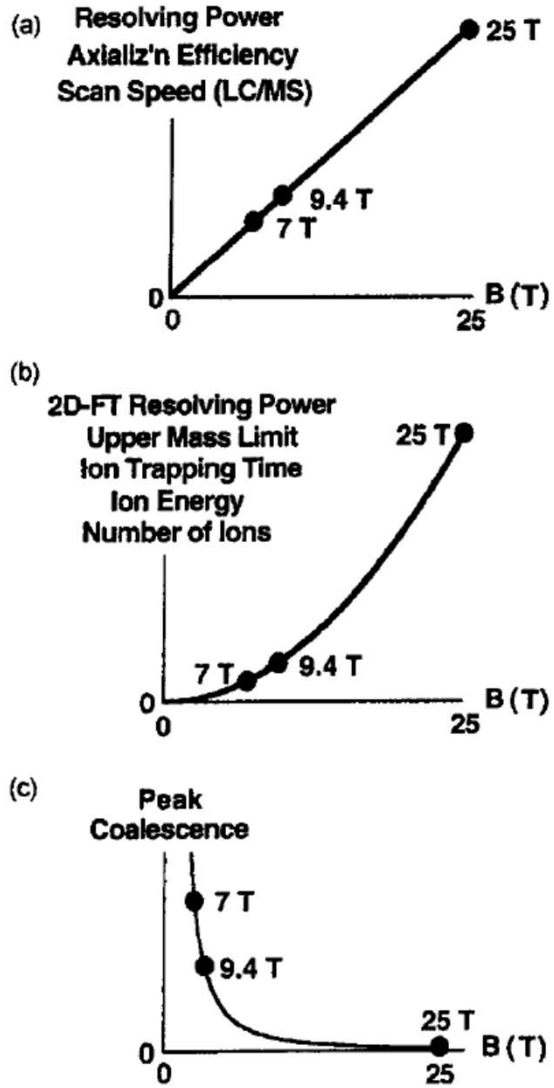


Accuracy better than 100 ppb

Meas. m/z	#	Ion Formula	m/z	err [ppm]
377.191059	1	C28H25O	377.191089	0.1
377.194431	1	C25H29OS	377.194460	0.1
377.248612	1	C26H33O2	377.248604	0
377.251936	1	C23H37O2S	377.251975	0.1
377.284998	1	C27H37O	377.284989	0
377.342524	1	C25H45O2	377.342504	-0.1

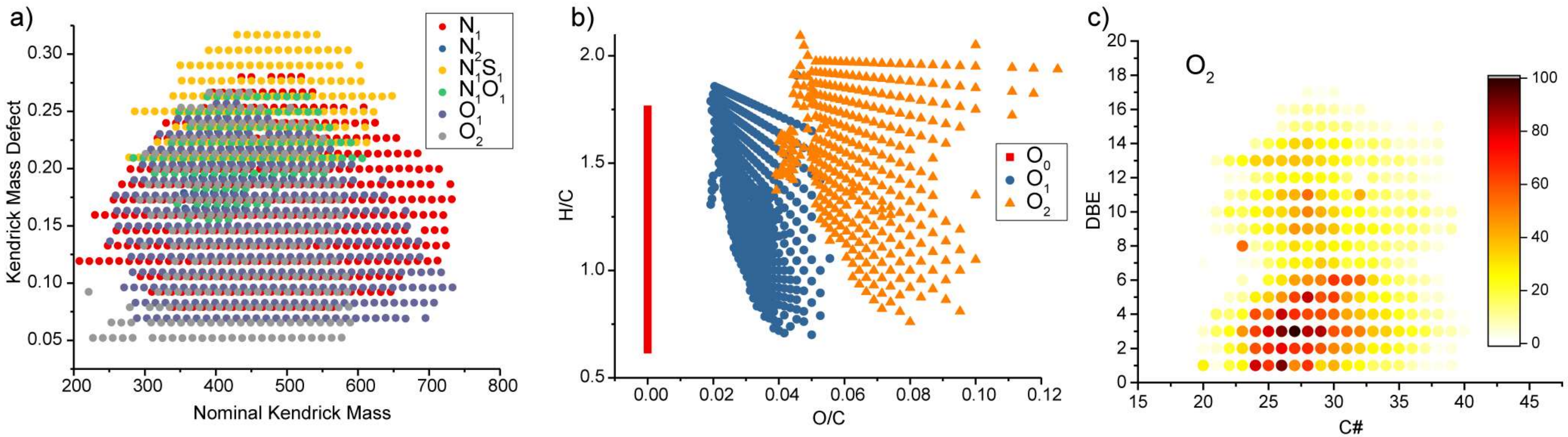
What is important for complex mixtures

- Properties
  - Resolving Power
  - Mass accuracy
  - Dynamic range
  - Number of ions
- High field FTICR
  - All properties increase
  - Linear
  - Quadratic



Marshall, *Rapid Commun. Mass Spectrom.*, 1996, 10, 1819

Molecular map



Kendrick Diagram

Van Krevelen Diagram

DBE vs C#

S. Gutierrez Sama, M. Farenc, C. Barrère-Mangote, R. Lobinski, C. Afonso, B. Bouyssiere, P. Giusti. Molecular Fingerprints and Speciation of Crude Oils and Heavy Fractions Revealed by Molecular and Elemental Mass Spectrometry: Keystone between Petroleomics, Metallopetroleomics, and Petrointeractomics. *Energy Fuels* **2018**.

Data treatment

- PetroOrg
  - http://petroorg.com
- Composer (Sierra Analytics)
  - http://massspec.com/composer/

Ion source comparison

- ESI

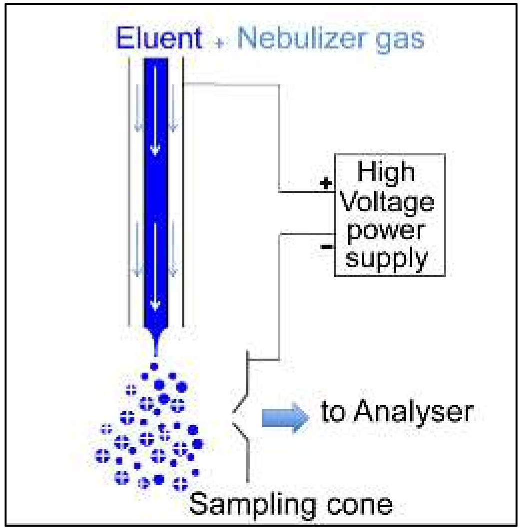
Electrospray ionization

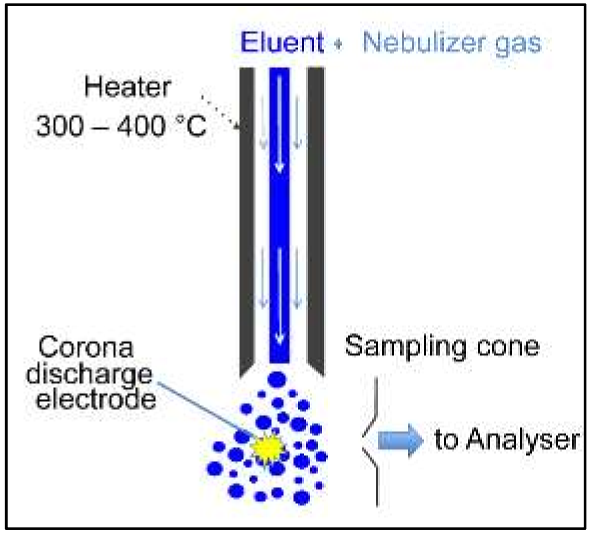
- APCI

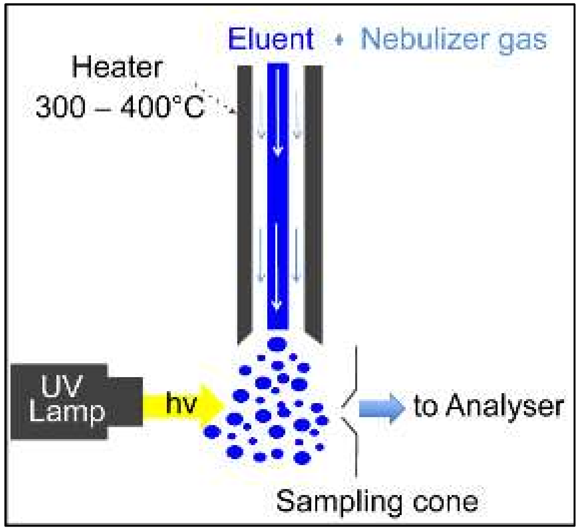
Atmospheric Pressure Chemical Ionization

- APPI

Atmospheric Pressure Photo Ionization







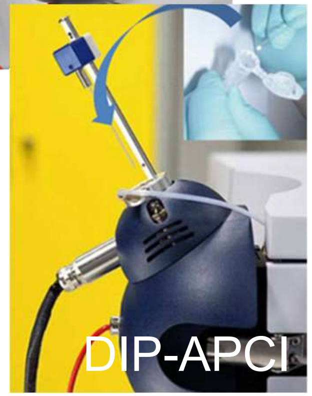
Liquid phase ionization

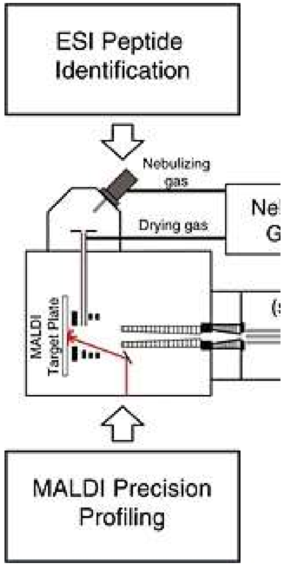
Gaseous phase ionization
Using a corona discharge

Gaseous phase ionization
Using a UV lamp hυ = 10.6 eV

Equipment

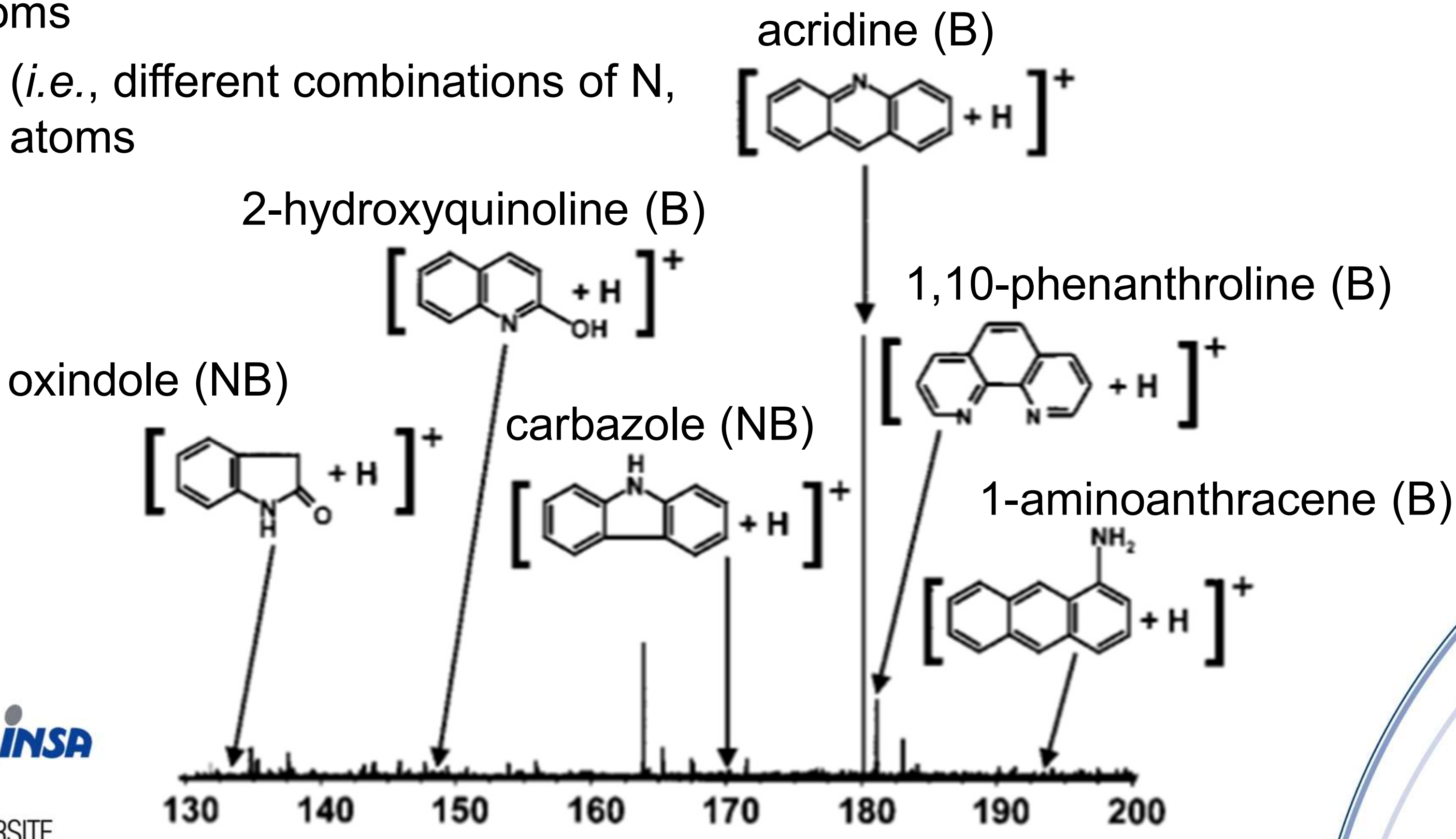
- API sources
  - ESI
  - APCI
  - APPI
  - Direct insertion probe APCI
- MALDI





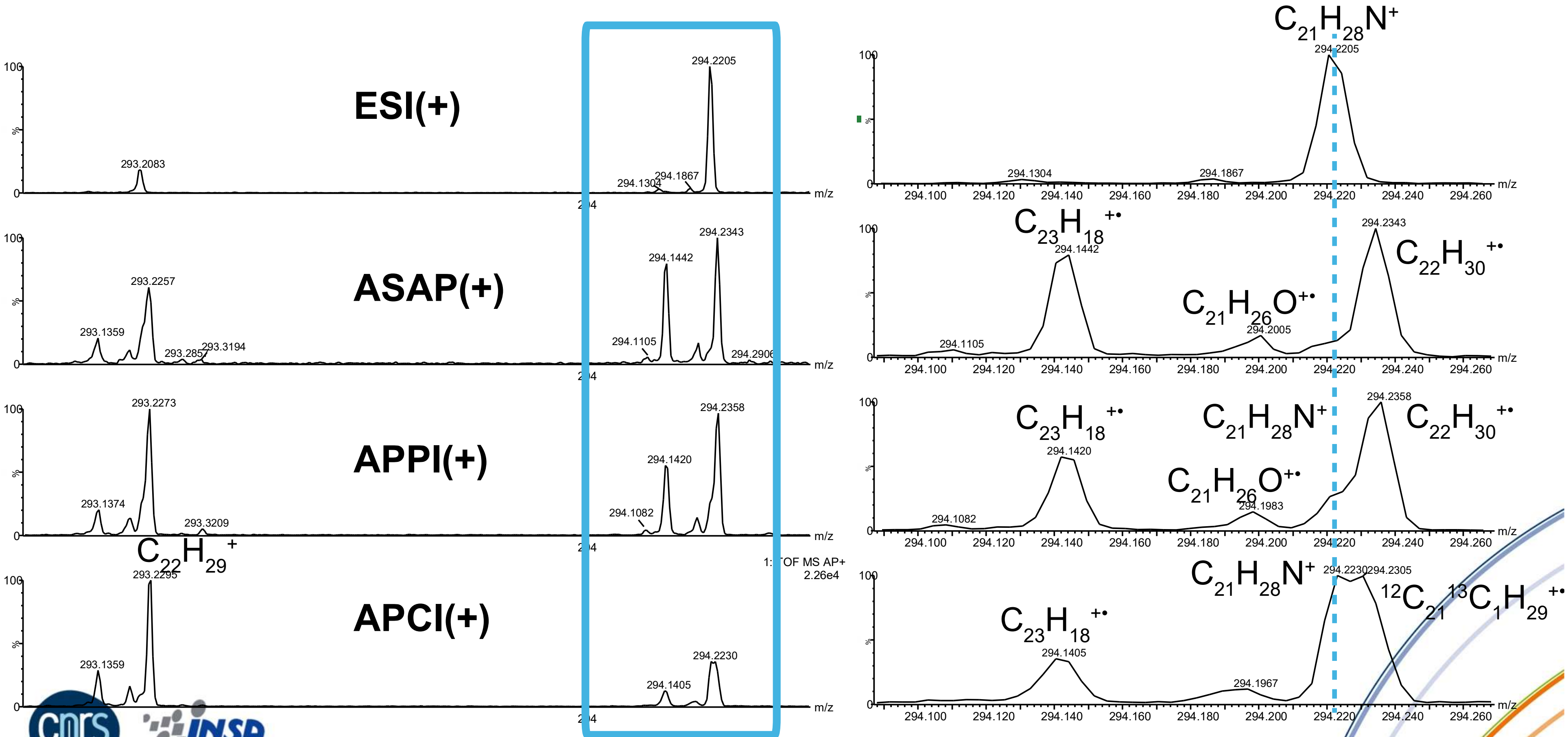
Exemple: Complex petroleum mixtures

- Basic *vs* Non Basic N
- Z types (Z is the “hydrogen deficiency” relative to alkanes, C_cH_{2c}+zX, in which X denotes heteroatoms
- classes (*i.e.*, different combinations of N, O, and S atoms

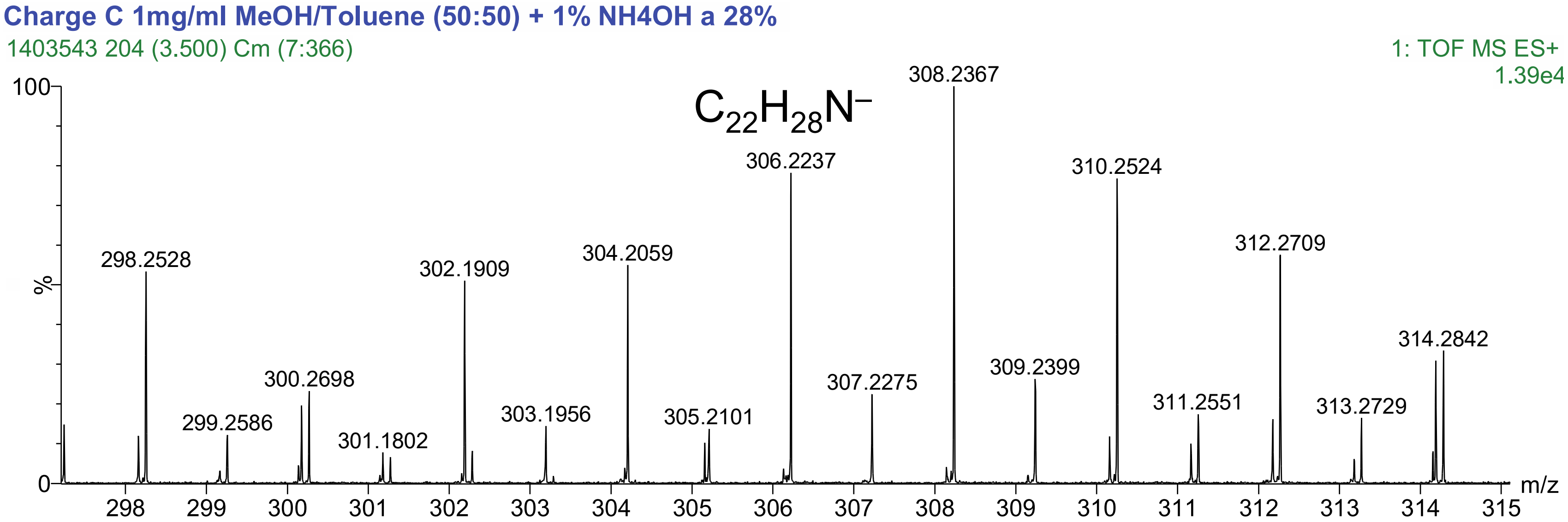


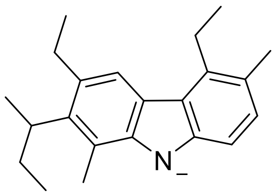
Marshall, *Energy & Fuels* 2001, 15, 1186-1193

Ionization discrimination



ESI(-) NB nitrogen

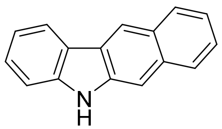




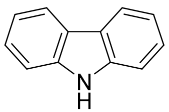
Chemical Formula: $C_{22}H_{28}N^-$
Exact Mass: 306.22272

DBE vs C#

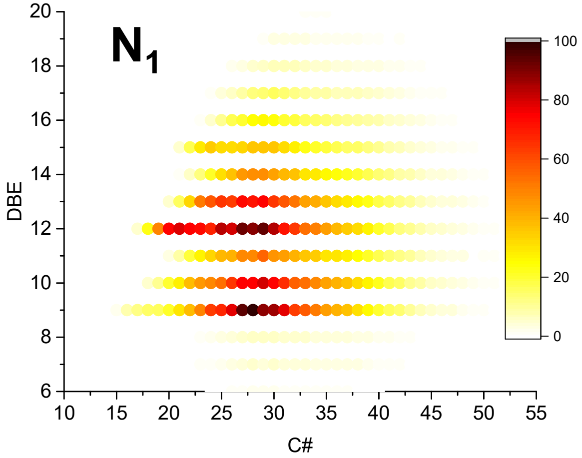
DBE = c − h/2 + n/2 + 1
(for $C_cH_hN_nO_oS_s$)

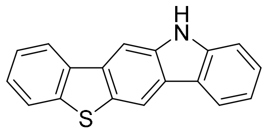


benzocarbazole
DBE=12

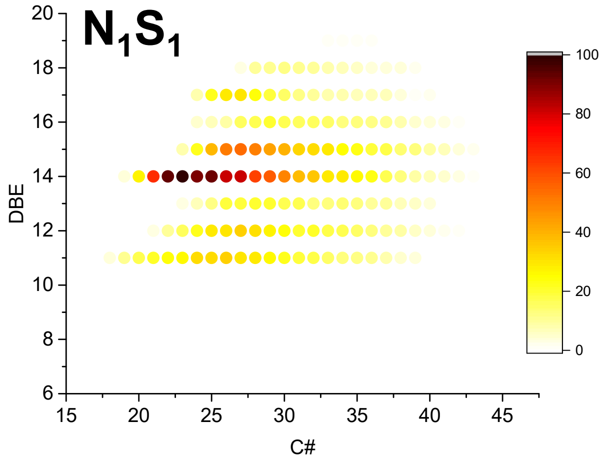


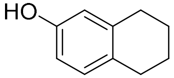
carbazole
DBE=9



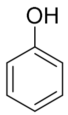


DBE =14

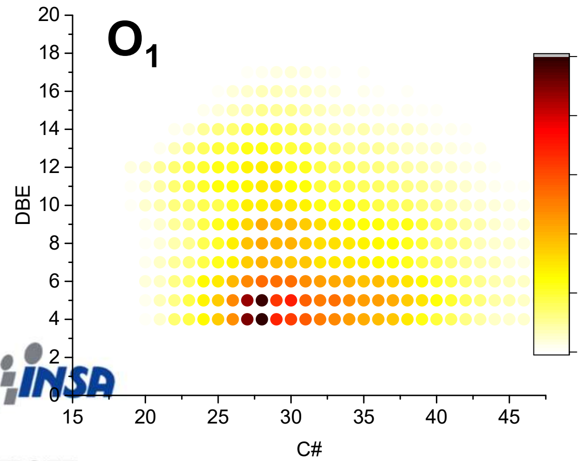


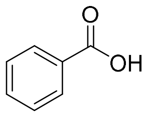


DBE=5

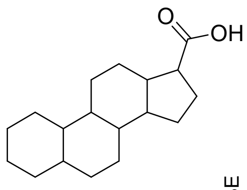


Phenol
DBE=4

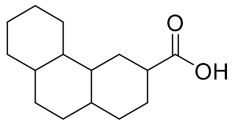




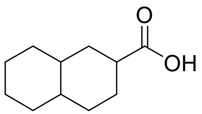
DBE =5



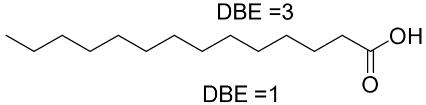
DBE =5



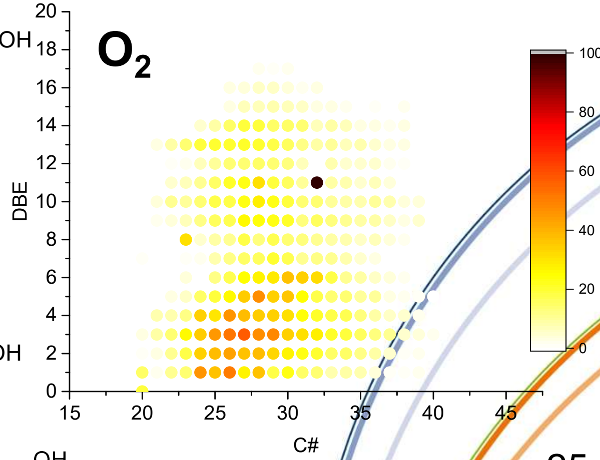
DBE =4



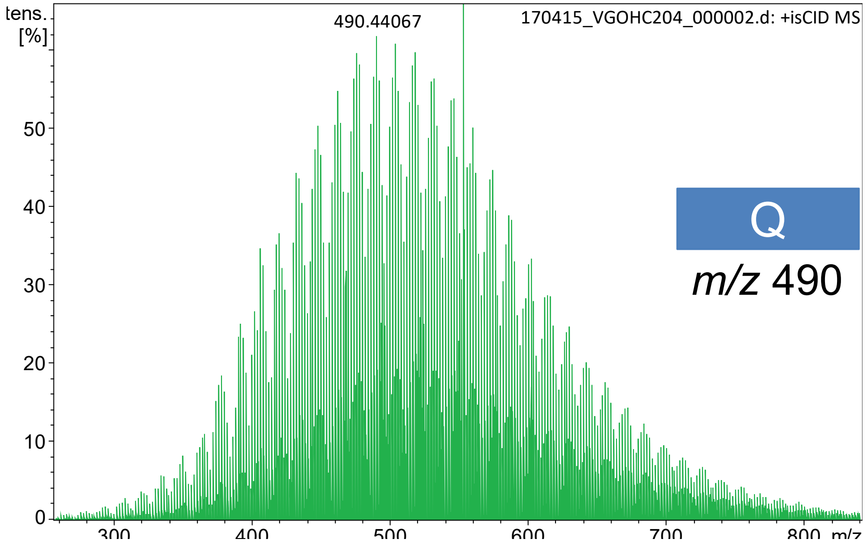
DBE =3

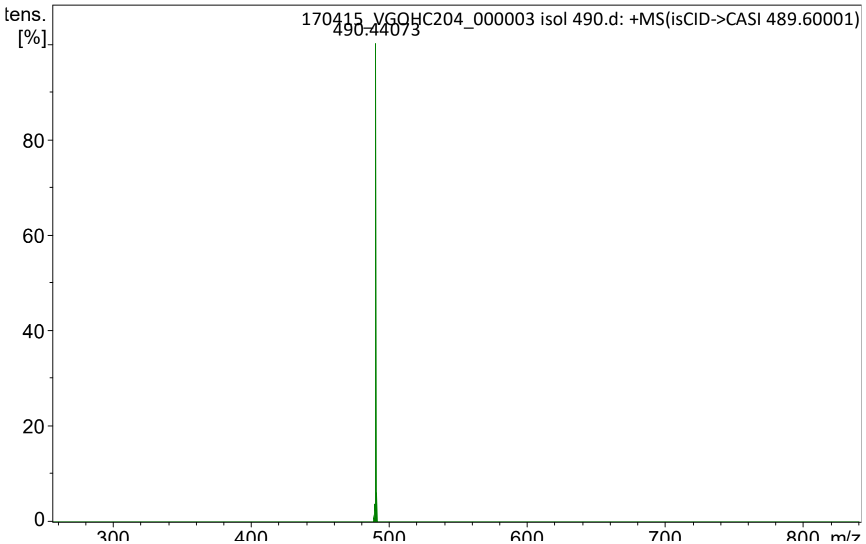


DBE =1

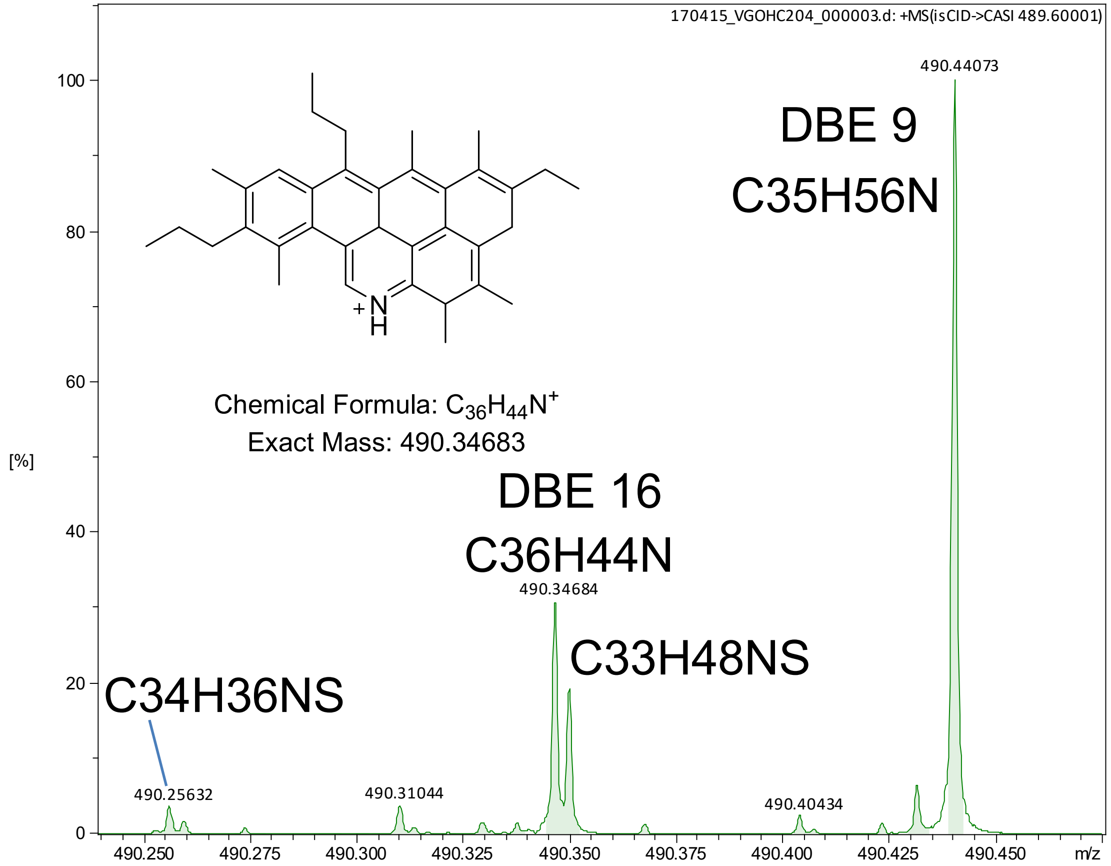


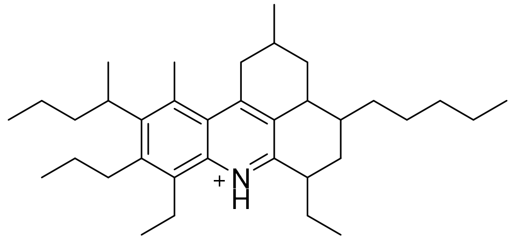
Un peu de chimie structurale





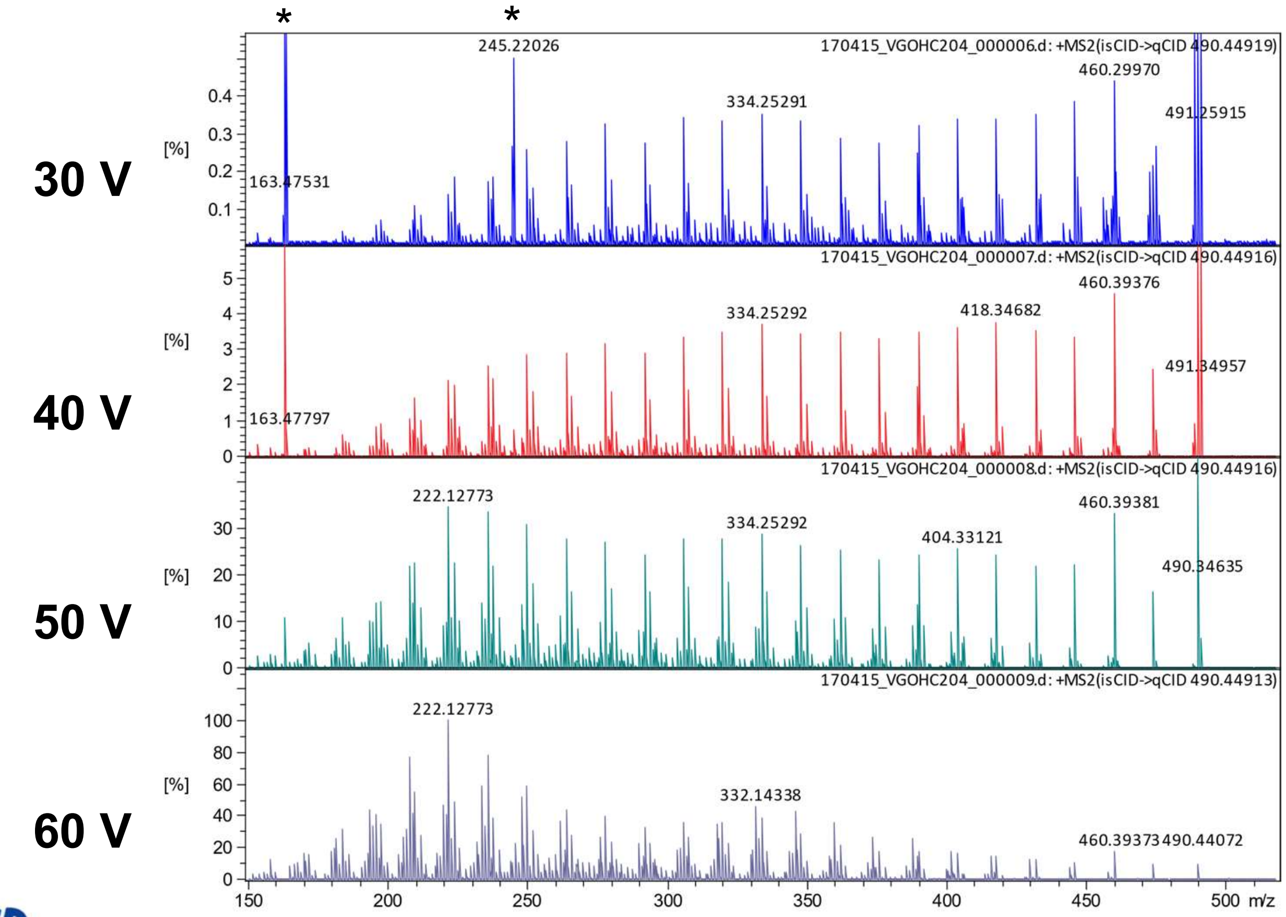
Isolation *m/z* 490.449





Chemical Formula: $C_{35}H_{56}N^{+}$
Exact Mass: 490.44073

Spectres CID

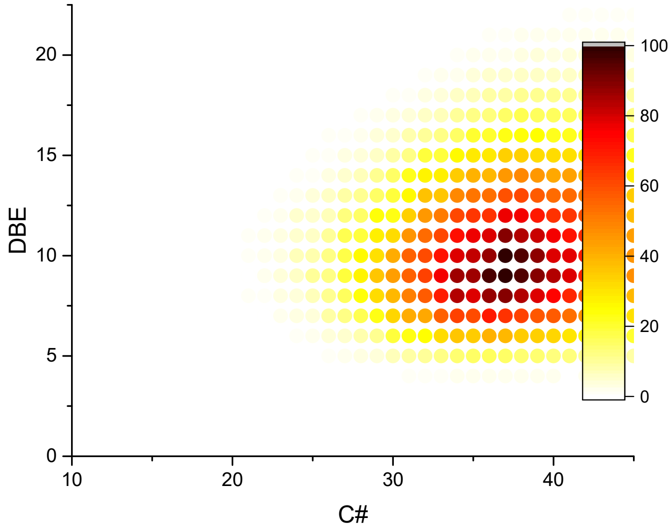


*harmonics

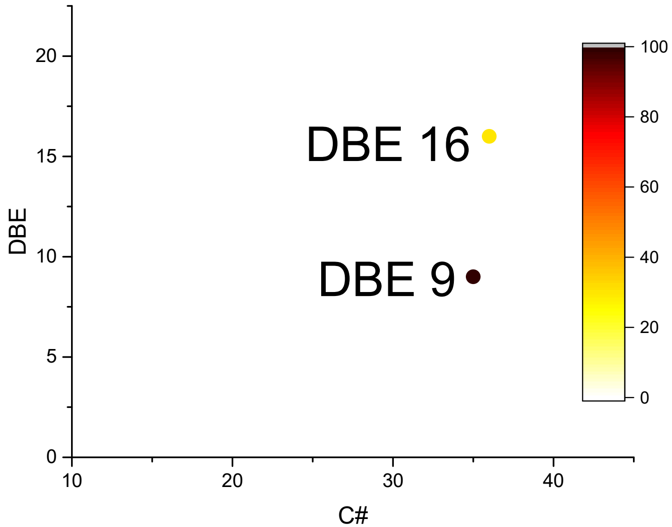
Selection m/z 490.449

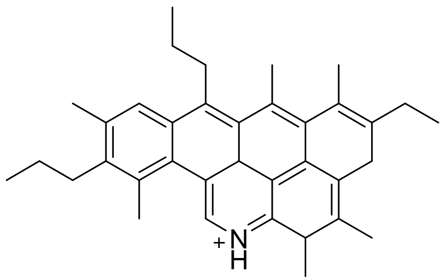
m/z 490

N1 Class

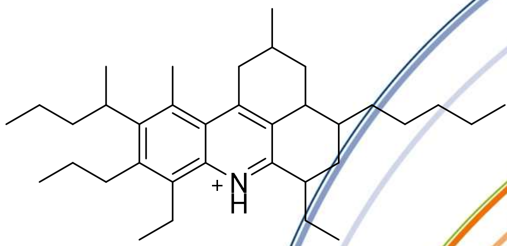


N1 Class
Selection 490.4



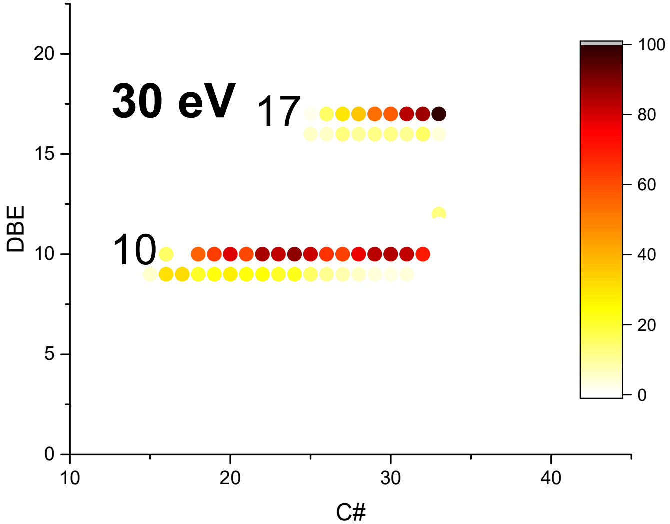


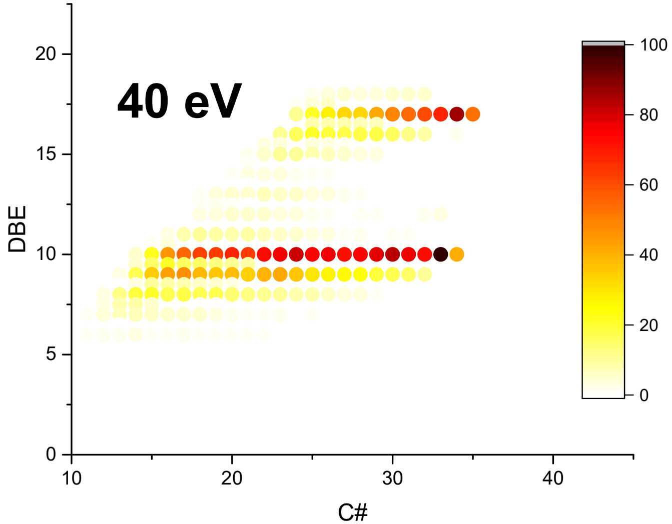
Chemical Formula: $C_{36}H_{44}N^+$
Exact Mass: 490.34683

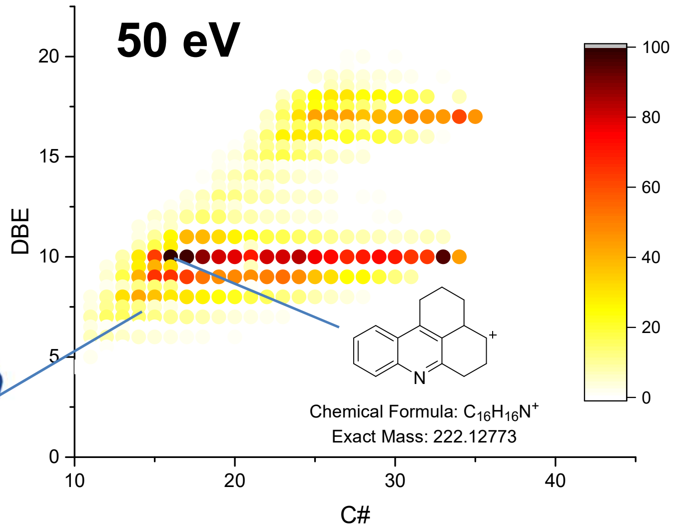


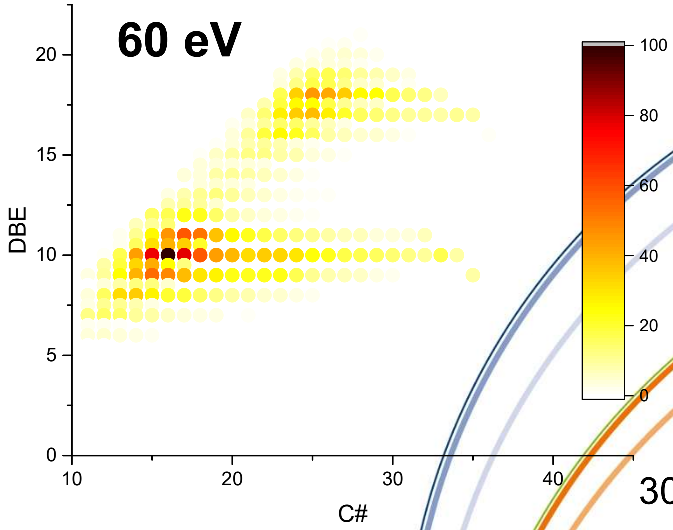
Chemical Formula: $C_{35}H_{56}N^+$
Exact Mass: 490.44073

Losses of DBE through ring opening

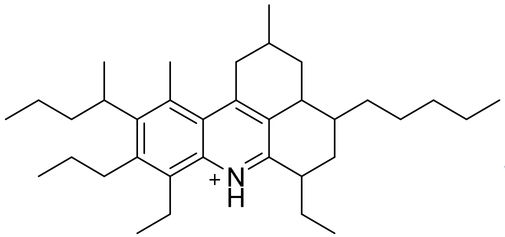






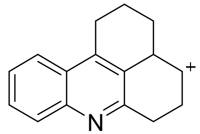


DBE 10 N1 fragment series



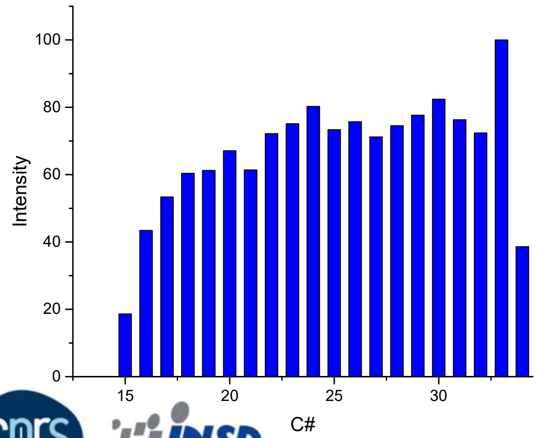
Chemical Formula: $C_{35}H_{56}N^{+}$
Exact Mass: 490.44073

Ion core

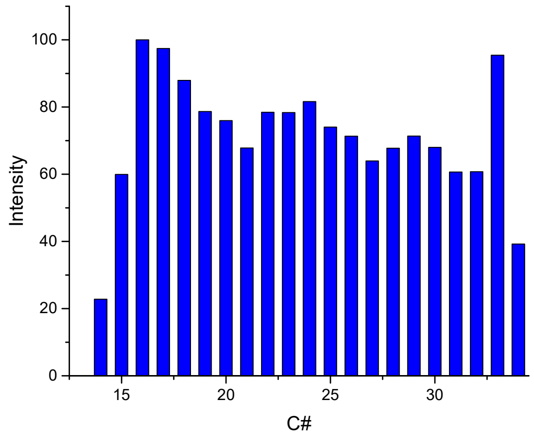


Chemical Formula: $C_{16}H_{16}N^{+}$
Exact Mass: 222.12773

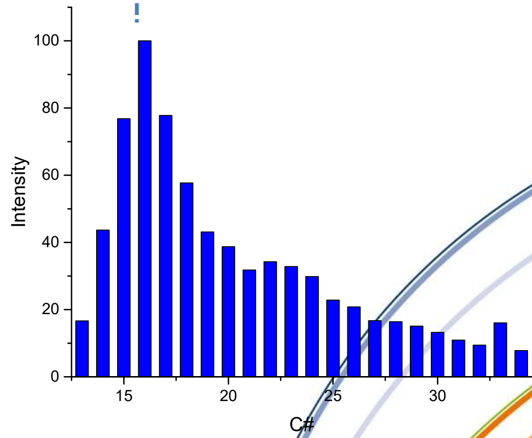
40 V



50 V



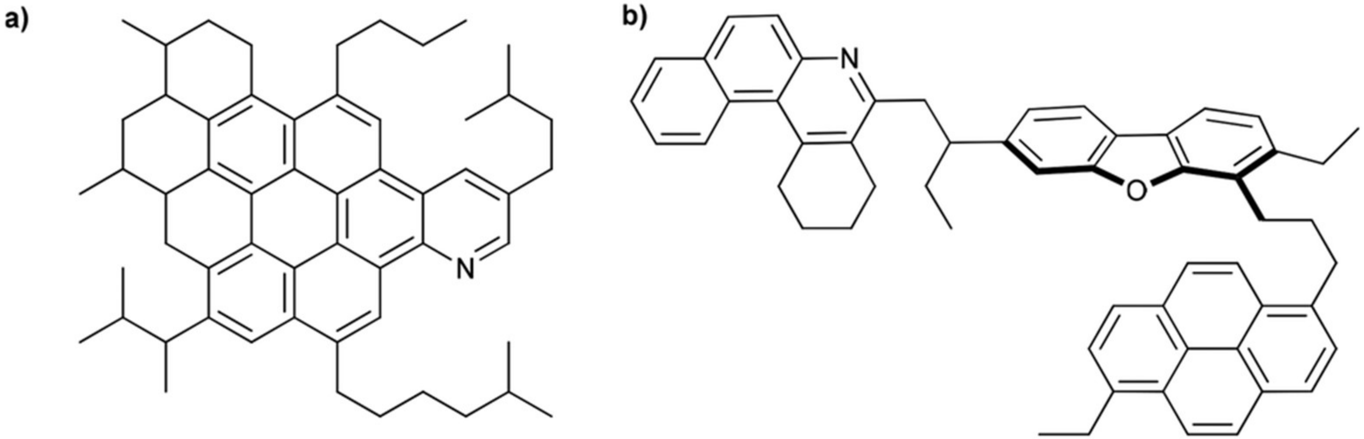
60 V



Asphaltenes

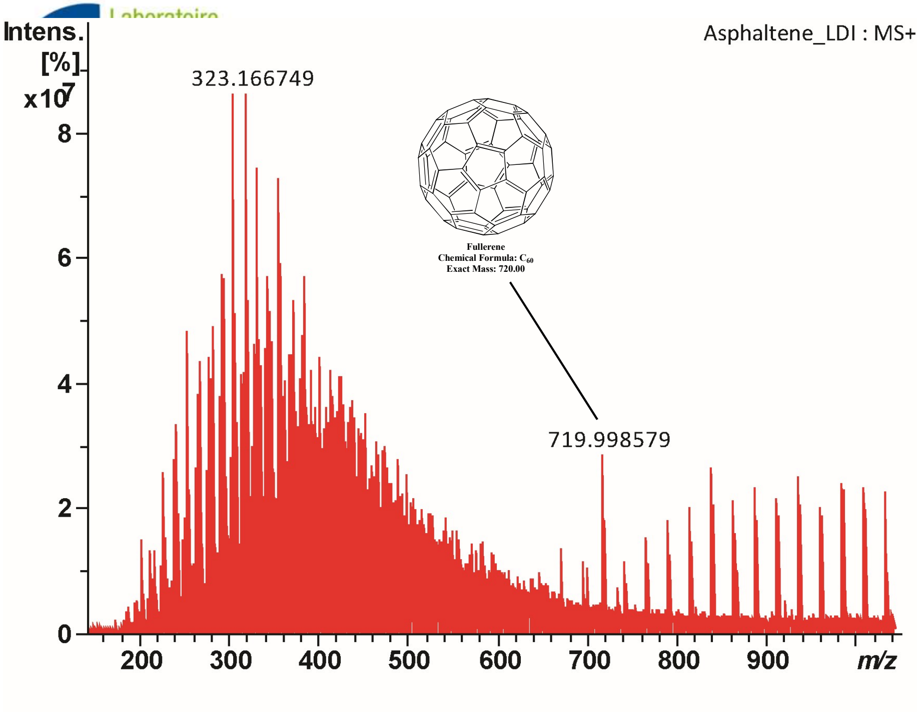
- Reference asphaltene de in the framework of PetroPhase 2017 Le Havre.

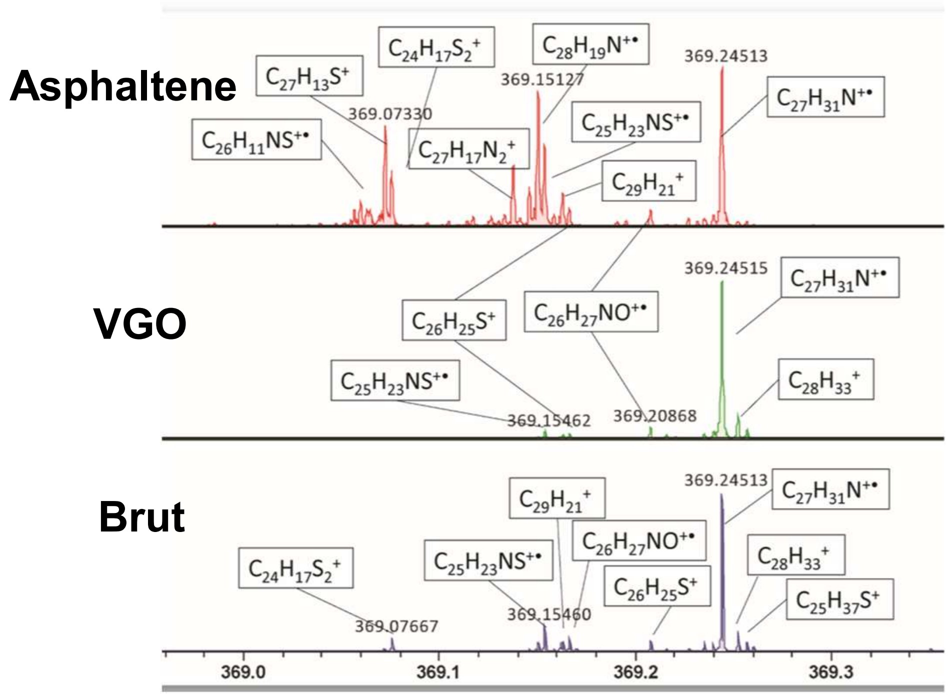
Non-soluble in pentane or heptane but soluble in toluene



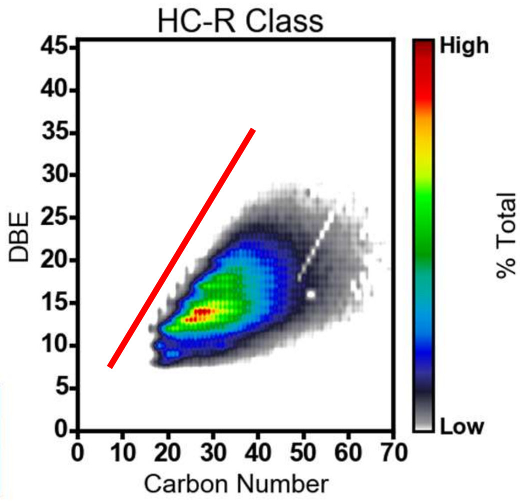
Island ***Archipelago***

Org. Biomol. Chem., 2015, 13, 6984-6991

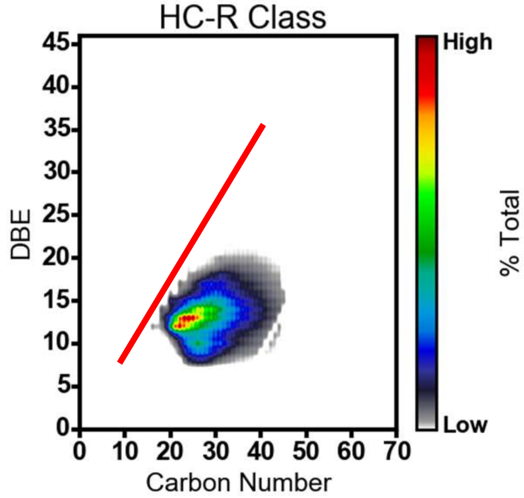




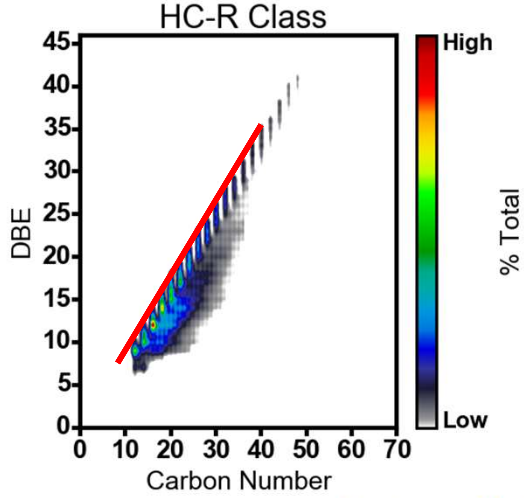
Brut



VGO

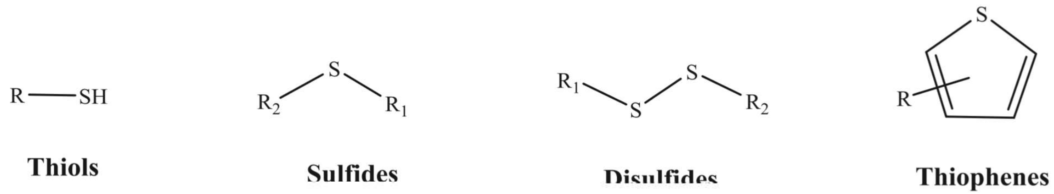


Asphaltene

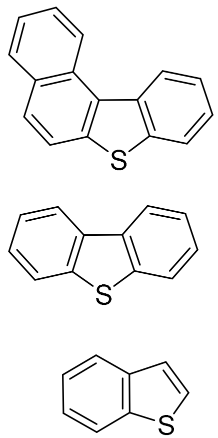


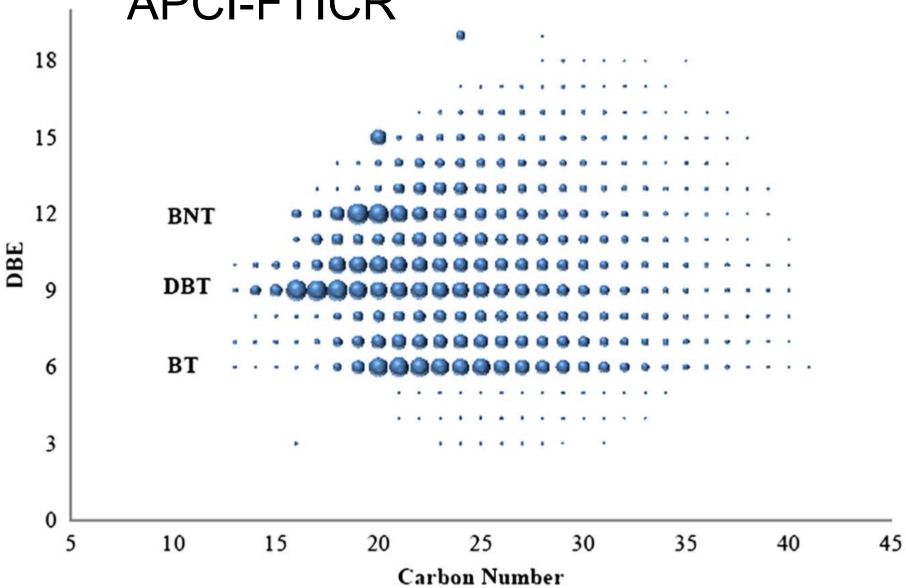
Marianny Combariza

Sulfur



APCI-FTICR





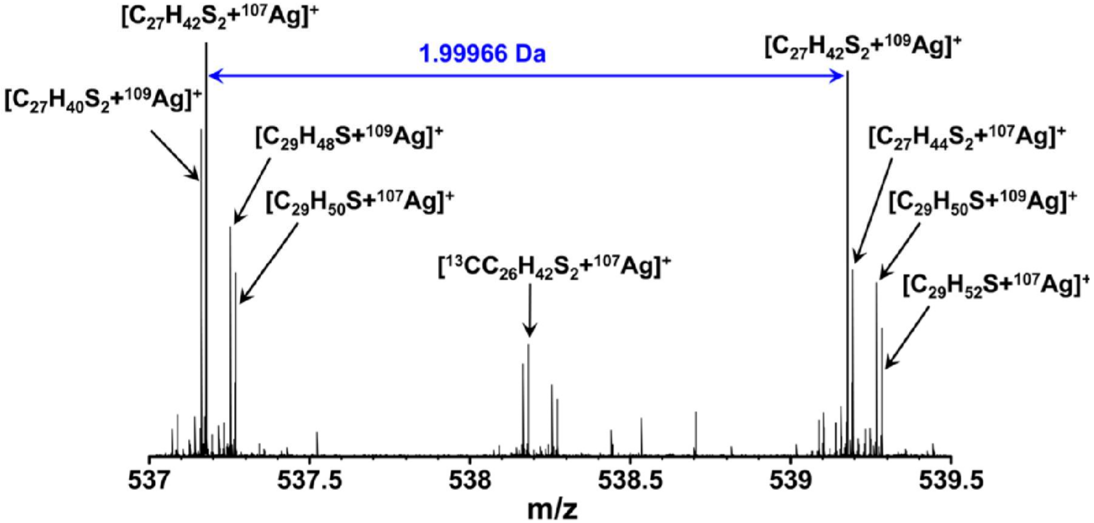
Y. Han, Y. Zhang, C. Xu, C. S. Hsu. Molecular characterization of sulfur-containing compounds in petroleum. *Fuel* **2018**, *221*, 144.

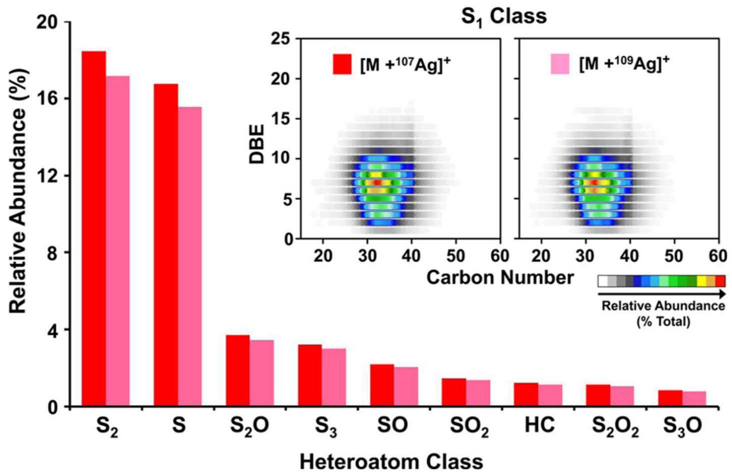
N. Hourani, J. T. Andersson, I. Moller, M. Amad, M. Witt, S. M. Sarathy. Atmospheric pressure chemical ionization Fourier transform ion cyclotron resonance mass spectrometry for complex thiophenic mixture analysis. *Rapid commun. mass spectrom.* **2013**, *27*, 2432.

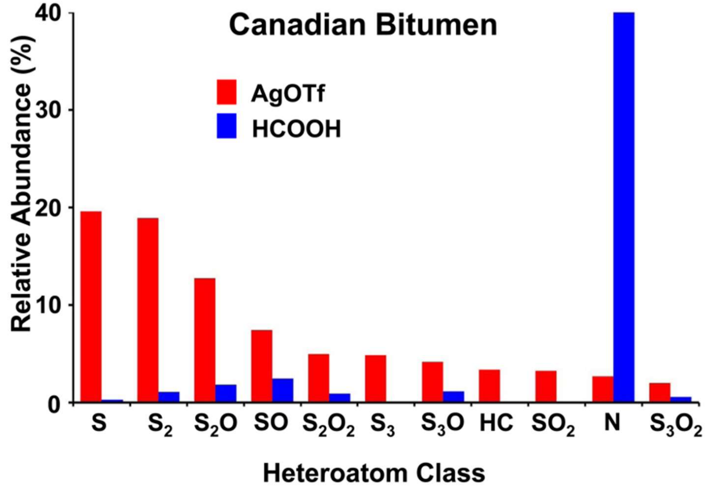
Cationization

- Ag(I)
  - [M + ^{107}Ag]$^+$ and [M + ^{109}Ag]$^+$
  - AgOTf
  - Selective ionization

ESI(+) Canadian HVGO



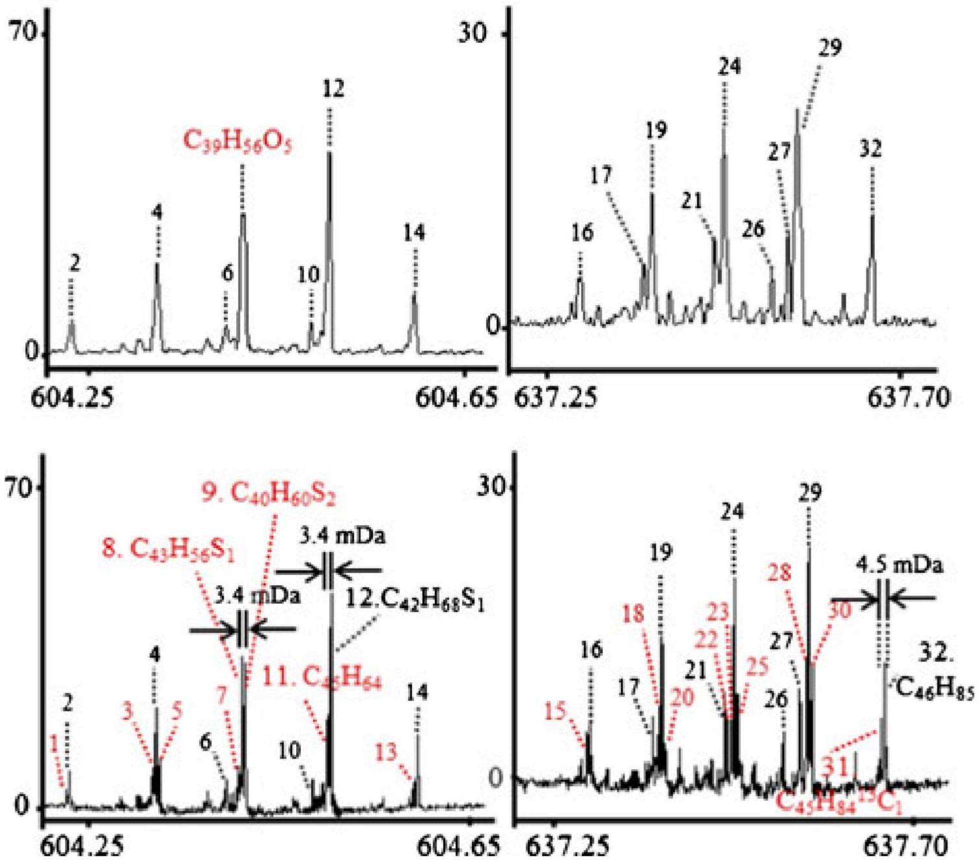


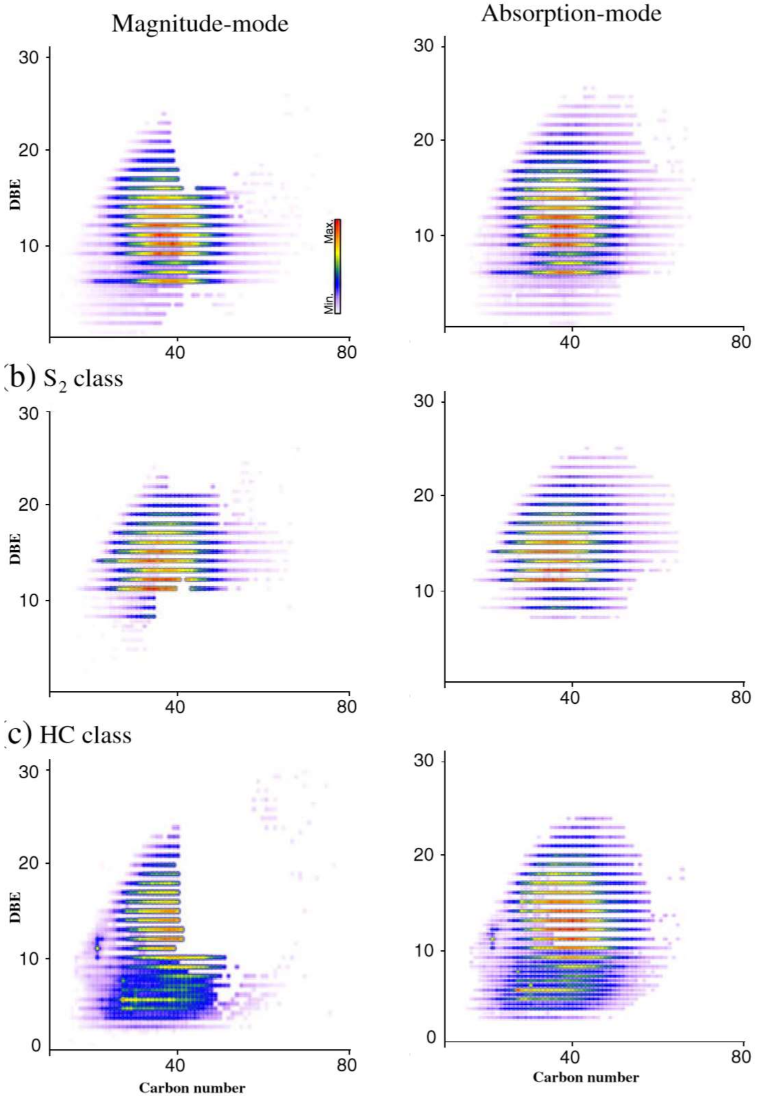


V. V. Lobodin, P. Juyal, A. M. McKenna, R. P. Rodgers, A. G. Marshall. Silver Cationization for Rapid Speciation of Sulfur-Containing Species in Crude Oils by Positive Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2014**, *28*, 447.

Absorption mode

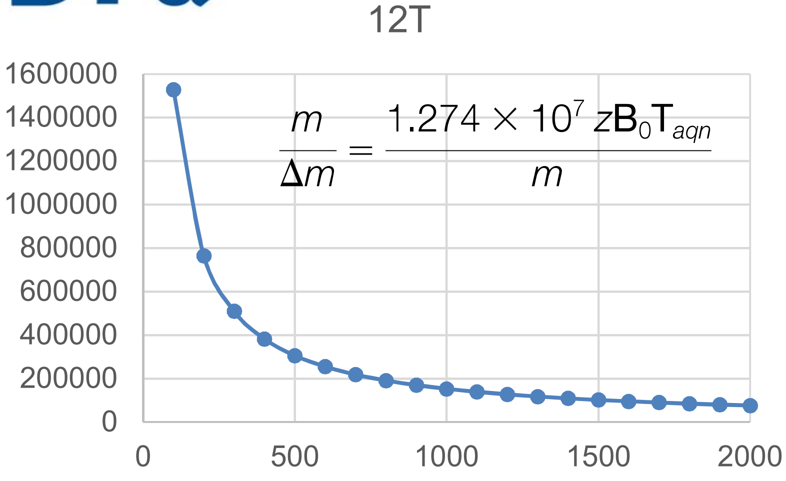
- 7T FTICR, 2s transient

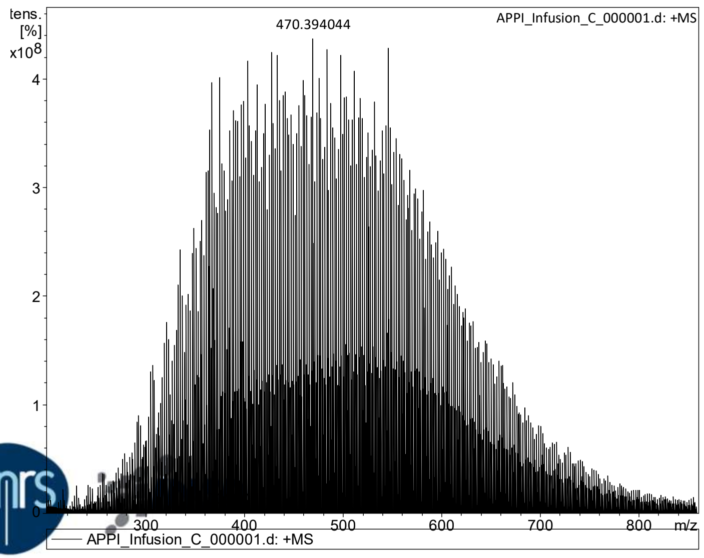


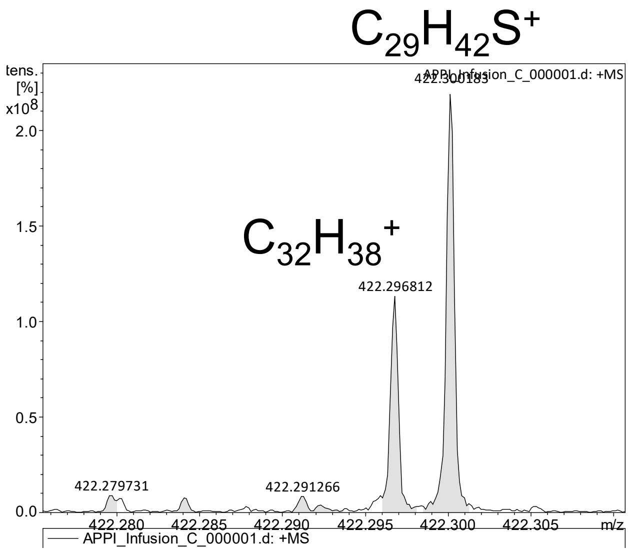


Y. Cho, Y. Qi, P. B. O'Connor, M. P. Barrow, S. Kim. Application of phase correction to improve the interpretation of crude oil spectra obtained using 7 T Fourier transform ion cyclotron resonance mass spectrometry. *J Am Soc Mass Spectrom* **2014**, *25*, 154.

Evolution of RP with *m/z*

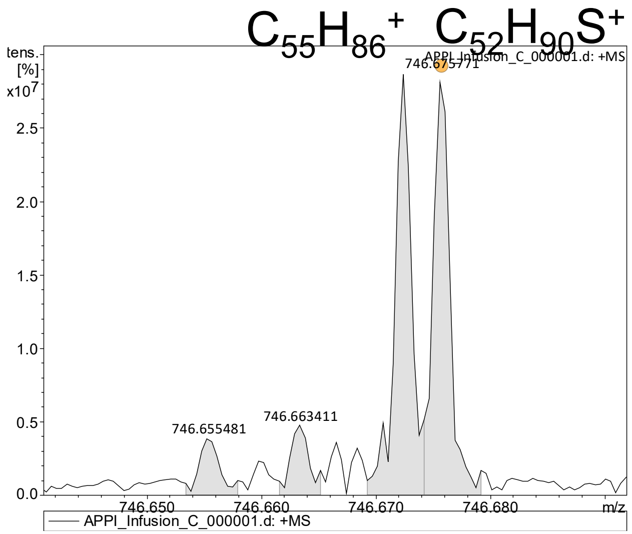






3.3 s transient

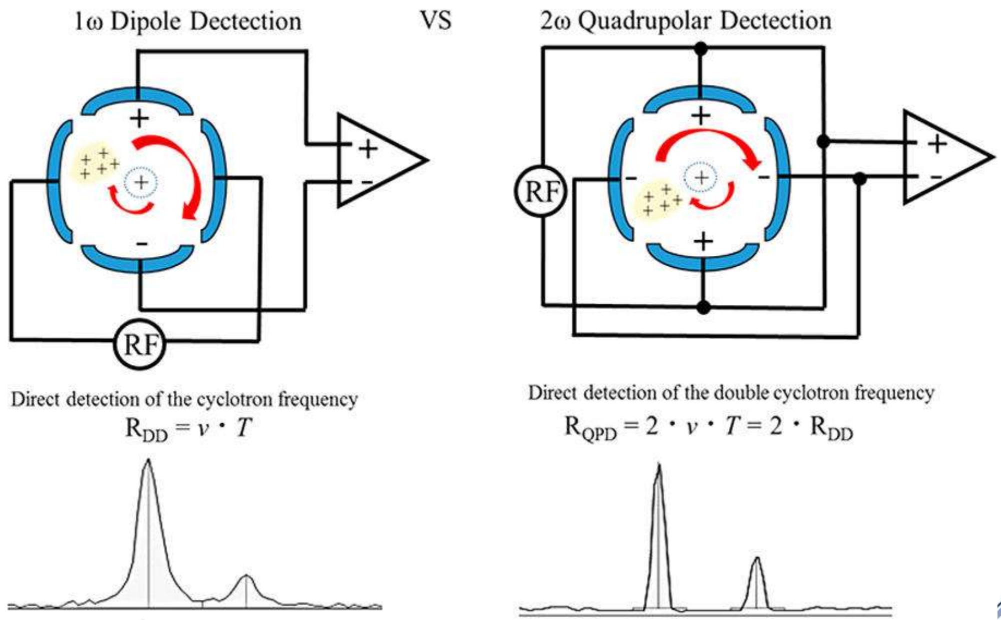
R 850000



R 550000

Quadripolar detection

- 7 T
- RP150000 m/z
  400 4s transient



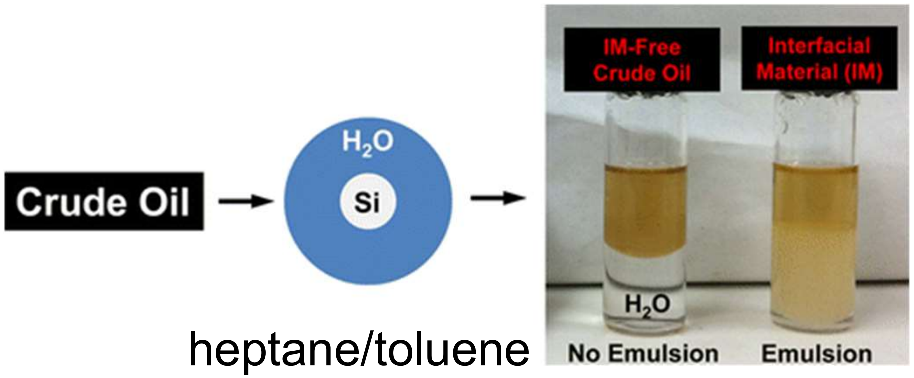
E. Cho, M. Witt, M. Hur, M. J. Jung, S. Kim. Application of FT-ICR MS Equipped with Quadrupole Detection for Analysis of Crude Oil. *Anal Chem* **2017**, *89*, 12101.

Limits

- Isomers ?
  - *m/z* depends only on molecular formula
- Ionization discrimination
  - In complex mixtures charge tend to go to the more basic/acidic species
  - Observation of species with higher ionization efficiency
- Compounds with low ionization efficiency?
- Addition of separation
  - Fractionation
  - Liquid chromatography (on line and off line)
  - Gas chromatography

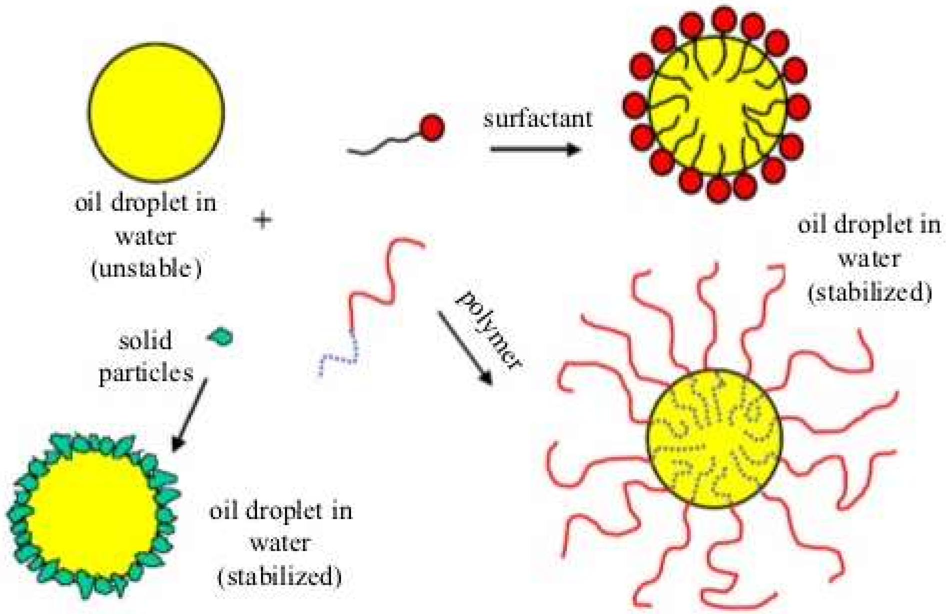
Emulsions

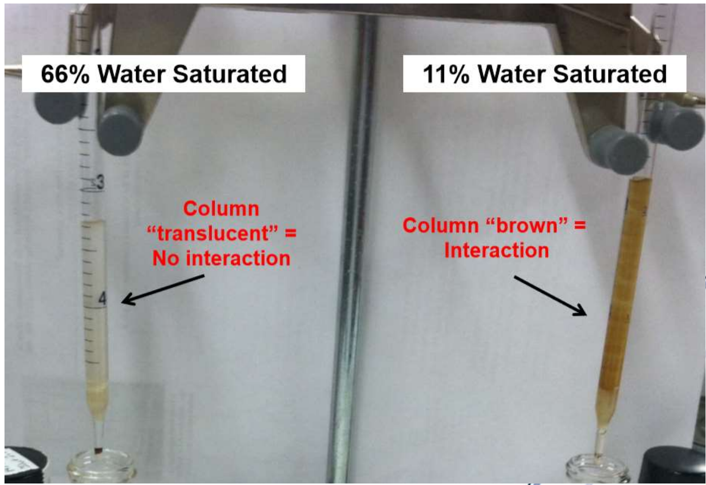
- Formation of emulsions can be a issue for oil production
- Some oils lead to higher amount of emulsions



heptane/toluene

10:25 MeOH/toluene





J. M. Jarvis, W. K. Robbins, Y. E. Corilo, R. P. Rodgers. Novel Method To Isolate Interfacial Material. *Energy Fuels* **2015**, *29*, 7058.

Off line chromatographic separation

HPLC-2

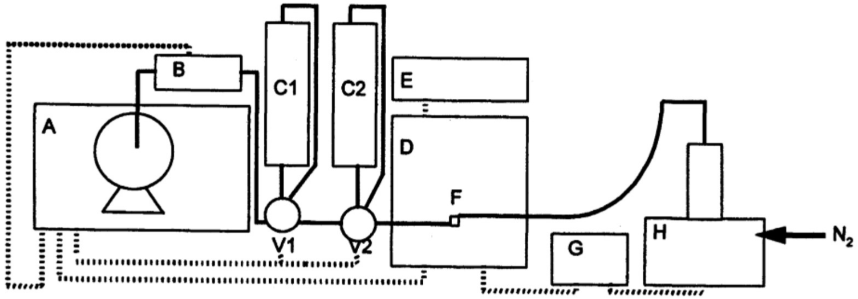
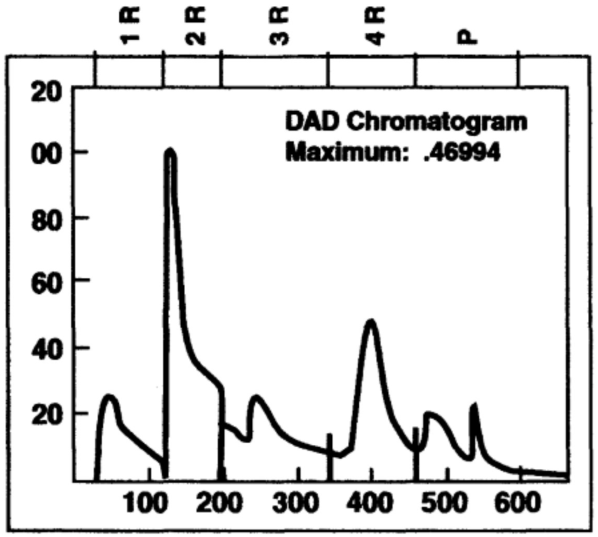
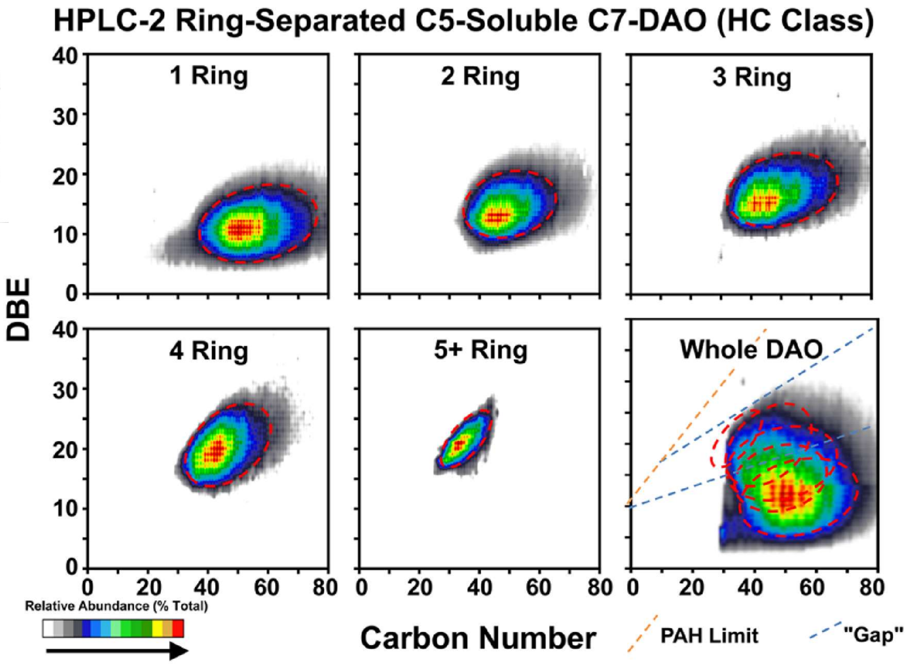


Figure 1. Commercial components assembled into the HPLC-2 system. A, Varian 5560 ternary solvent pump; B, Varian 8055 autosampler; C1, 4.6 × 2500 mm DNAP column; C2, 4.6 × 250 mm PAC column; D, HP 8451 diode array spectrophotometer (DAD); E, HP 9133 dual disk drive; F, Isco 1-mm flowcell; G, Kiethey 195A digital voltmeter; H, Applied Chromatography Systems 750/14 evaporative mass detector; V1 and V2, Rheodyne 7040 six-port switching valves.



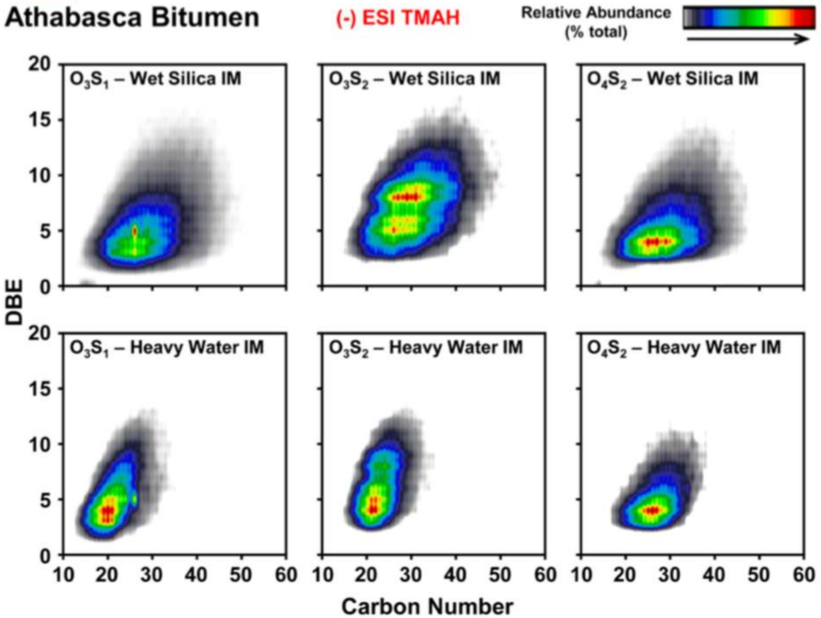
C1 - dinitroanilinopropyl (DNAP) column for separating the larger rings

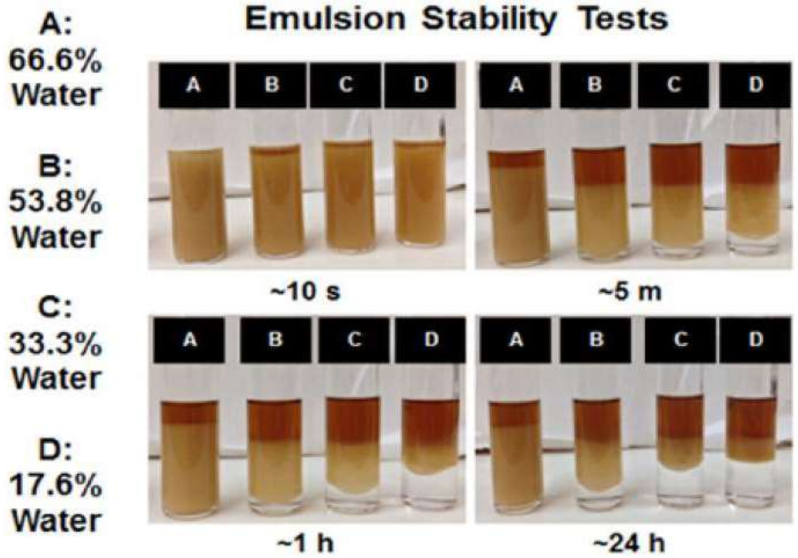
C2 - propylaminocyano (PAC) column for separating saturates and mono-aromatics

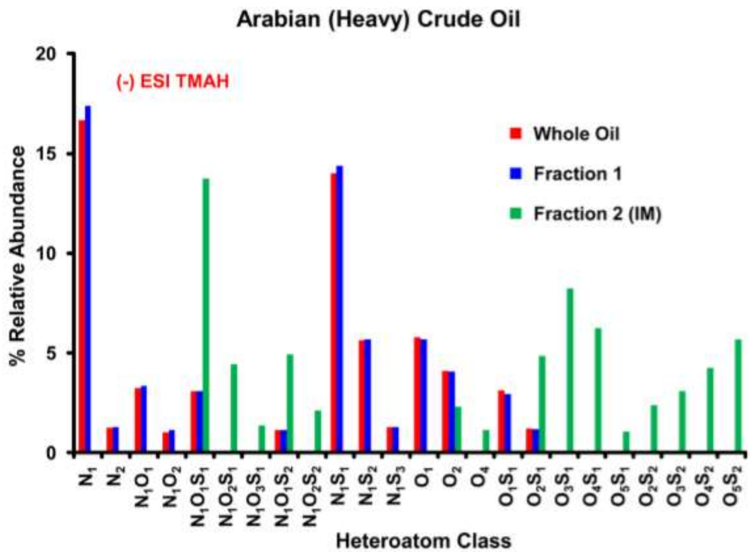


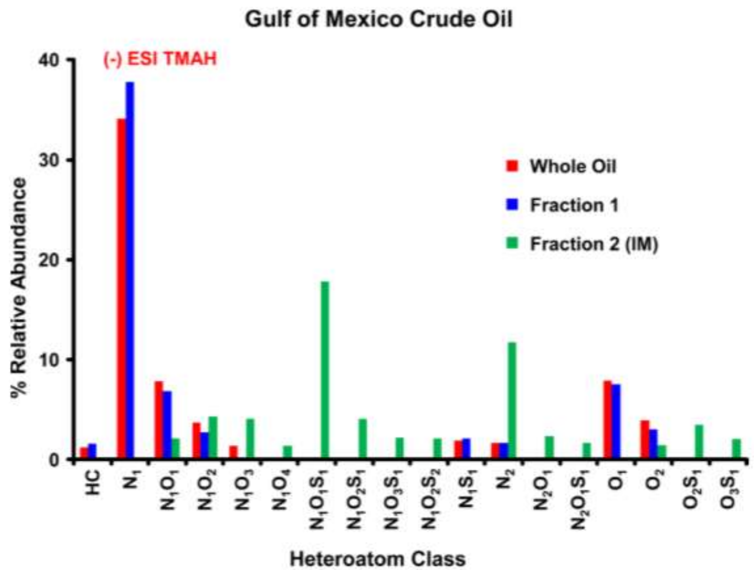
W. K. Robbins. Quantitative Measurement of Mass and Aromaticity Distributions for Heavy Distillates 1. Capabilities of the HPLC-2 System. *J. Chrom. Sci.* **1998**, *36*, 457.

D. C. Podgorski, Y. E. Corilo, L. Nyadong, V. V. Lobodin, B. J. Bythell, W. K. Robbins, A. M. McKenna, A. G. Marshall, R. P. Rodgers. Heavy Petroleum Composition. 5. Compositional and Structural Continuum of Petroleum Revealed. *Energy Fuels* **2013**, *27*, 1268.


Athabasca Bitumen
(-) ESI TMAH
Relative Abundance (% total)
O_3S_1 – Wet Silica IM
O_3S_2 – Wet Silica IM
O_4S_2 – Wet Silica IM
O_3S_1 – Heavy Water IM
O_3S_2 – Heavy Water IM
O_4S_2 – Heavy Water IM
DBE
Carbon Number

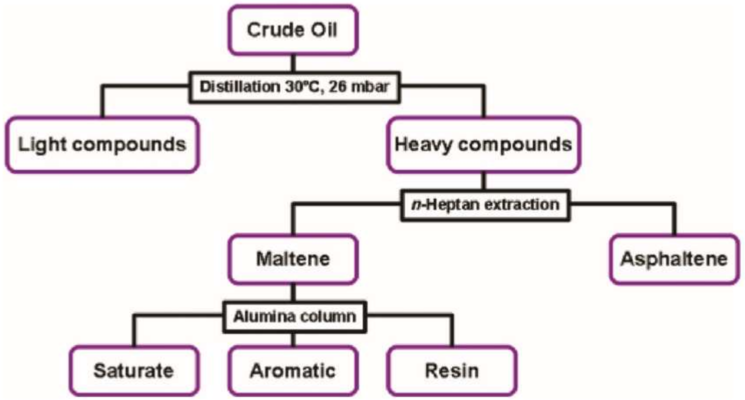

Emulsion Stability Tests
A: 66.6% Water
B: 53.8% Water
C: 33.3% Water
D: 17.6% Water
A B C D
~10 s
~5 m
~1 h
~24 h

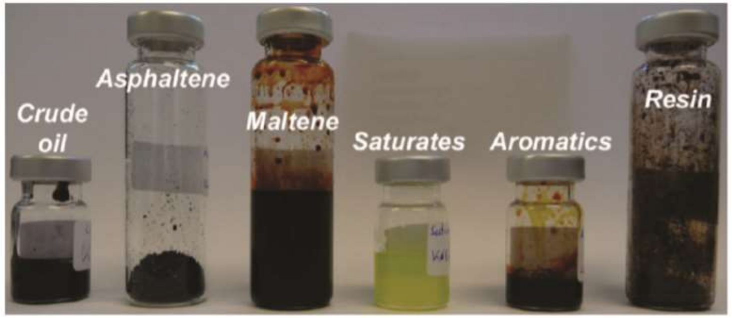

Arabian (Heavy) Crude Oil
(-) ESI TMAH
Whole Oil
Fraction 1
Fraction 2 (IM)
% Relative Abundance
Heteroatom Class
N_1 N_2 N_1O_1 N_1O_2 $N_1O_1S_1$ $N_1O_2S_1$ $N_1O_3S_1$ $N_1O_1S_2$ $N_1O_2S_2$ N_1S_1 N_1S_2 N_1S_3 O_1 O_2 O_4 O_1S_1 O_2S_1 O_3S_1 O_4S_1 O_5S_1 O_2S_2 O_3S_2 O_4S_2 O_5S_2

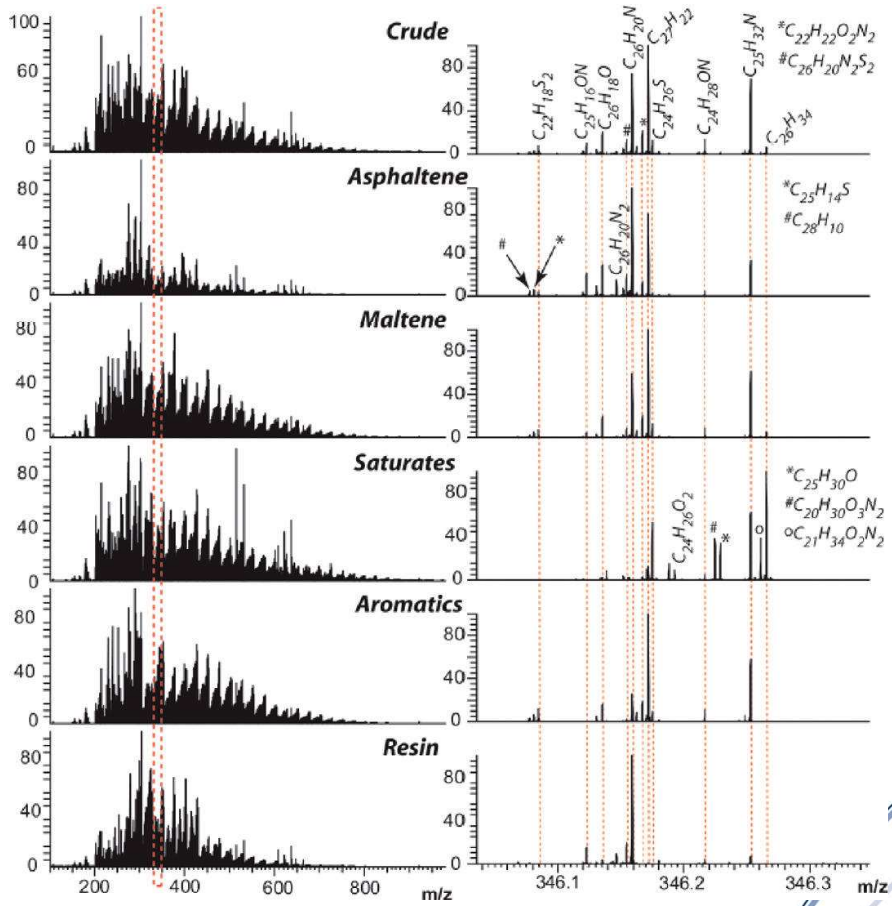

Gulf of Mexico Crude Oil
(-) ESI TMAH
Whole Oil
Fraction 1
Fraction 2 (IM)
% Relative Abundance
Heteroatom Class
HC N_1 N_1O_1 N_1O_2 N_1O_3 N_1O_4 $N_1O_1S_1$ $N_1O_2S_1$ $N_1O_3S_1$ $N_1O_2S_2$ N_1S_1 N_2 N_2O_1 $N_2O_1S_1$ O_1 O_2 O_2S_1 O_3S_1

SARA

Saturated, Aromatics, Resins, Asphaltens





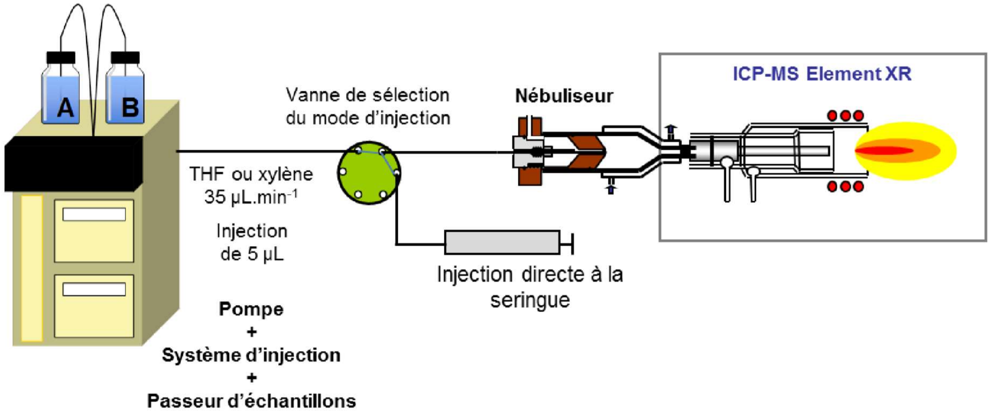


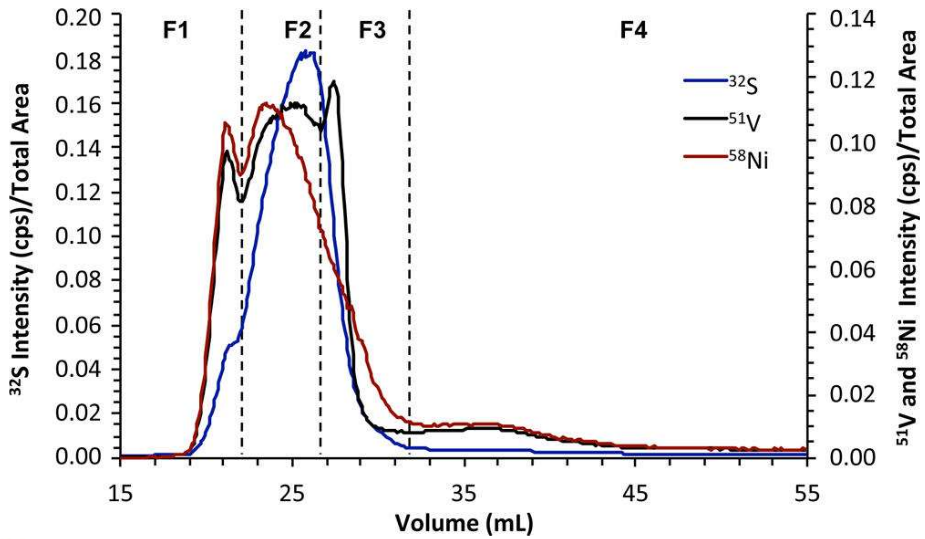
APLI-FTICR

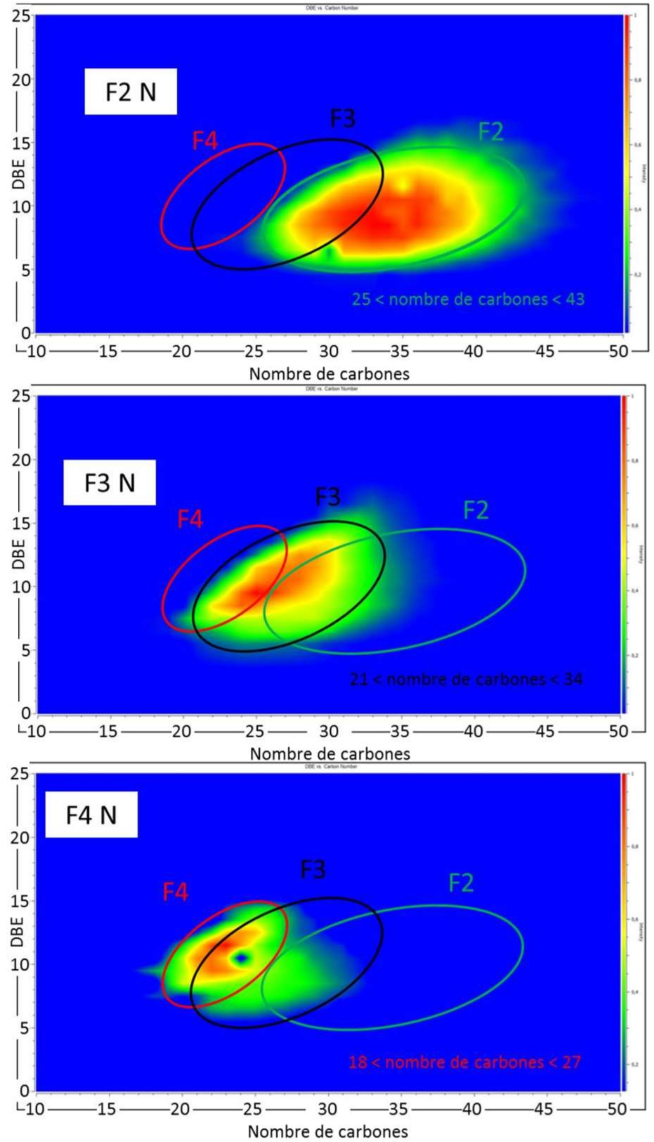
A. Gaspar, E. Zellermann, S. Lababidi, J. Reece, W. Schrader. Characterization of Saturates, Aromatics, Resins, and Asphaltenes Heavy Crude Oil Fractions by Atmospheric Pressure Laser Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2012**, *26*, 3481.

- GPC-ICPMS

GPC



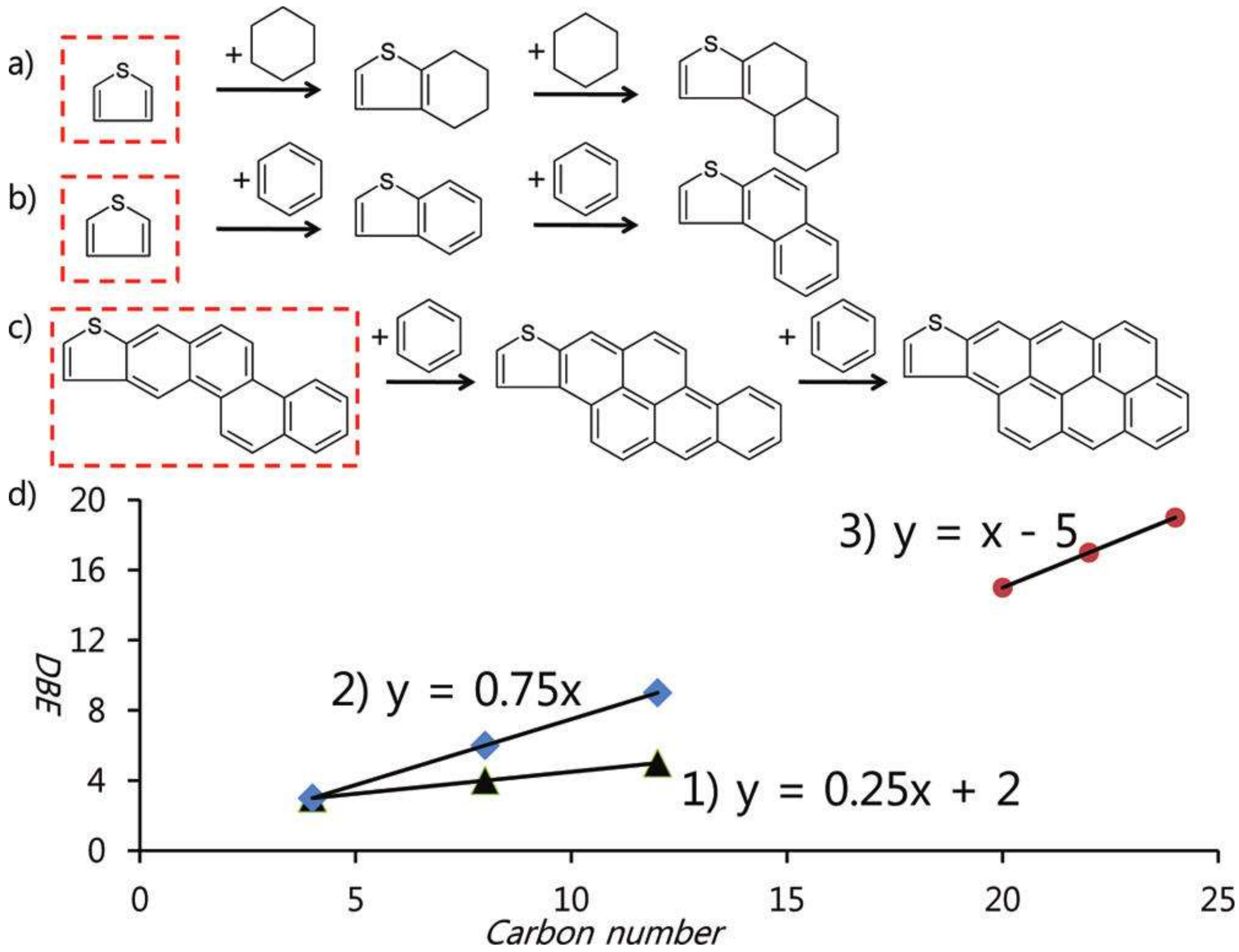




S. Gutierrez Sama, A. Desprez, G. Krier, C.-P. Lienemann, J. Barbier, R. Lobinski, C. Barrere-Mangote, P. Giusti, B. Bouyssiere. Study of the Aggregation of Metal Complexes with Asphaltenes Using Gel Permeation Chromatography Inductively Coupled Plasma High-Resolution Mass Spectrometry. *Energy Fuels* **2016**, *30*, 6907.

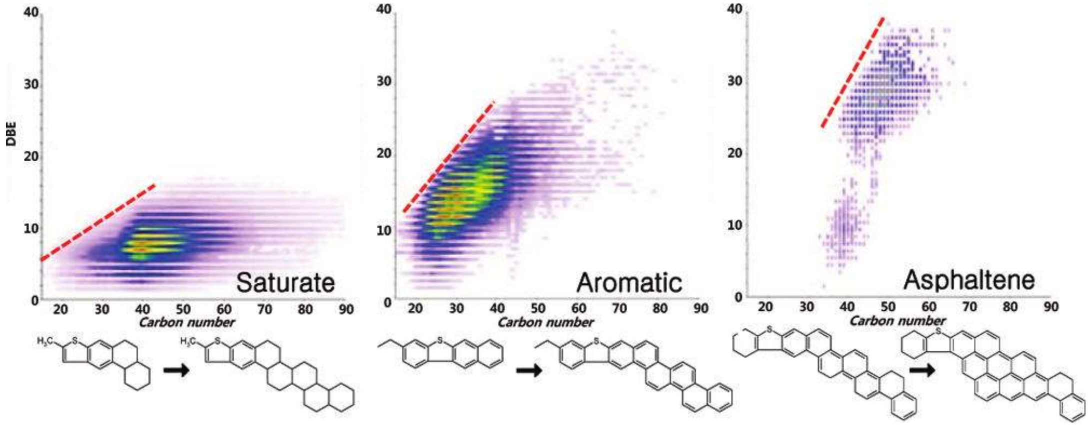
Thesis Alain Desprez

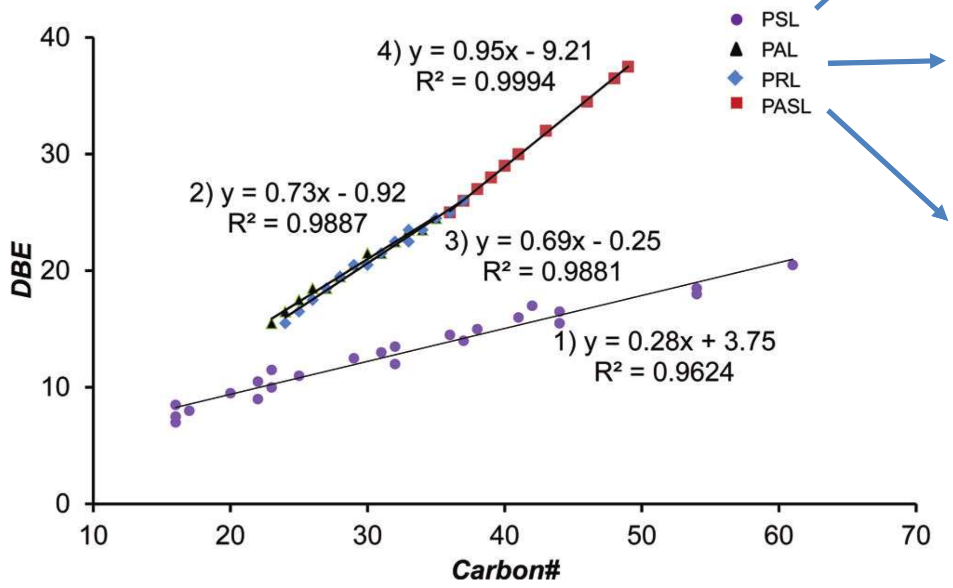
Planar limit



Y. Cho, Y. H. Kim, S. Kim. Planar limit-assisted structural interpretation of saturates/aromatics/resins/asphaltenes fractionated crude oil compounds observed by Fourier transform ion cyclotron resonance mass spectrometry. *Anal Chem* **2011**, *83*, 6068.

Application SARA fractions





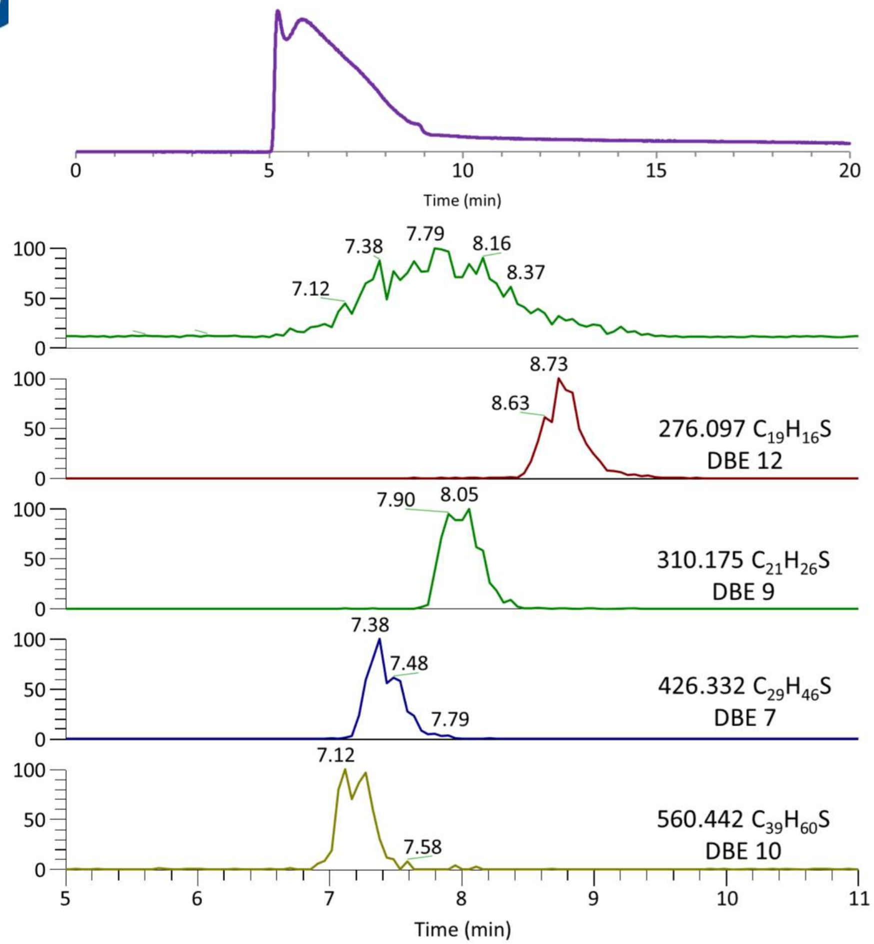
Slope 0.25 — addition of a saturated cyclic ring

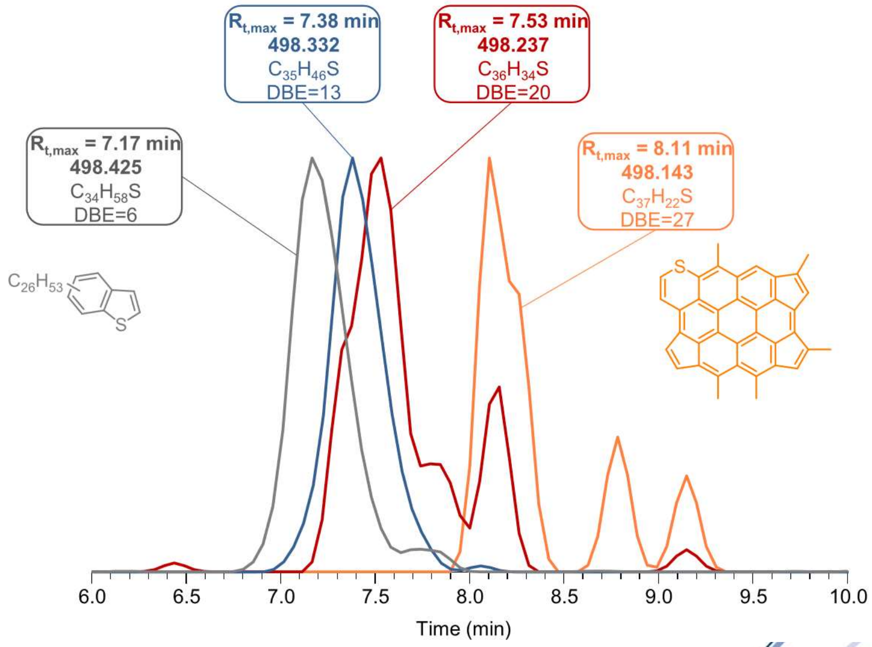
Slope 0.75 — serial linear addition of aromatic rings

Slope 1 — nonlinear addition of benzene rings

APPI-LTQ-Orbitrap

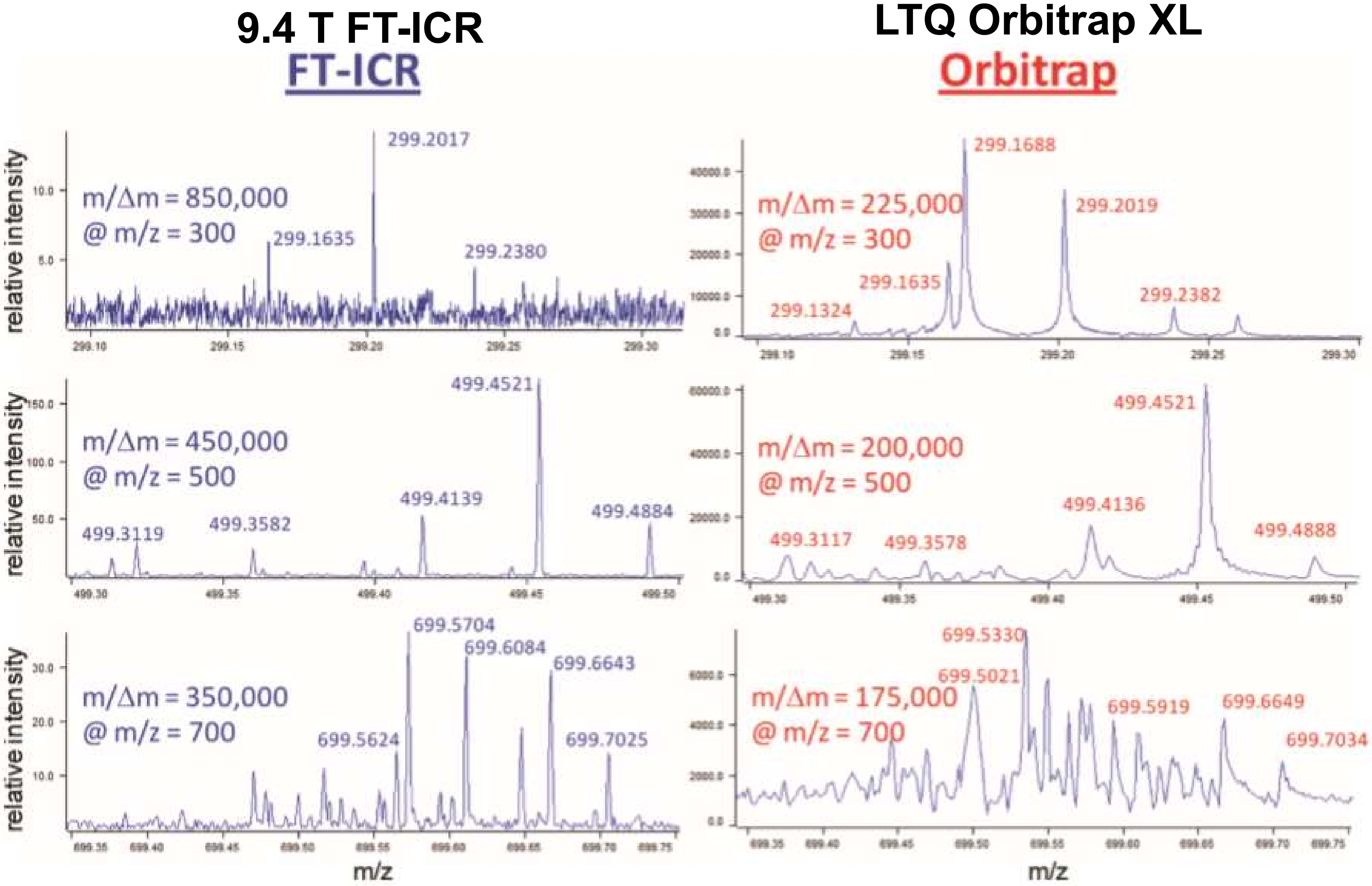
On line LC/MS





T. Ghislain, L. Molnarne Guricza, W. Schrader. Characterization of crude oil asphaltenes by coupling size-exclusion chromatography directly to an ultrahigh-resolution mass spectrometer. Rapid commun. mass spectrom. 2017, 31, 495.

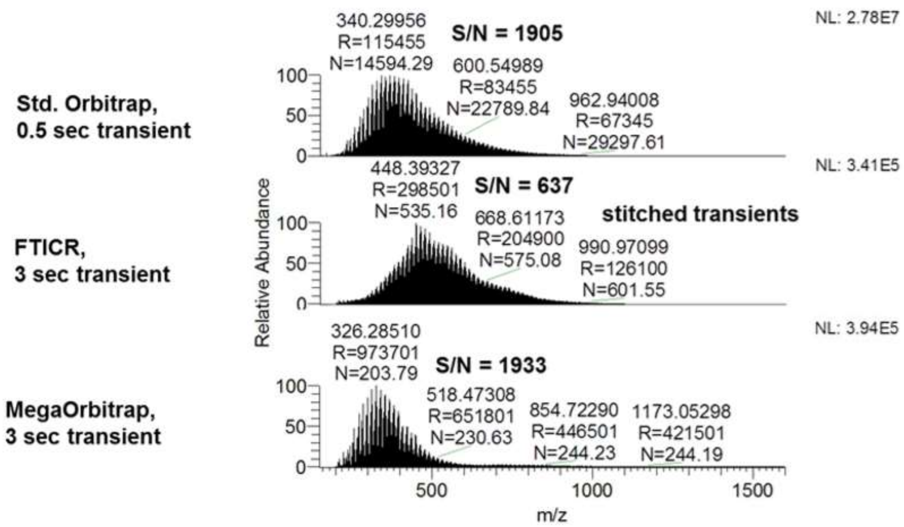
Orbitrap



A. E. Pomerantz, O. C. Mullins, G. Paul, J. Ruzicka, M. Sanders. Orbitrap Mass Spectrometry: A Proposal for Routine Analysis of Nonvolatile Components of Petroleum. *Energy Fuels* **2011**, *25*, 3077.

Orbitrap

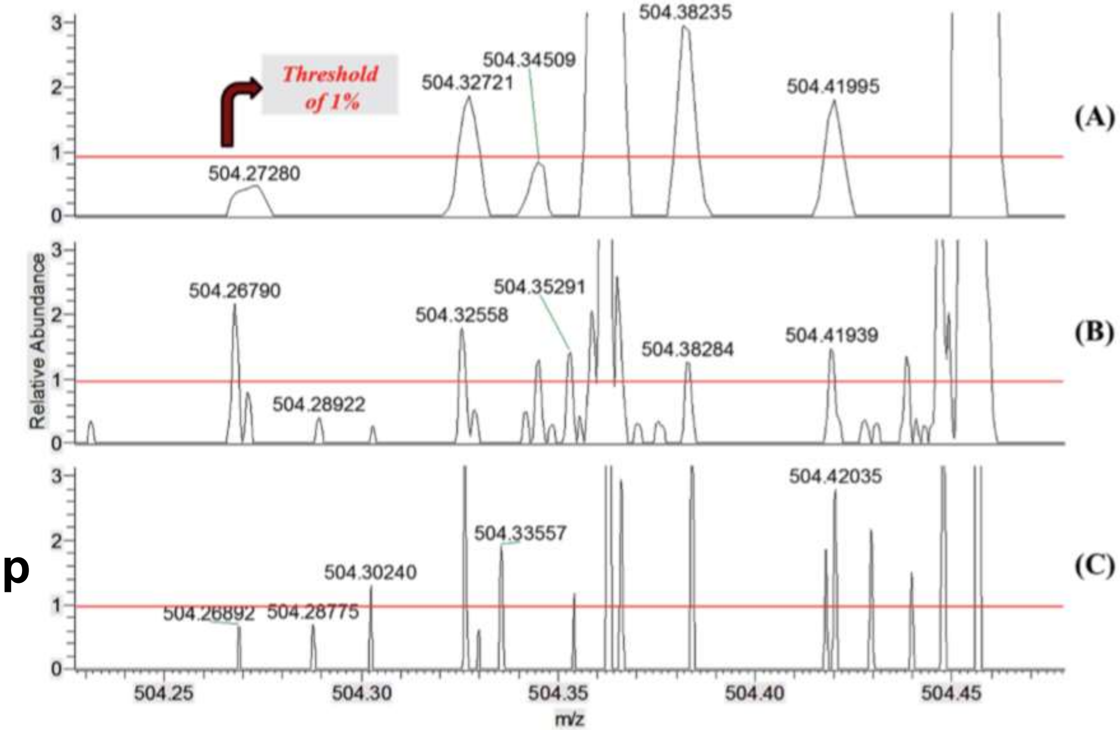
ESI(+)



Std Orbitrap
0.5 s

7 T FTICR
3 s

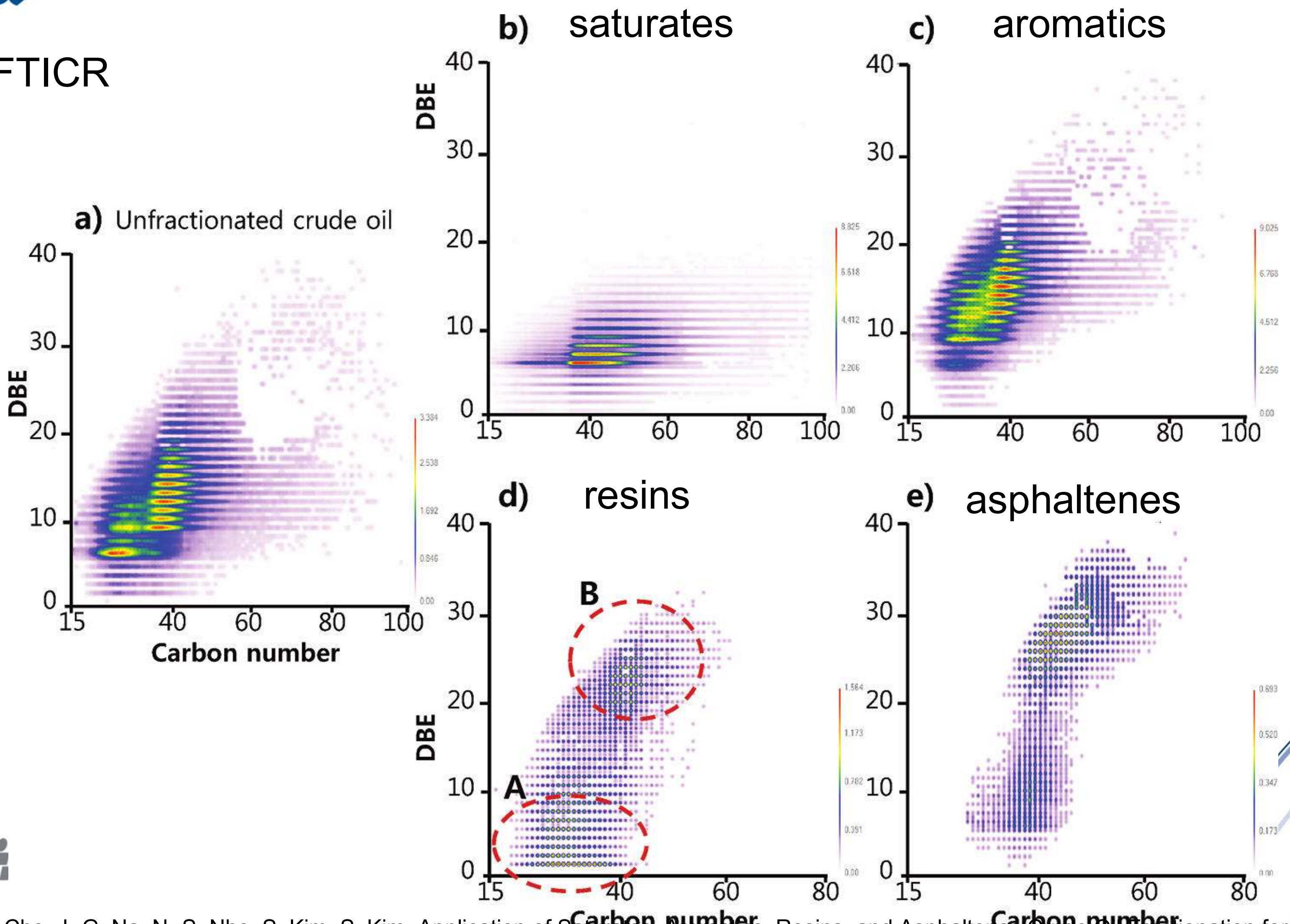
Mega Orbitrap
3 s (eFT)



E. M. Schmidt, M. A. Pudenzi, J. M. Santos, C. F. F. Angolini, R. C. L. Pereira, Y. S. Rocha, E. Denisov, E. Damoc, A. Makarov, M. N. Eberlin. Petroleomics via Orbitrap mass spectrometry with resolving power above 1 000 000 at m/z 200. *RSC Advances* **2018**, *8*, 6183

SARA APPI

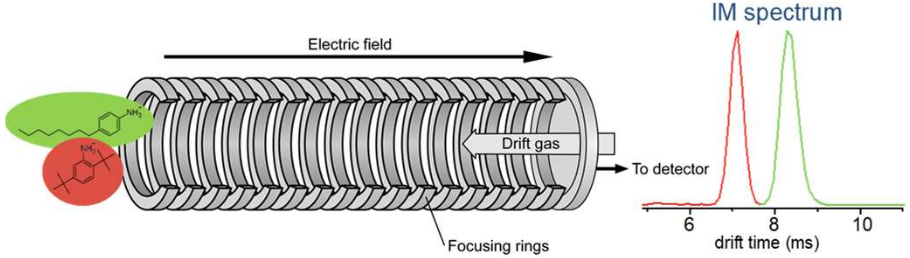
APPI-FTICR



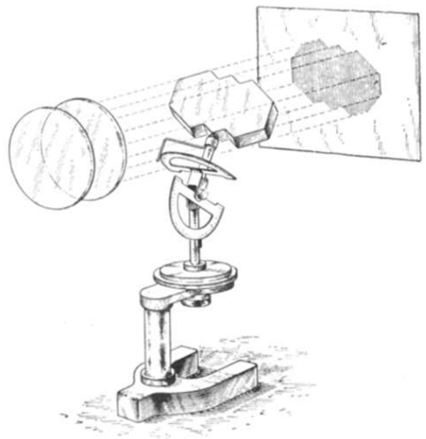
Y. Cho, J.-G. Na, N.-S. Nho, S. Kim, S. Kim. Application of Saturates, Aromatics, Resins, and Asphaltenes Crude Oil Fractionation for Detailed Chemical Characterization of Heavy Crude Oils by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Equipped with Atmospheric Pressure Photoionization. *Energy Fuels* **2012**, *26*, 2558.

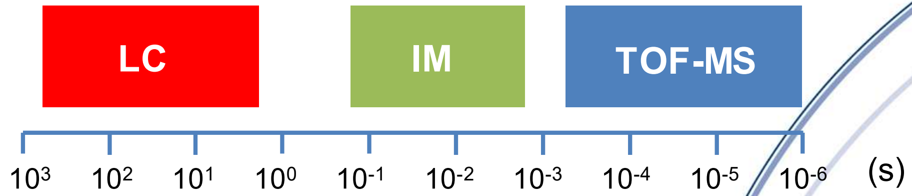
Ion Mobility

- Separation based on size and shape
  - Drift time (1-30 ms)
  - Access to collision cross section
    - Intrinsic property of the ion
    - Predictable
- IM-MS coupling
  - 2D separation
  - Information on isomers
  - Coupling with TOF (acquisition in µs range)
- IM-FTMS coupling
  - Second time scale



$$v_d = K \times E$$

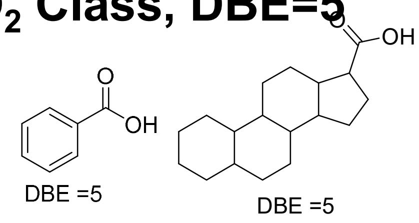


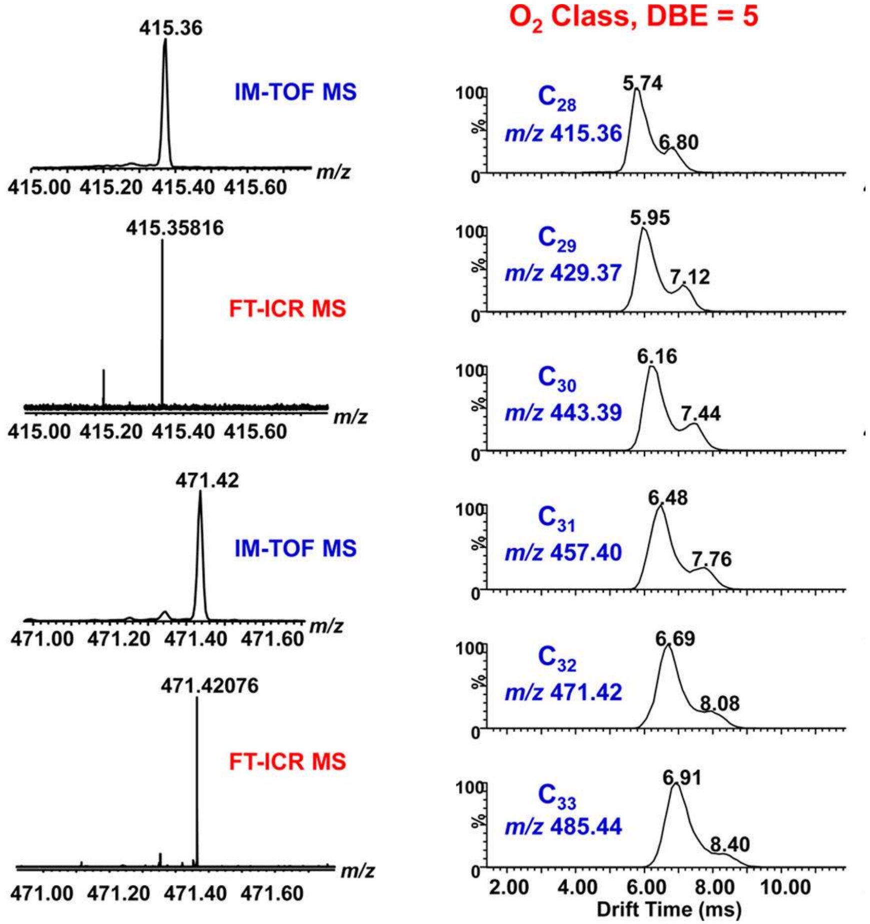


Edward Mack, Jr, *J. Am. Chem. Soc.* 1925, 47, 2468

IMS-TOF and FTMS

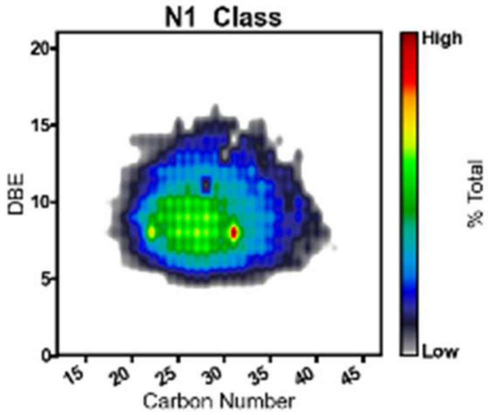
ESI(-)
O_2 Class, DBE=5

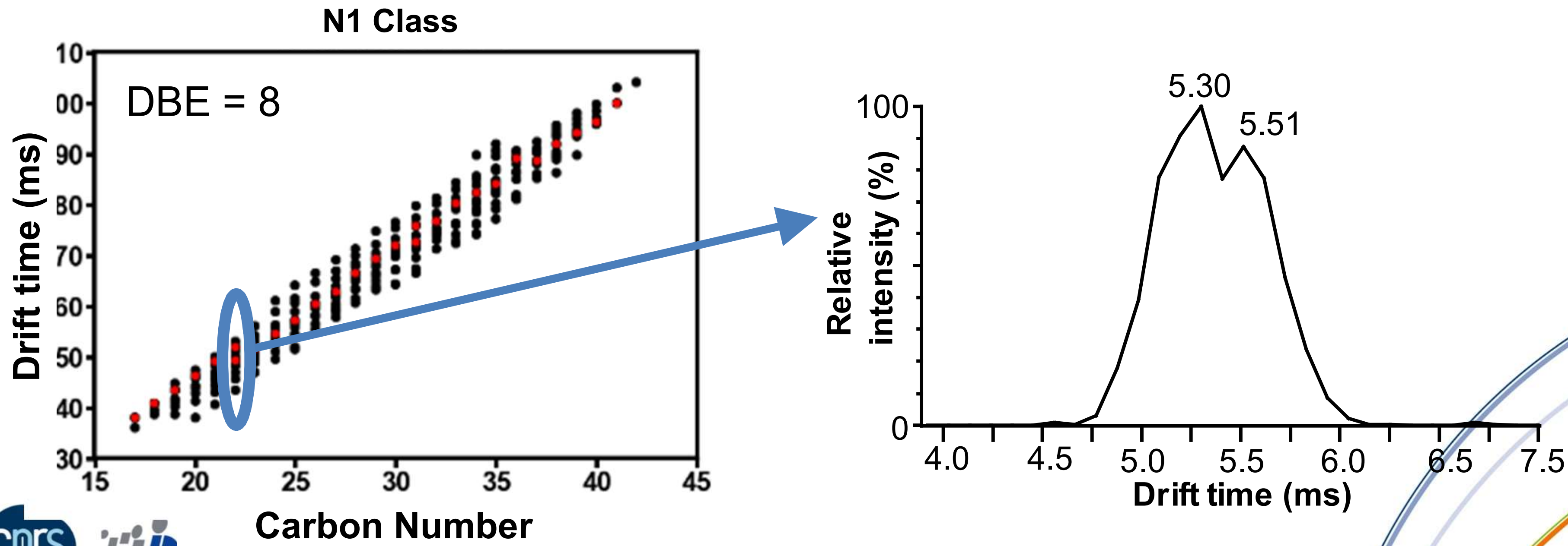




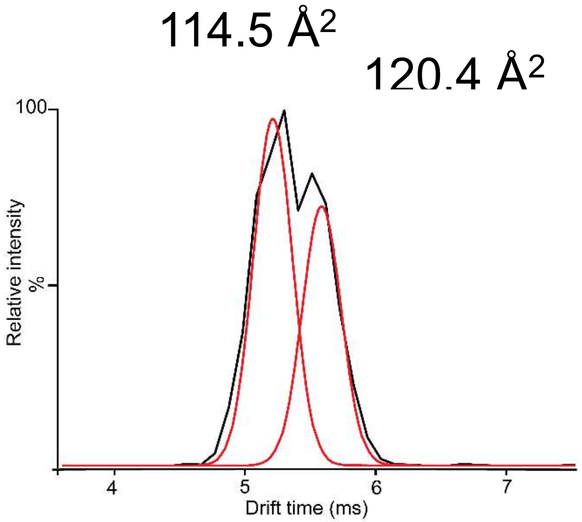
P. M. Lalli, Y. E. Corilo, S. M. Rowland, A. G. Marshall, R. P. Rodgers. Isomeric Separation and Structural Characterization of Acids in Petroleum by Ion Mobility Mass Spectrometry. *Energy Fuels* **2015**, *29*, 3626.

ESI(+)





M. Farenc, Y. E. Corilo, P. M. Lalli, E. Riches, R. P. Rodgers, C. Afonso, P. Giusti. Comparison of Atmospheric Pressure Ionization for the Analysis of Heavy Petroleum Fractions with Ion Mobility-Mass Spectrometry. *Energy Fuels* **2016**, *30*, 8896.



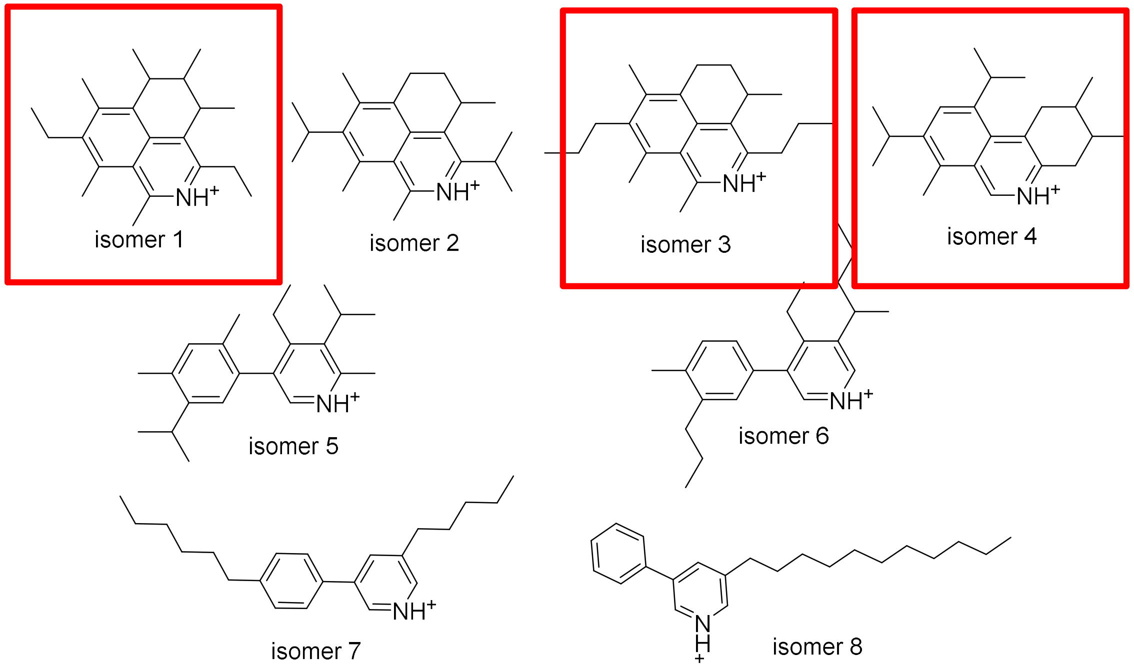


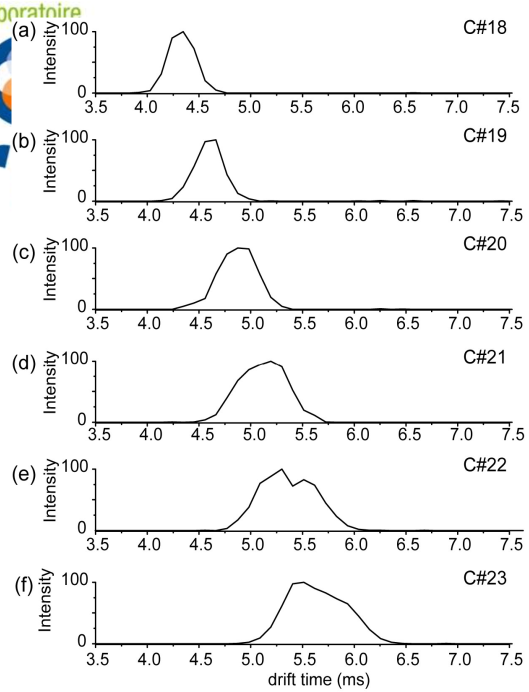
Table 1: Theoretical CCS (Å²) values for putative $C_{22}H_{32}N^+$ isomers

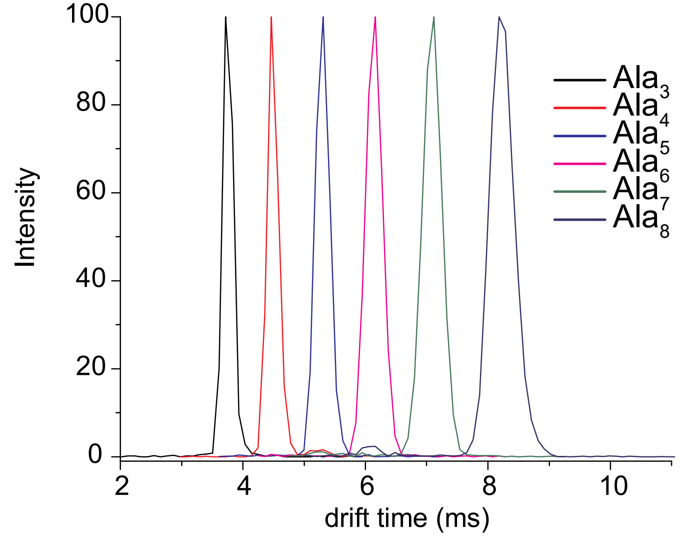
isomer	TM CS (Å²)
1	115.0
2	117.5
3	119.8
4	120.4
5	121.8
6	127.4
7	139.0
8	136.8

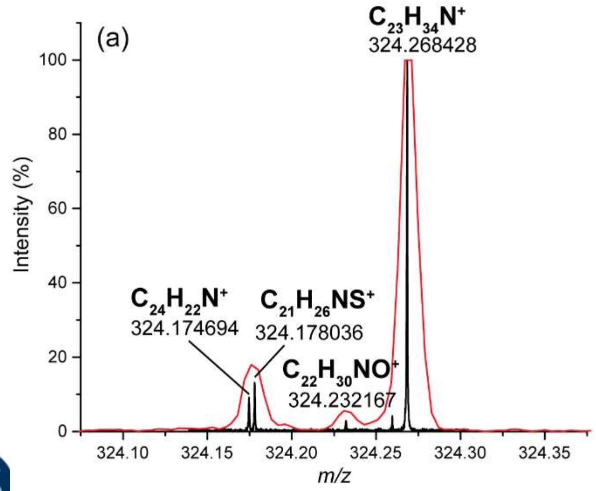
MMFF94 force field

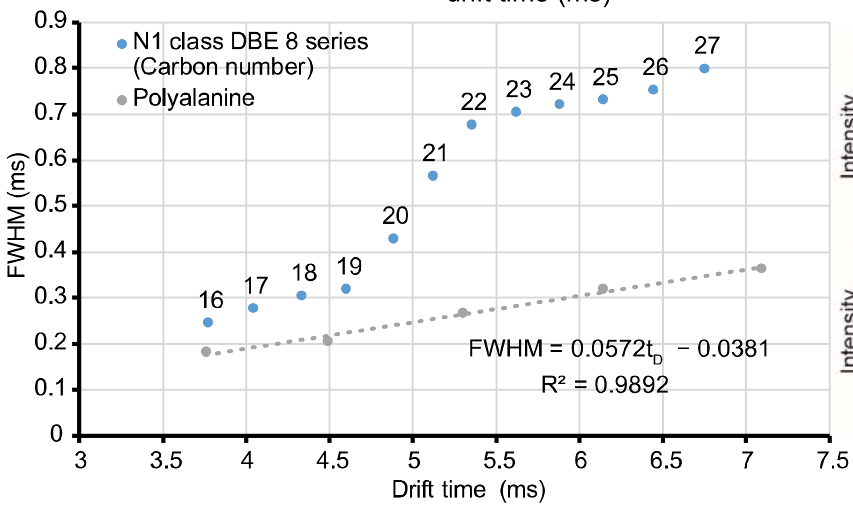
IMS Peak width

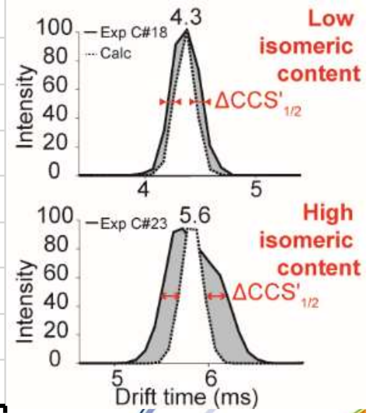
DBE=8







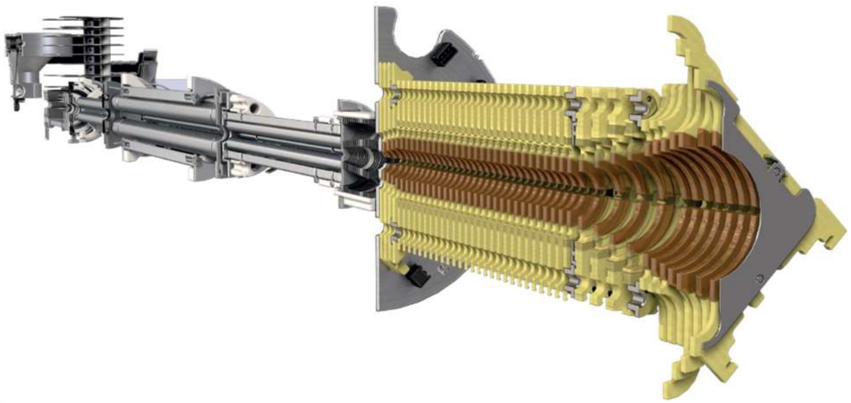




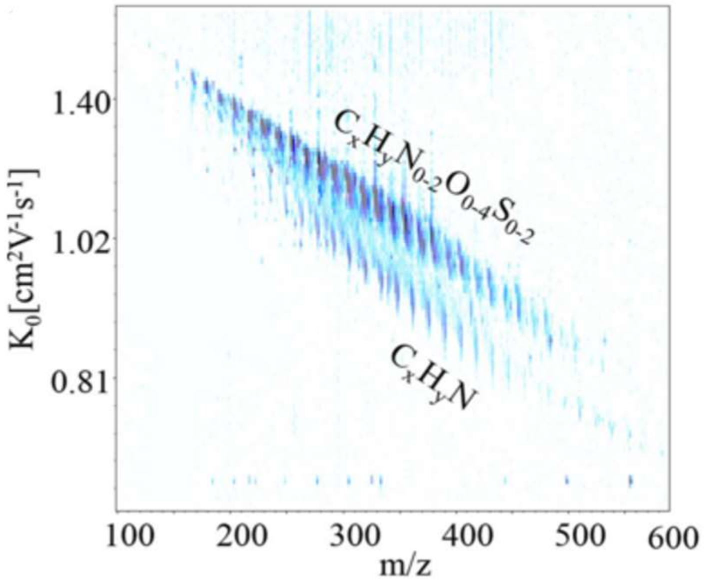
M. Farenc, B. Paupy, S. Marceau, E. Riches, C. Afonso, P. Giusti. Effective Ion Mobility Peak Width as a New Isomeric Descriptor for the Untargeted Analysis of Complex Mixtures Using Ion Mobility-Mass Spectrometry. *J Am Soc Mass Spectrom* **2017**, *28*, 2476.

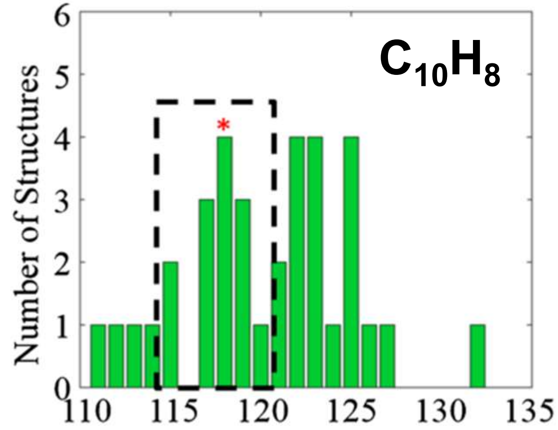
IMS with FTMS

- IMS coupling with FTICR?
  - Second time scale
  - FAIMS
  - TIMS-FTMS

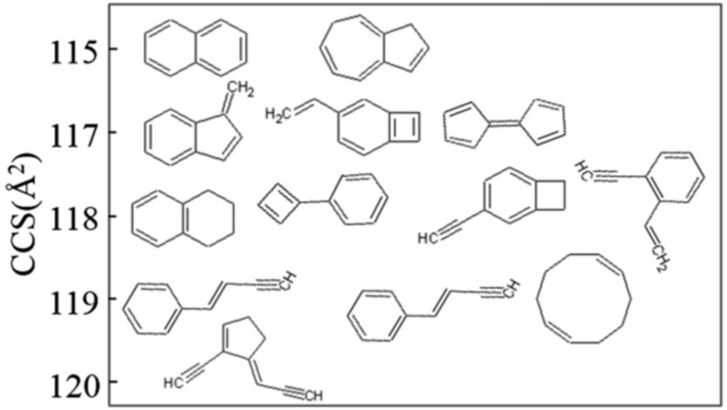


TIMS-FTICR





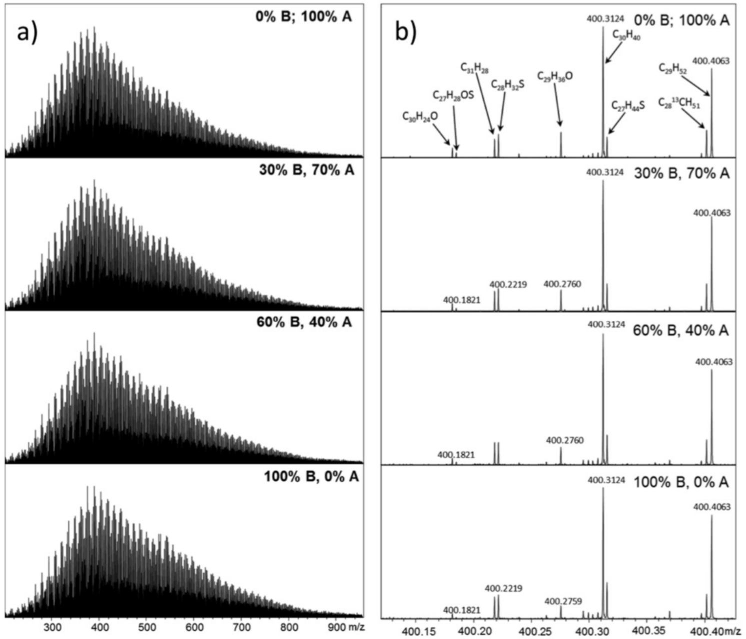
* 2% experimental value

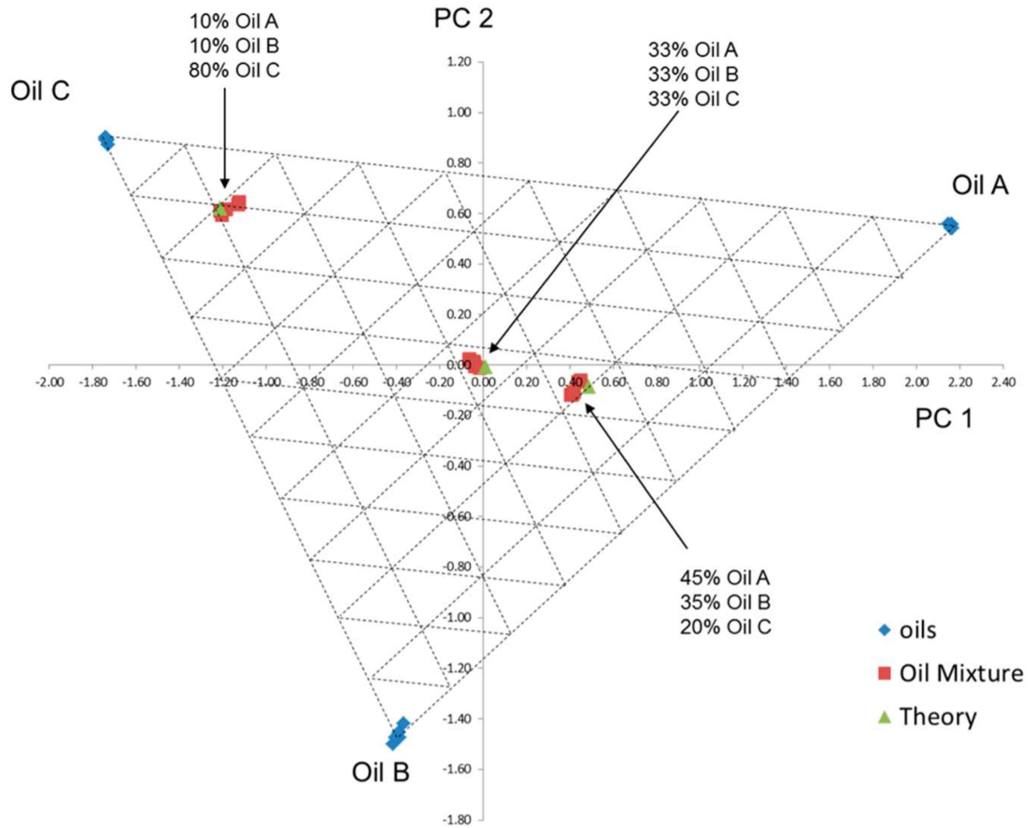


P. Benigni, R. Marin, F. Fernandez-Lima. Towards unsupervised polyaromatic hydrocarbons structural assignment from SA-TIMS-FTMS data. *Int J Ion Mobil Spectrom* **2015**, *18*, 15

Chemometrics

Evaluation of the accurate determination of calculated mixing ratios of similar crude oils





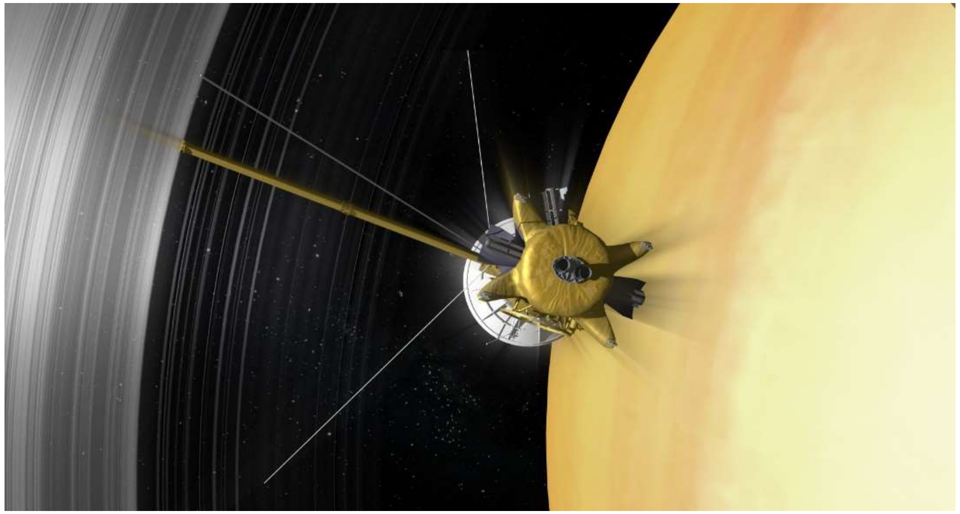
M. Witt, W. Timm. Determination of Simulated Crude Oil Mixtures from the North Sea Using Atmospheric Pressure Photoionization Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2015**, *30*, 3707.

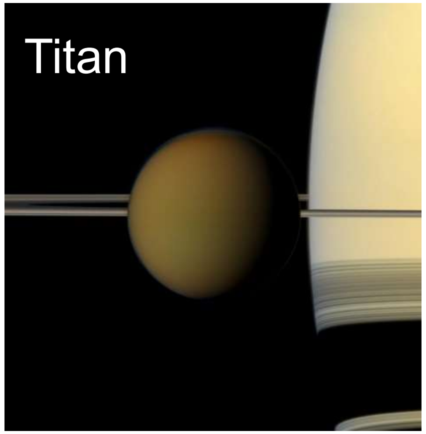
Tholins

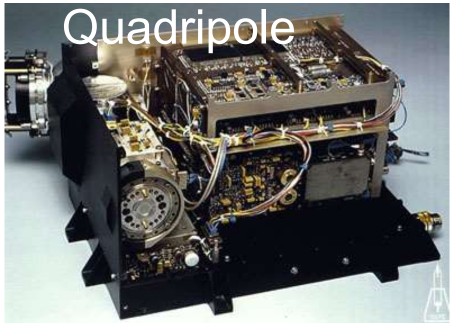
Nathalie Carasco (Univ. Paris Saclay)

Thèse de Julien Maillard

Cassini Mission

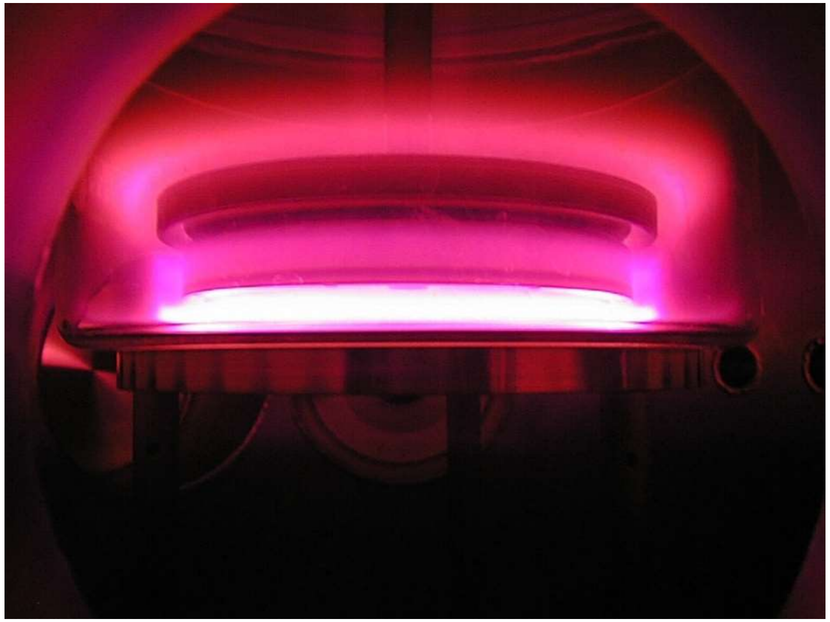




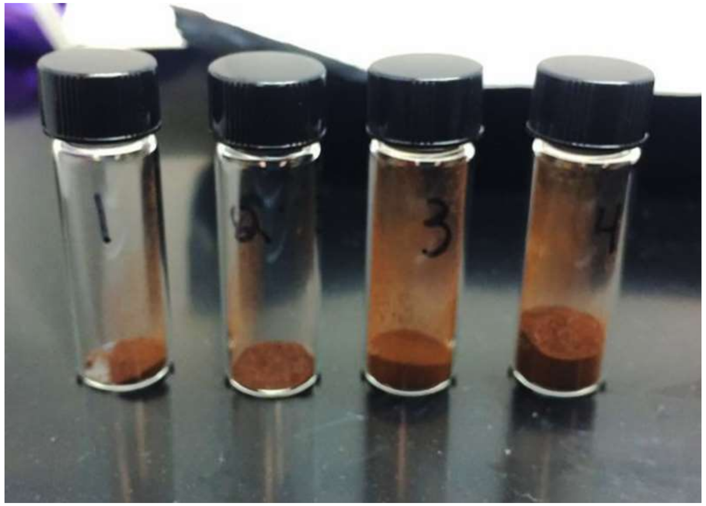


95 % à 98,4 % d'azote
1,6 % à 5 % de méthane

Tholins



Vue de l’intérieur du réacteur de l’expérience PAMPRE



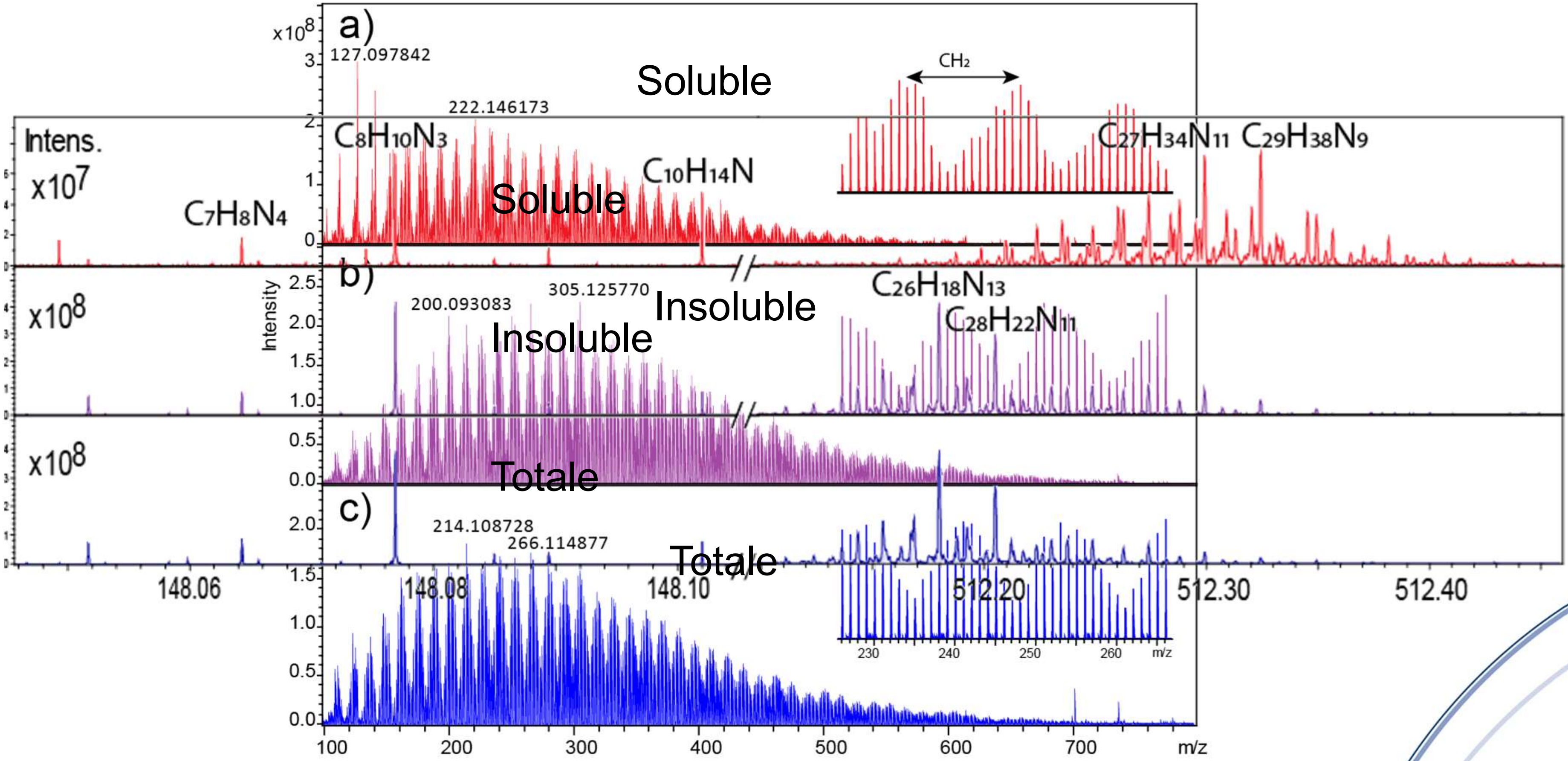
Que savions nous avant cette étude ?

- **Propriétés physiques des Tholins (Carrasco et al. 2009) :**
  Analyse élémentaire,
  Solubilité,
  (Le tholins préparées avec 5% de méthane sont solubles à 35% dans le méthanol)
  Absorption IR,
  (Validation par rapport aux données de Titan)

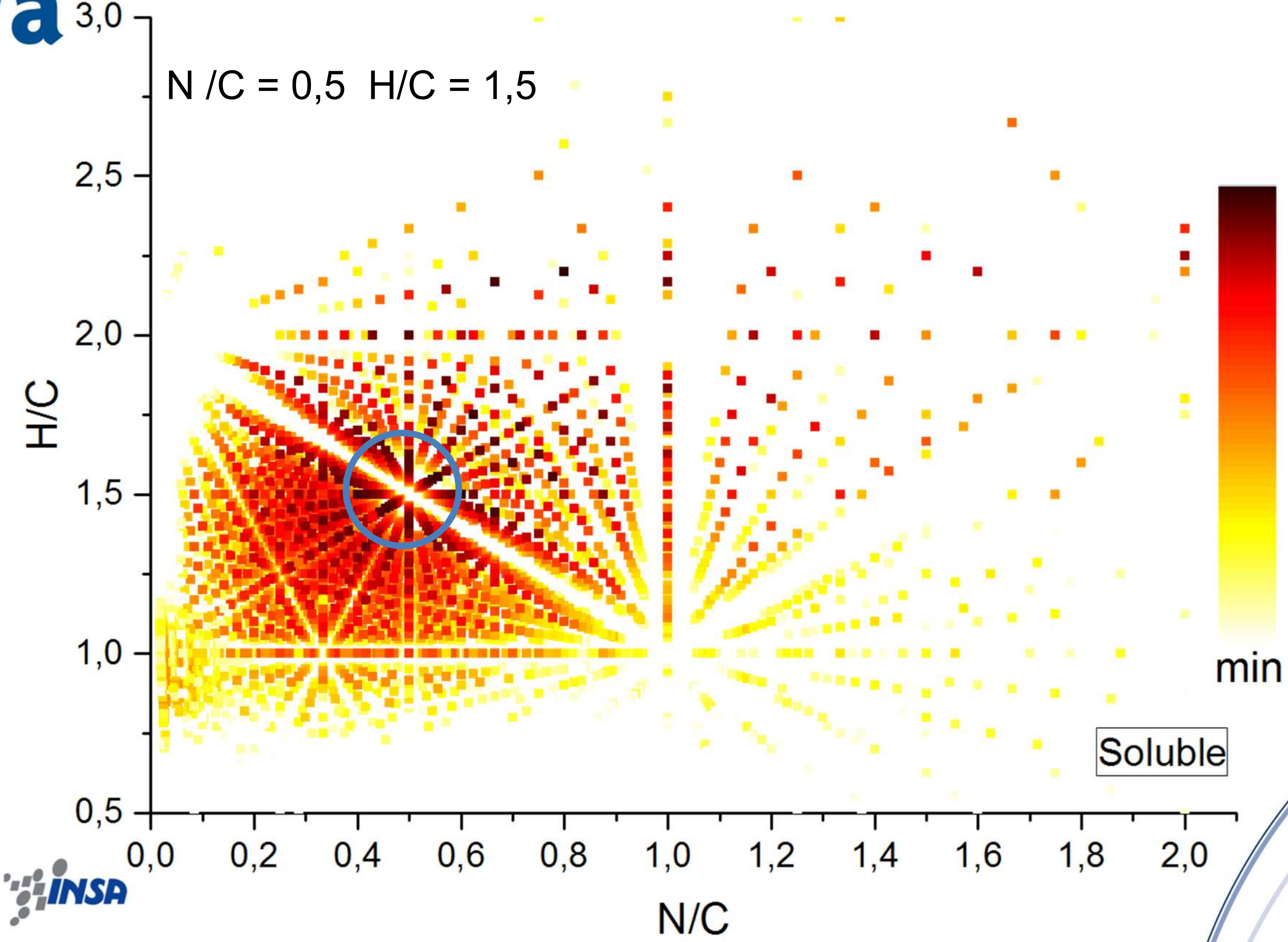
- **Etude de la fraction soluble en ESI-Orbitrap (Gautier et al. 2014):**
  Polymère, motifs CH_2 et HCN

  Postulat fraction soluble représentative de la globalité

Analyse par desorption laser des fractions solubles et insolubles



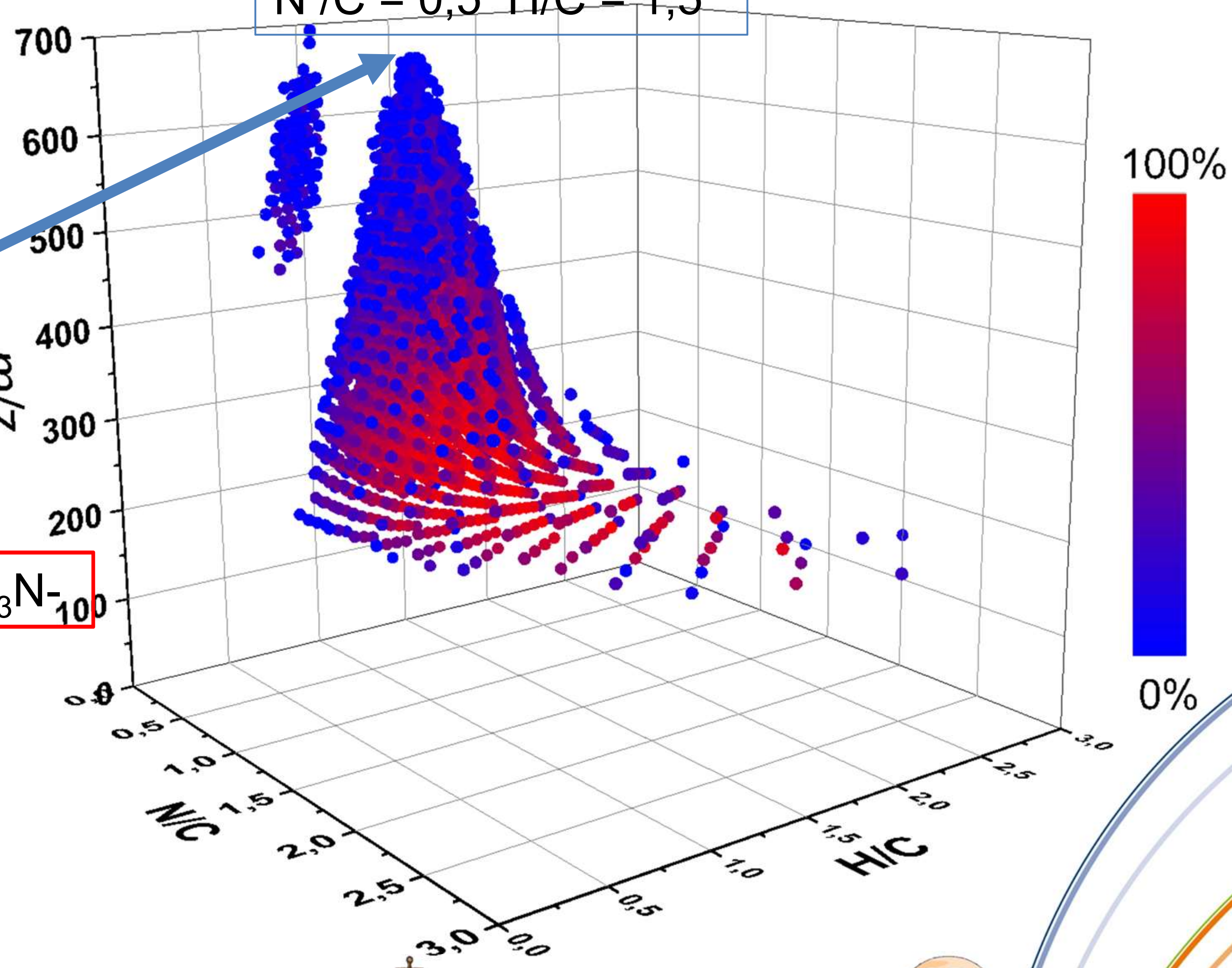
Diagrammes de Van Krevelen de la fraction soluble



Van Krevelen avec x = N/C, y = H/C et z = m/z

- Fraction soluble
- Convergence des espèces

N /C = 0,5 H/C = 1,5

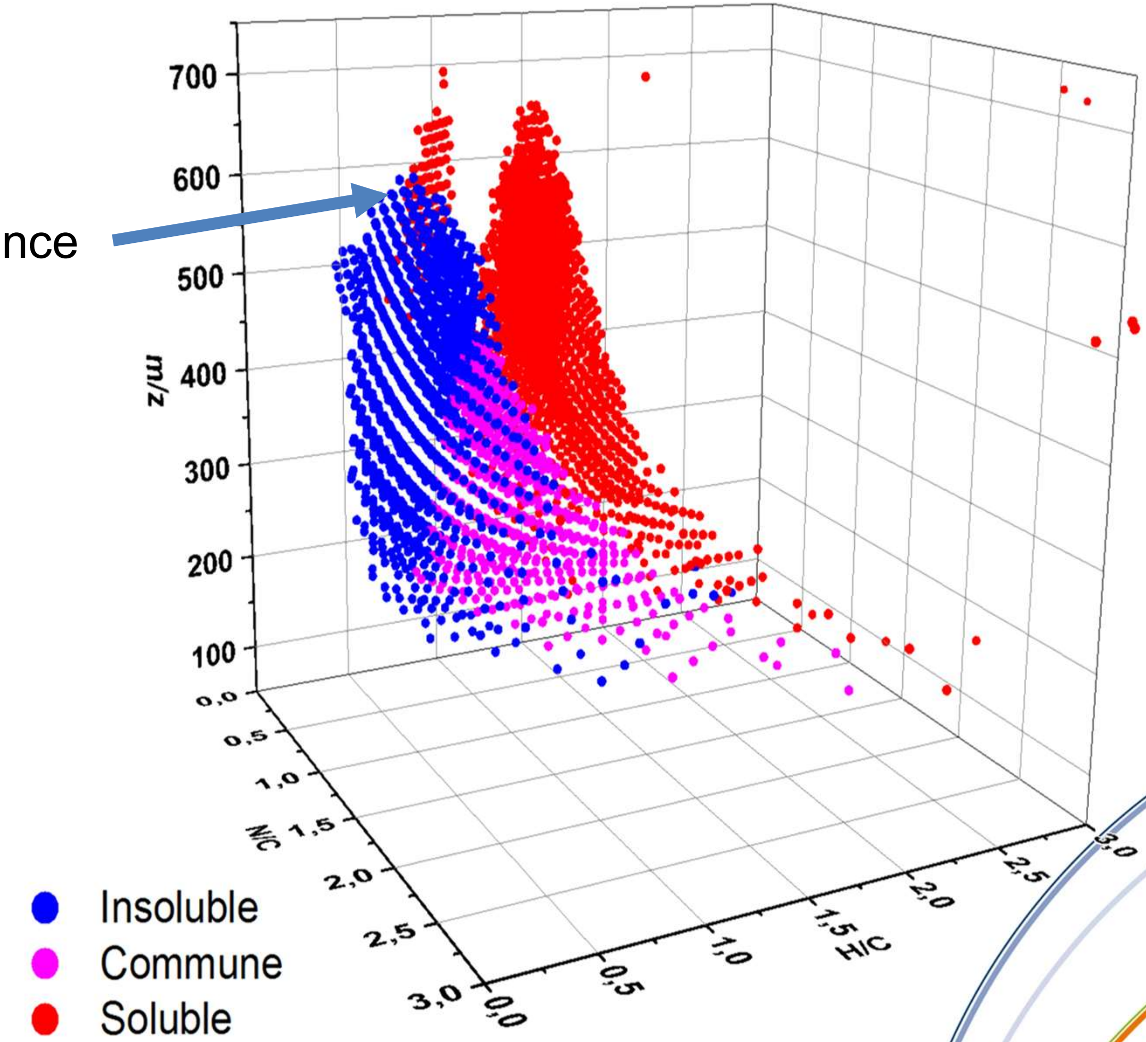


Polymère de motif $–C_2H_3N–$

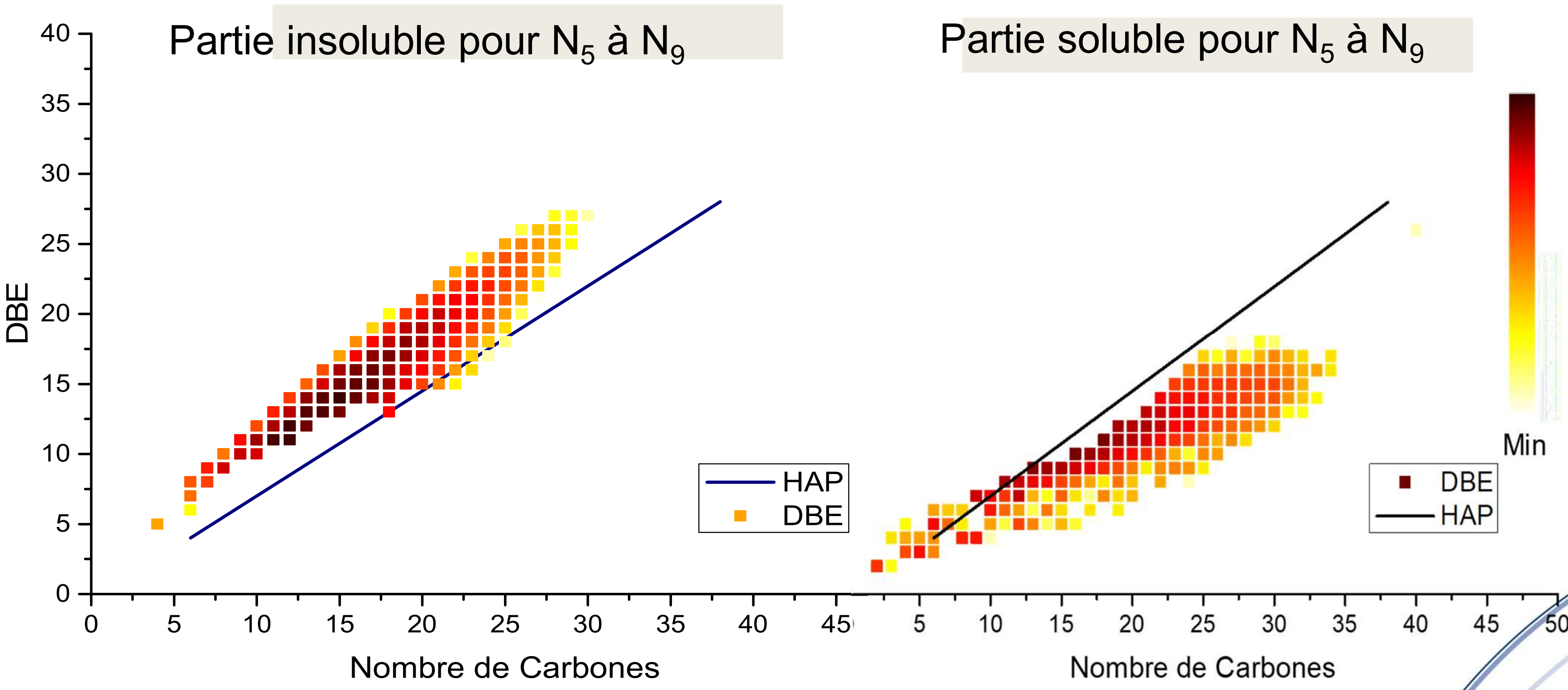
Diagrammes de Van Krevelen de la fraction insoluble

- Deuxième motif de croissance

N/C = 0,5; H/C = 0,75
Motif: $C_4H_3N_2$

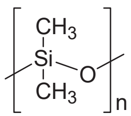


Comparaison de la saturation des fractions

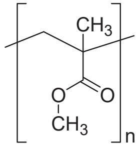


Polymères et MS

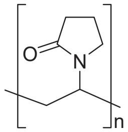
- Polymères
  - Motif de répétition
  - Terminaisons
  - Masse moyenne



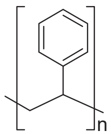
PDMS **1**



PMMA **2**

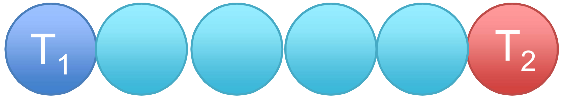


PVP **3**

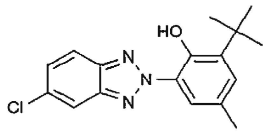
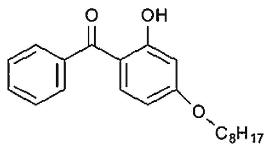
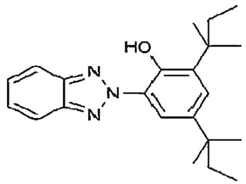
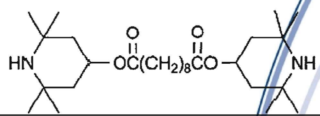


PS **7**

- Additifs
  - Anti-UV
  - Antioxydants
  - Photostabilisants de type amines encombrées
    - HALS (hindered amine light stabilizants)

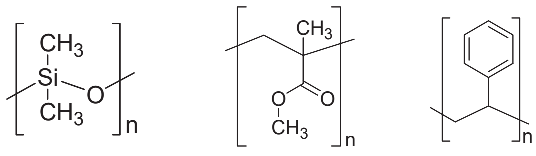


$M_N = \Sigma M_i N_i / \Sigma N_i$
$M_W = \Sigma (M_i) N_i / \Sigma M_i N_i$
polydispersité $D = M_W / M_N$

Substance	Formula	$[M+H]^+$ calculated
Chimassorb 81		316.1211
Tinuvin 326		327.1955
Tinuvin 328		352.2383
Tinuvin 770		481.4000

Ionization of Polymers

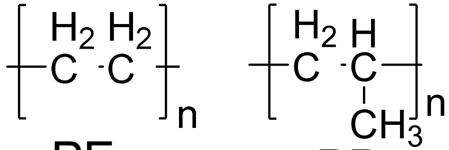
- Ionization
  - $M^{+\bullet}$
  - $[M+H]^+$, $[M+Na]^+$, $[M+Met]^+$
- Polymers : large molecular diversity
  - Heteroatoms (PEG, PMMA…)
  - Unsaturated (PB)
  - Aromatics (PS)
  - Saturated (PE, PP…)
- Solubility
  - In MS most ionization imply that the sample is soluble



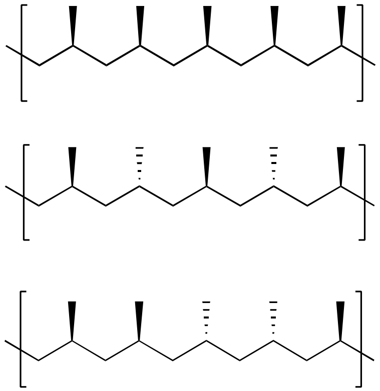
PDMS **1** PMMA **2** PS **7**

Polyolefins

- Saturated polymers
  - Most common polymers
  - PE (80 million tonnes)
  - PP (55 million tonnes)
- Solubility
  - Insoluble in most solvents
  - Most ionization method requires solutions
- Ionization
  - How to ionize large alkanes ?



PE PP

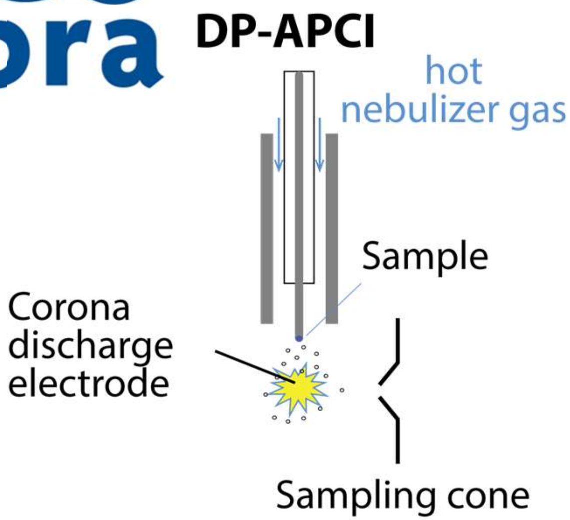


iPP

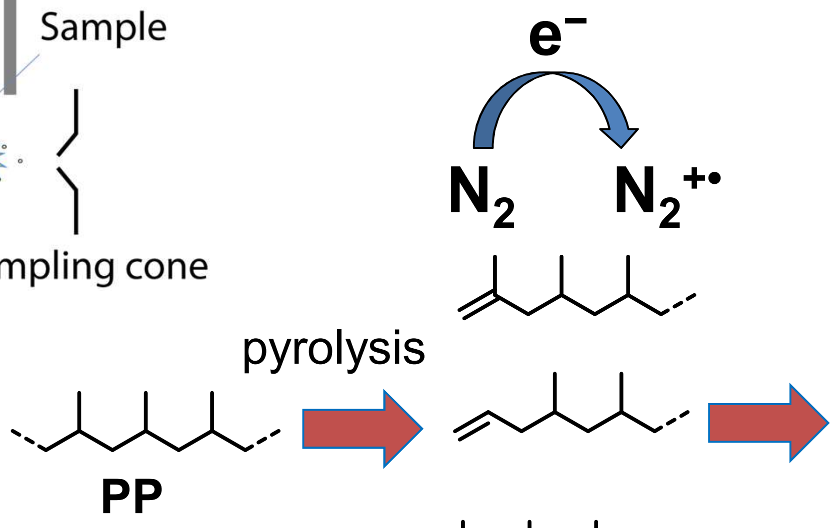
sPP

aPP

ASAP or DIP-APCI: a complex ionization process

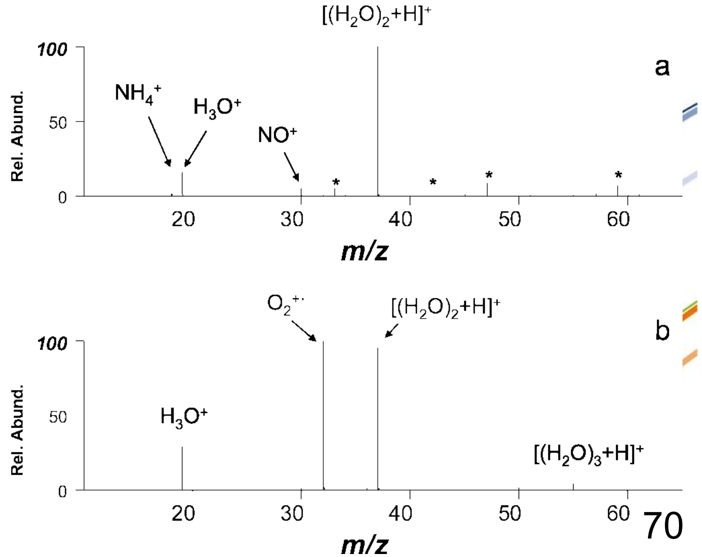


Ionization
By charge exchange



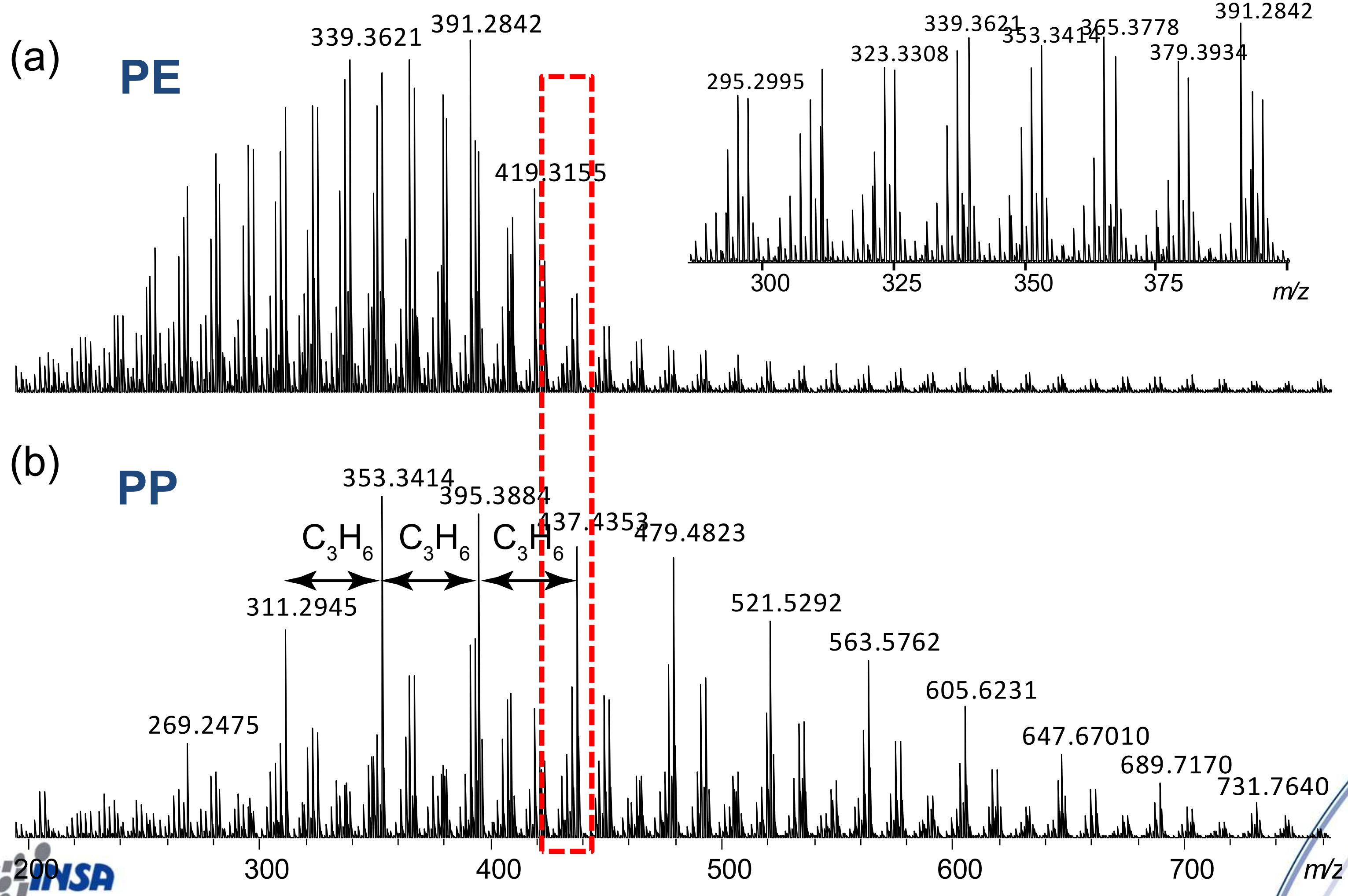
Traces of O_2 and H_2O

Pyrolysis products



R.B. Cody, Anal. Chem. **2009,** *81,* 1101–1107

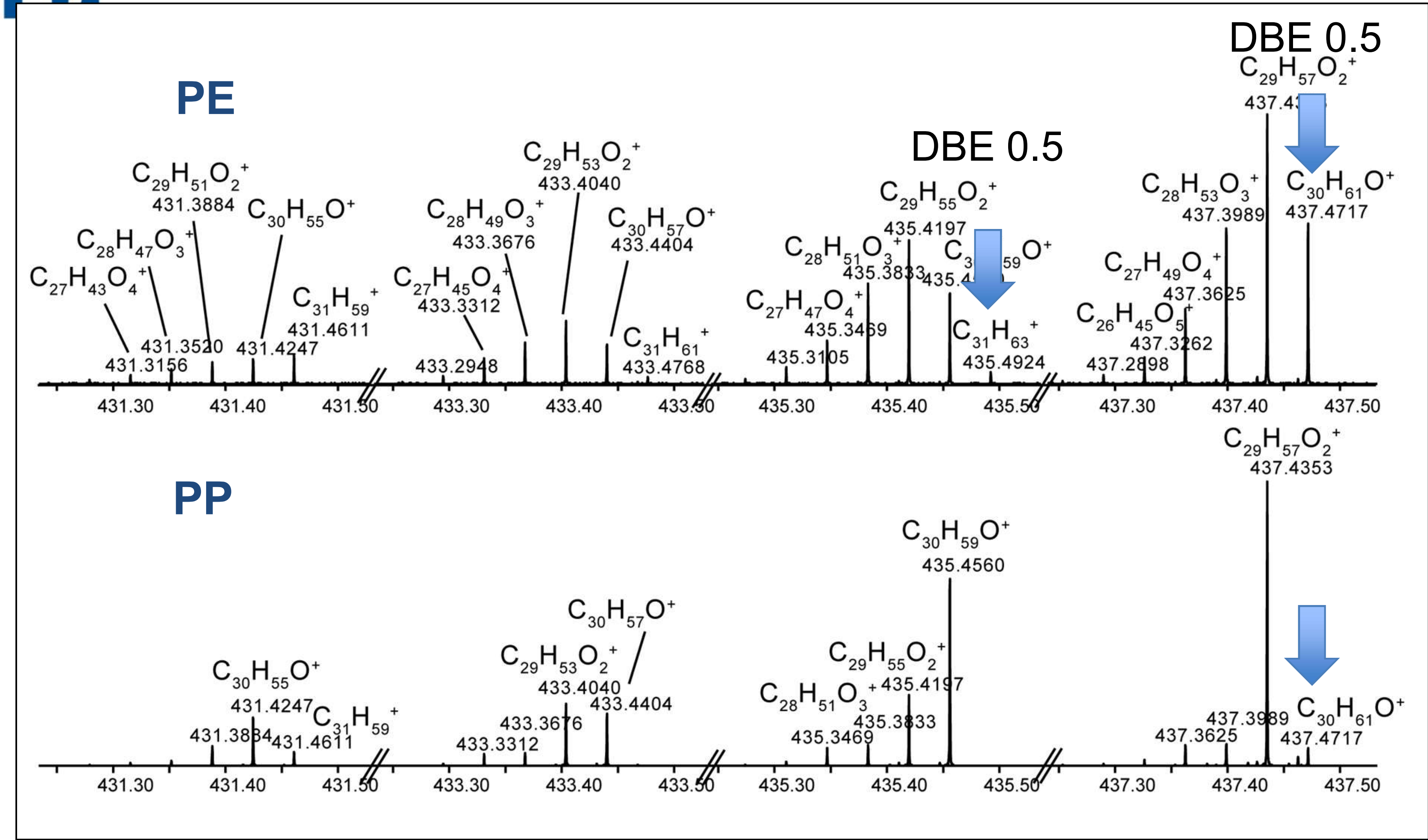
FTICR analysis



Differentiation of PP and PE

FT-ICR Analysis

RP=900000

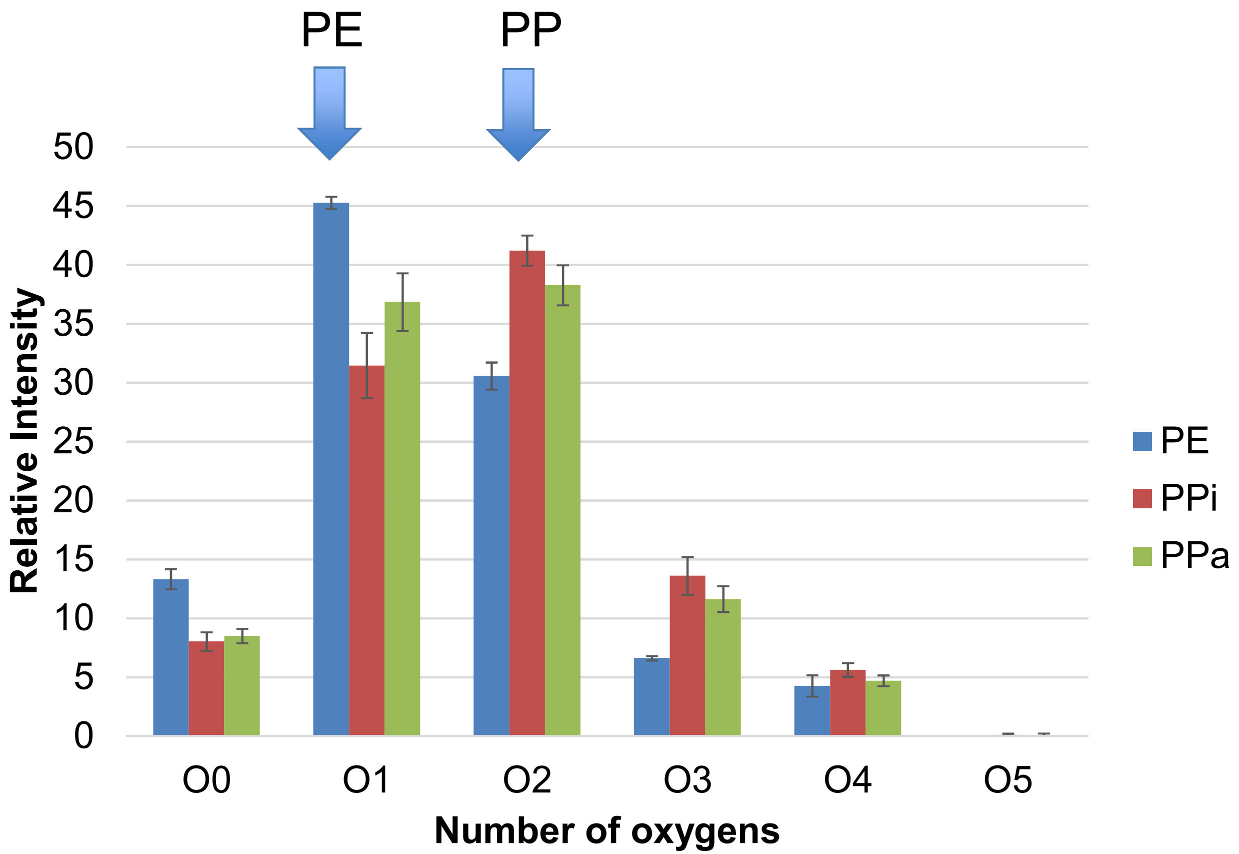


Oxygen containing species for PE and PP

Low DBE species detected for PE not for PP

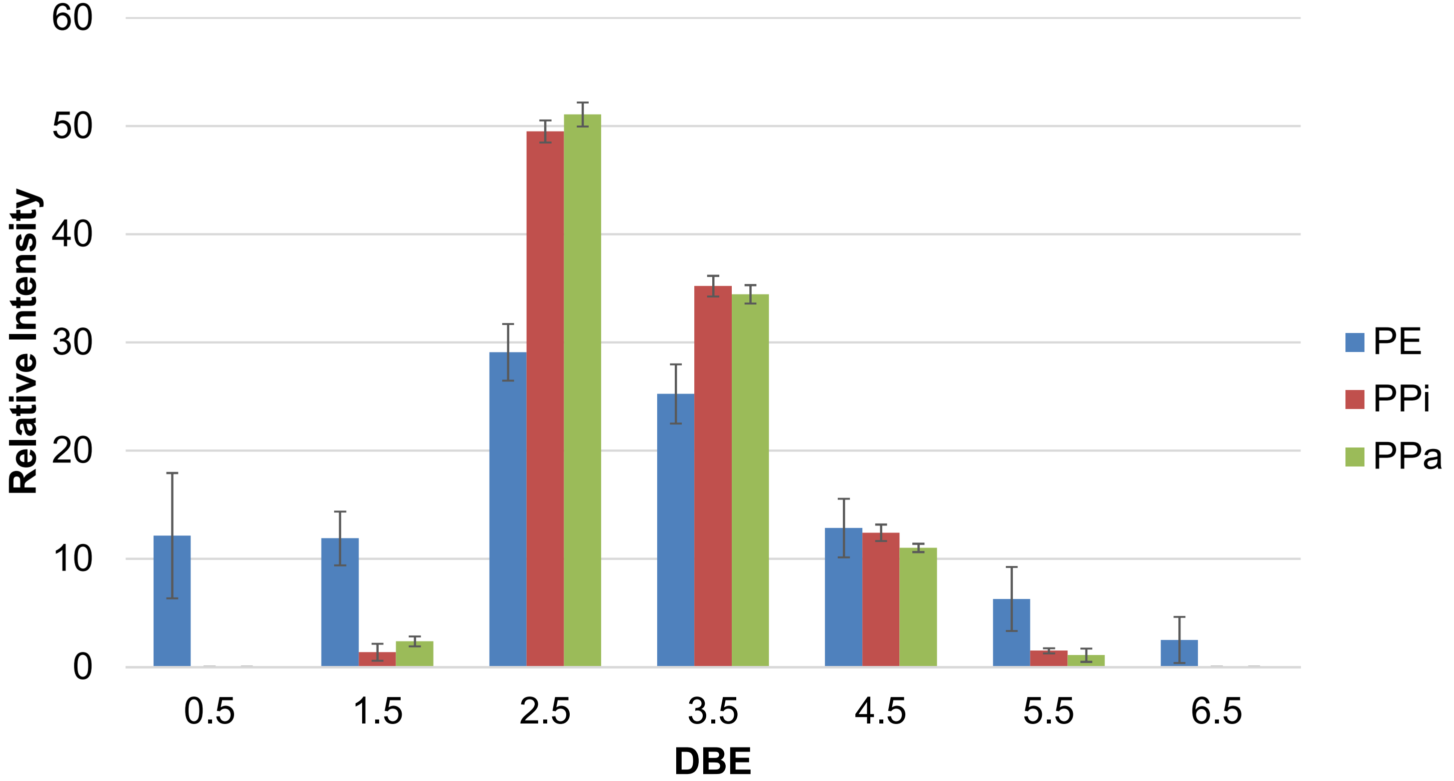
M. Farenc, M. Witt, K. Craven, C. Barrere-Mangote, C. Afonso, P. Giusti. Characterization of Polyolefin Pyrolysis Species Produced Under Ambient Conditions by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry and Ion Mobility-Mass Spectrometry. *J Am Soc Mass Spectrom* **2017**, *28*, 507.

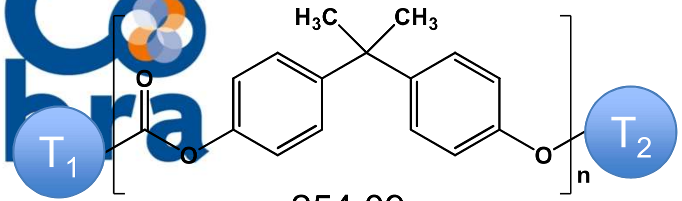
Oxygen number distribution (FT-ICR)



Higher number of oxygens for PP related to ramifications ?

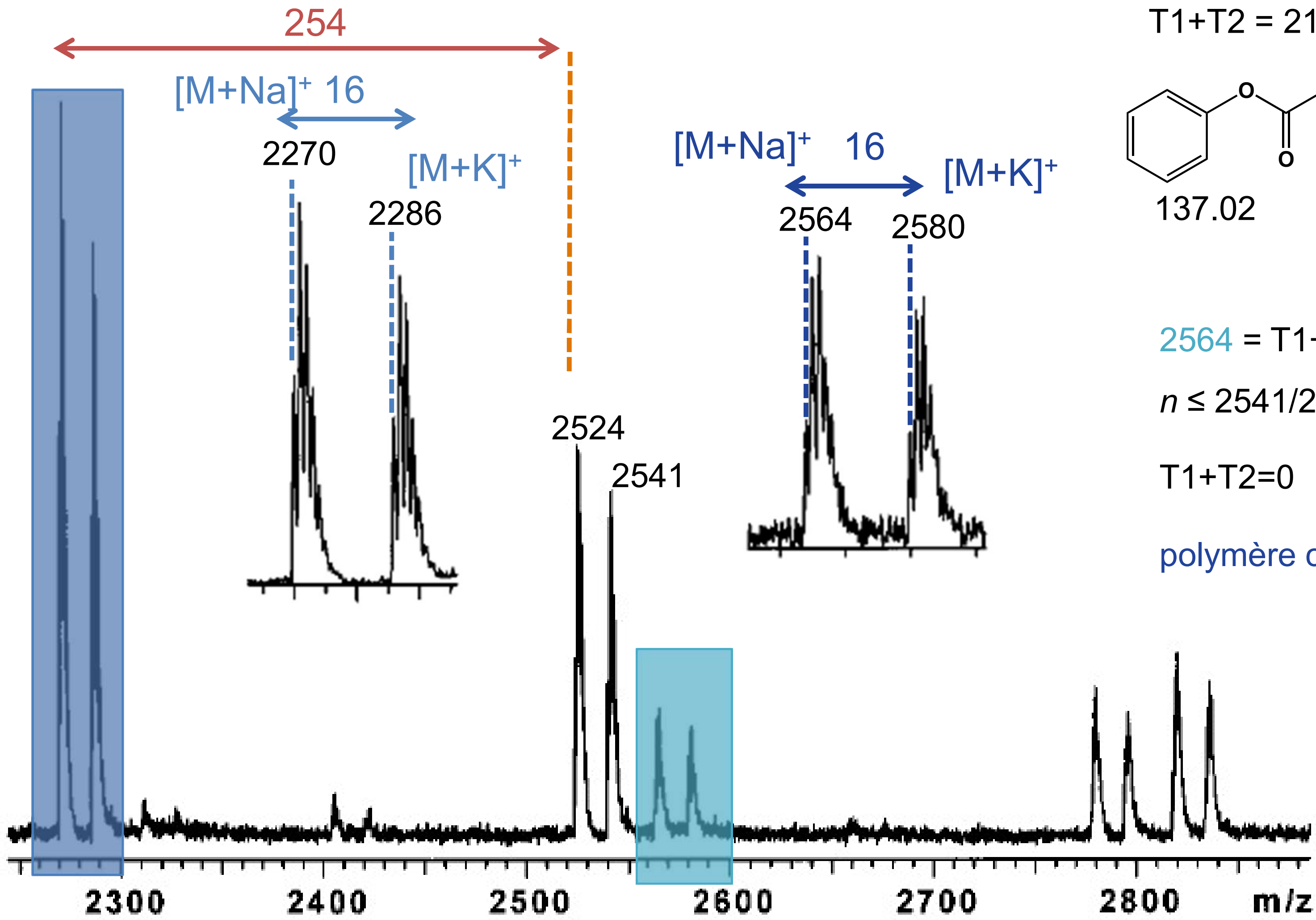
DBE distribution C_xH_y (no oxygen) (FTICR)





254.09 u

polybisphenol A carbonate (PC)

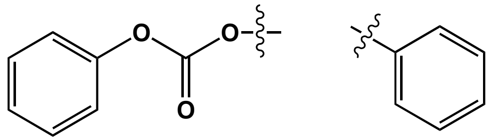


2270 = T1+T2+n×254.09+23

n ≤ 2247/254=8.8

n=8 254.09 x 8 = 2032.7

T1+T2 = 214.3



137.02 77.04

2564 = T1+T2+n×254.09+23

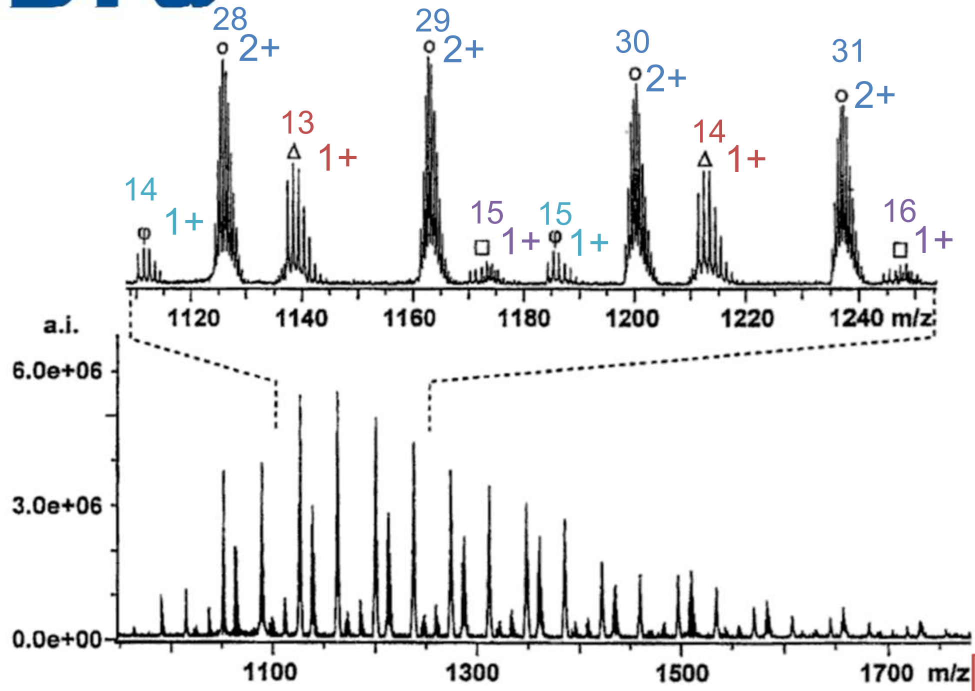
n ≤ 2541/254.09=10.00

T1+T2=0

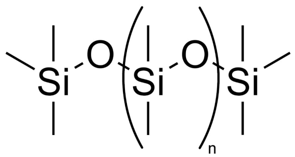
polymère cyclique

Michel W. F. Nielen, Anal. Chem. 1998, 70, 1563-1568

ESI-FTICR PDMS



ESI-FTICR
poly(dimethylsiloxane)



	Suspected oligomer series	n[a]	Theor. mass	Exp. mass	Error (ppm)
Δ	$H_3\overset{+}{N}C_3H_6-[Si(CH_3)_2-O]_n-Si(CH_3)_2-C_3H_6NH_2$	13	1137.4067	1137.4121	4.7
○	$H_3\overset{+}{N}C_3H_6-[Si(CH_3)_2-O]_n-Si(CH_3)_2-C_3H_6\overset{+}{N}H_3$	29	2322.7152	2322.7144	0.3
φ	$H_3\overset{+}{N}C_3H_6-[Si(CH_3)_2-O]_n-CH_3$	14	1110.3595	1110.3599	0.4
□	$H_3\overset{+}{N}C_3H_6-[Si(CH_3)_2-O]_n-H$	15	1170.3626	1170.3588	3.2

[a] Degree of polymerization

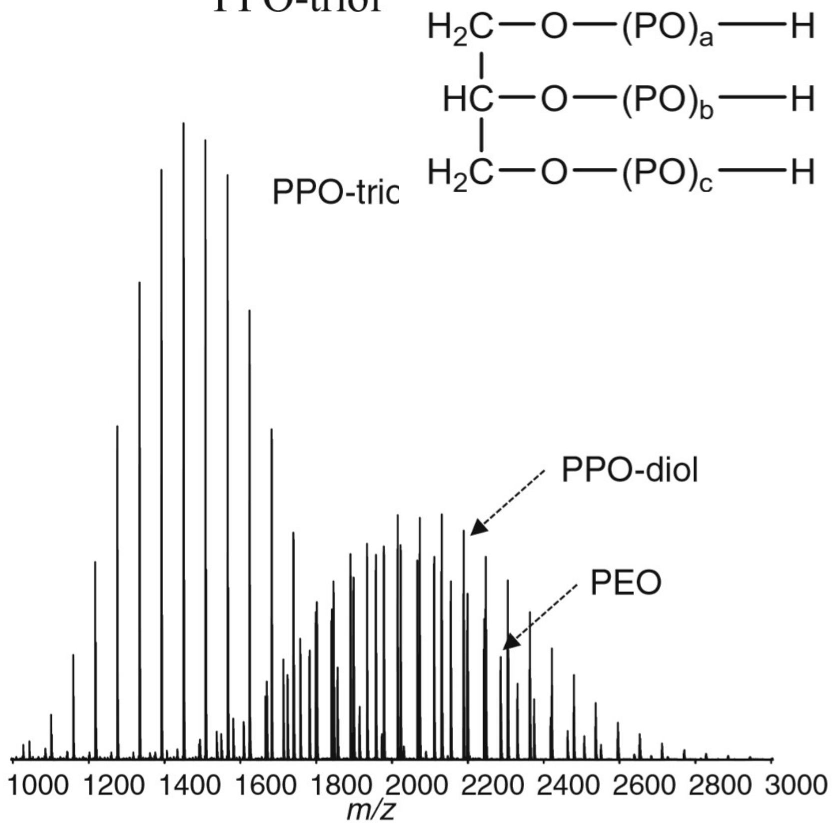
Maziarz et al. *Macromolecules*,1999,32,4411

Polymer mix

PEO $HO\text{-}(EO)_n\text{-}H$

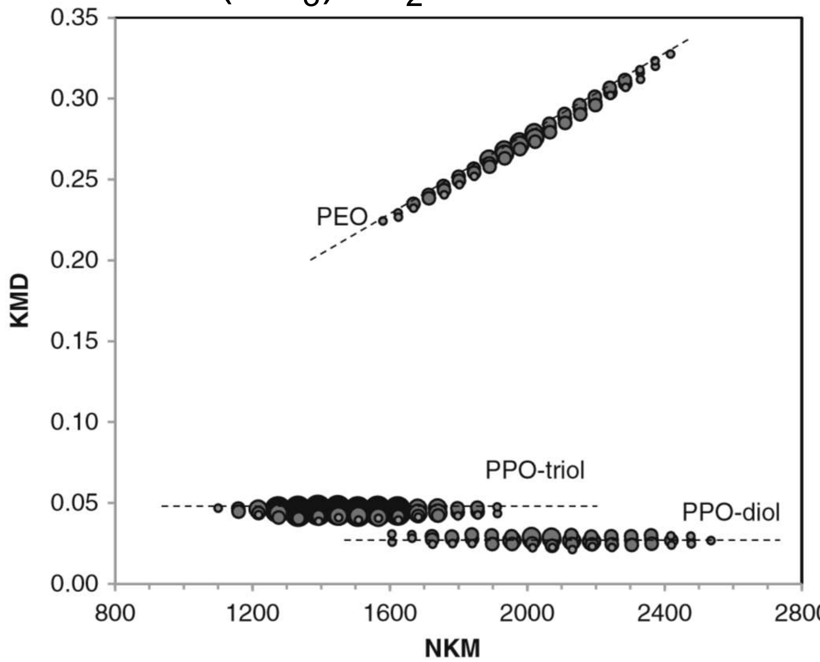
PPO-diol $HO\text{-}(PO)_n\text{-}H$

PPO-triol



$$KM = observed\ IUPAC\ mass \times \frac{nominal\ mass\ of\ base\ unit}{IUPAC\ mass\ of\ base\ unit}$$

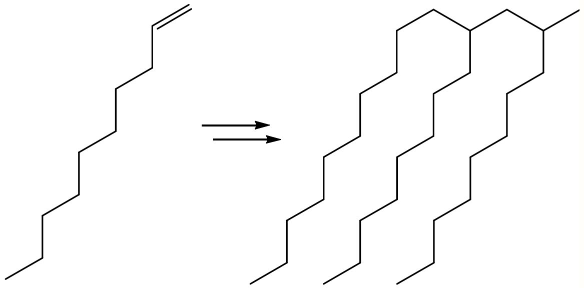
mass scale based on PO units $\text{-}CH(CH_3)CH_2O$



H. Sato, S. Nakamura, K. Teramoto, T. Sato. Structural characterization of polymers by MALDI spiral-TOF mass spectrometry combined with Kendrick mass defect analysis. *J Am Soc Mass Spectrom* **2014**, 25, 1346.

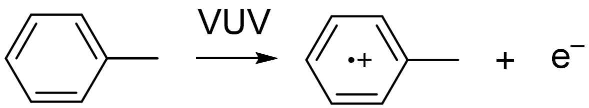
Alkanes: halide attachment

lubrifiants



Alpha-olefin poly-alpha-olefin

photoionization

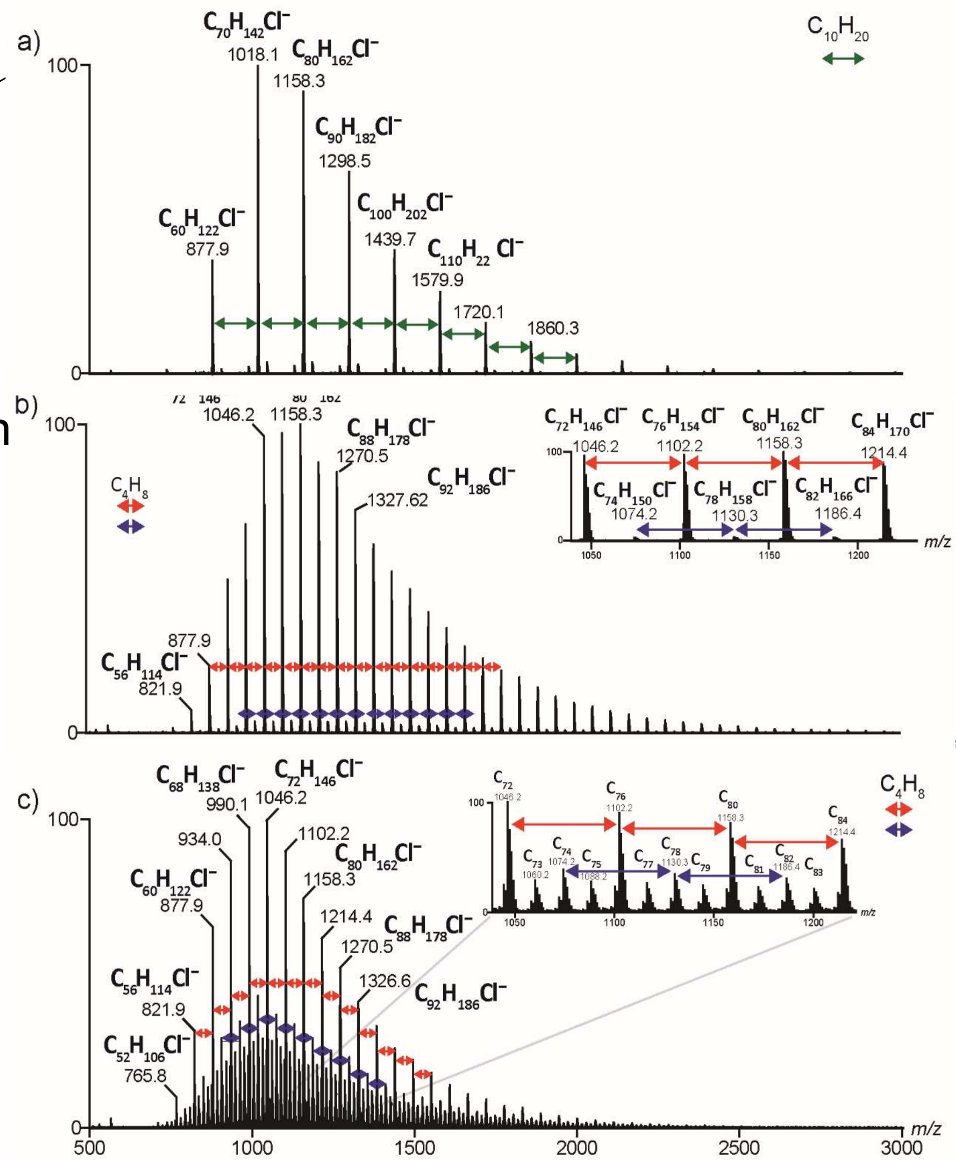


Electron capture dissocation

$$e^- + CH_2Cl_2 \longrightarrow Cl^- + CH_2Cl^\bullet$$

Anion attachment

$$\text{Alcane} + Cl^- \longrightarrow [\text{Alcane+Cl}]^-$$



Thesis Anna Siqueira

Macromolecules 2008, 41, 3772-3774

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Laboratoire d'excellence SynOrg – Des molécules pour le vivant

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