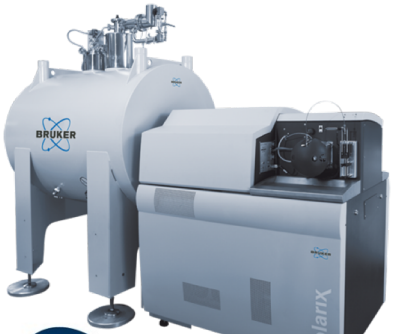
Highly complex analysis from petroleum to polymers

Carlos Afonso

Laboratoire Cobra



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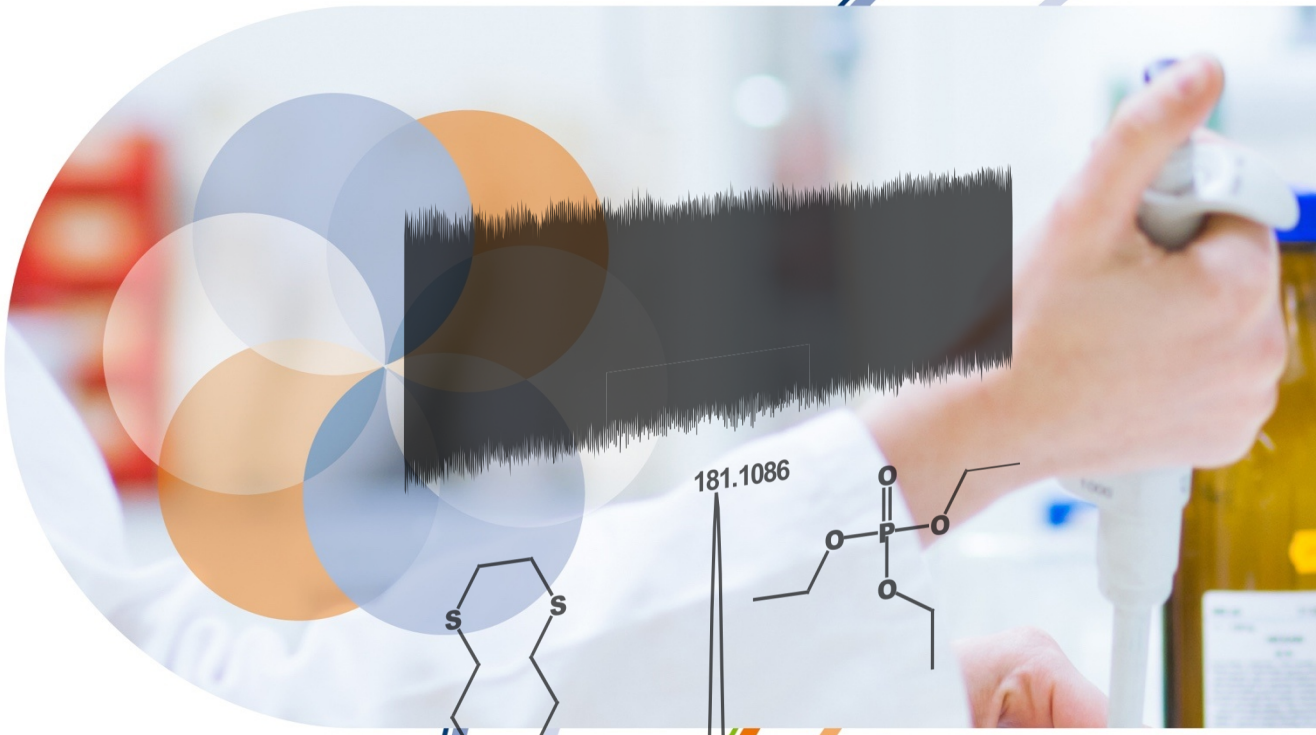
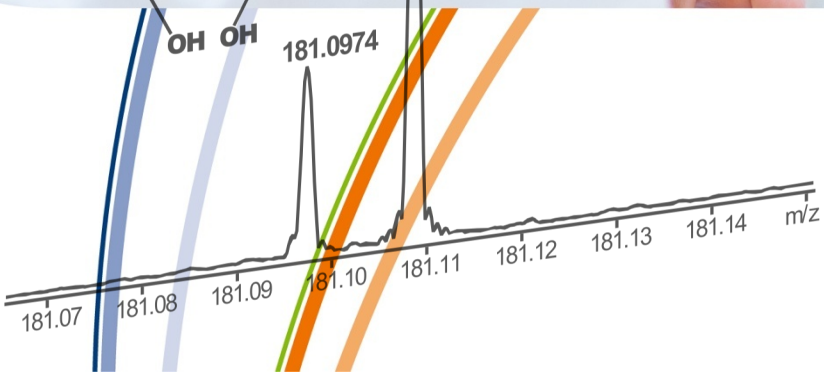




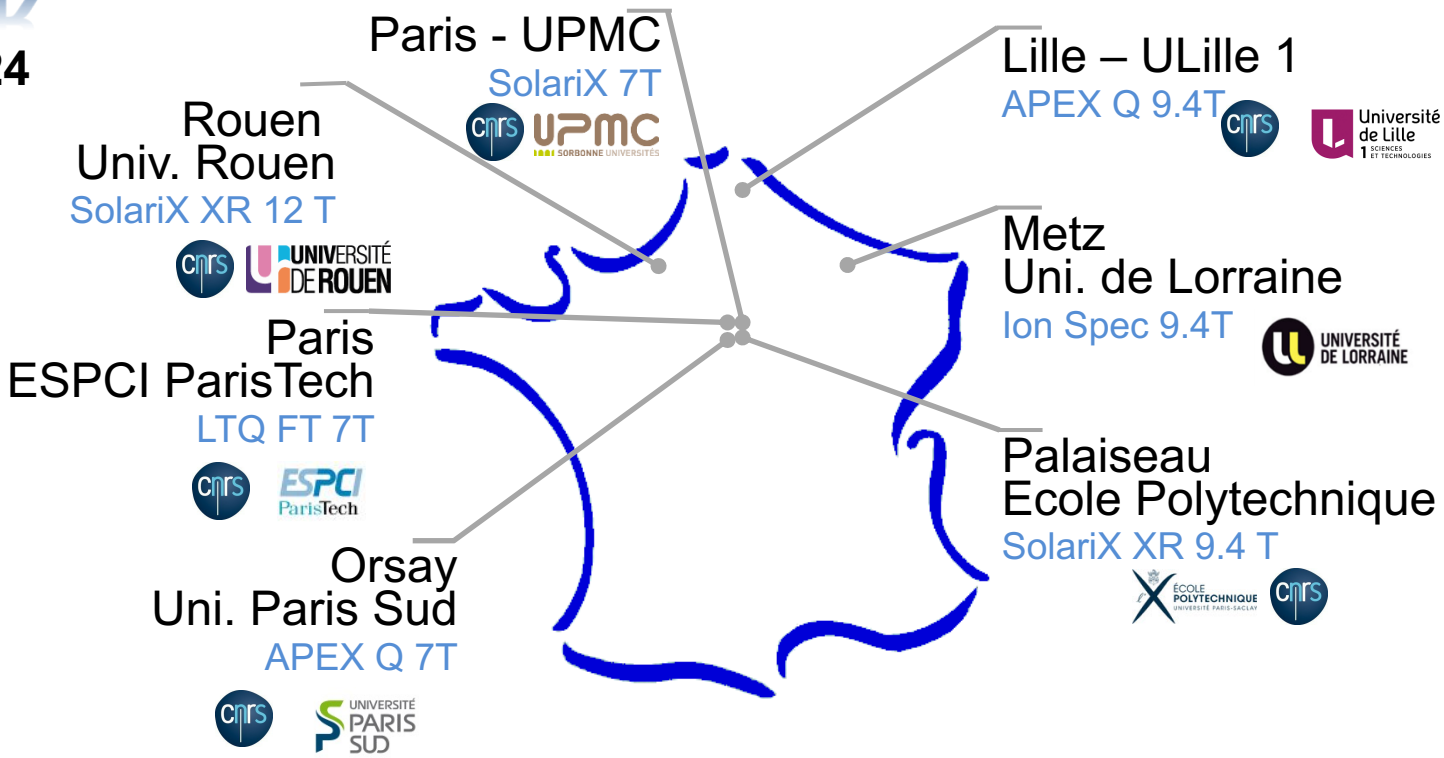
CNRS French FTICR network

Very field FTICR mass spectrometer

Responsable Guillaume Van der Rest

FR FT-ICR

FR 3624

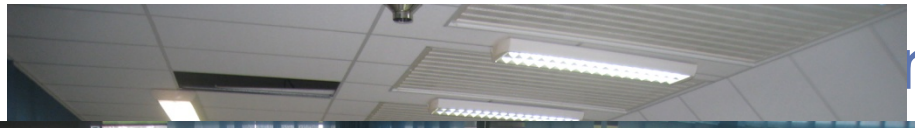


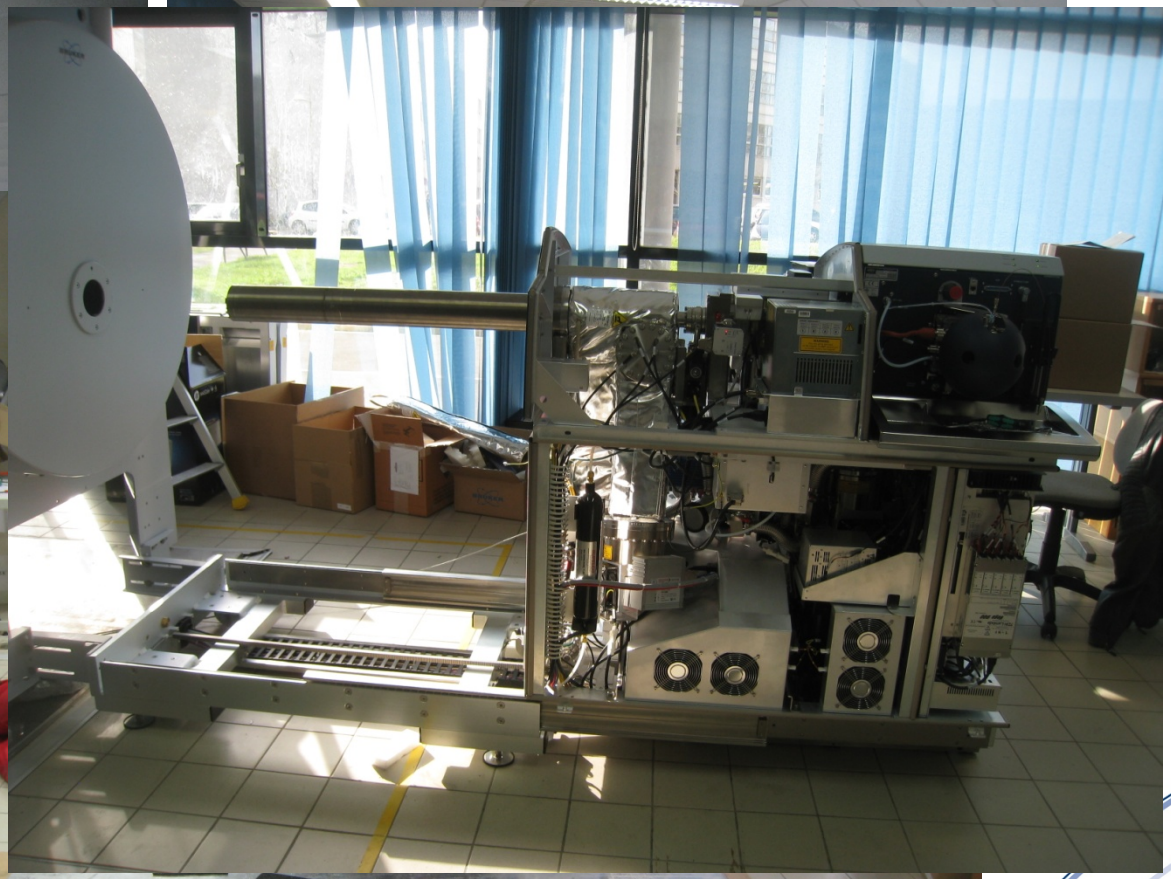
www.fticr.org

Hélène Lavanant: Scientific advisor
Isabelle Schmitz: Research engineer

Laboratoire

Cobra





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Laboratoire

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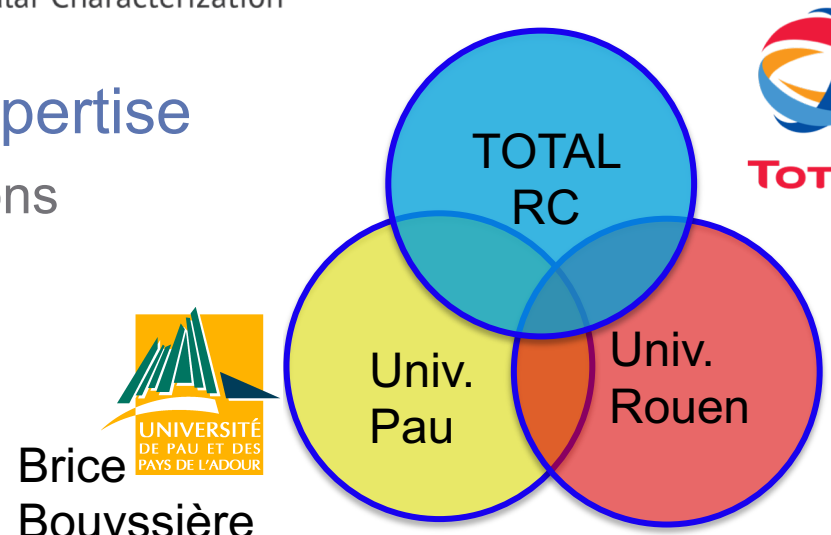
C2MC joint lab

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

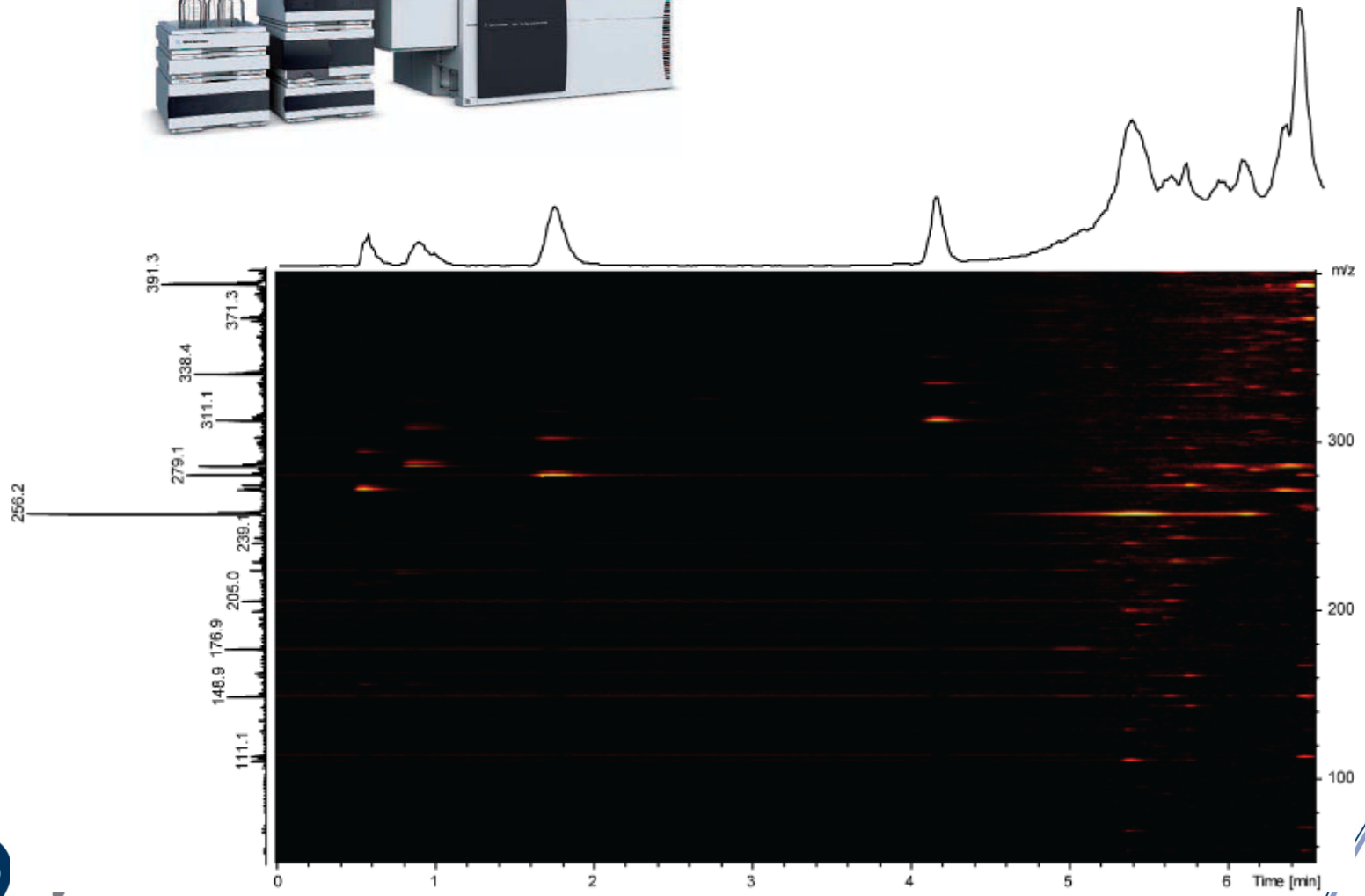


Pierre Giusti

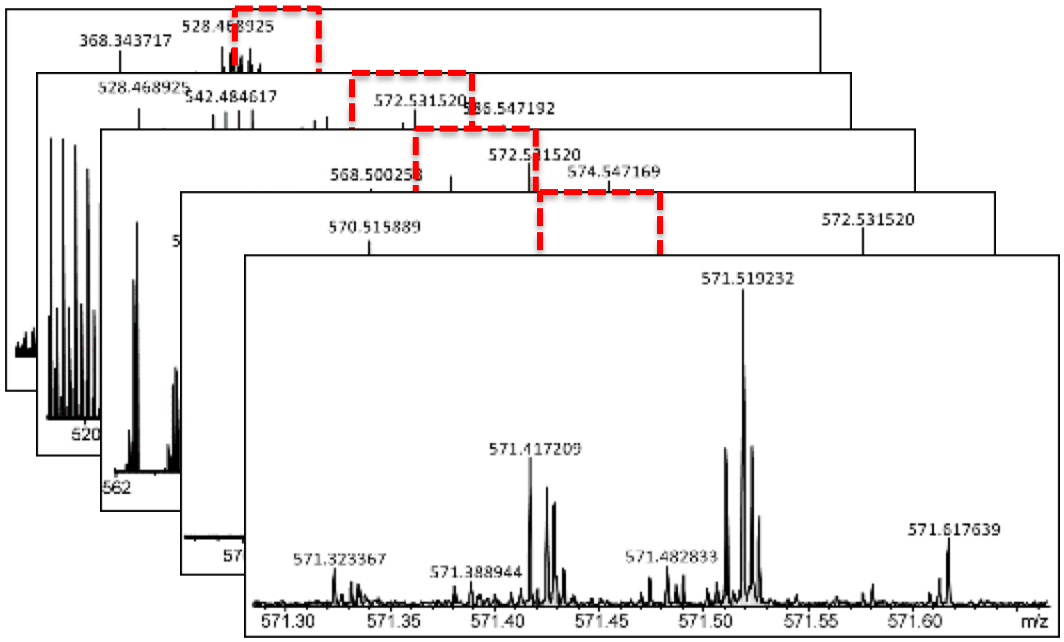
Brice Bouyssière

Complex mixtures

LC/MS a 2D separation



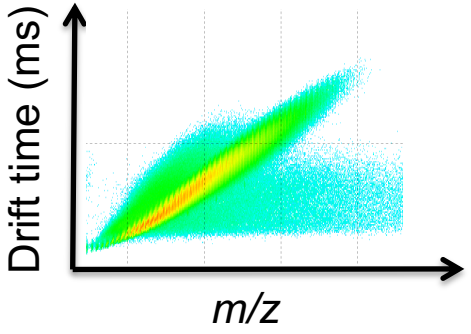
Analysis of heavy petroleum product



Post ionization separation

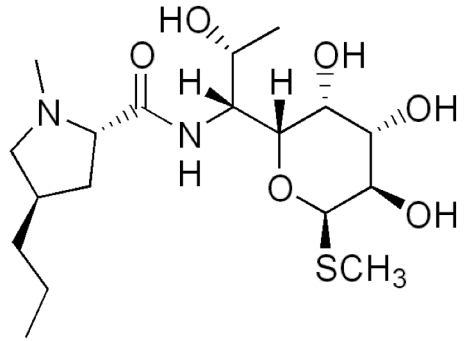
1D separation
Ultra high resolution
FT-MS

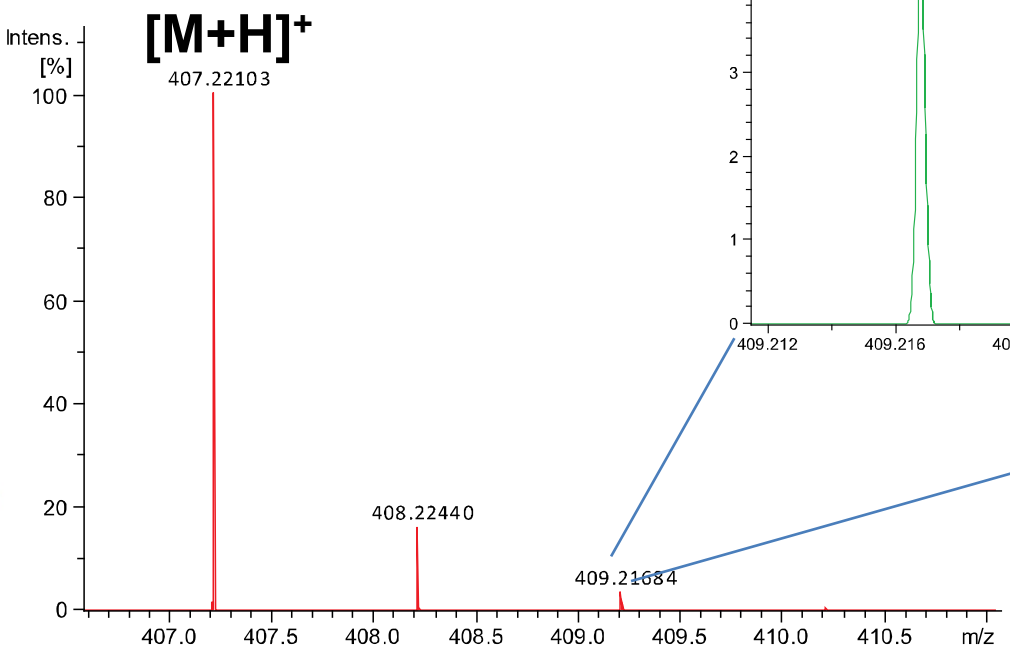
2D separation
Ion mobility – mass spectrometry

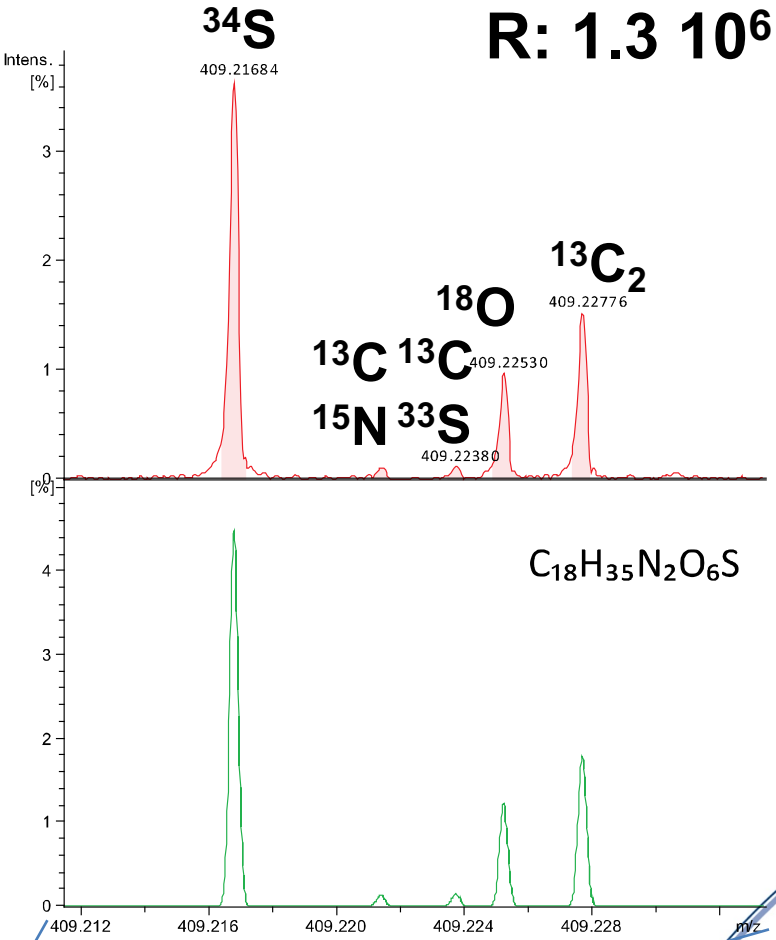


Isotopic Fine Structure

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

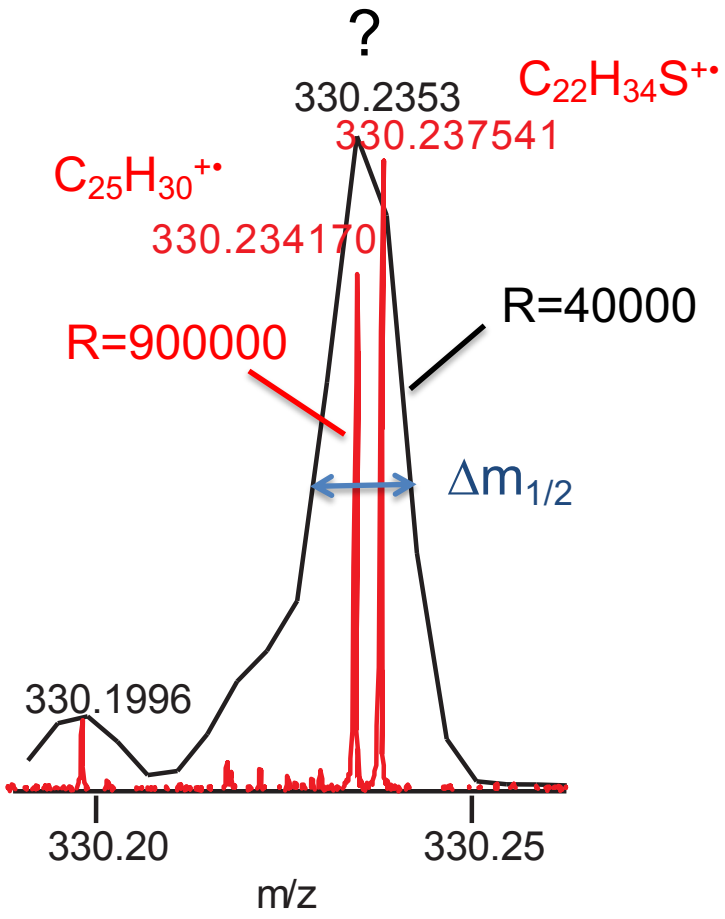






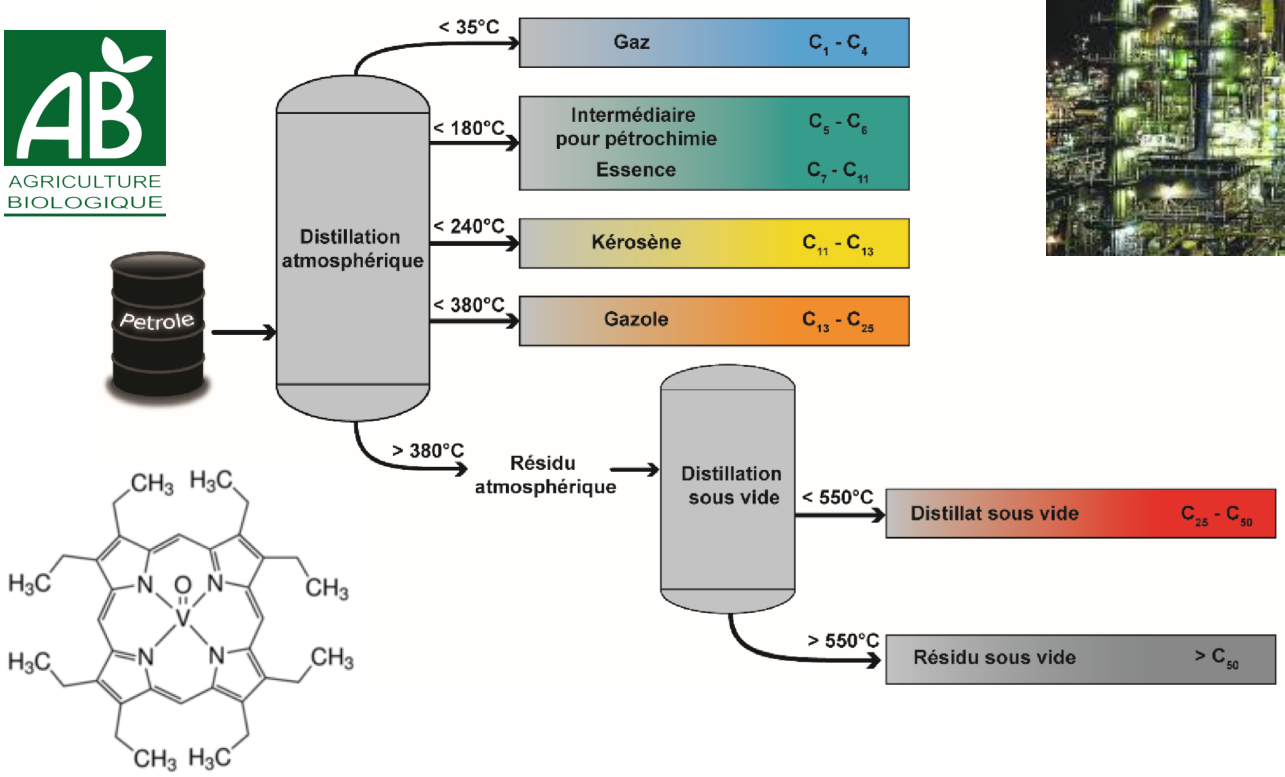
Petroleum complexity

- C_3 *vs* SH_4
  - 3.4 mDa

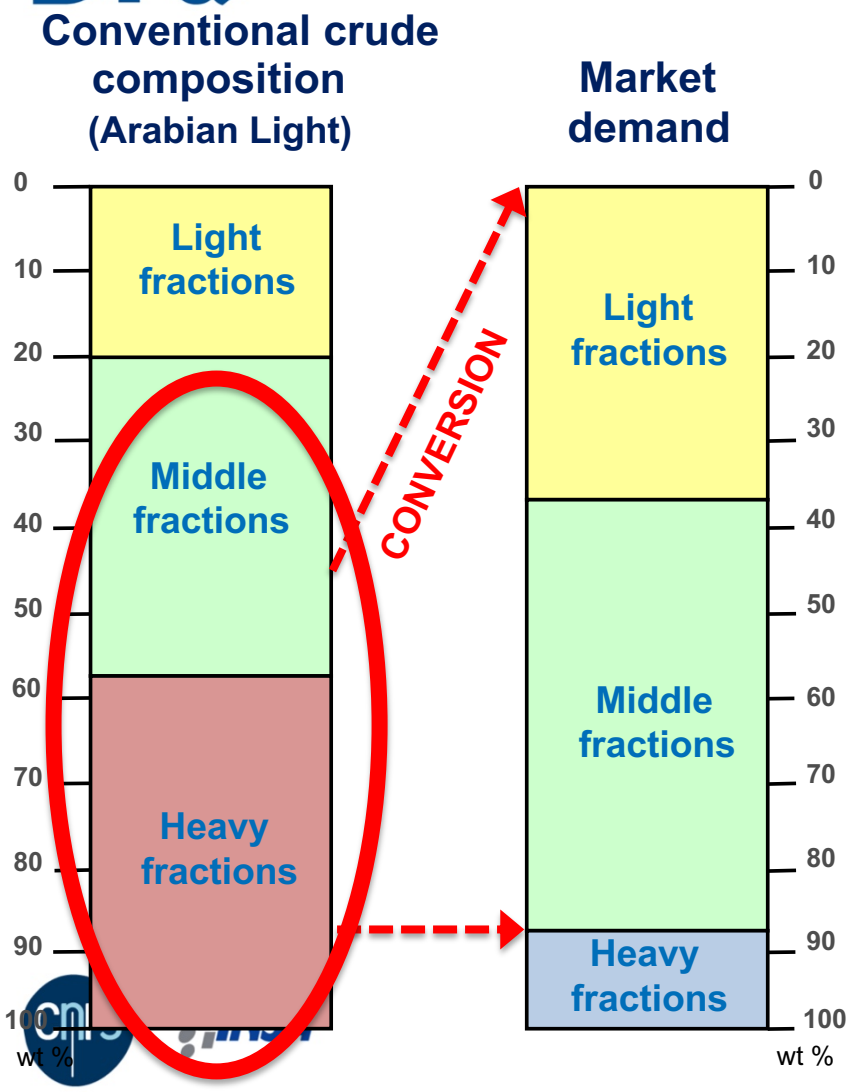


$R=m/\Delta m_{1/2}$

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

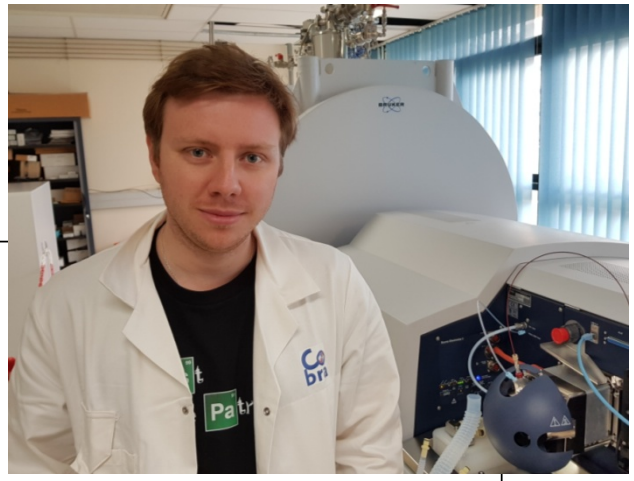
Why molecular characterization

- 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…
- Problem: petroleums with similar macroscopic descriptors may have different properties

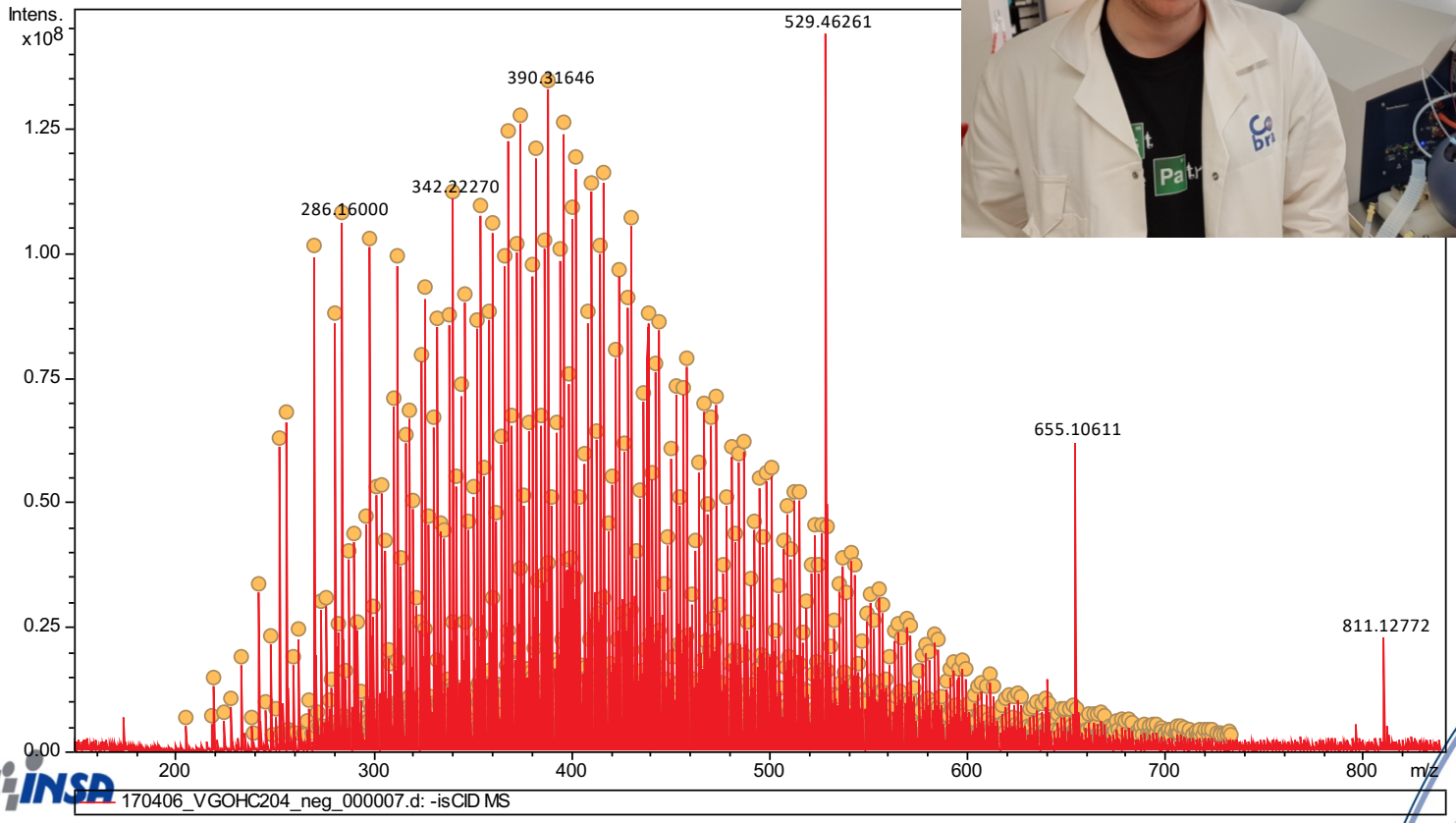
Crude Oil	Country of Origin	Crude Oil Class	Properties		Price USD (2018/03)
			Gravity °API	Sulfur (wt.%)	
Brent	UK	Light Sweet	40.0	0.5	69.0
West Texas Intermediate	USA		39.8	0.3	64.8
Arabian Extra Lt. Export	Saudi Arabia	Light Sour	38.1	1.1	68.9
Daqing	China	Medium Medium Sour	33.0	0.1	63.1
Arabian 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

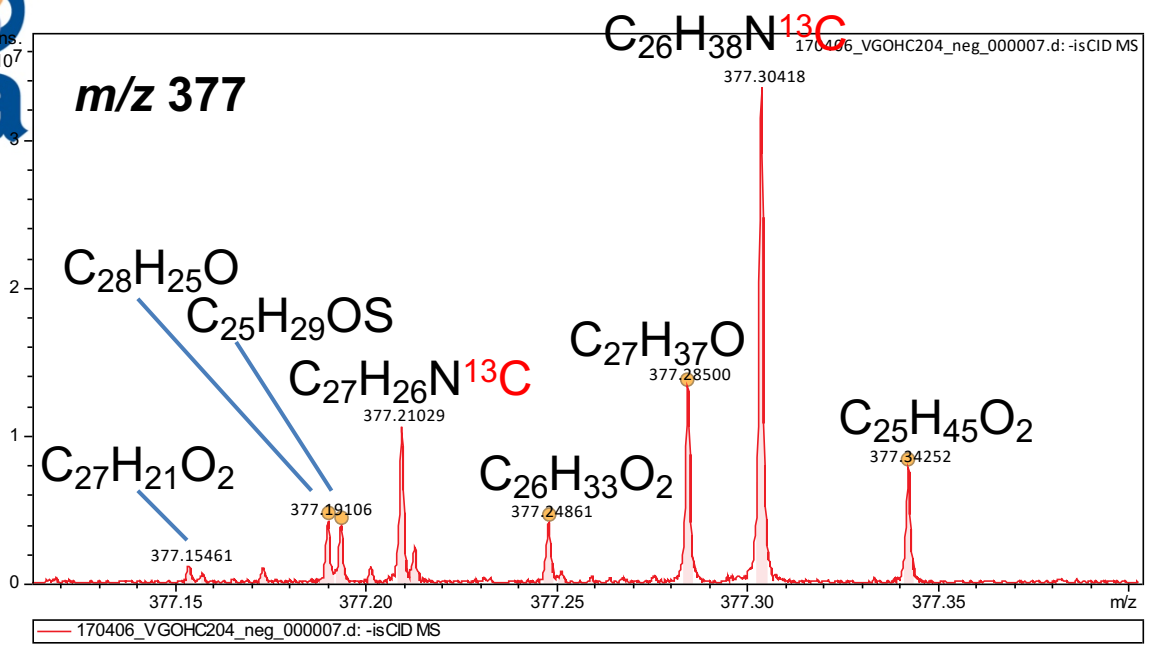
Theses Johann Le Maitre

Vacuum Gasoil ESI(−)



VGO 0.5 mg/mL toluene/MeOH 3% NH_4OH

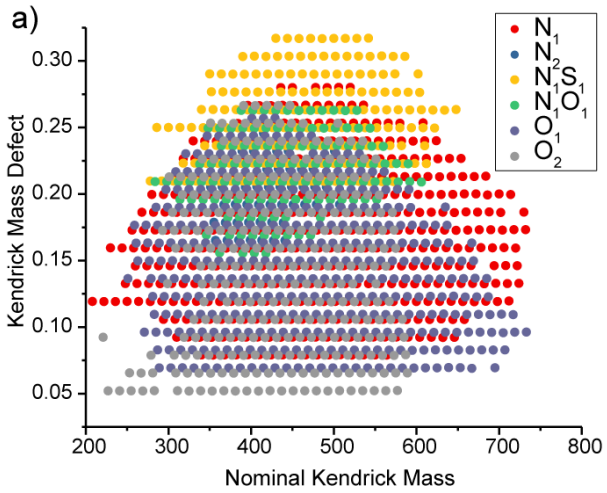




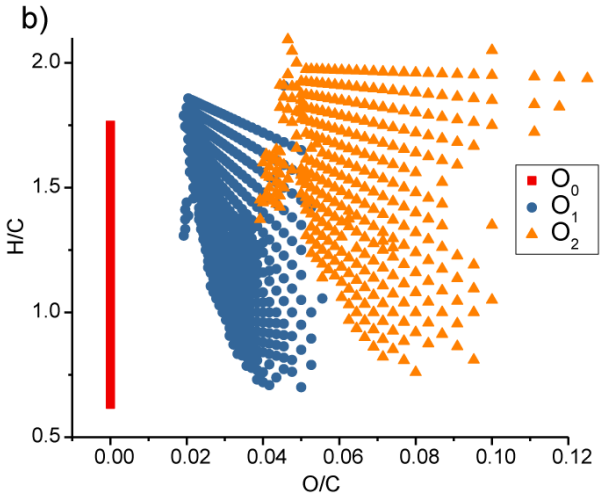
Accuracy better than 100 ppb

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

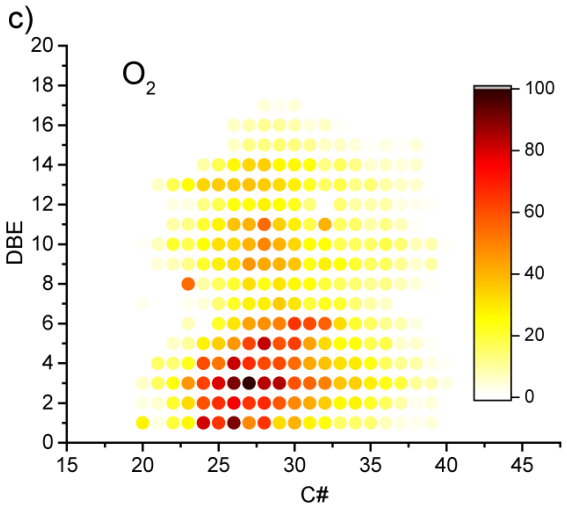
Molecular map



Kendrick Diagram



Van Krevelen Diagram

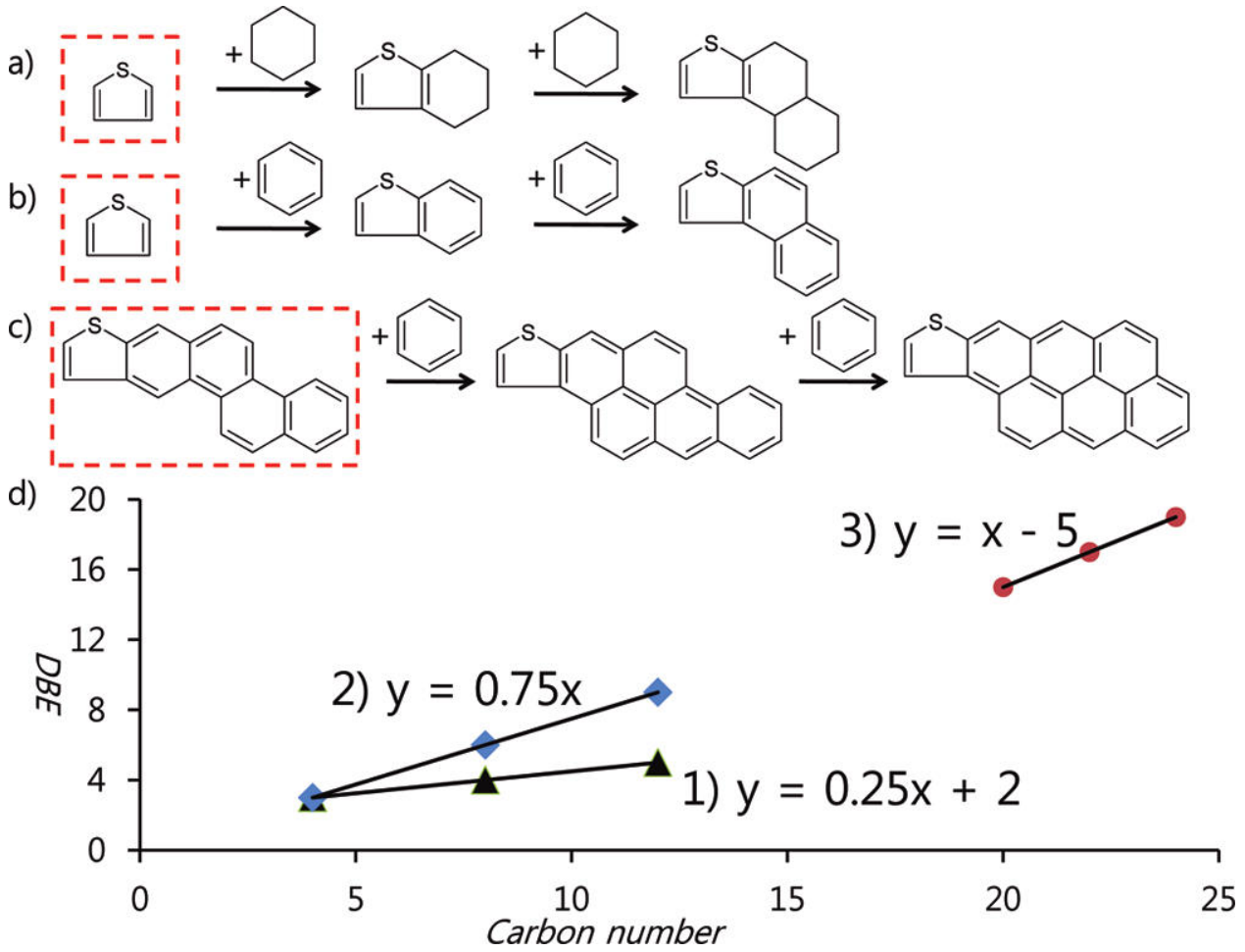


DBE vs C#

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

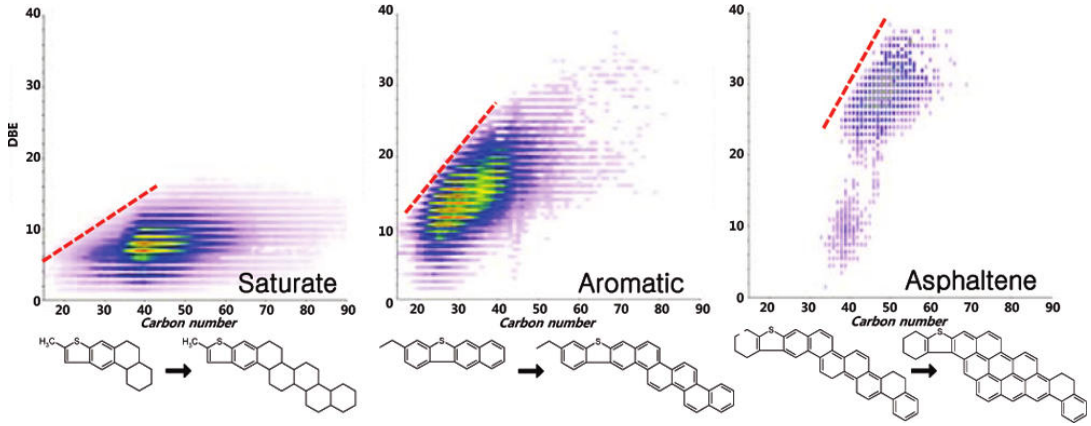
S. Gutierrez Sama, M. Farenc, C. Barrère-Mangote, R. Lobinski, C. Afonso, B. Bouyssiere, P. Giusti. Molecular Fingerprints and Speciation of Crude Oils and Heavy Fractions Revealed by Molecular and Elemental Mass Spectrometry: Keystone between Petroleomics, Metallopetroleomics, and Petrointeractomics.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

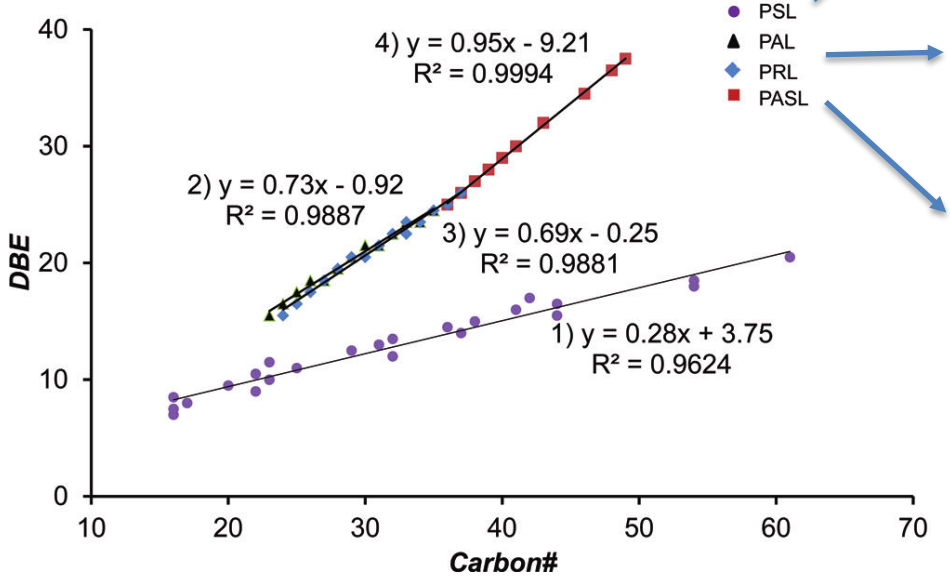
Planar limit



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





PSL
PAL
PRL
PASL

Slope 0.25 — addition of a saturated cyclic ring

Slope 0.75 — serial linear addition of aromatic rings

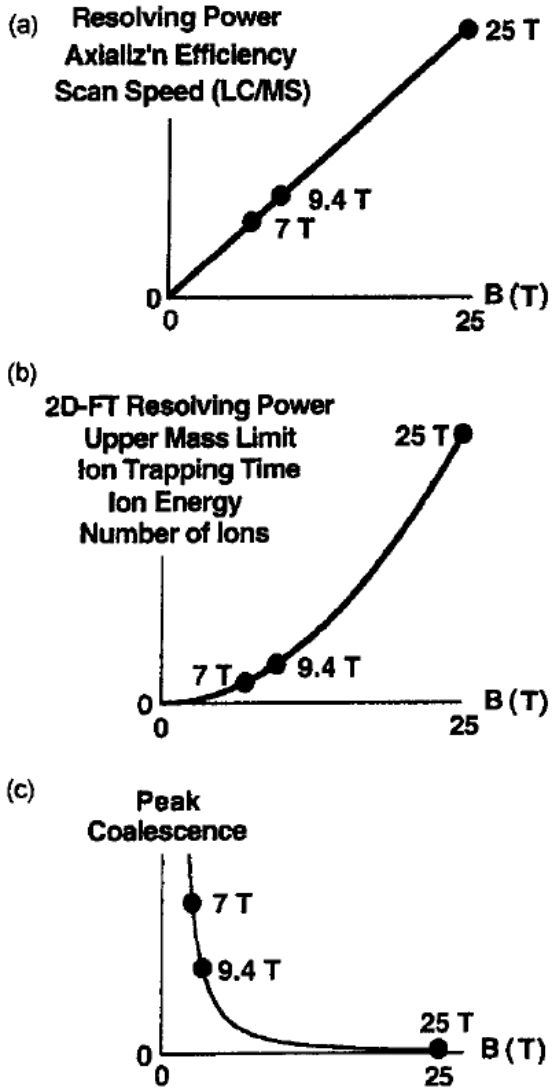
Slope 1 — nonlinear addition of aromatic rings

Data treatment

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

What is important for complex mixtures

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

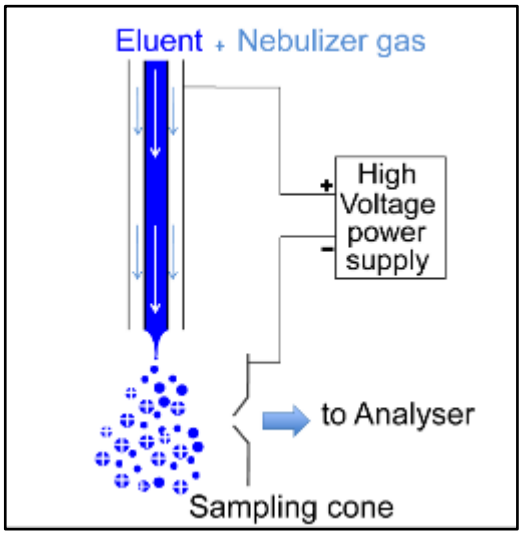


Marshall, *Rapid Commun. Mass Spectrom.*, 1996, 10, 1819

Ion source comparison

- ESI

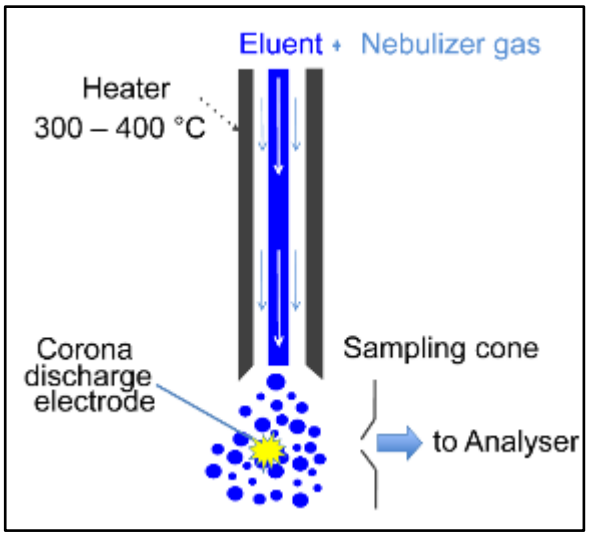
Electrospray ionization



Liquid phase ionization

- APCI

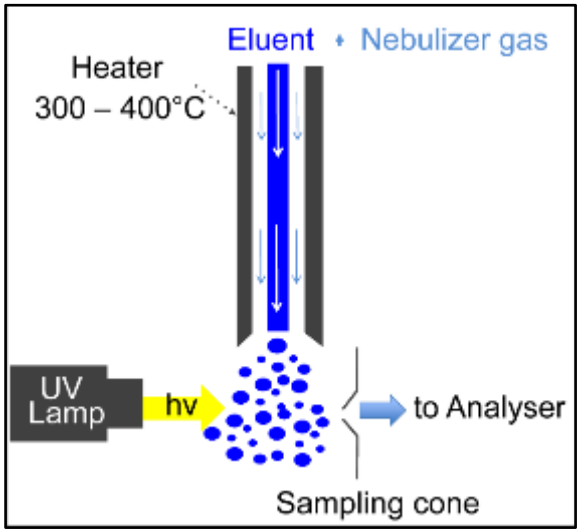
Atmospheric Pressure Chemical Ionization



Gaseous phase ionization
Using a corona discharge

- APPI

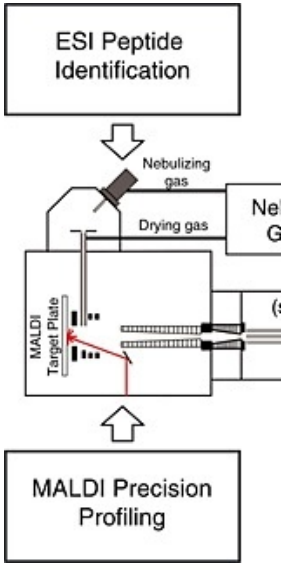
Atmospheric Pressure Photo Ionization

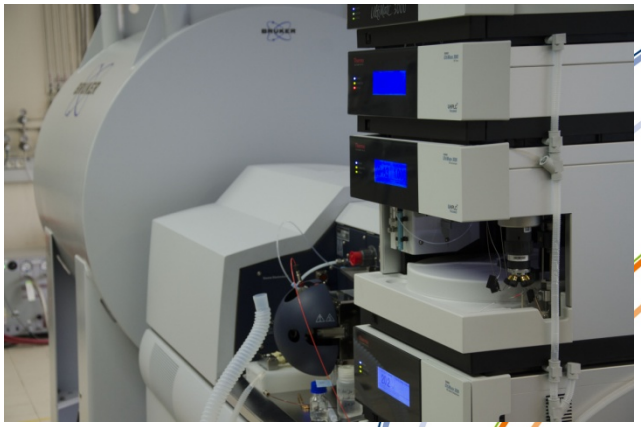


Gaseous phase ionization
Using a UV lamp $h\upsilon$ = 10.6 eV

Equipment

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



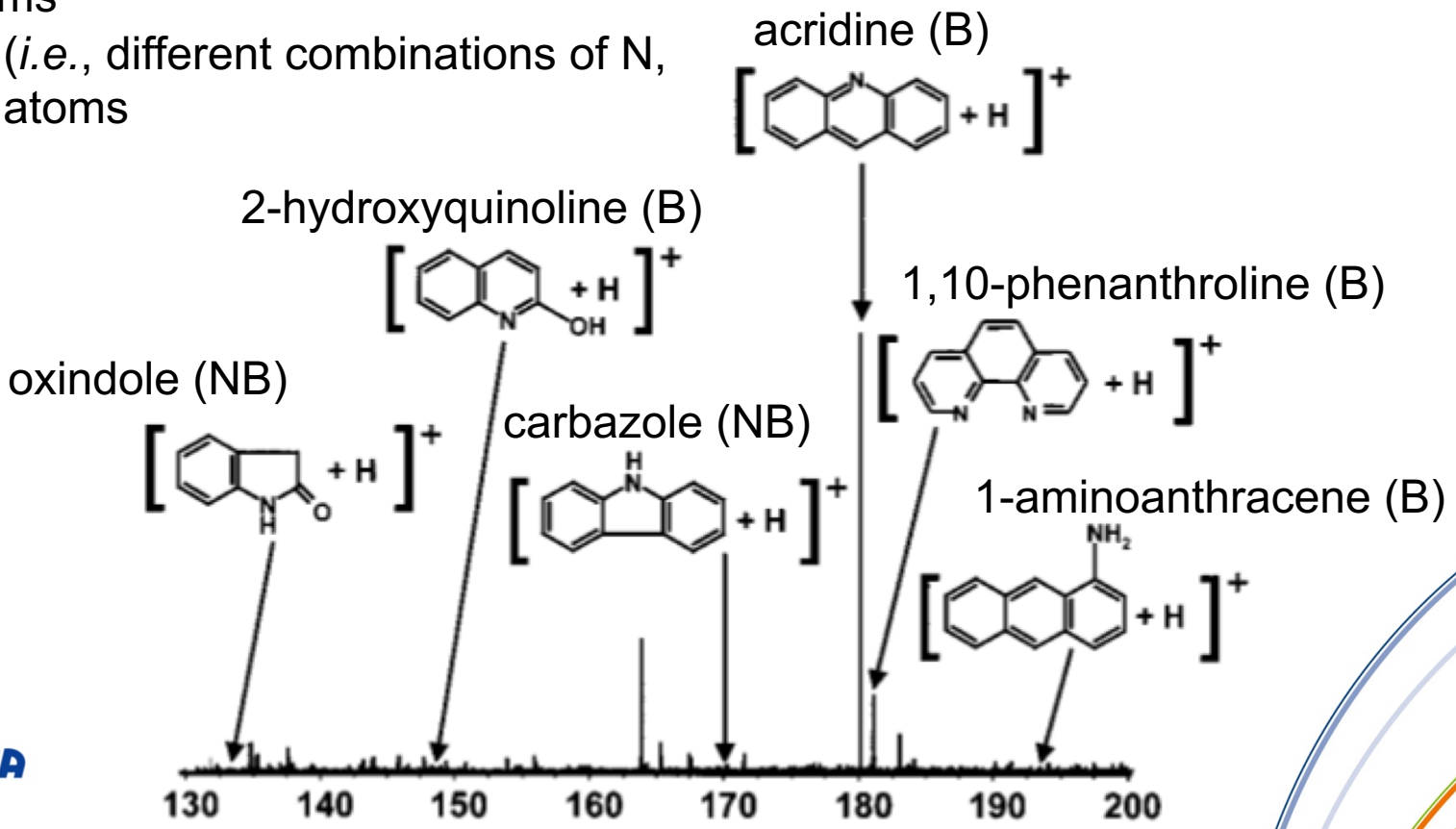


ESI(+): Complex petroleum mixtures

- Basic *vs* Non Basic N

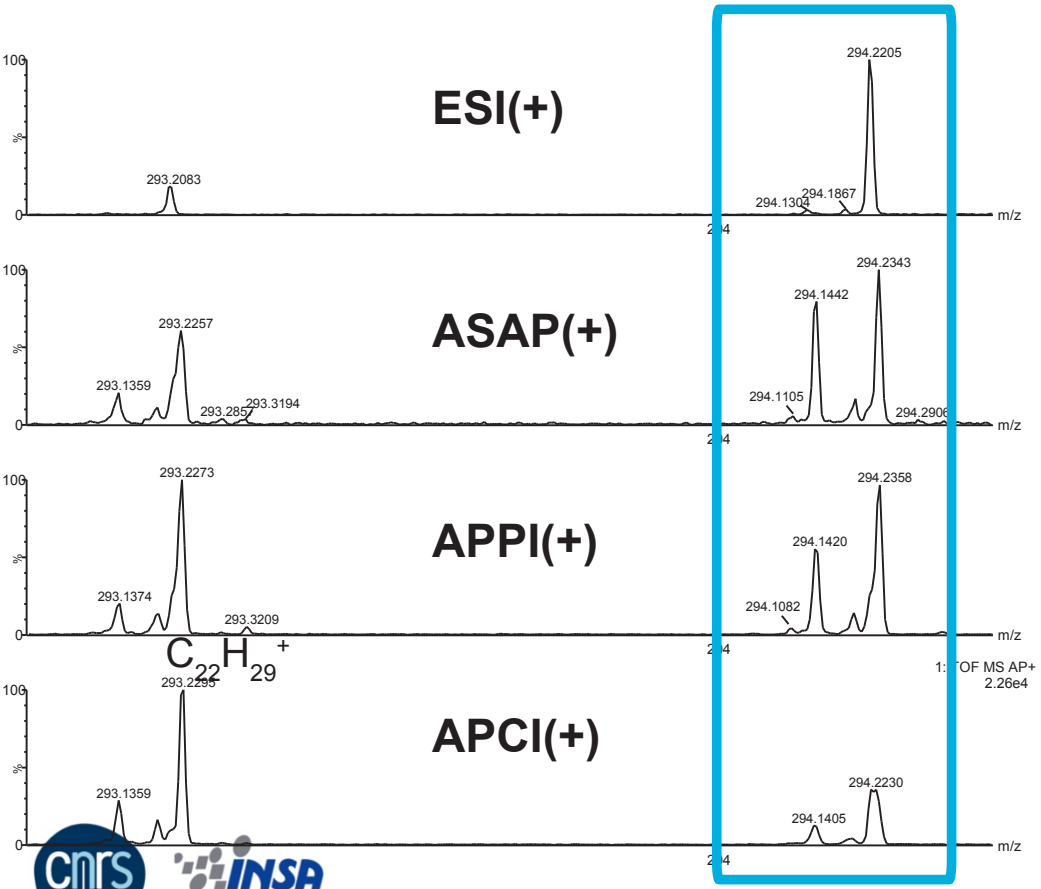
- Z types (Z is the “hydrogen deficiency” relative to alkanes, C_cH_{2c}+zX, in which X denotes heteroatoms

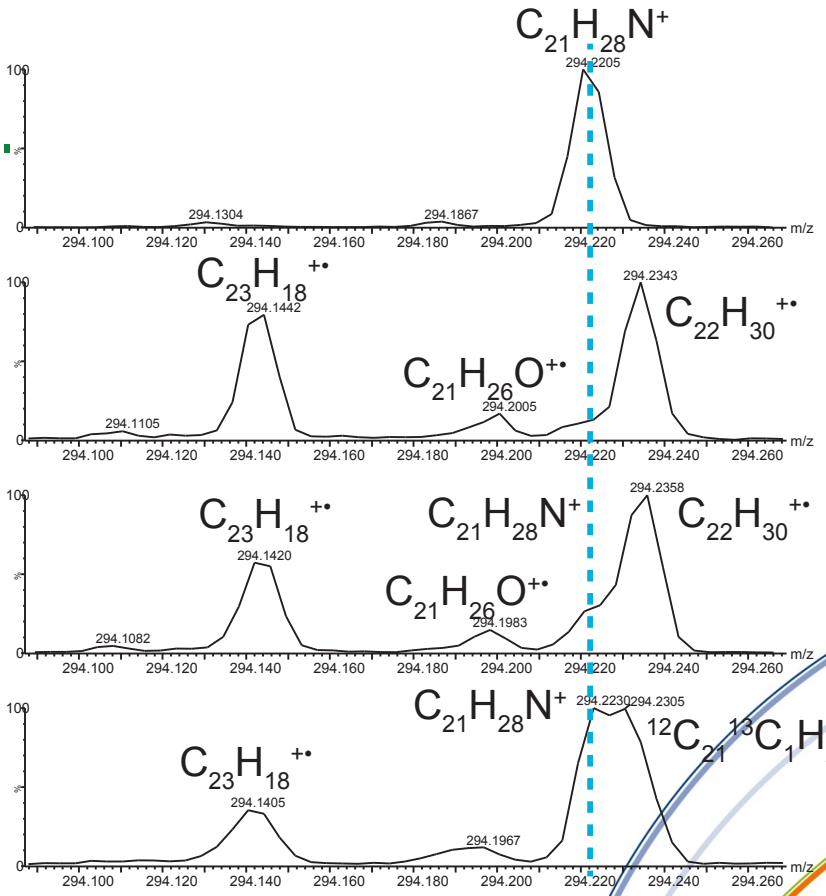
- classes (*i.e.*, different combinations of N, O, and S atoms



C. A. Hughey, C. L. Hendrickson, R. P. Rodgers, A. G. Marshall. Elemental composition analysis of processed and unprocessed diesel fuel by electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. Energy Fuels 2001, 15, 1186.

Ionization discrimination



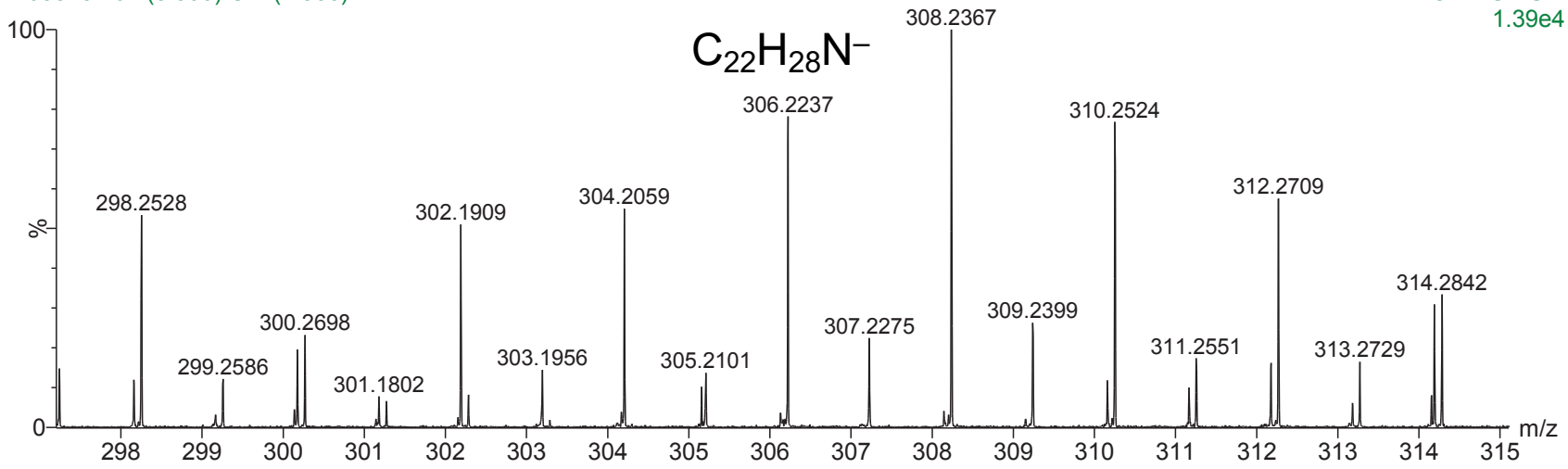


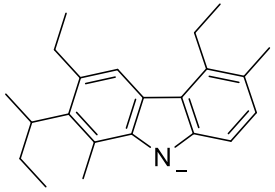
ESI(-) NB nitrogen

Charge C 1mg/ml MeOH/Toluene (50:50) + 1% NH4OH a 28%

1403543 204 (3.500) Cm (7:366)

1: TOF MS ES+
1.39e4

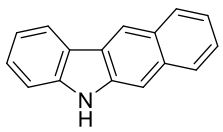




Chemical Formula: $C_{22}H_{28}N^-$
Exact Mass: 306.22272

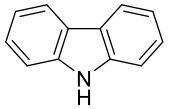
DBE = c − h/2 + n/2 + 1 (for $C_cH_hN_nO_oS_s$)

DBE vs C#



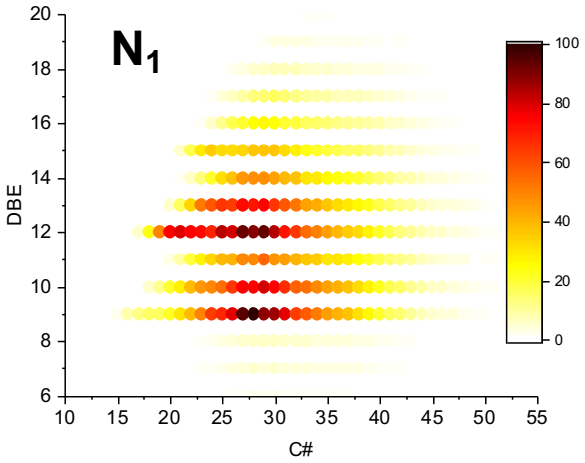
benzocarbazole

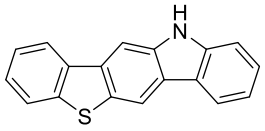
DBE=12



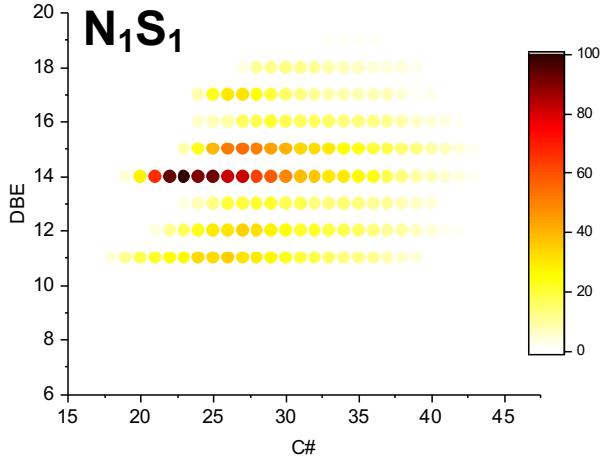
carbazole

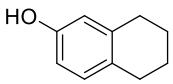
DBE=9



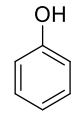


DBE =14



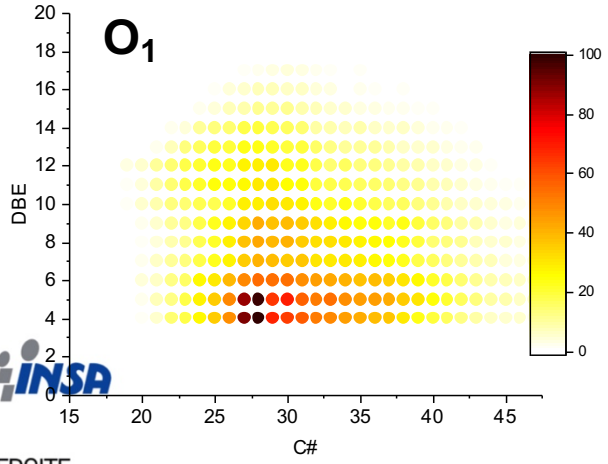


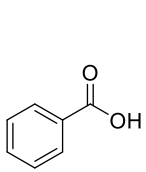
DBE=5



Phenol

DBE=4





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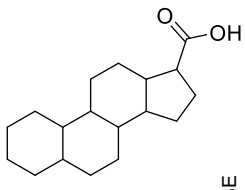

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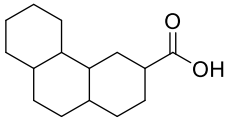
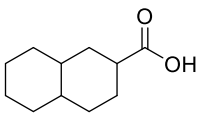


DBE =4



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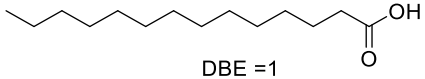

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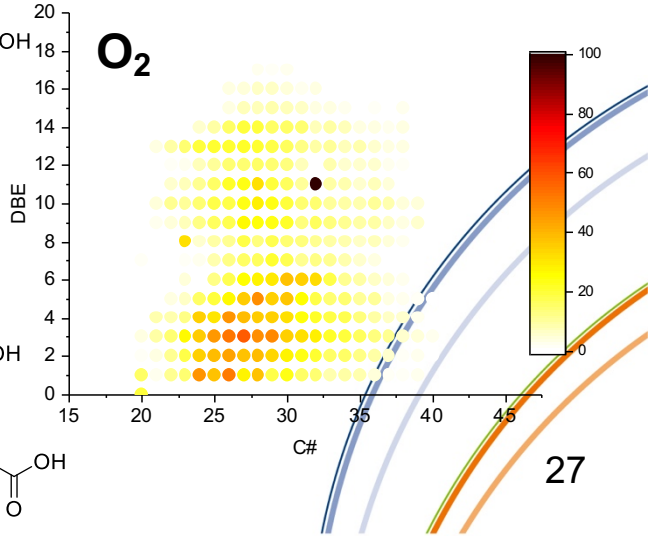
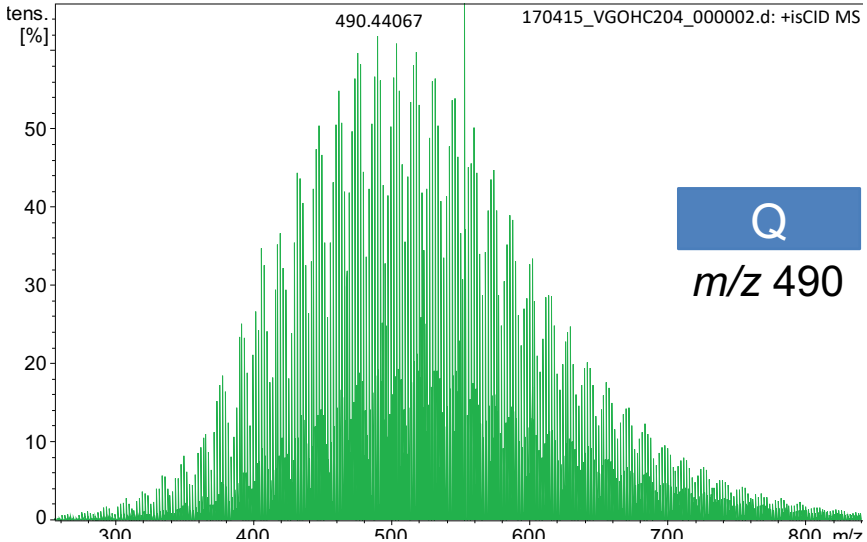
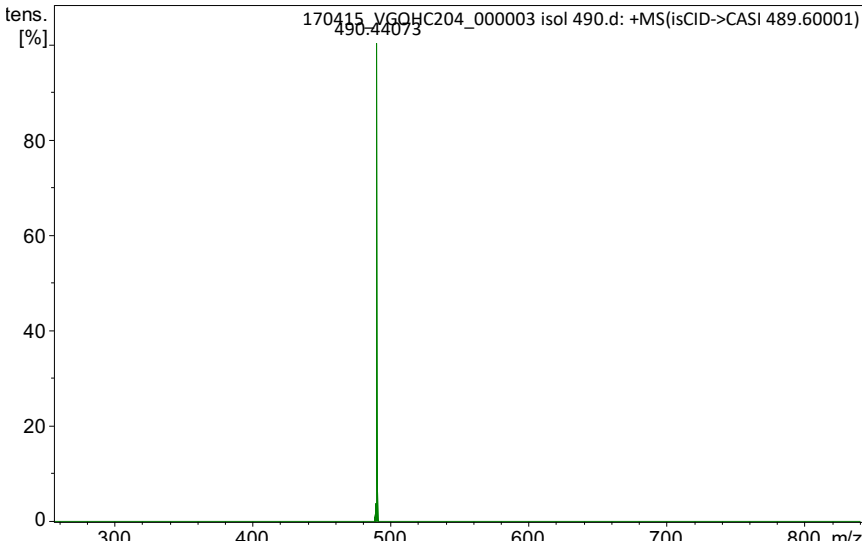
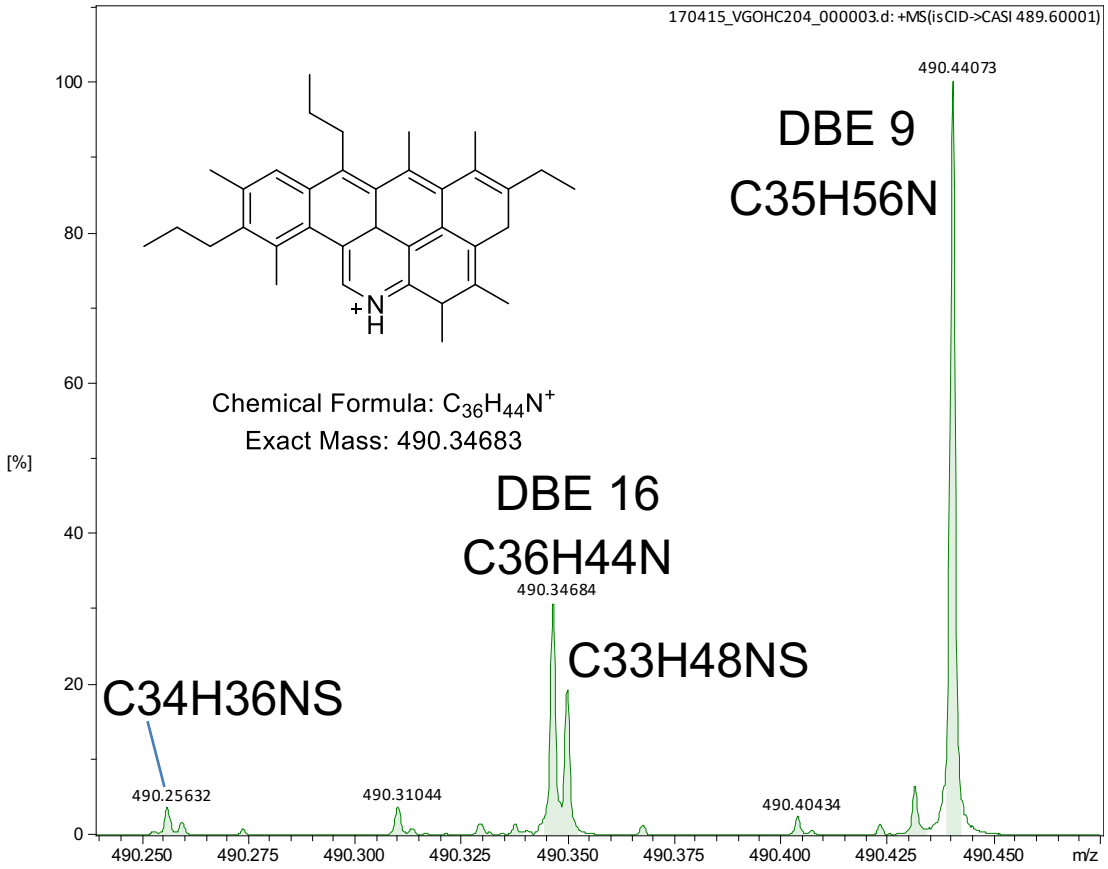


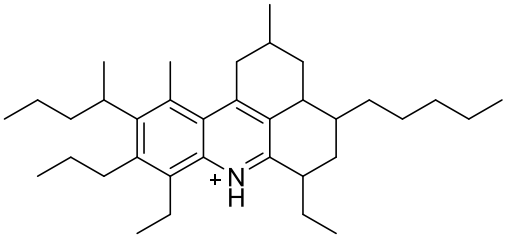
Un peu de chimie structurale





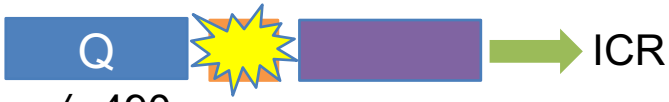
Isolation *m/z* 490.449



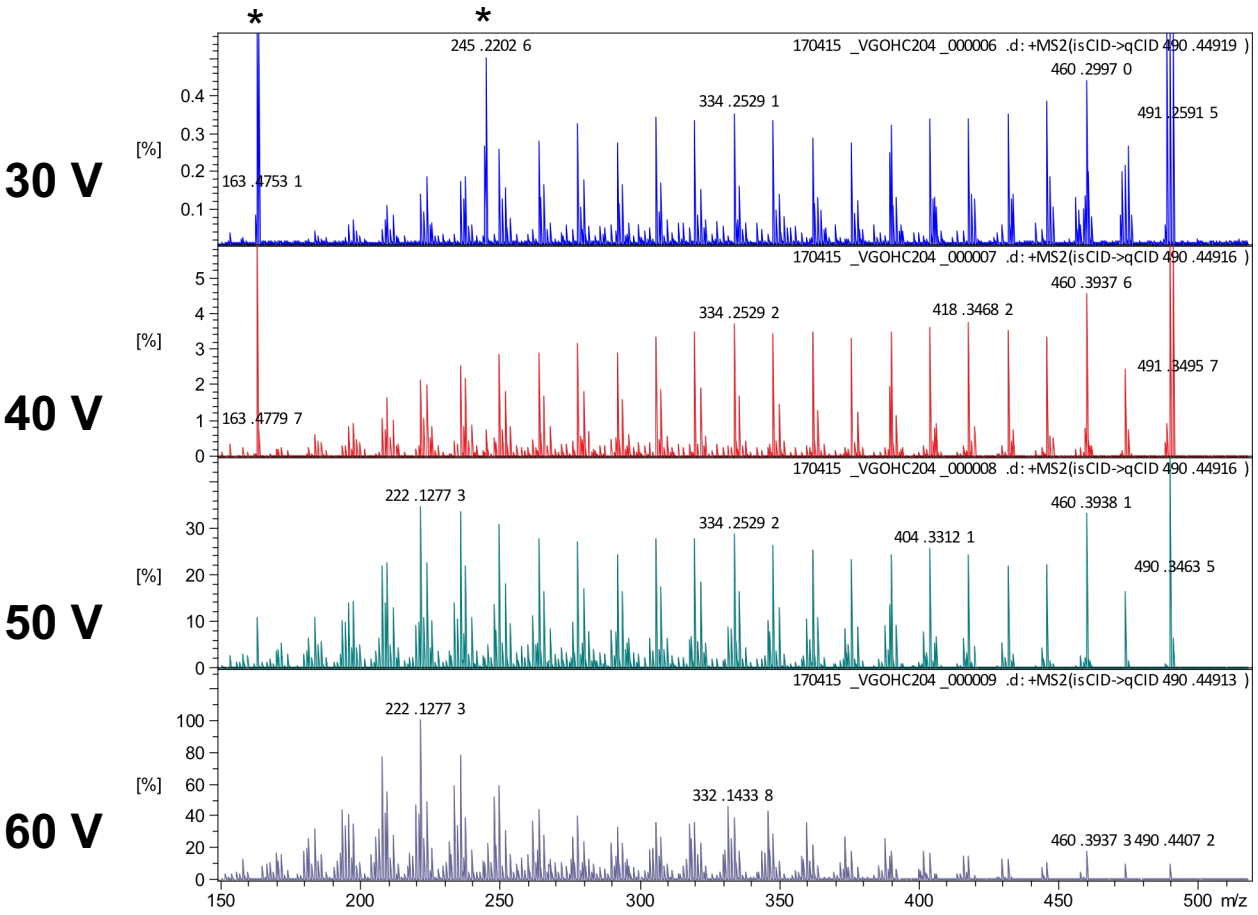


Chemical Formula: $C_{35}H_{56}N^+$
Exact Mass: 490.44073

Spectres CID



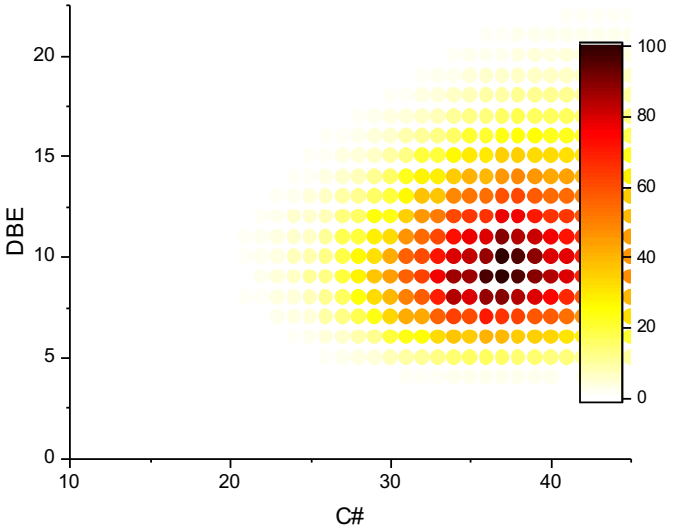
m/z 490



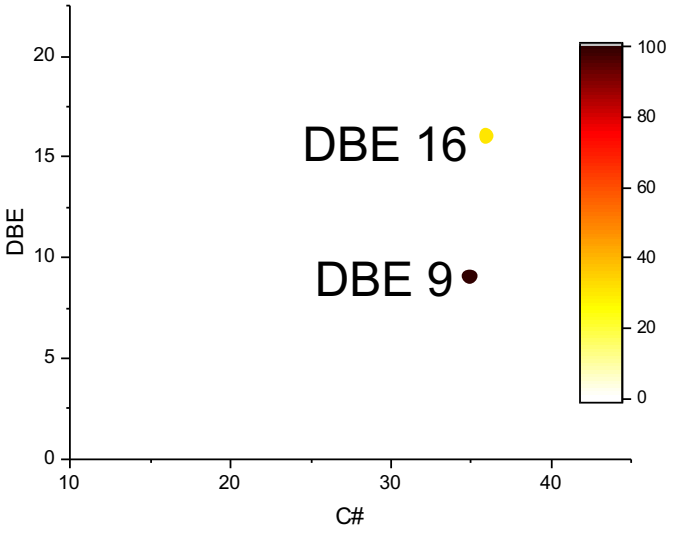
Selection m/z 490.449

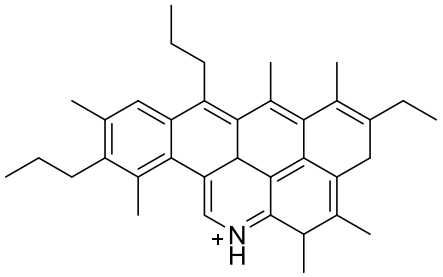
m/z 490

N1 Class

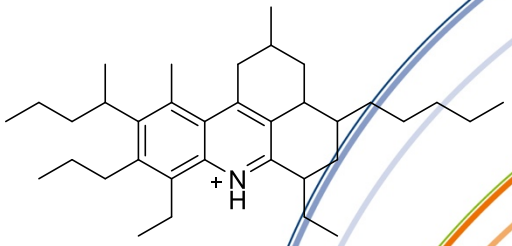


N1 Class
Selection 490.4

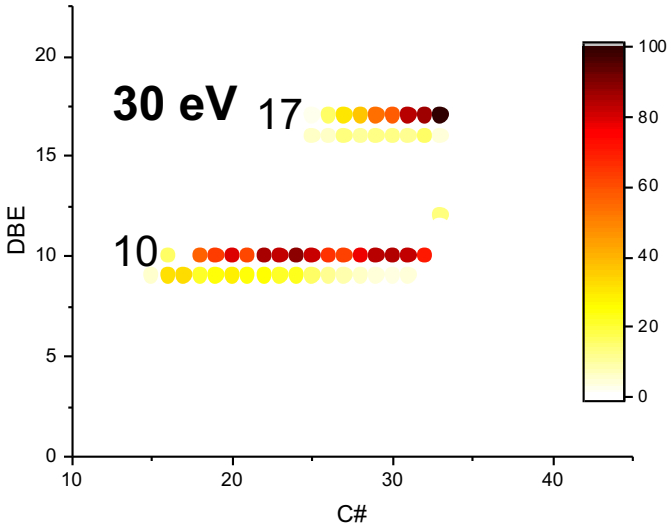


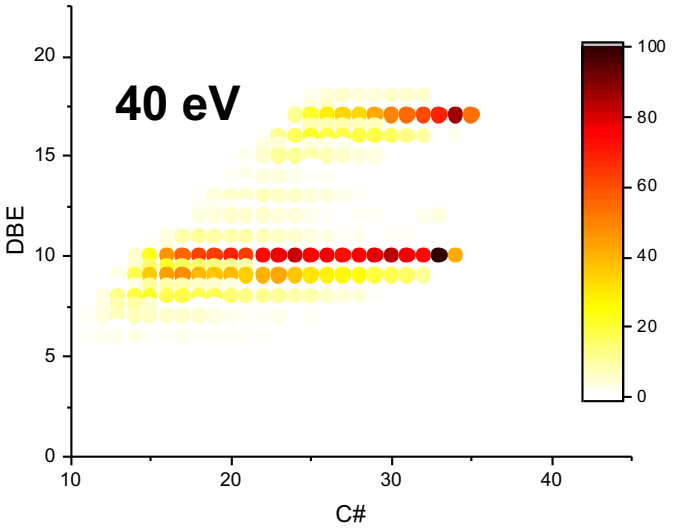


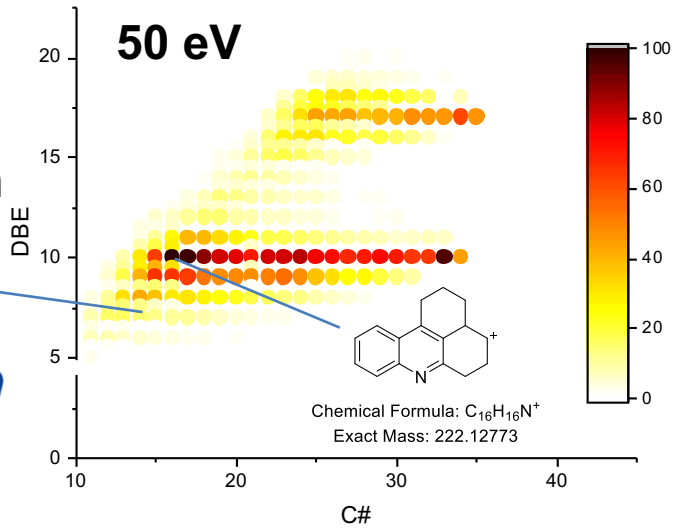
Chemical Formula: $C_{36}H_{44}N^+$
Exact Mass: 490.34683

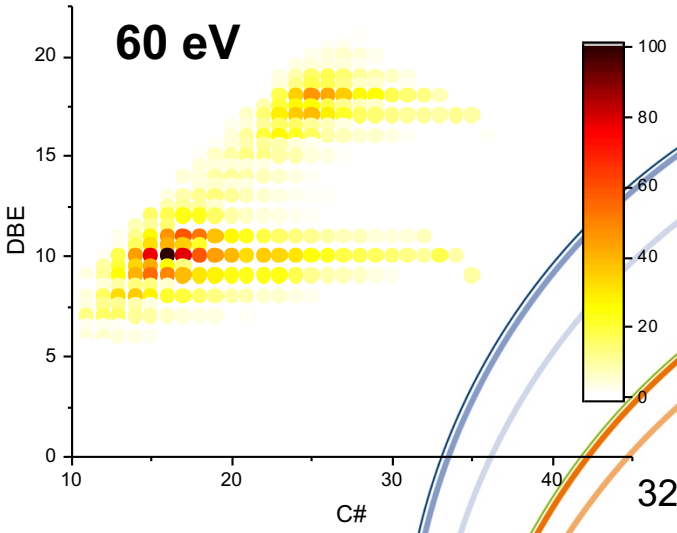


Chemical Formula: $C_{35}H_{56}N^+$
Exact Mass: 490.44073



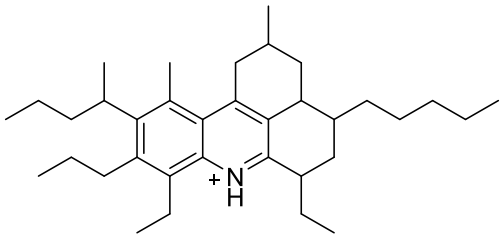






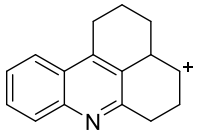
Losses of DBE through ring opening

DBE 10 N1 fragment series



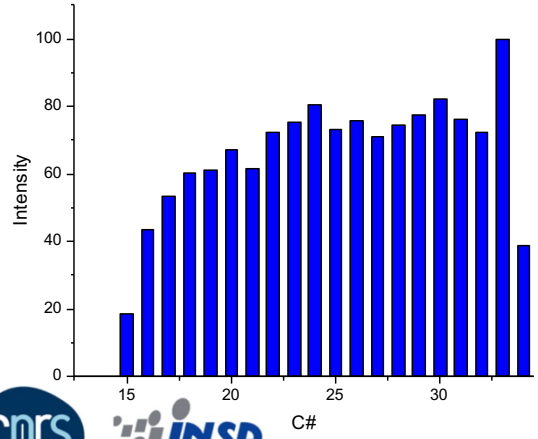
Chemical Formula: $C_{35}H_{56}N^+$
Exact Mass: 490.44073

Ion core

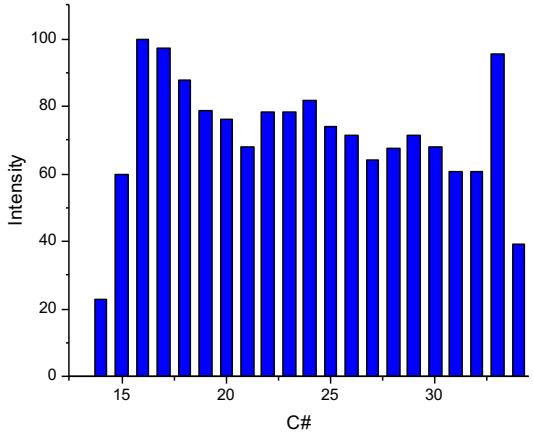


Chemical Formula: $C_{16}H_{16}N^+$
Exact Mass: 222.12773

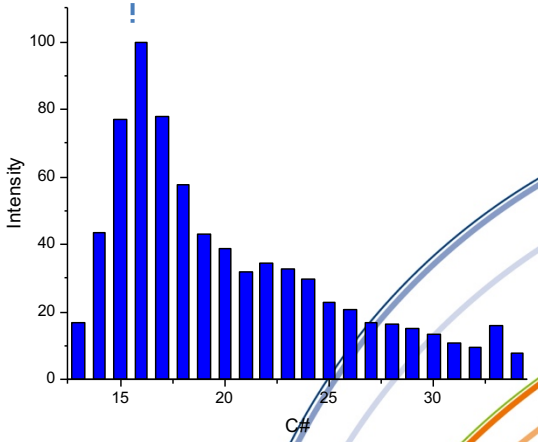
40 V



50 V



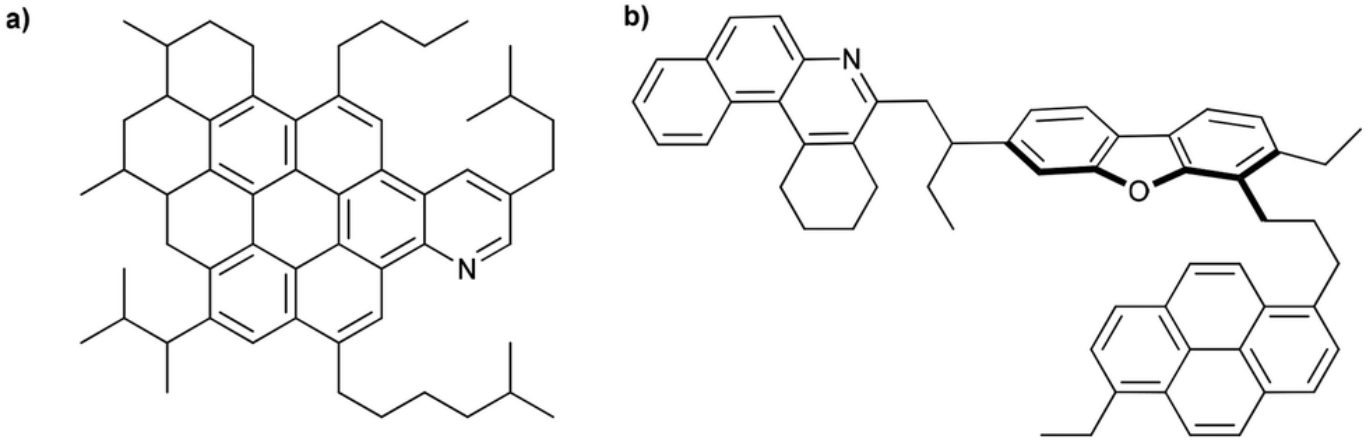
60 V



Asphaltenes

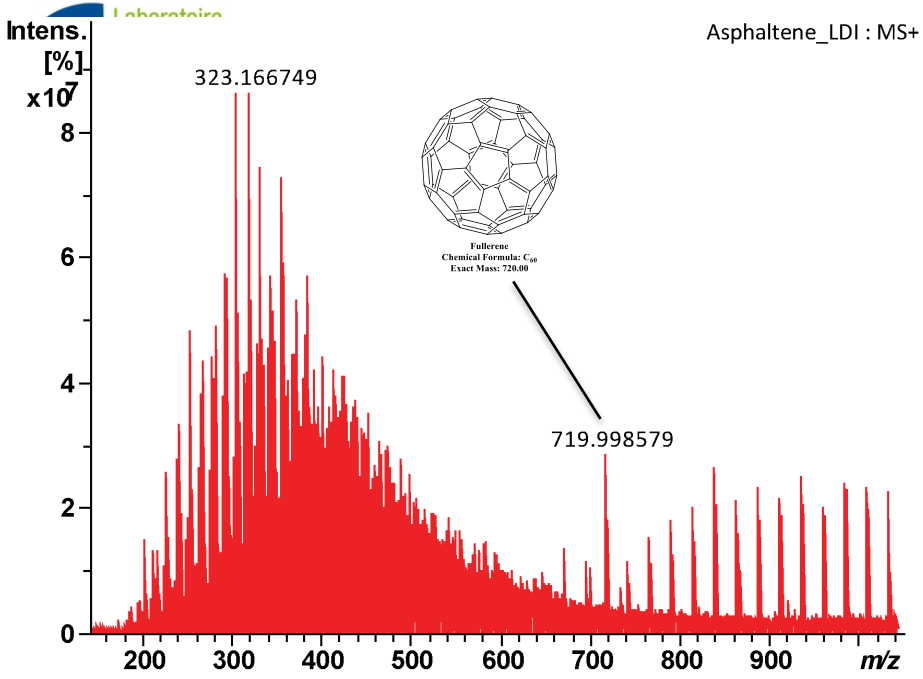
- Reference asphaltene de in the framework of PetroPhase 2017 Le Havre.

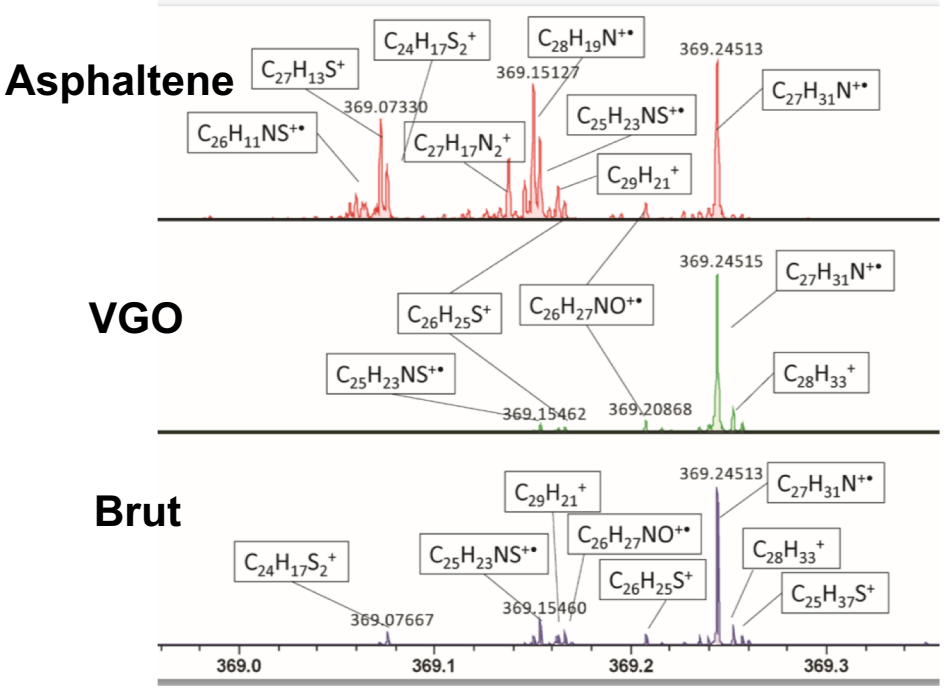
Non-soluble in pentane or heptane but soluble in toluene

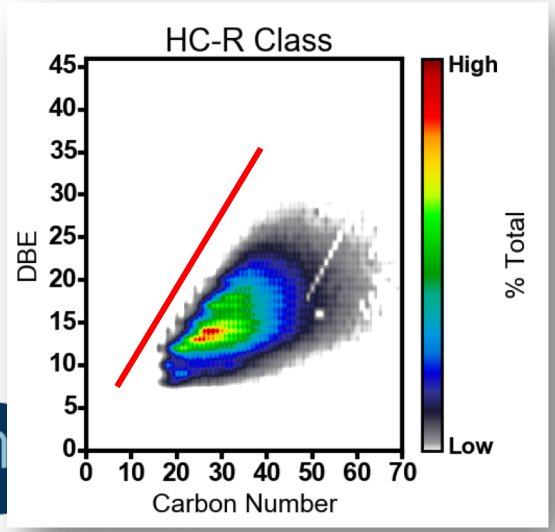


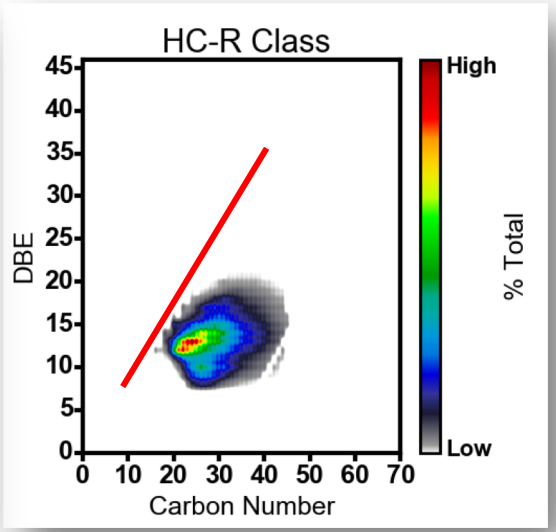
Island ***Archipelago***

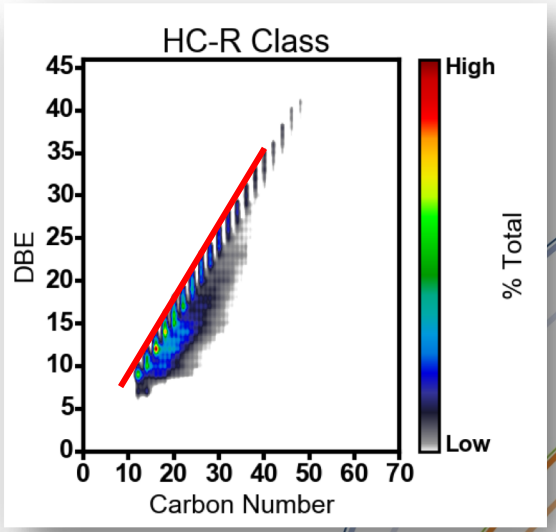
Org. Biomol. Chem., 2015, 13, 6984-6991





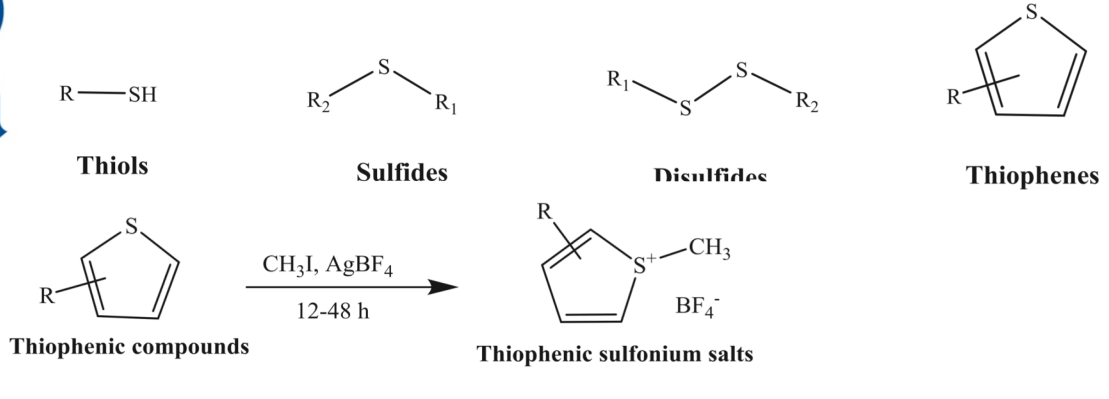


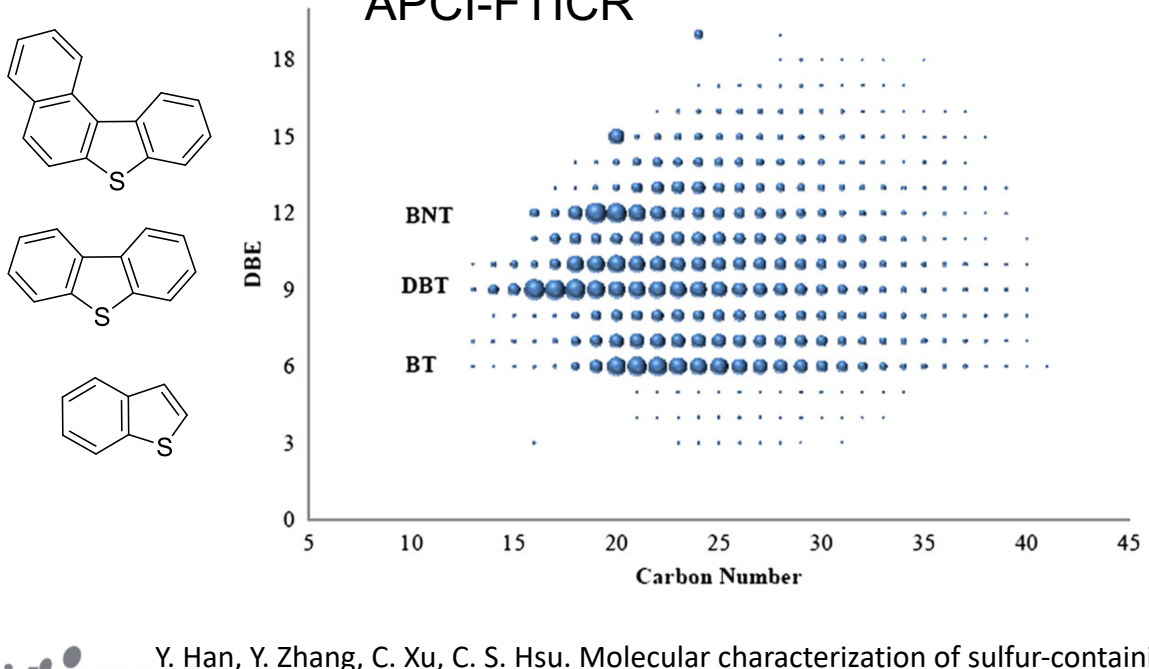




Marianny Combariza

Sulfur





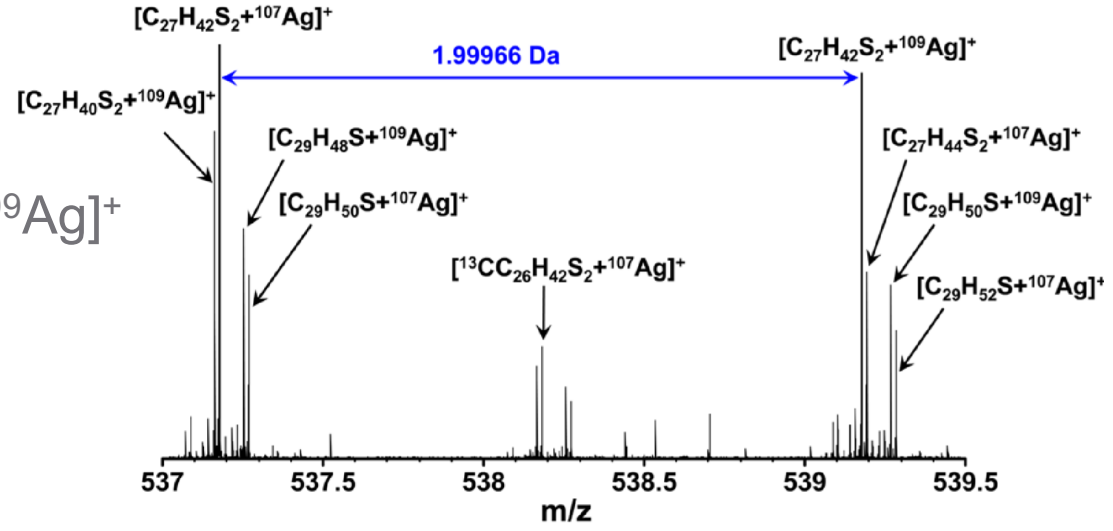
Y. Han, Y. Zhang, C. Xu, C. S. Hsu. Molecular characterization of sulfur-containing compounds in petroleum. *Fuel* **2018**, *221*, 144.

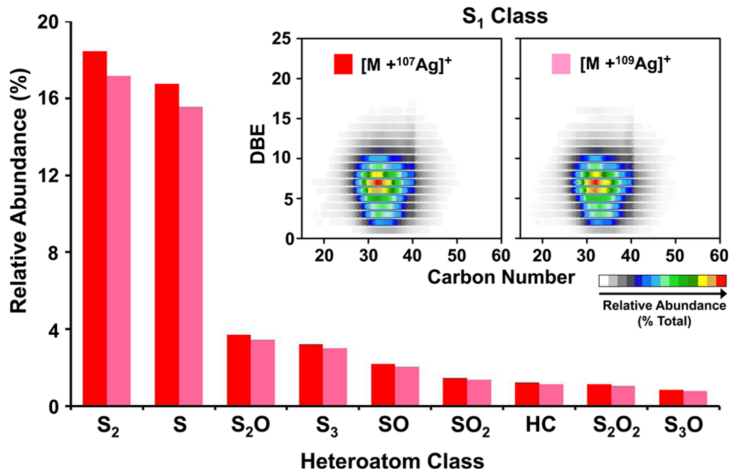
N. Hourani, J. T. Andersson, I. Moller, M. Amad, M. Witt, S. M. Sarathy. Atmospheric pressure chemical ionization Fourier transform ion cyclotron resonance mass spectrometry for complex thiophenic mixture analysis. *Rapid commun. mass spect.* **2013**, *27*, 2432.

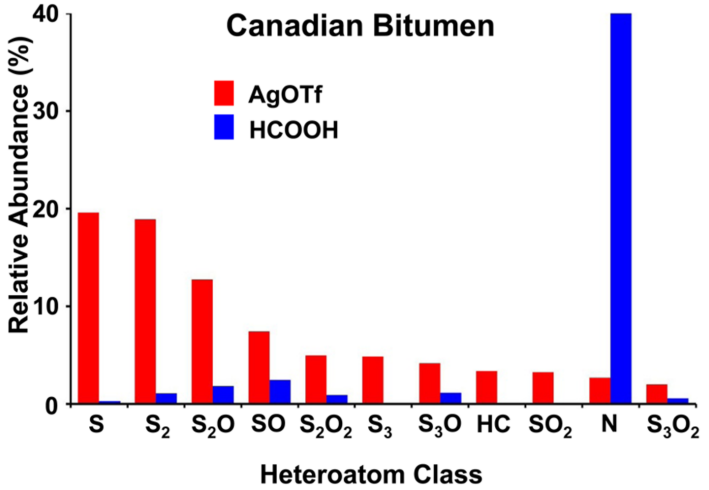
Cationization

ESI(+) Canadian HVGO

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

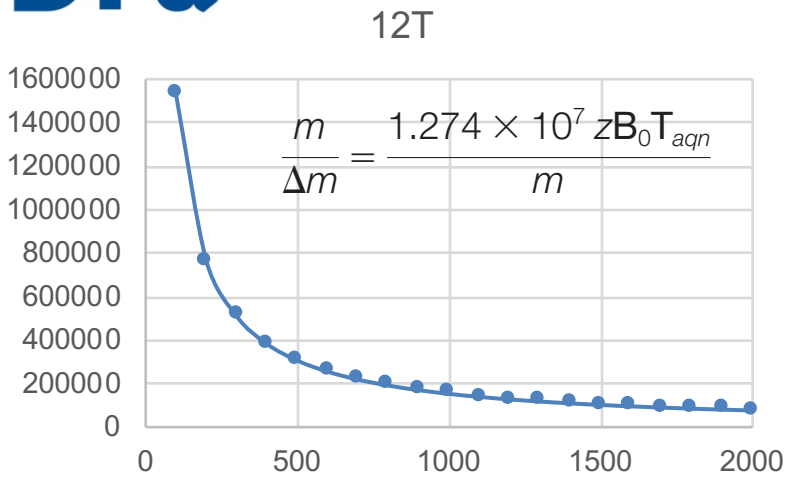


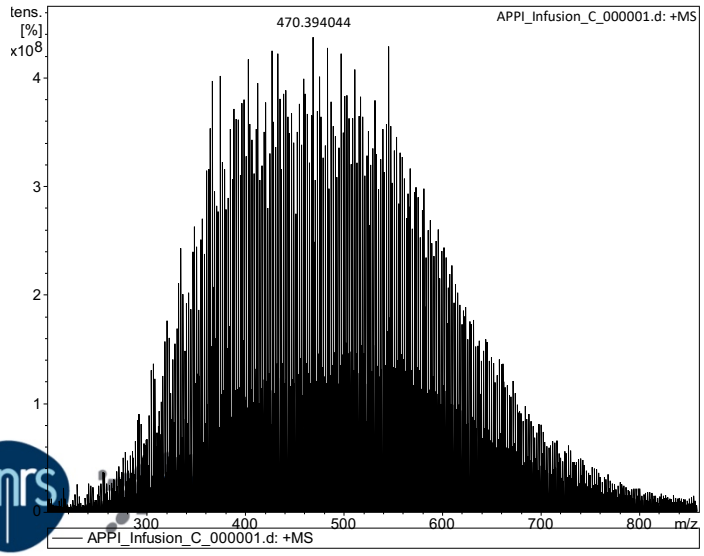




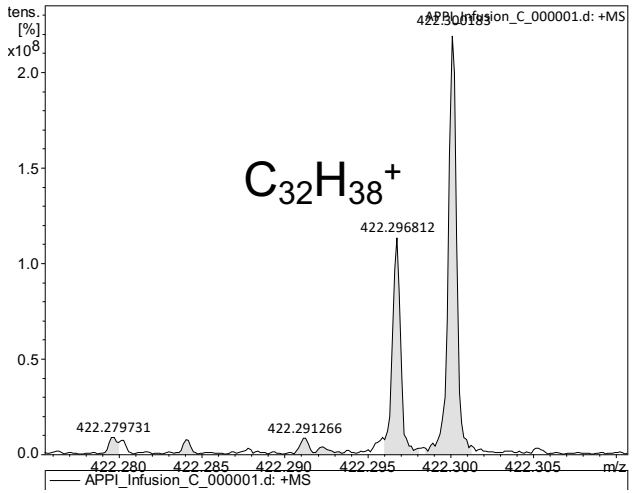
V. V. Lobodin, P. Juyal, A. M. McKenna, R. P. Rodgers, A. G. Marshall. Silver Cationization for Rapid Speciation of Sulfur-Containing Species in Crude Oils by Positive Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2014**, *28*, 447.

Evolution of RP with *m/z*





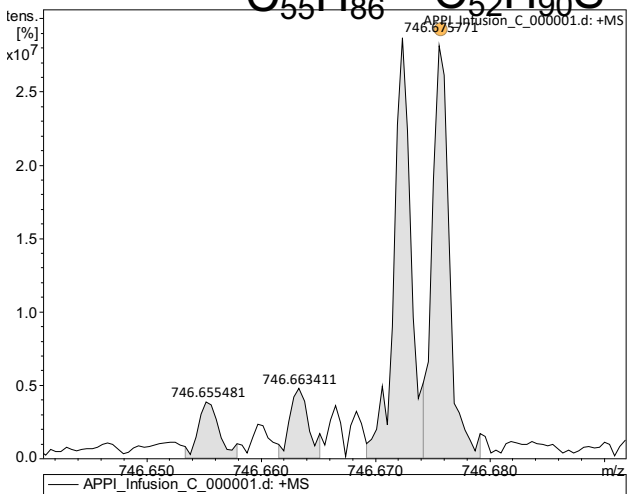
$C_{29}H_{42}S^+$



3.3 s transient

R 850000

$C_{55}H_{86}^+$ $C_{52}H_{90}S^+$

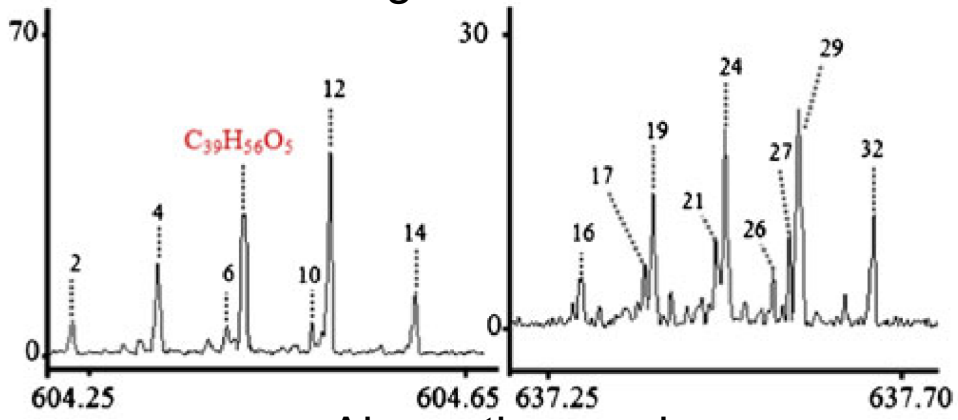


R 550000

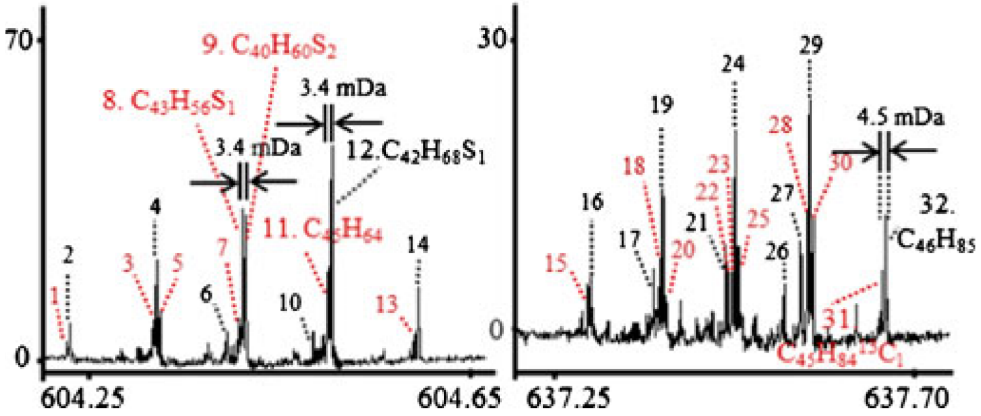
Absorption mode

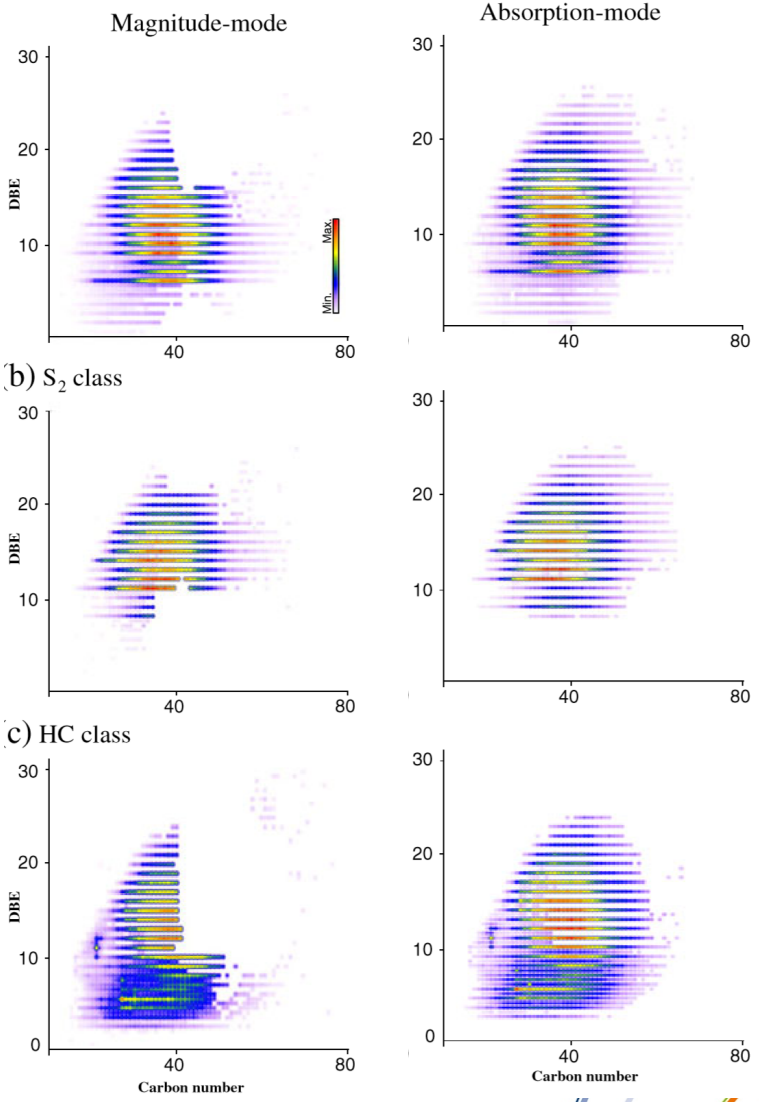
- 7T FTICR, 2s transient

magnitude-mode



Absorption-mode

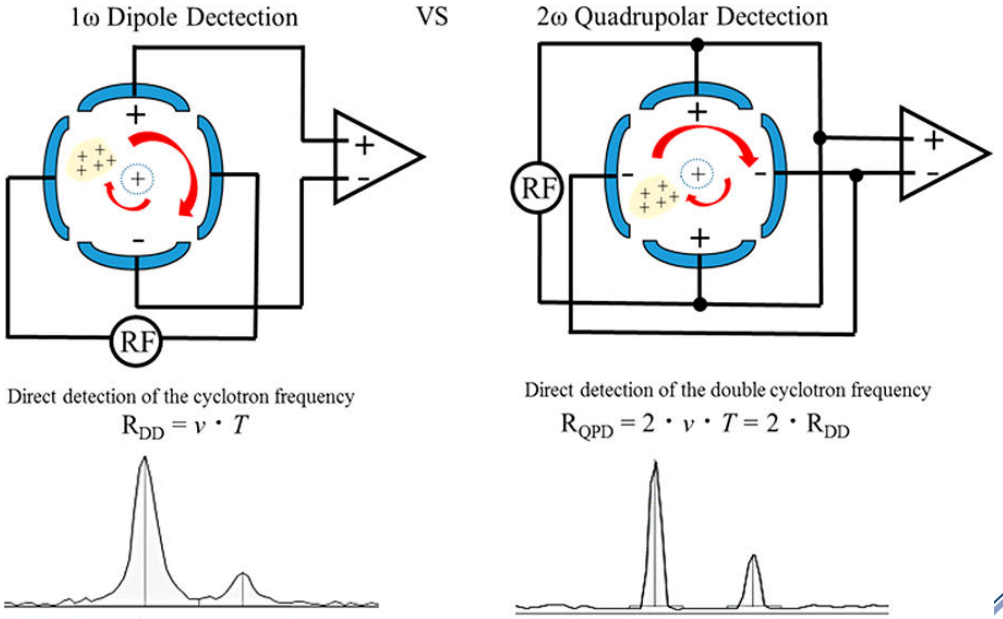




Y. Cho, Y. Qi, P. B. O'Connor, M. P. Barrow, S. Kim. Application of phase correction to improve the interpretation of crude oil spectra obtained using 7 T Fourier transform ion cyclotron resonance mass spectrometry. *J Am Soc Mass Spectrom* **2014**, *25*, 154.

Quadripolar detection

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



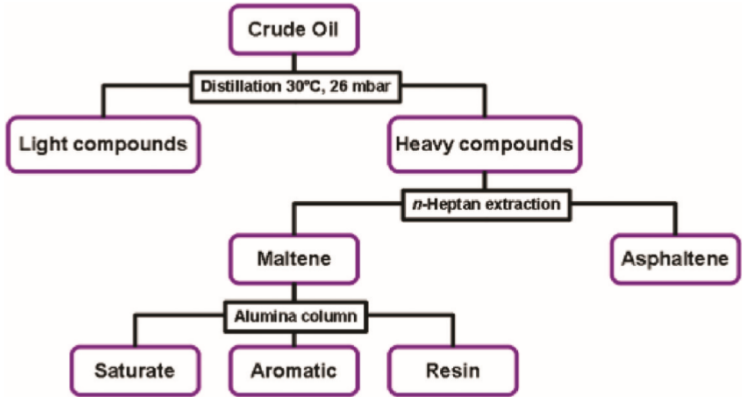
E. Cho, M. Witt, M. Hur, M. J. Jung, S. Kim. Application of FT-ICR MS Equipped with Quadrupole Detection for Analysis of Crude Oil. *Anal Chem* **2017**, *89*, 12101.

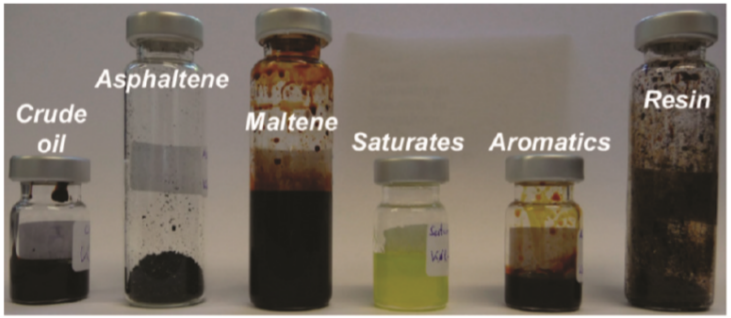
Limits

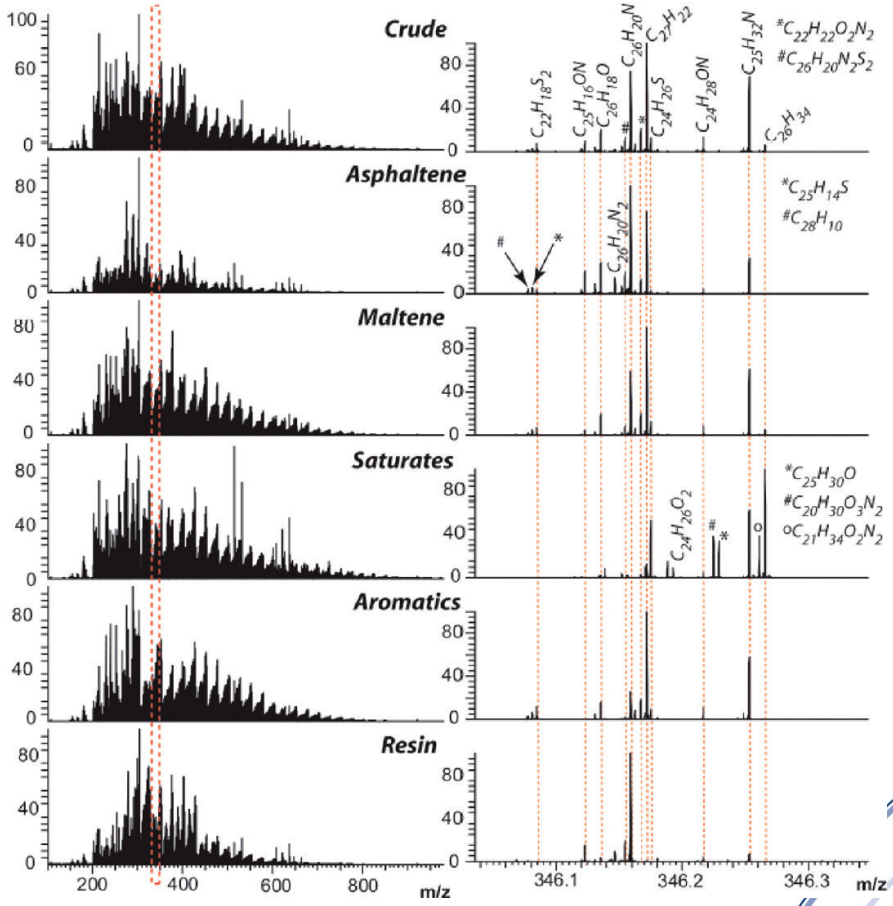
- Isomers ?
  - *m/z* depends only on molecular formula
- Ionization discrimination
  - In complex mixtures charge tend to go to the more basic/acidic species
  - Observation of species with higher ionization efficiency
- Compounds with low ionization efficiency?
- Addition of separation
  - Fractionation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

Saturated, Aromatics, Resins, Asphaltens

SARA





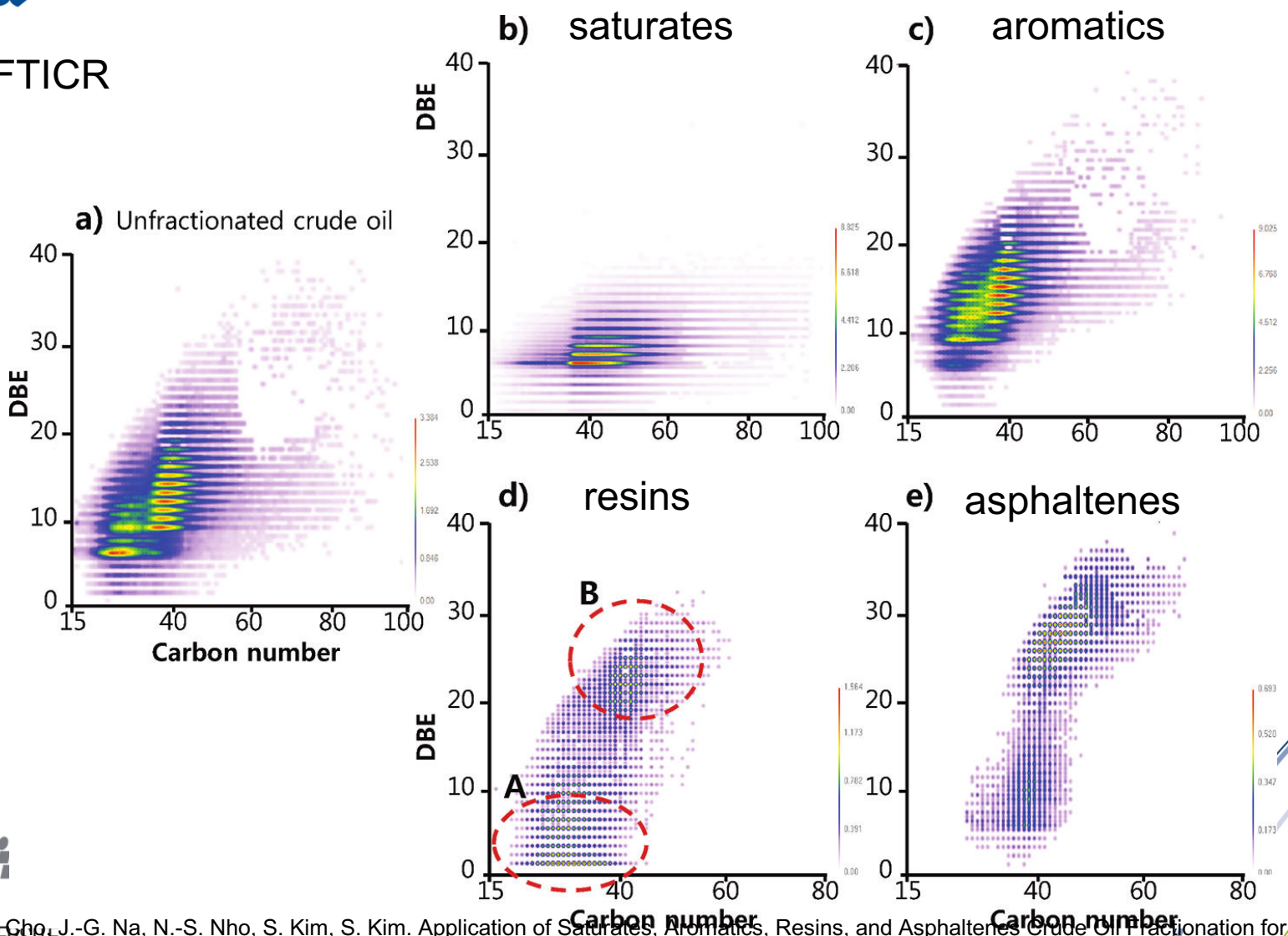


APLI-FTICR

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.

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.

Off line chromatographic separation

HPLC-2

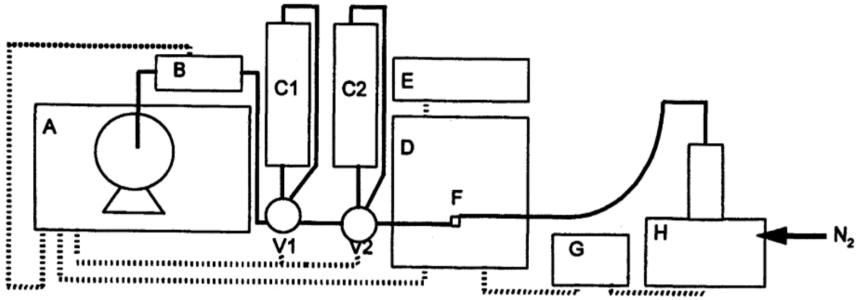
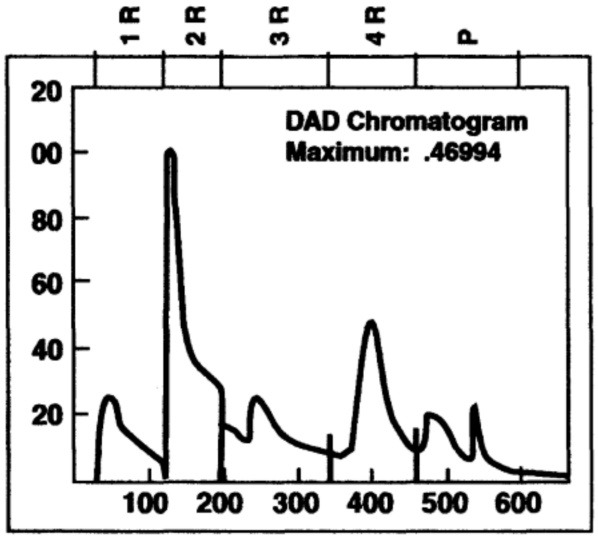
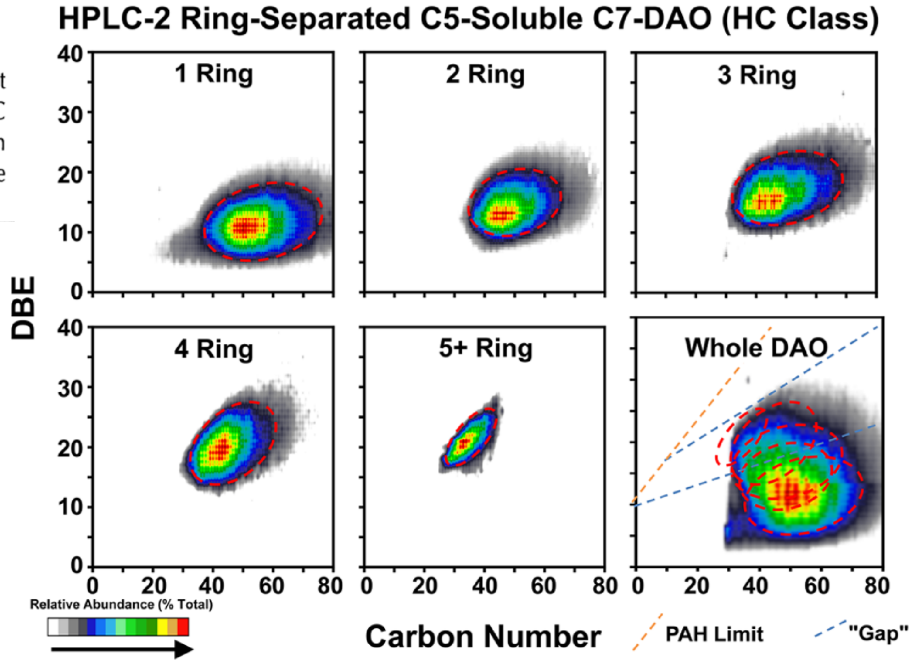


Figure 1. Commercial components assembled into the HPLC-2 system. A, Varian 5560 ternary solvent pump; B, Varian 8055 autosampler; C1, 4.6 × 2500 mm DNAP column; C2, 4.6 × 250 mm PAC column; D, HP 8451 diode array spectrophotometer (DAD); E, HP 9133 dual disk drive; F, Isco 1-mm flowcell; G, Kiethey 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

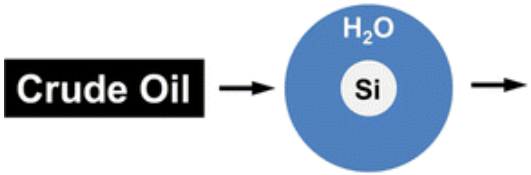


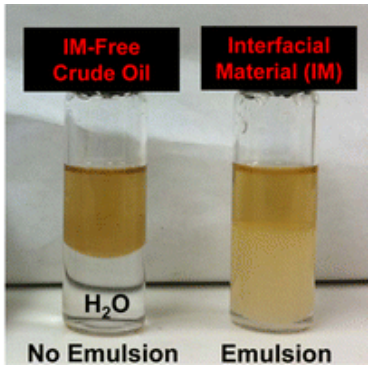
W. K. Robbins. Quantitative Measurement of Mass and Aromaticity Distributions for Heavy Distillates 1. Capabilities of the HPLC-2 System. *J. Chrom. Sci.* **1998**, *36*, 457.

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.

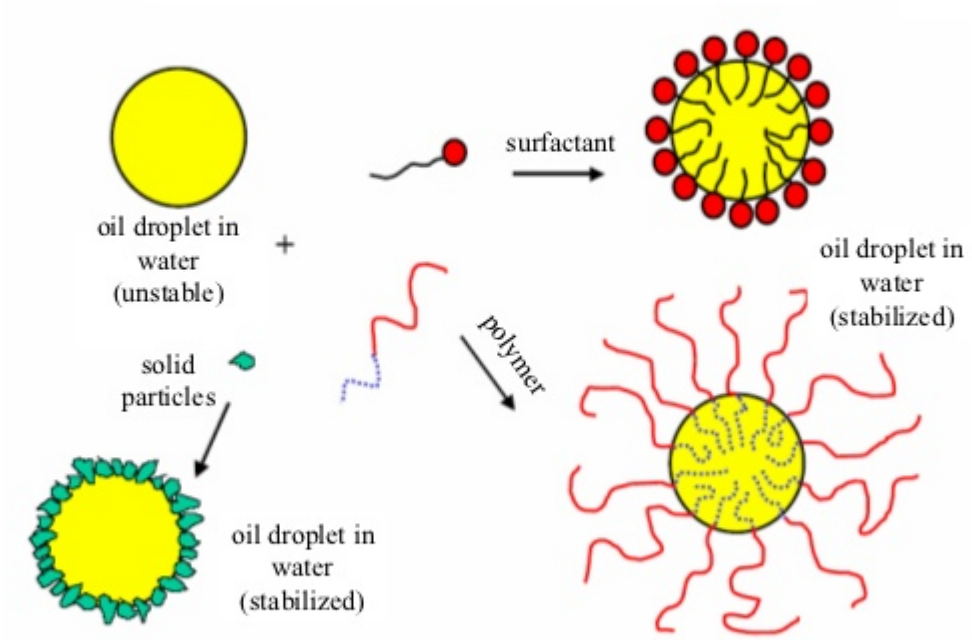
Emulsions

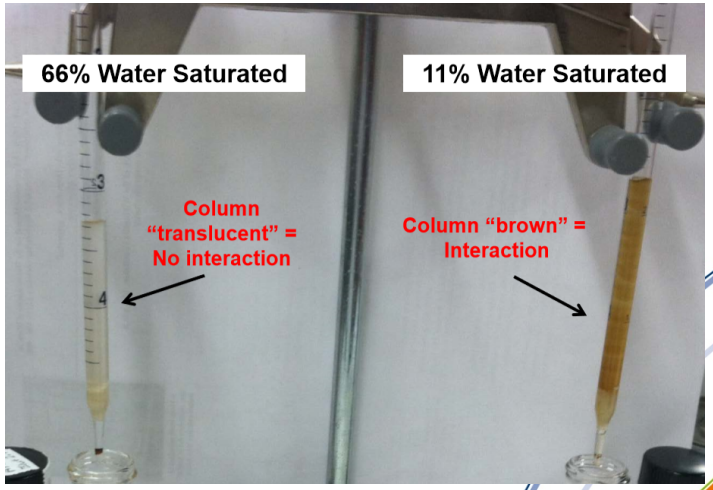
- Formation of emulsions can be a issue for oil production
- Some oils lead to higher amount of emulsions





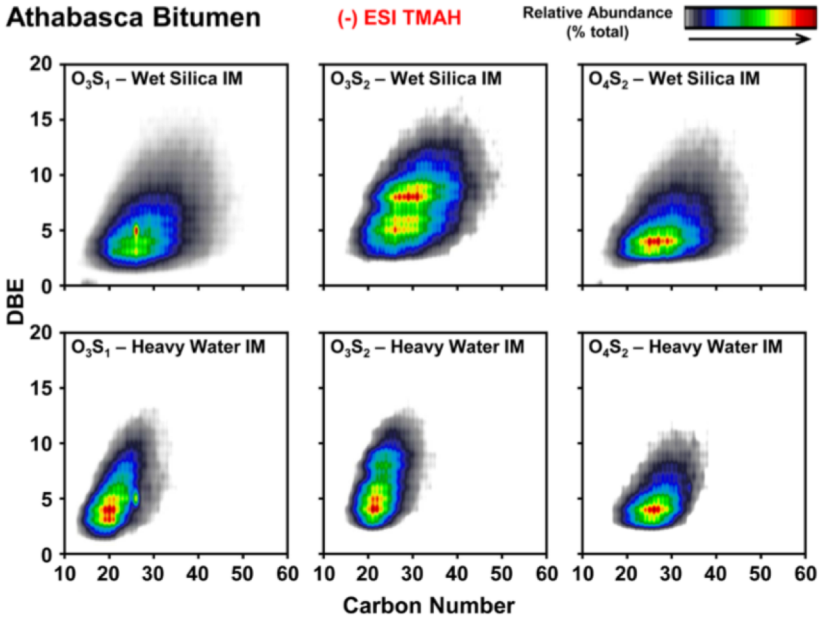
heptane/toluene
10:25 MeOH/toluene

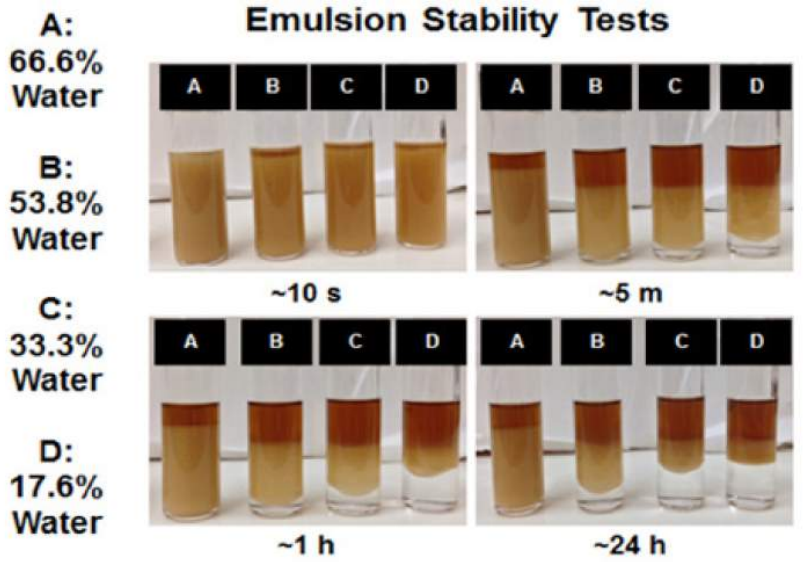


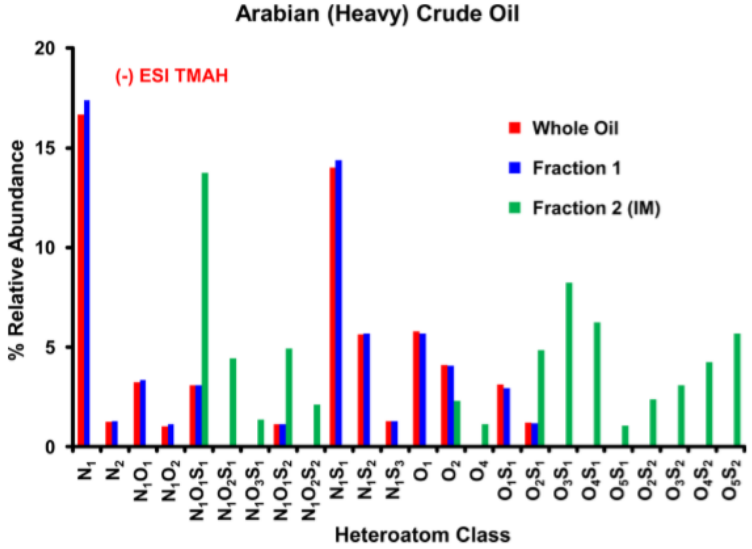


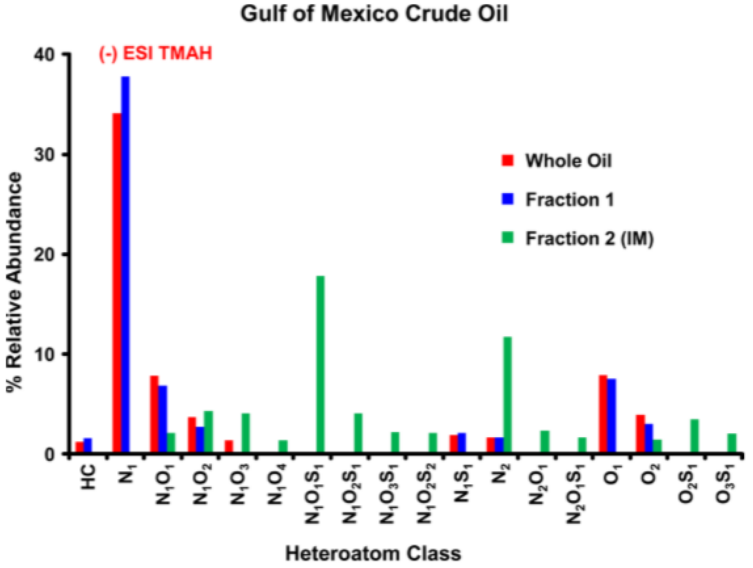
J. M. Jarvis, W. K. Robbins, Y. E. Corilo, R. P. Rodgers. Novel Method To Isolate Interfacial Material. *Energy Fuels* **2015**, *29*, 7058.

Laboratoire Cobra



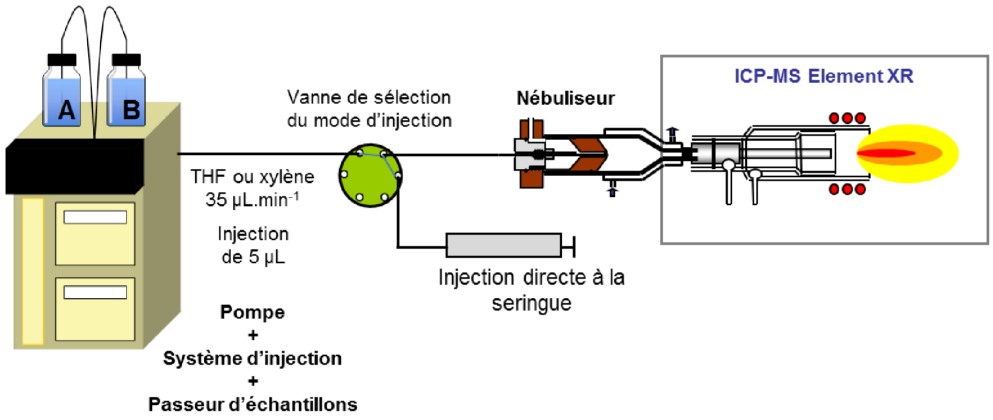


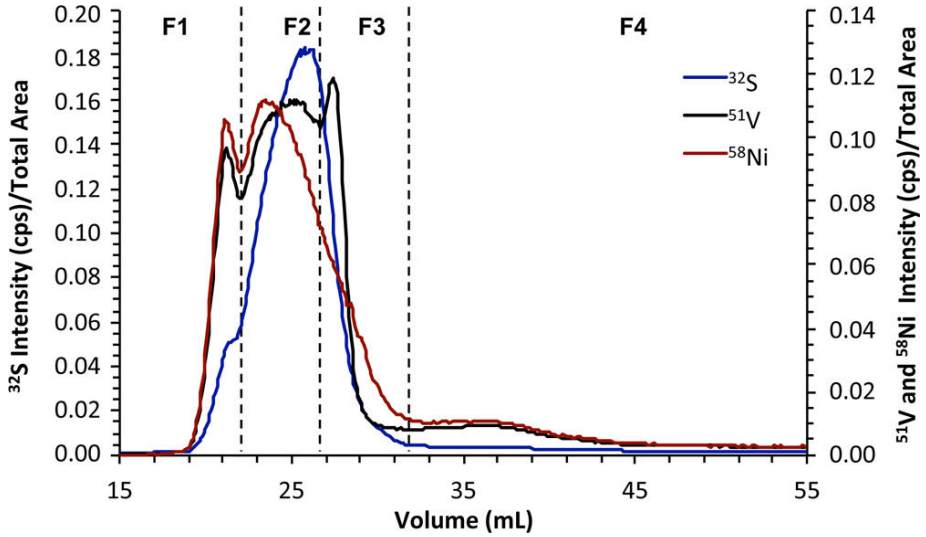


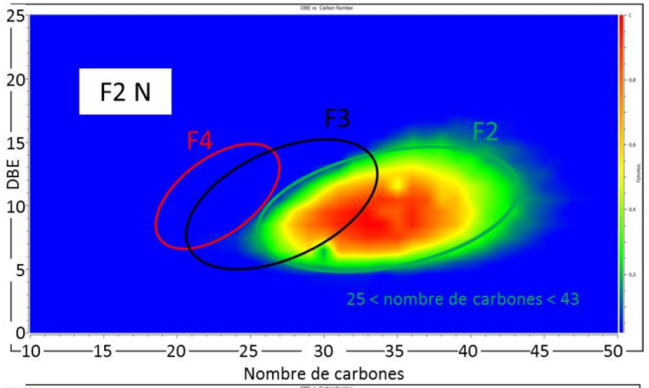


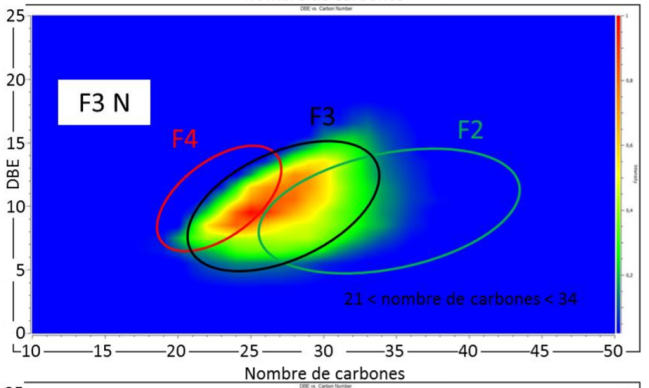
• GPC-ICPMS

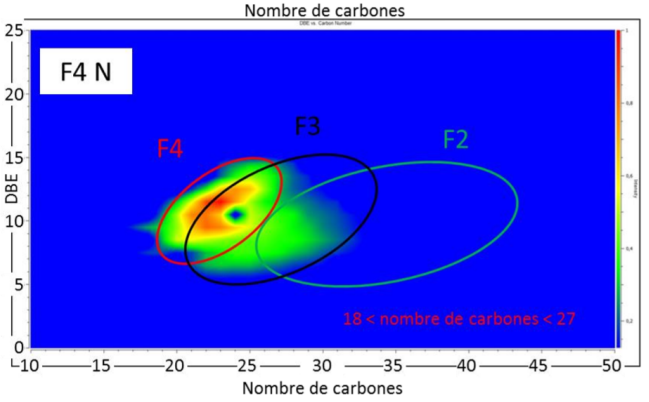
GPC











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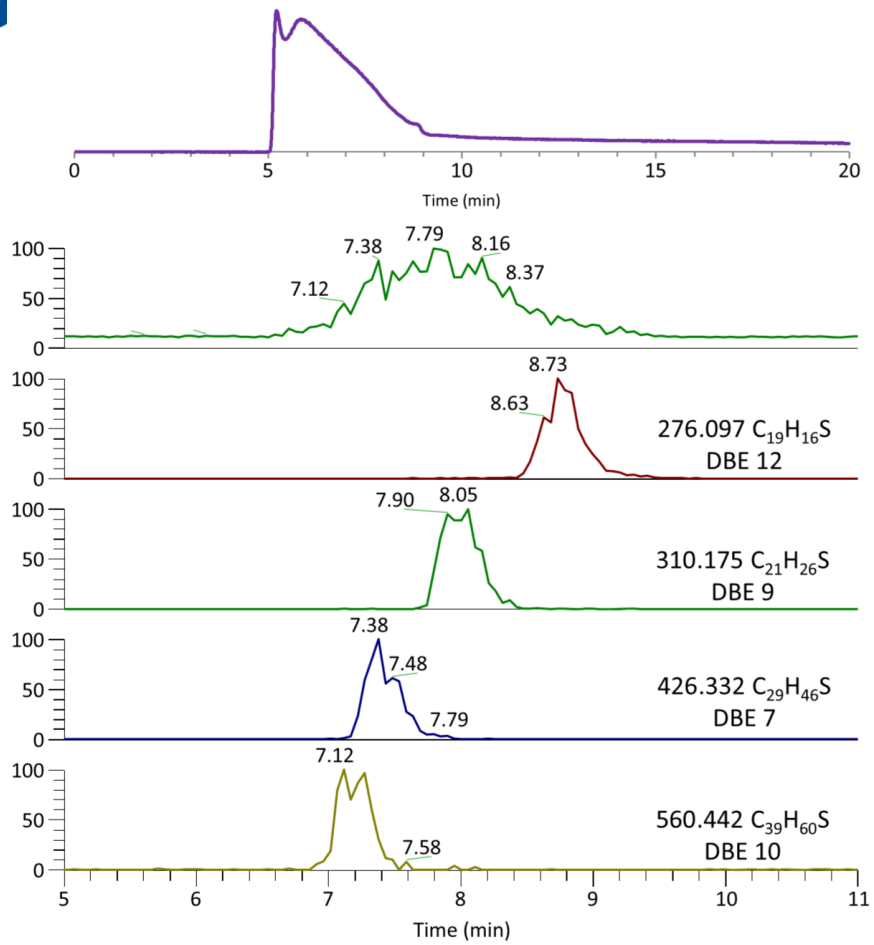
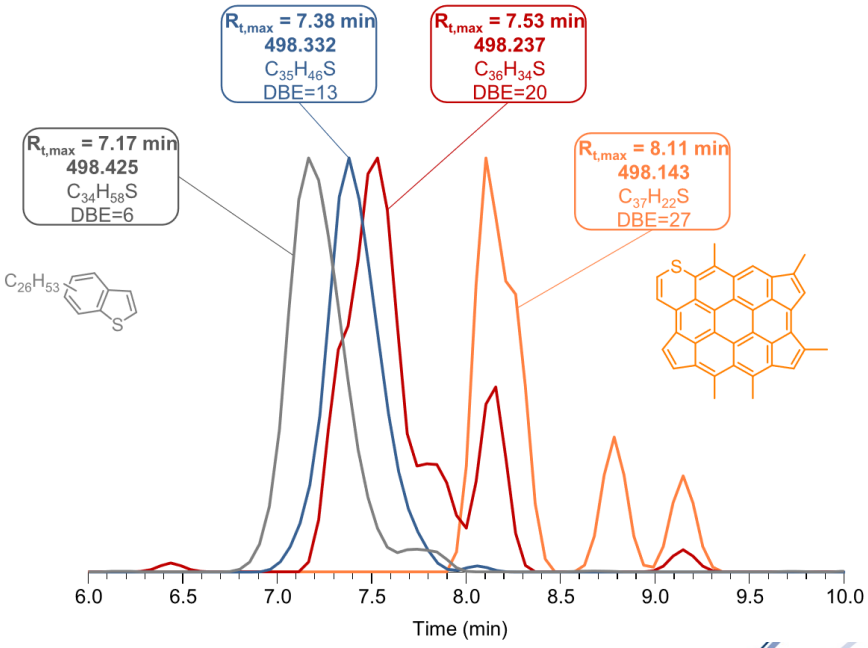
Thesis Alain Desprez

APPI-LTQ-Orbitrap

On line LC/MS



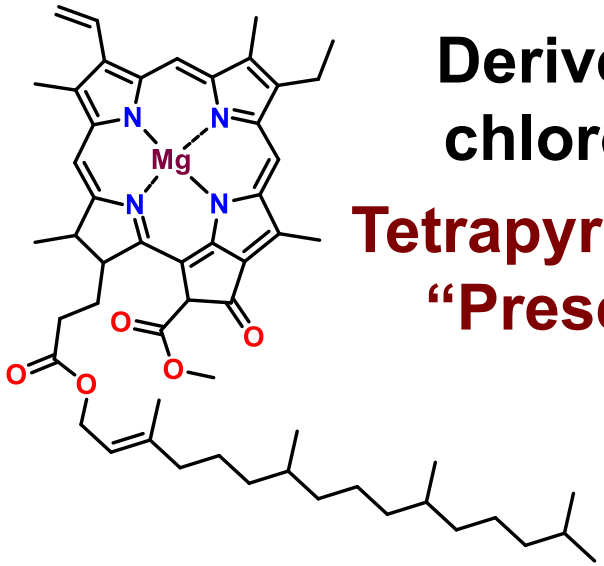


T. Ghislain, J. Molnarne Guricza, W. Schrader. Characterization of crude oil asphaltenes by coupling size-exclusion chromatography directly to an ultrahigh-resolution mass spectrometer. Rapid commun. mass spectrom. 2017, 31, 495.

Petroporphyrins

Low Concentration "<1%"

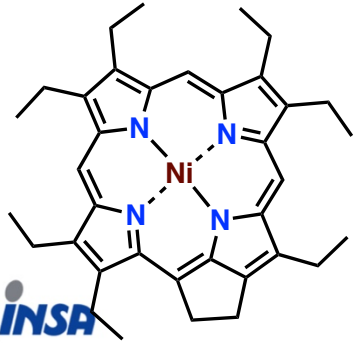
Need Purification Process

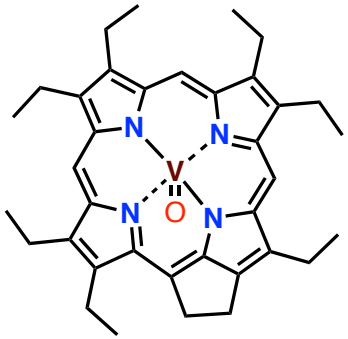


Derived from chlorophylls

Tetrapyrrole core "Preserved"

Nickel and Vanadyl Porphyrins





Catalyst Poisoning

Asphaltenes

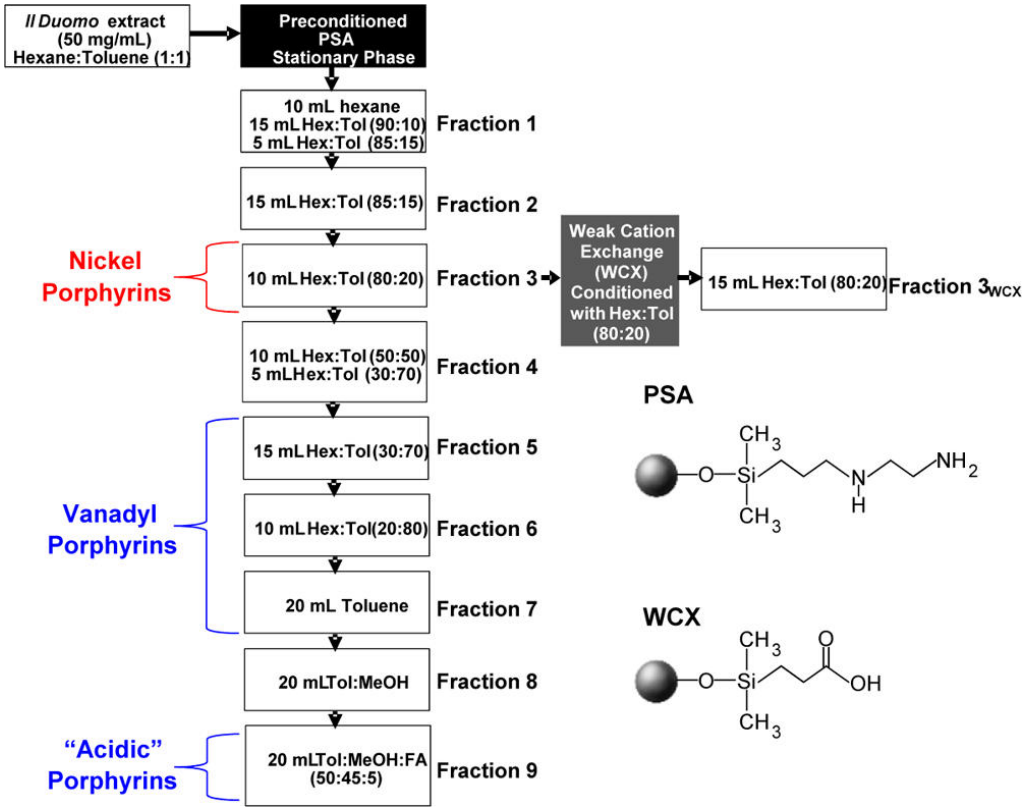
Heaviest fractions

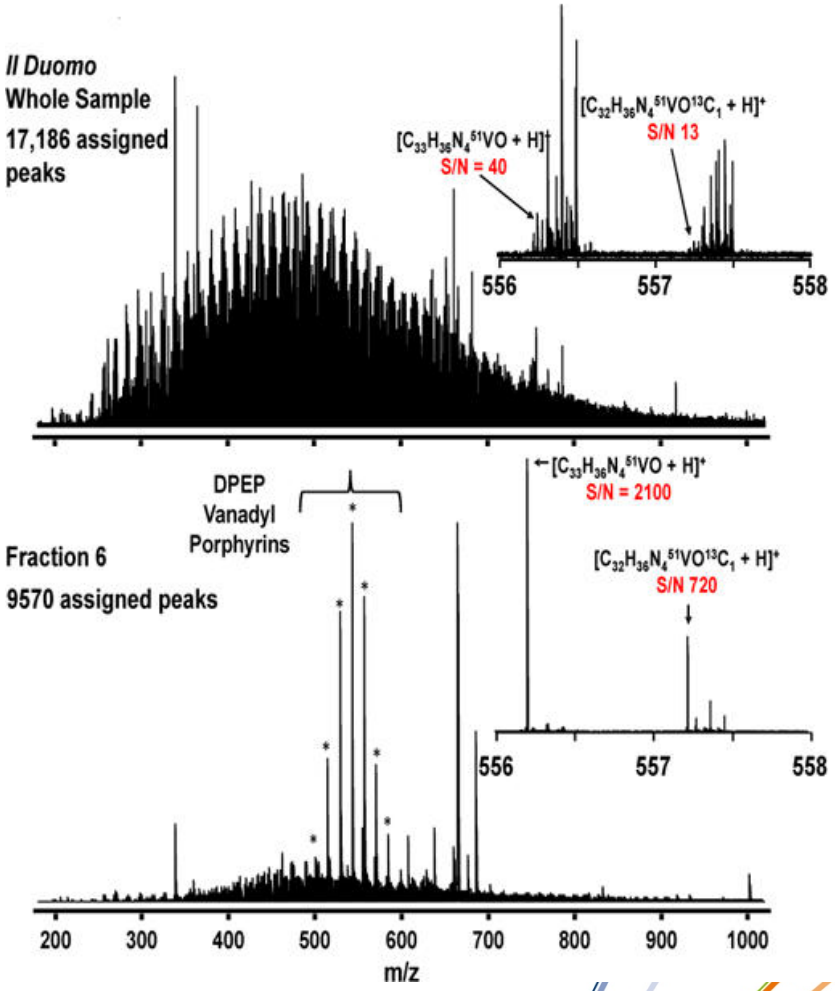
Maturity

Measure of maturity

Petroporphyrins fractionation

Chromatographic enrichment





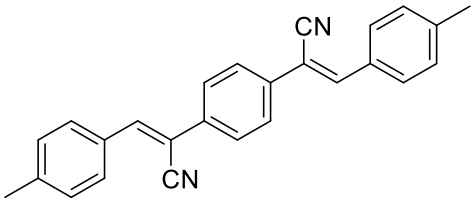
Putman JC, Rowland SM, Corilo YE, McKenna AM. *Anal Chem* 2014; 86: 10708-10715

Electron transfer MALDI

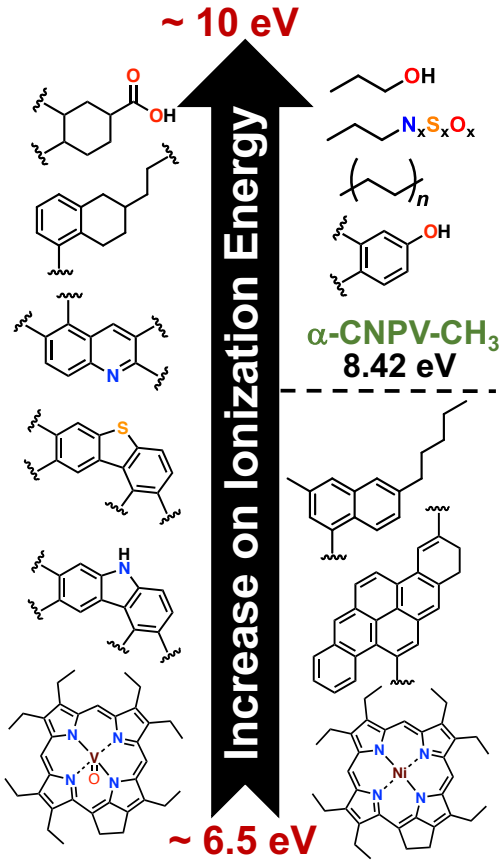
- Selective ionization

$$[M] + h\nu \rightarrow [M]^{+\bullet}$$

$$[M]^{+\bullet} + [A] \rightarrow [A]^{+\bullet} + [M] \qquad M(IE) > A(IE)$$

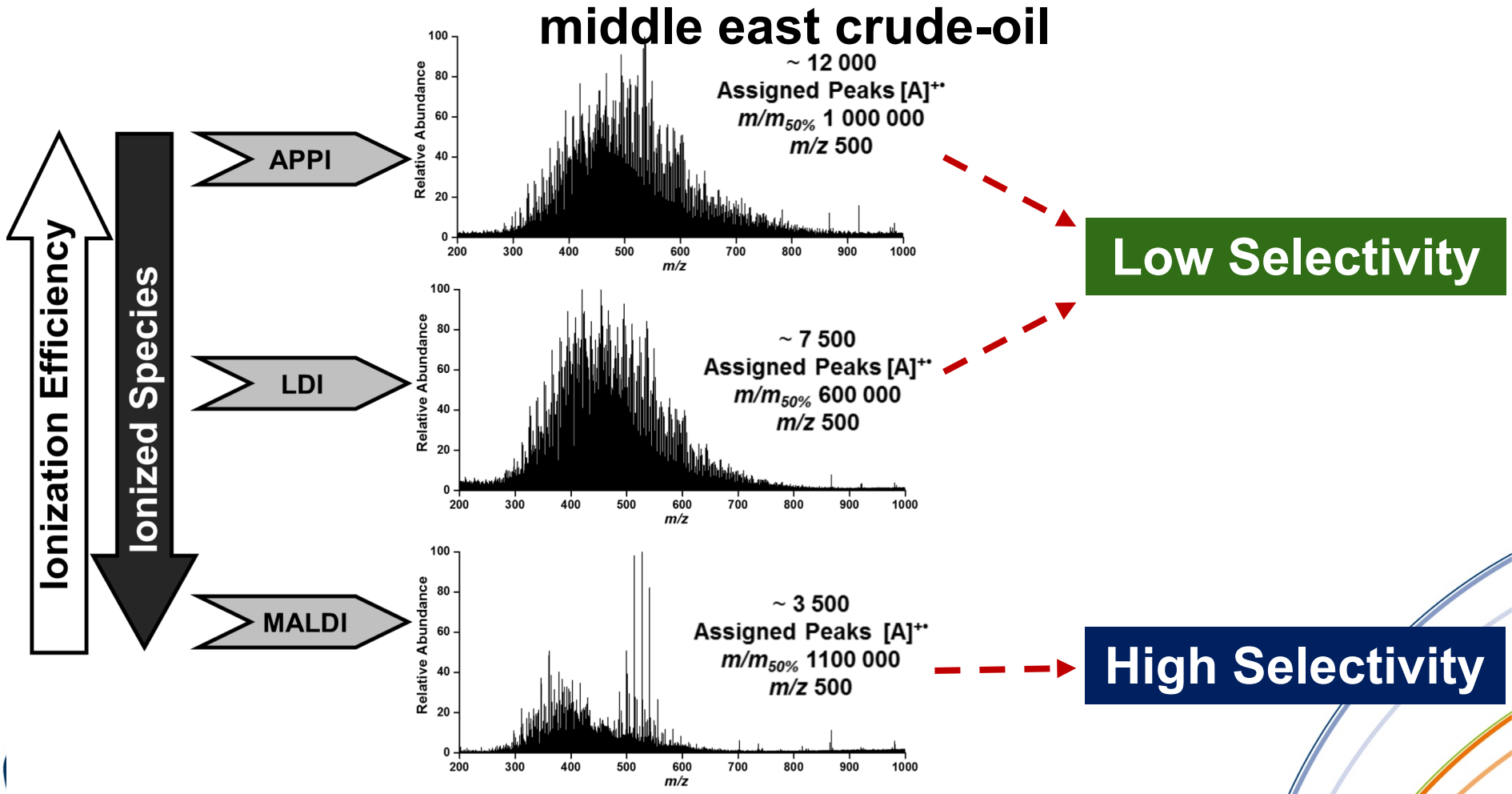


α-cyano-methyl-phenylenevinylene
α-CNPV-CH_3



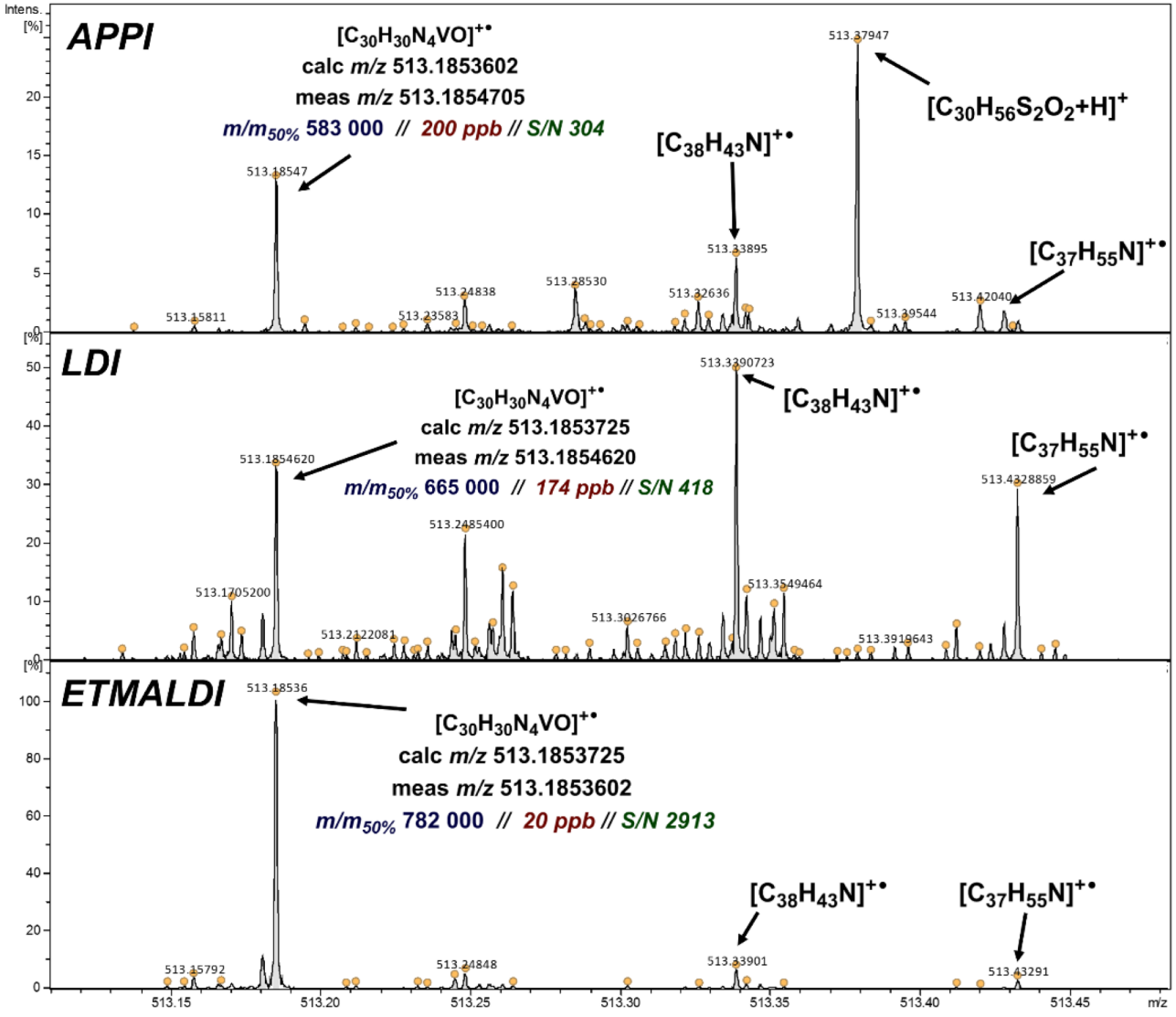
Giraldo-Dávila D, Chacón-Patiño ML, Ramirez-Pradilla JS, et al. Selective ionization by electron-transfer MALDI-MS of vanadyl porphyrins from crude oils. *Fuel* 2018; 226: 103-111.

ET-MALDI vs APPI and LDI

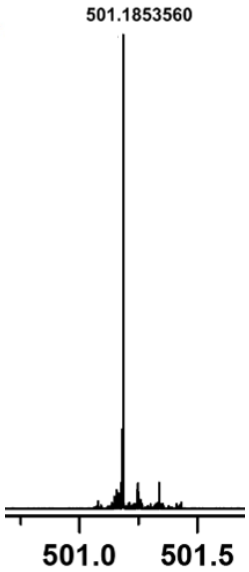


Juan S. Ramírez-Pradilla, Cristian Blanco-Tirado, Marie-Hubert-Roux, Pierre Giusti, Carlos Afonso and Marianny Y. Combariza, E&F in preparation

ET-MALDI vs APPI and LDI



Attribution of Ni and VO porphyrins

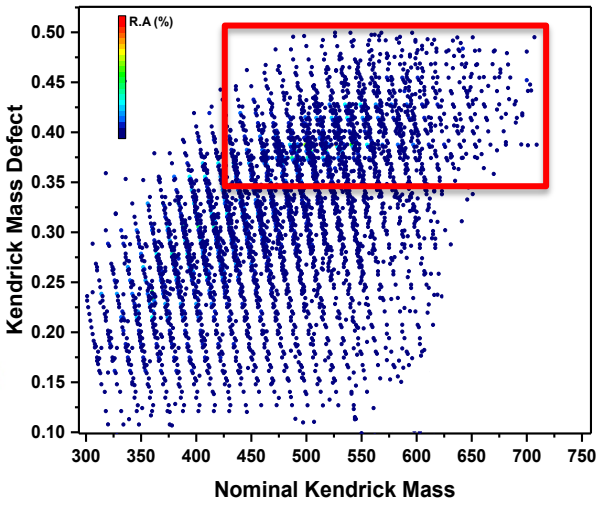


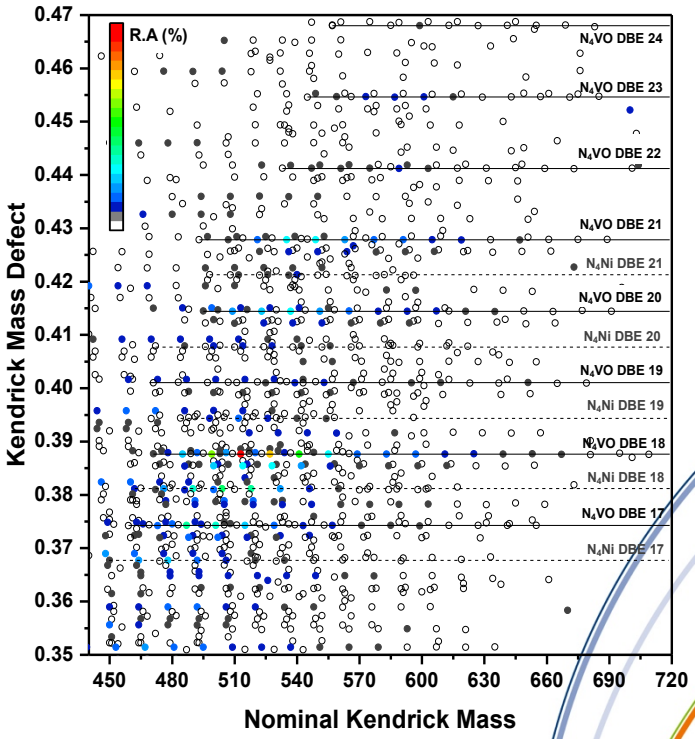
Max: $N_4Ni_1O_4S_2V_1$

Meas. m/z 513.185359

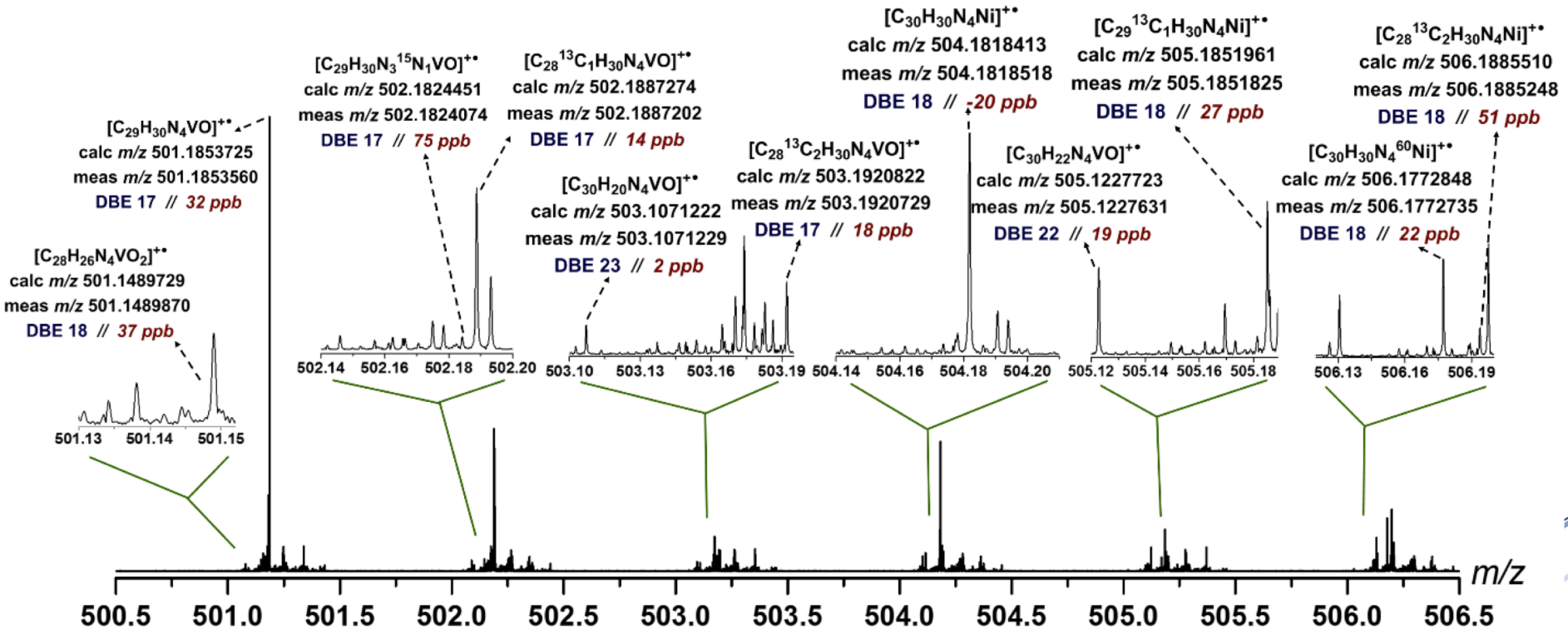
#	Ion Formula	m/z	err [ppm]
1	C30H30N4OV	513.185370	0.0
2	C38H25O2	513.184906	-0.9
3	C27H38N3NiV	513.185324	-0.1
4	C30H38S2V	513.184902	-0.9

Ni: 57.935342 u
V: 50.943957 u

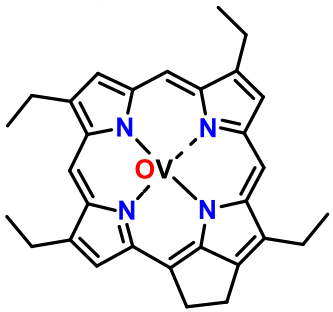




Isotope fine structue

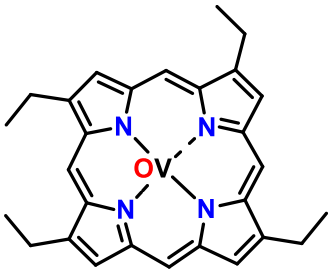


Assignments



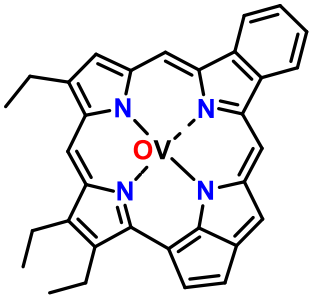
DBE=18

$C_{30}H_{30}N_4VO$



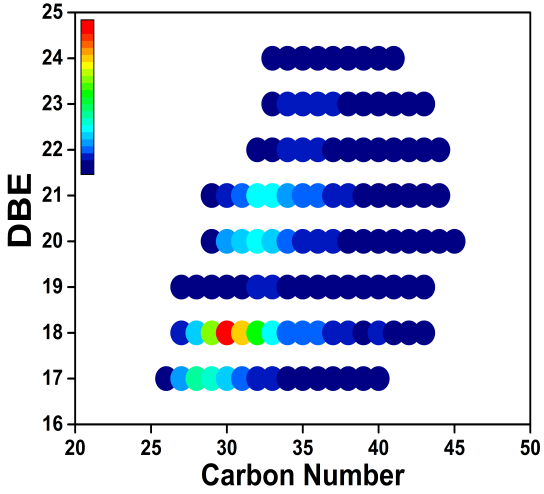
DBE=17

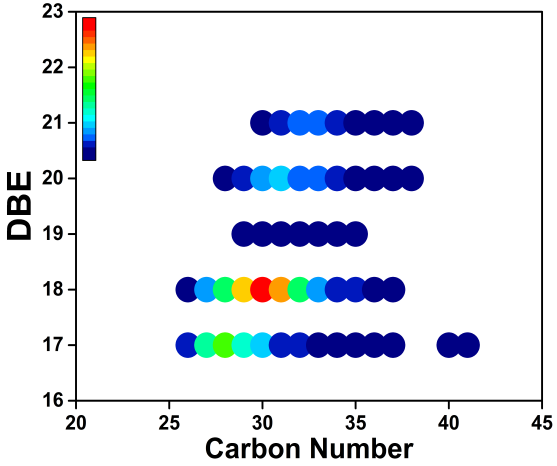
$C_{28}H_{28}N_4VO$

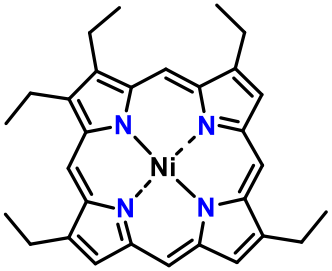


DBE=22

$C_{32}H_{26}N_4VO$

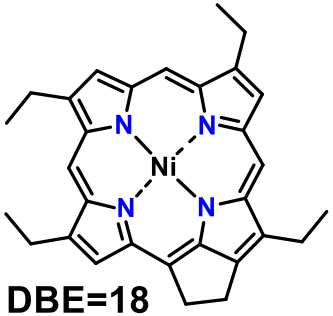






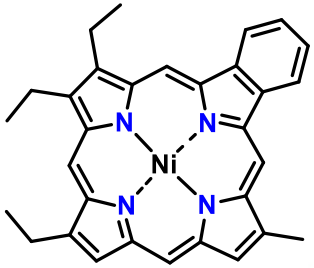
DBE=17

$C_{30}H_{32}N_4Ni$



DBE=18

$C_{30}H_{30}N_4Ni$

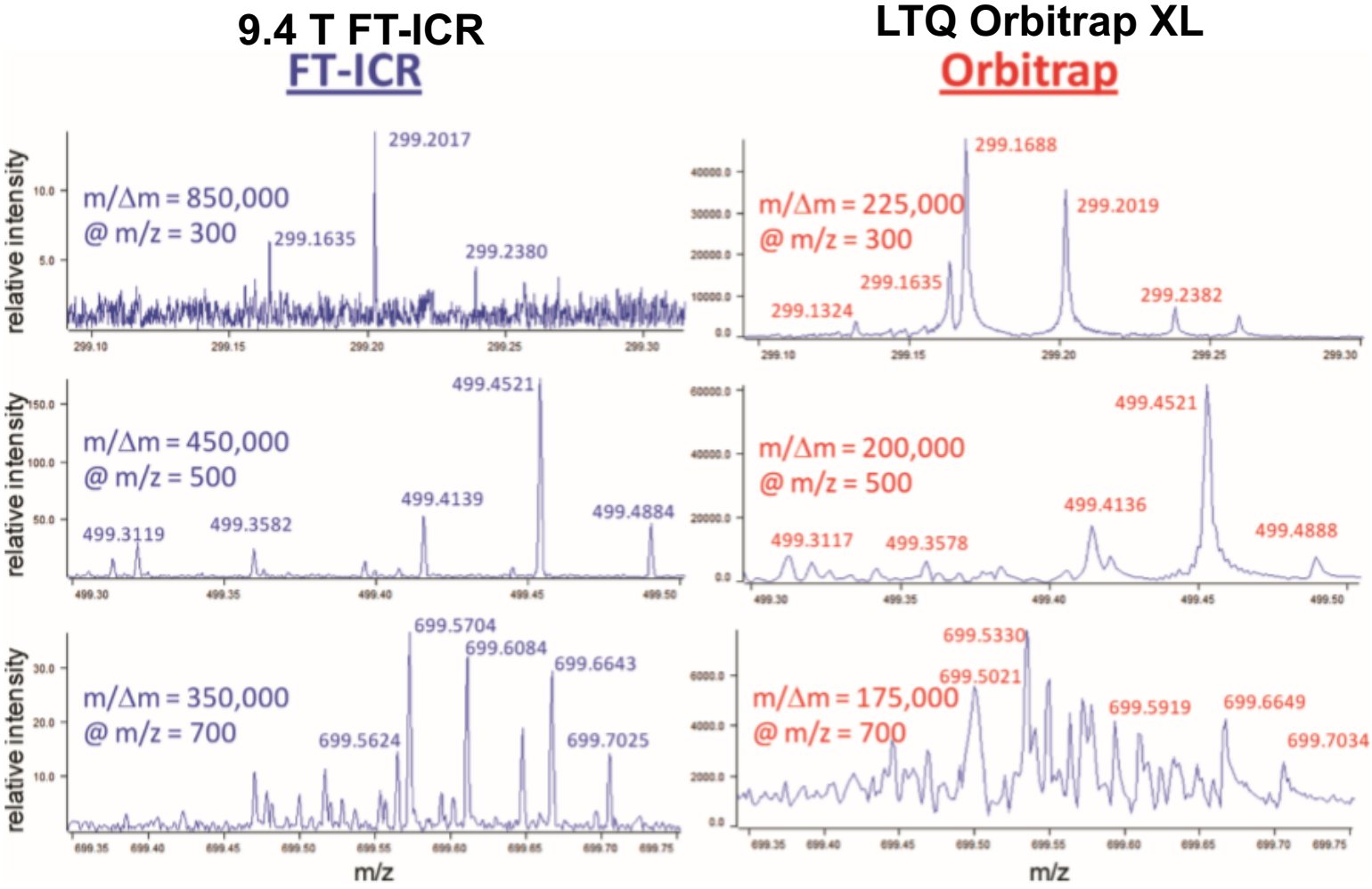


DBE=20

$C_{31}H_{28}N_4Ni$

150 vanadyl porphyrins
100 nickel porphyrins

Orbitrap



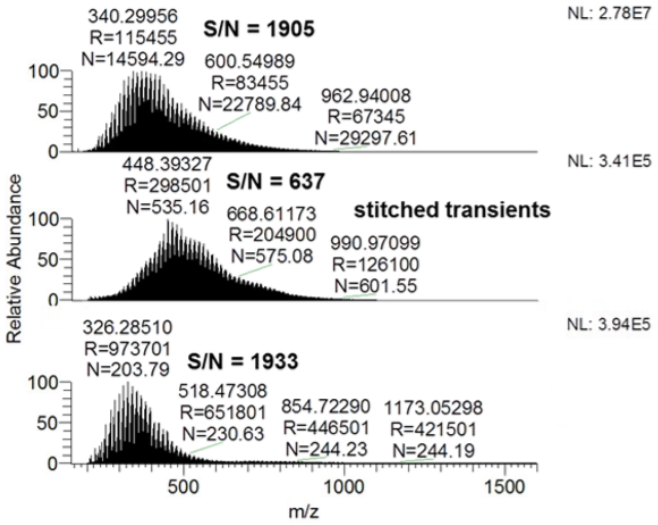
A. E. Pomerantz, O. C. Mullins, G. Paul, J. Ruzicka, M. Sanders. Orbitrap Mass Spectrometry: A Proposal for Routine Analysis of Nonvolatile Components of Petroleum. *Energy Fuels* **2011**, *25*, 3077.

Orbitrap

Std. Orbitrap, 0.5 sec transient

FTICR, 3 sec transient

MegaOrbitrap, 3 sec transient

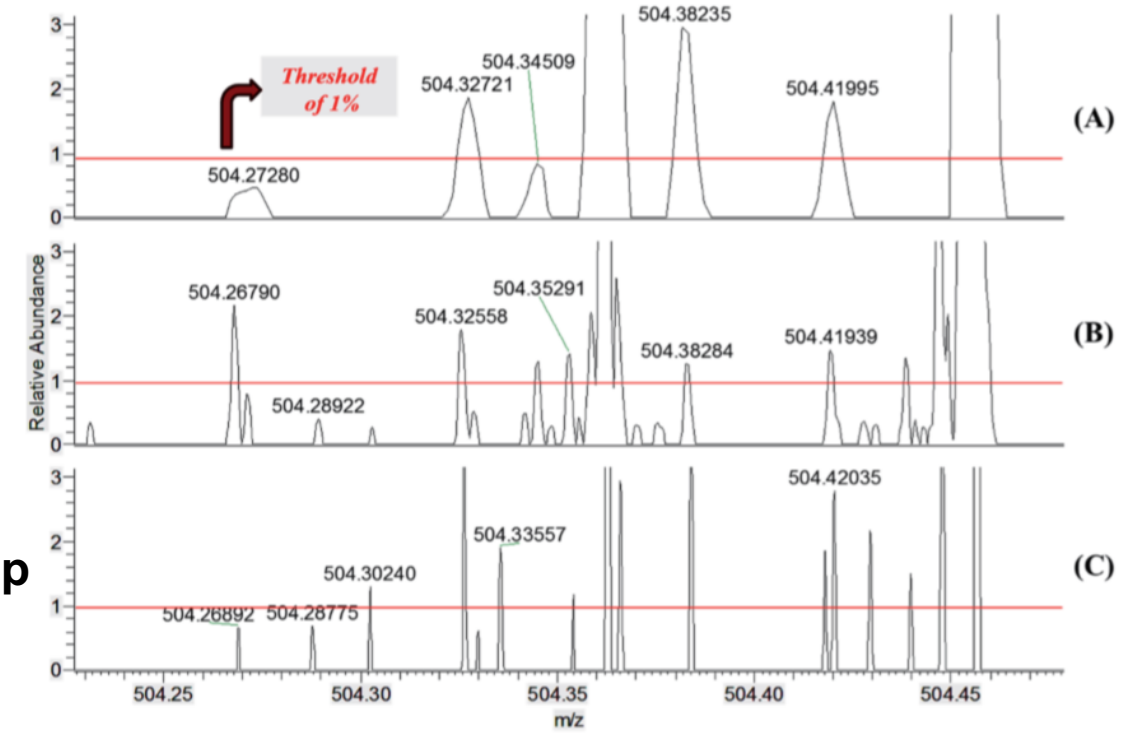


ESI(+)

Std Orbitrap 0.5 s

7 T FTICR 3 s

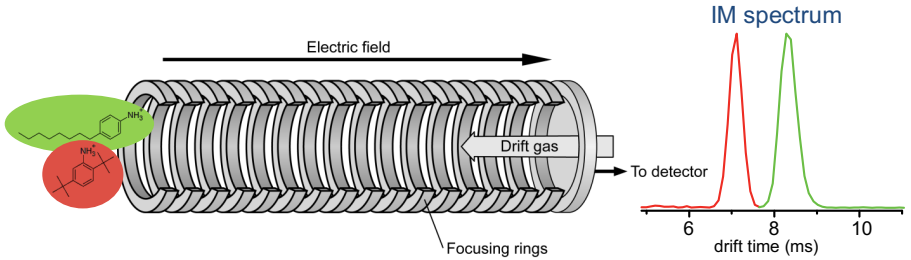
Mega Orbitrap 3 s (eFT)



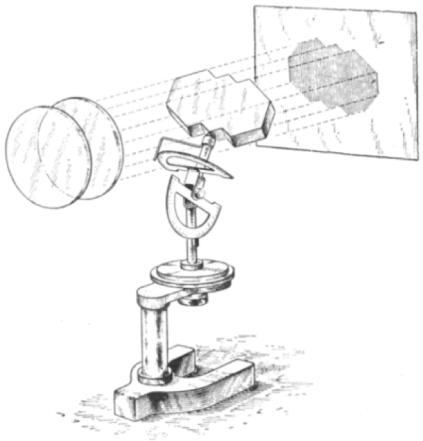
E. M. Schmidt, M. A. Pudenzi, J. M. Santos, C. F. F. Angolini, R. C. L. Pereira, Y. S. Rocha, E. Denisov, E. Damoc, A. Makarov, M. N. Eberlin. Petroleomics via Orbitrap mass spectrometry with resolving power above 1 000 000 at m/z 200. *RSC Advances* **2018**, *8*, 6183

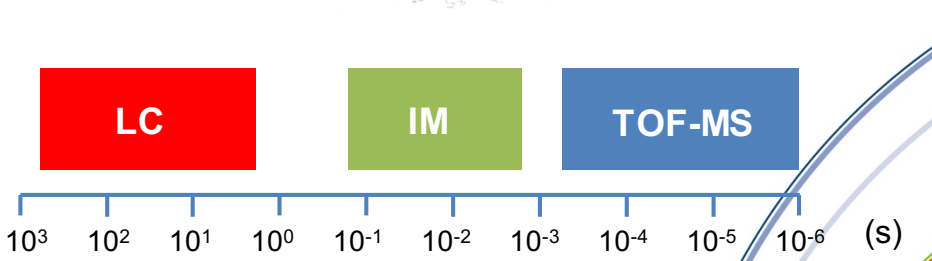
Ion Mobility

- 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



$$v_d = K \times E$$

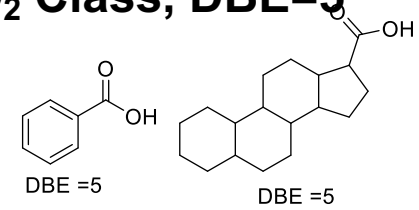


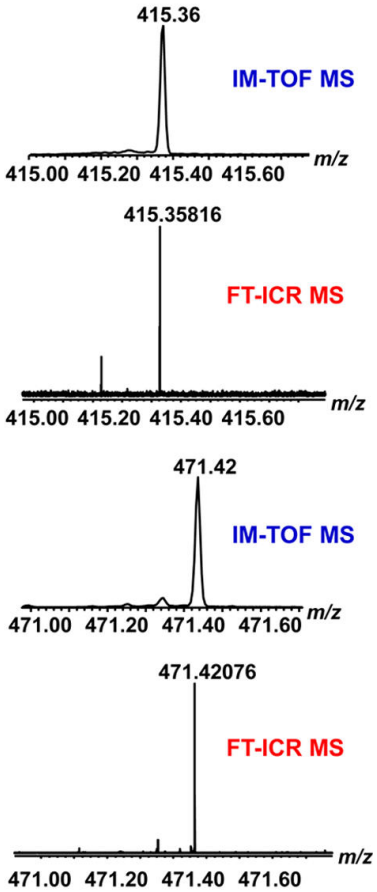


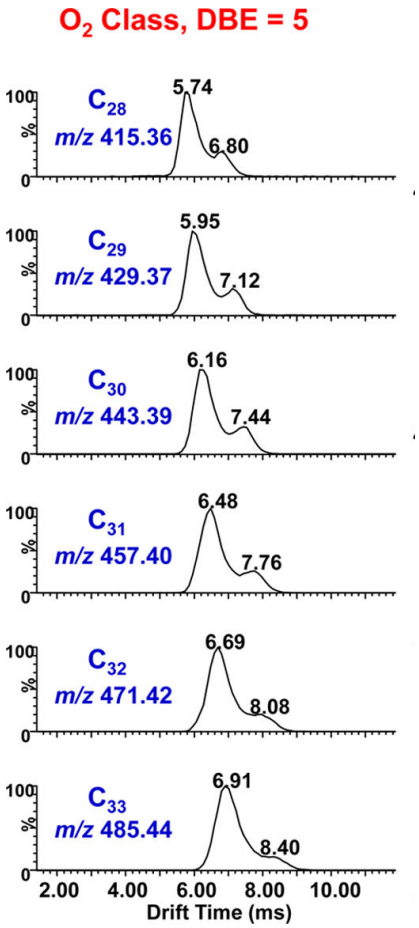
Edward Mack, Jr, *J. Am. Chem. Soc.* 1925, 47, 2468

IMS-TOF and FTMS

ESI(-)
O_2 Class, DBE=5

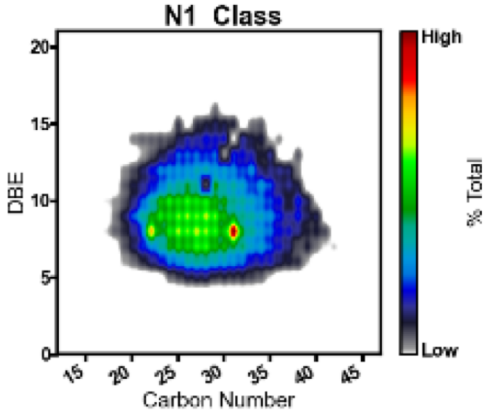


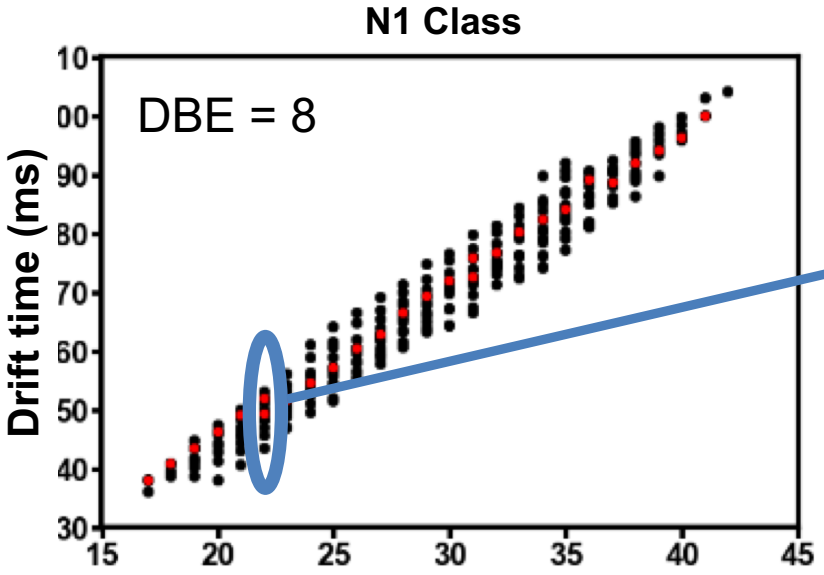


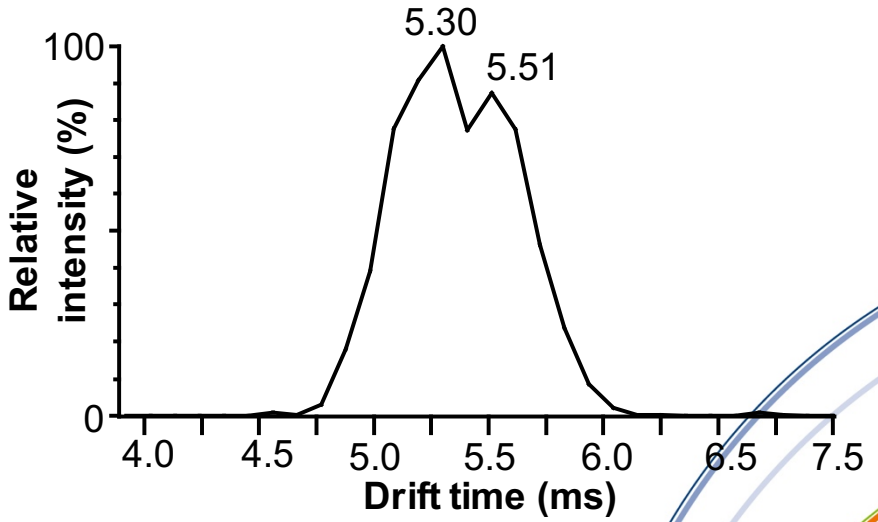


P. M. Lalli, Y. E. Corilo, S. M. Rowland, A. G. Marshall, R. P. Rodgers. Isomeric Separation and Structural Characterization of Acids in Petroleum by Ion Mobility Mass Spectrometry. *Energy Fuels* **2015**, *29*, 3626.

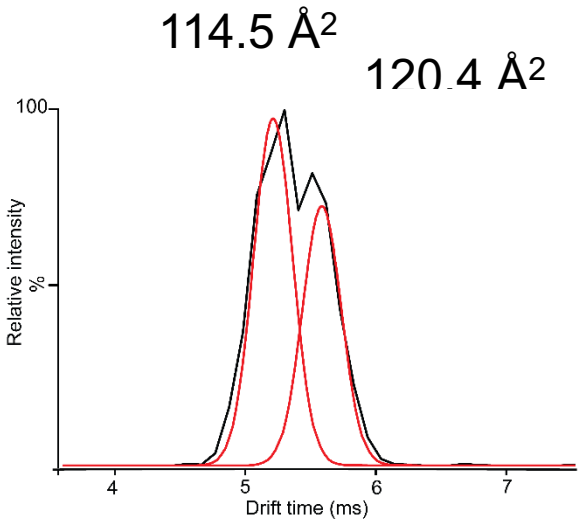
ESI(+)







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.



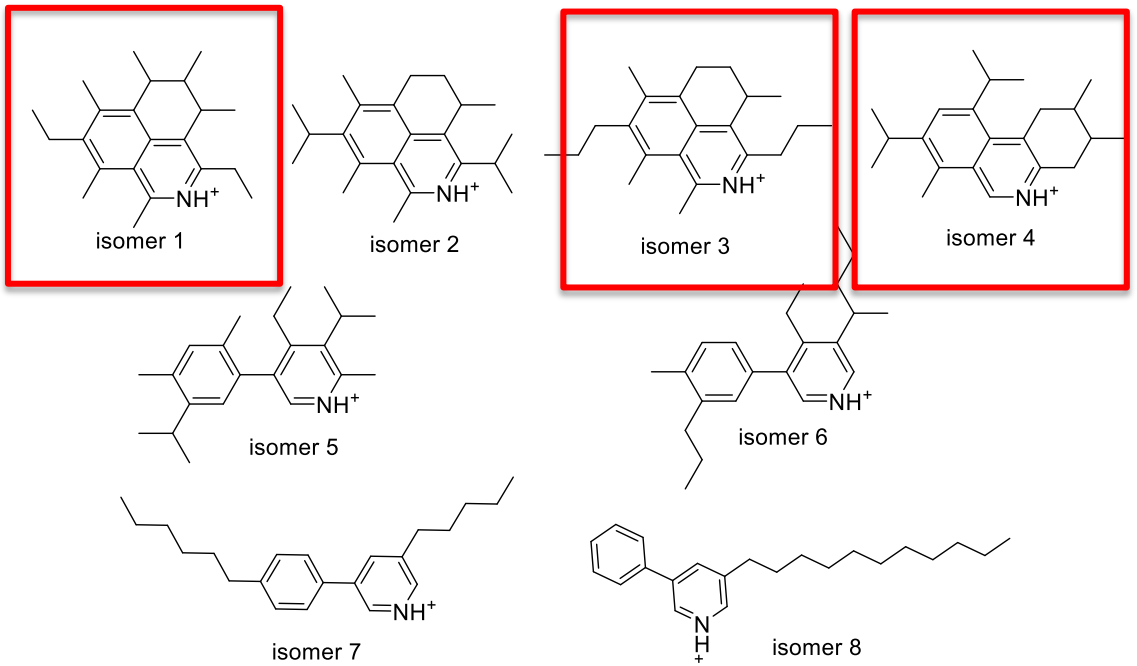
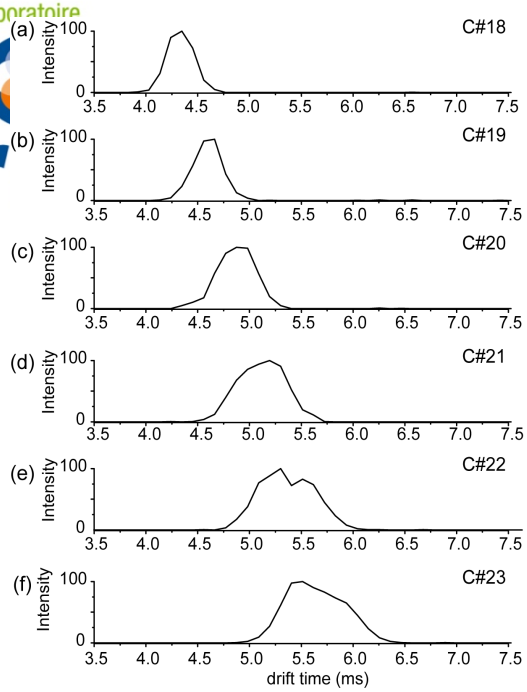


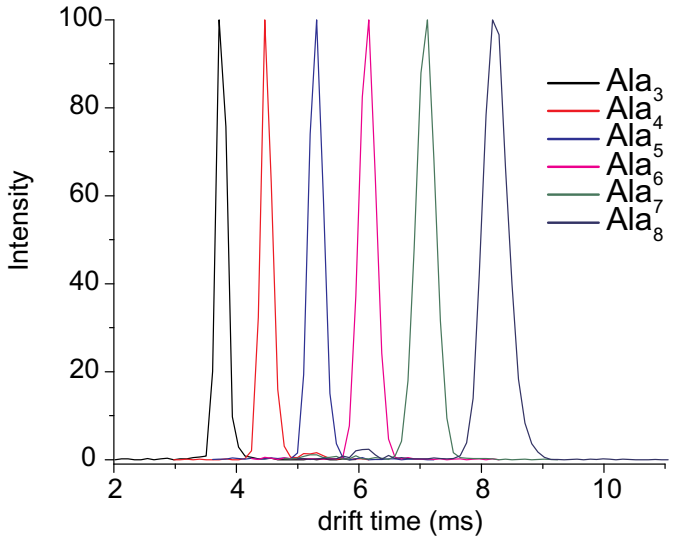
Table 1: Theoretical CCS (Å²) values for putative $C_{22}H_{32}N^+$ isomers	
isomer	TM CS (Å²)
1	115.0
2	117.5
3	119.8
4	120.4
5	121.8
6	127.4
7	139.0
8	136.8

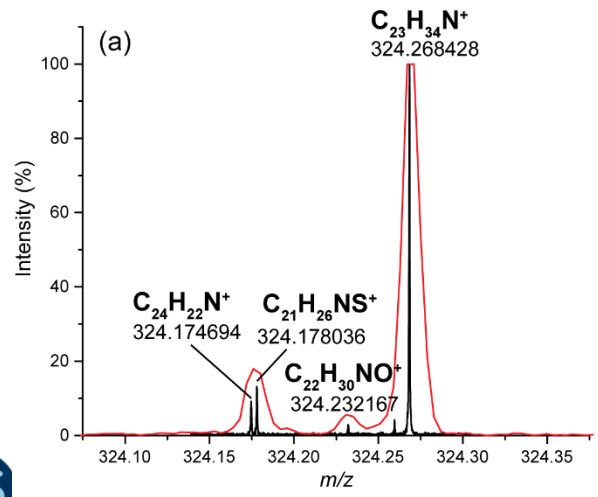
MMFF94 force field

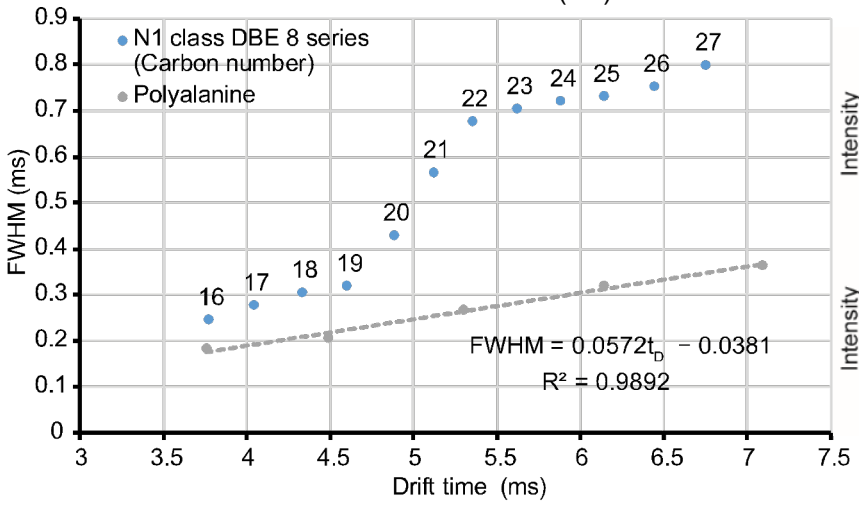
IMS Peak width

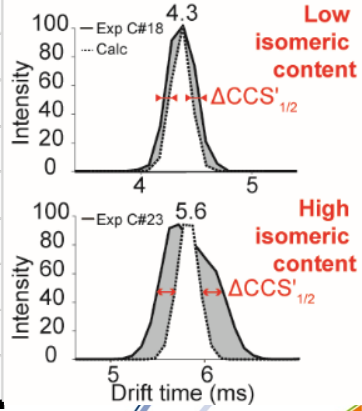
DBE=8







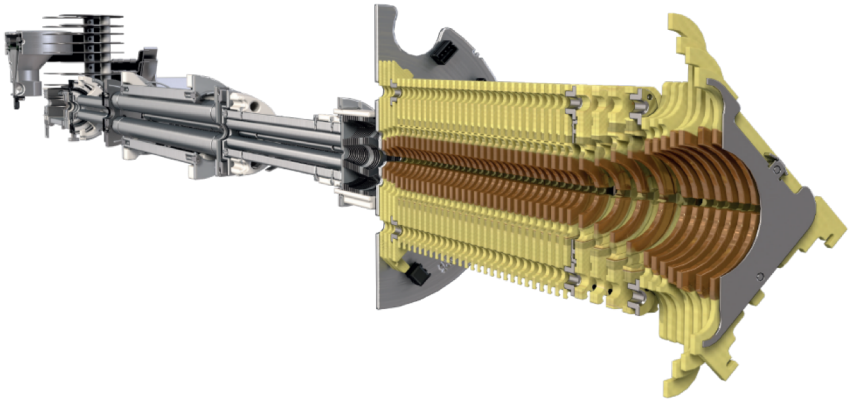




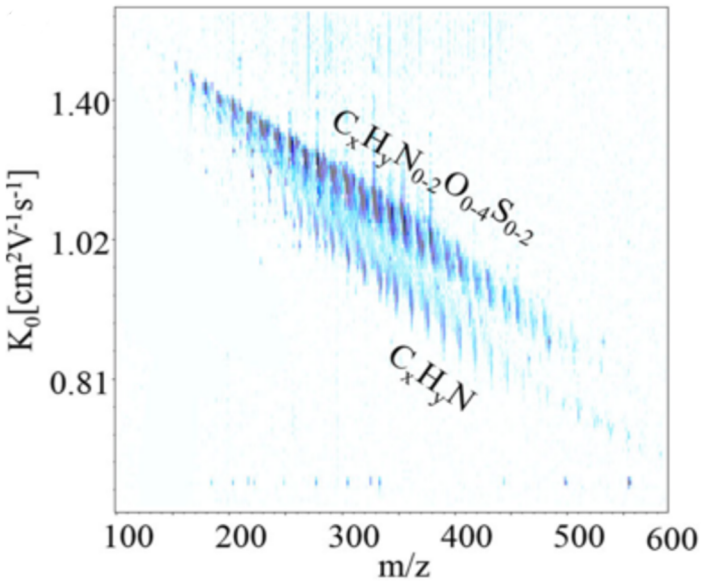
M. Farenc, B. Paupy, S. Marceau, E. Riches, C. Afonso, P. Giusti. Effective Ion Mobility Peak Width as a New Isomeric Descriptor for the Untargeted Analysis of Complex Mixtures Using Ion Mobility-Mass Spectrometry. *J Am Soc Mass Spectrom* **2017**, *28*, 2476.

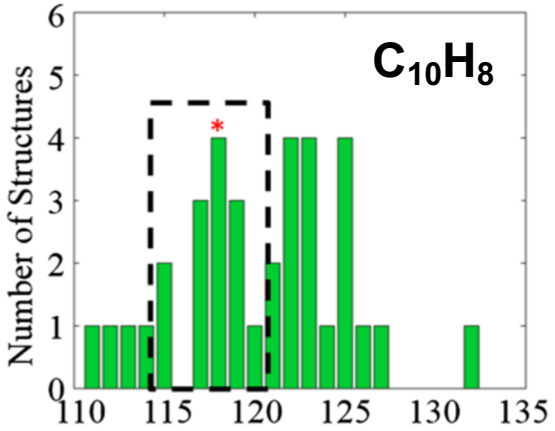
IMS with FTMS

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

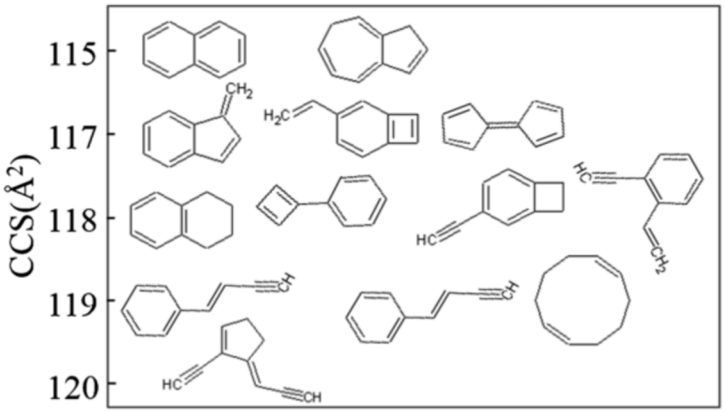


TIMS-FTICR





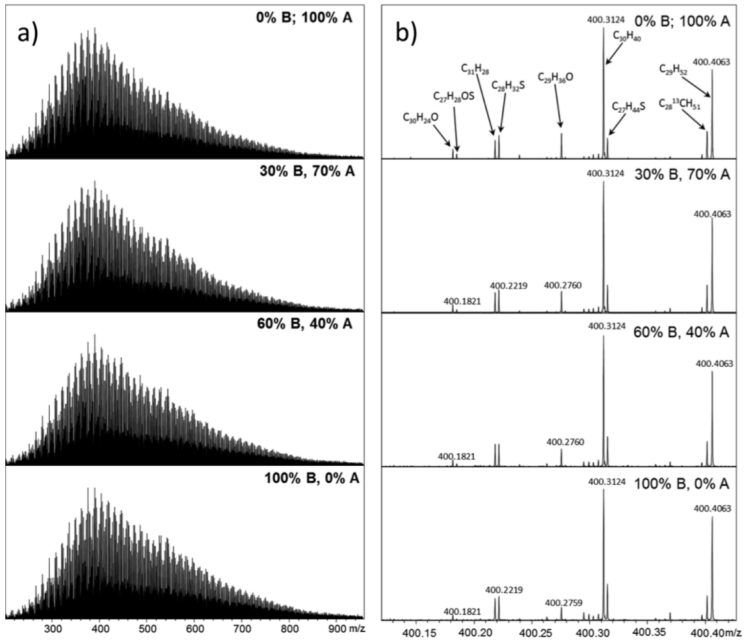
* 2% experimental value

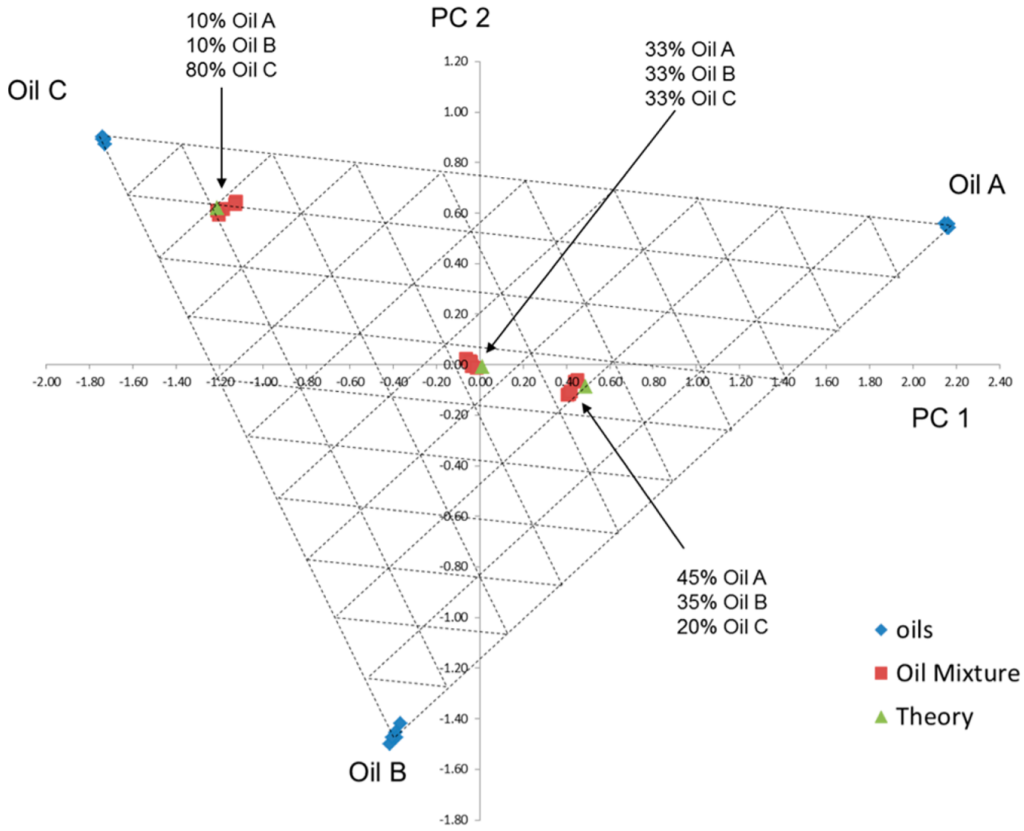


P. Benigni, R. Marin, F. Fernandez-Lima. Towards unsupervised polyaromatic hydrocarbons structural assignment from SA-TIMS-FTMS data. *Int J Ion Mobil Spectrom* **2015**, *18*, 15

Chemometrics

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





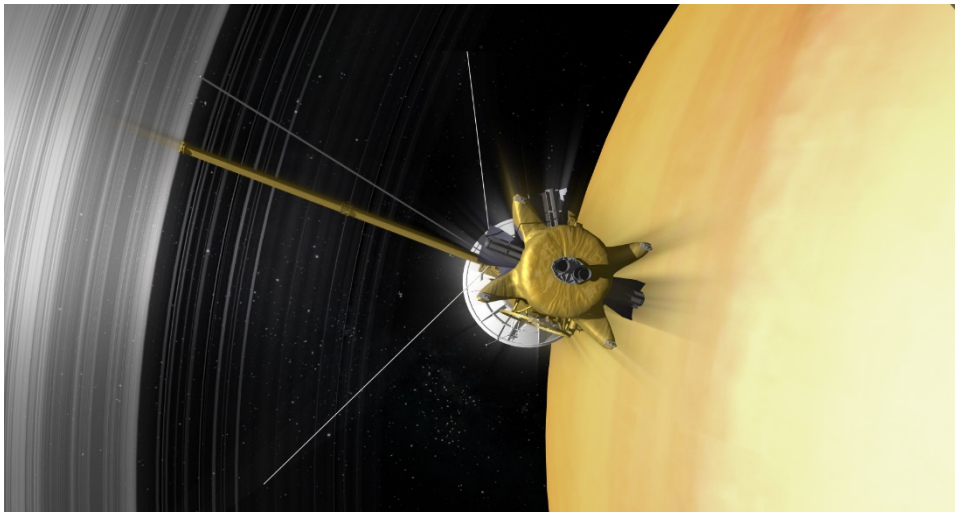
M. Witt, W. Timm. Determination of Simulated Crude Oil Mixtures from the North Sea Using Atmospheric Pressure Photoionization Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2015**, *30*, 3707.

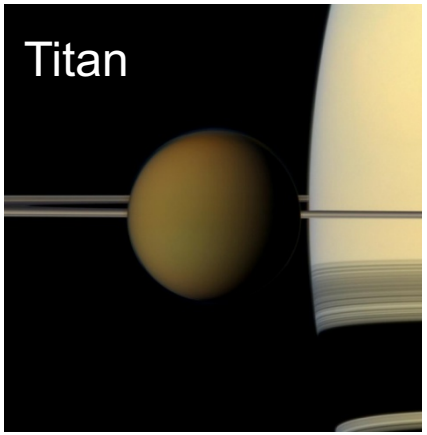
Nathalie Carasco (Univ. Paris Saclay)

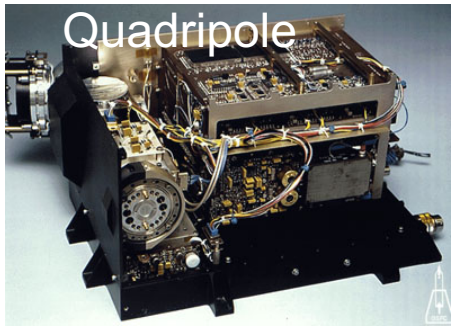
Tholins

Thèse de Julien Maillard

Cassini Mission



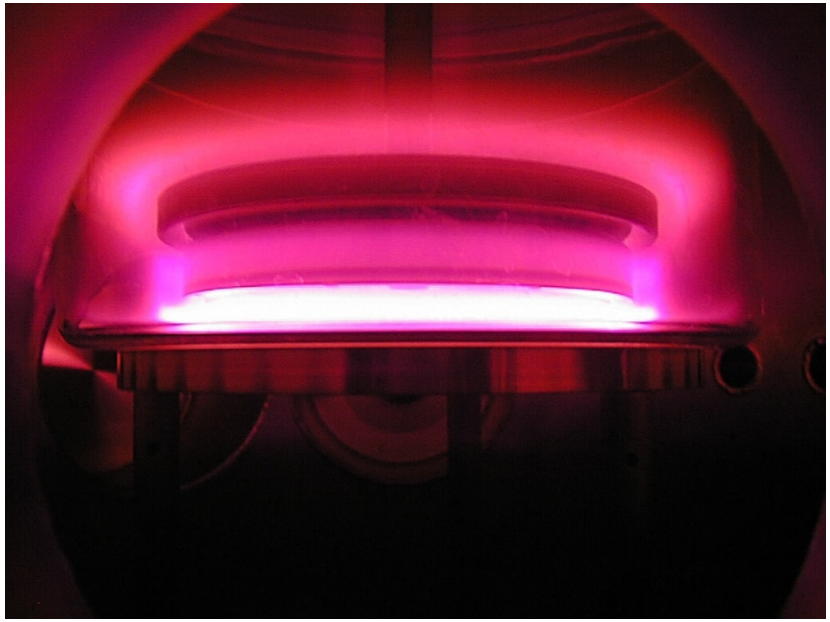




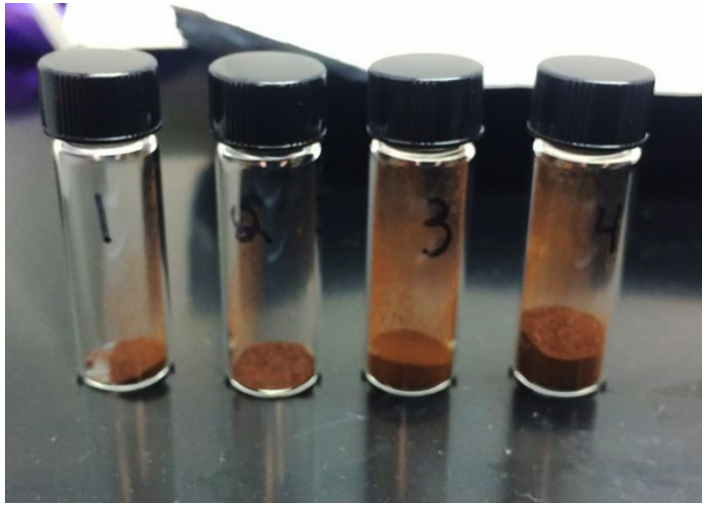
95 % à 98,4 % d'azote
1,6 % à 5 % de méthane

Tholins

Preparation of tholins in PAMPRE setup



View of the PAMPRE set up



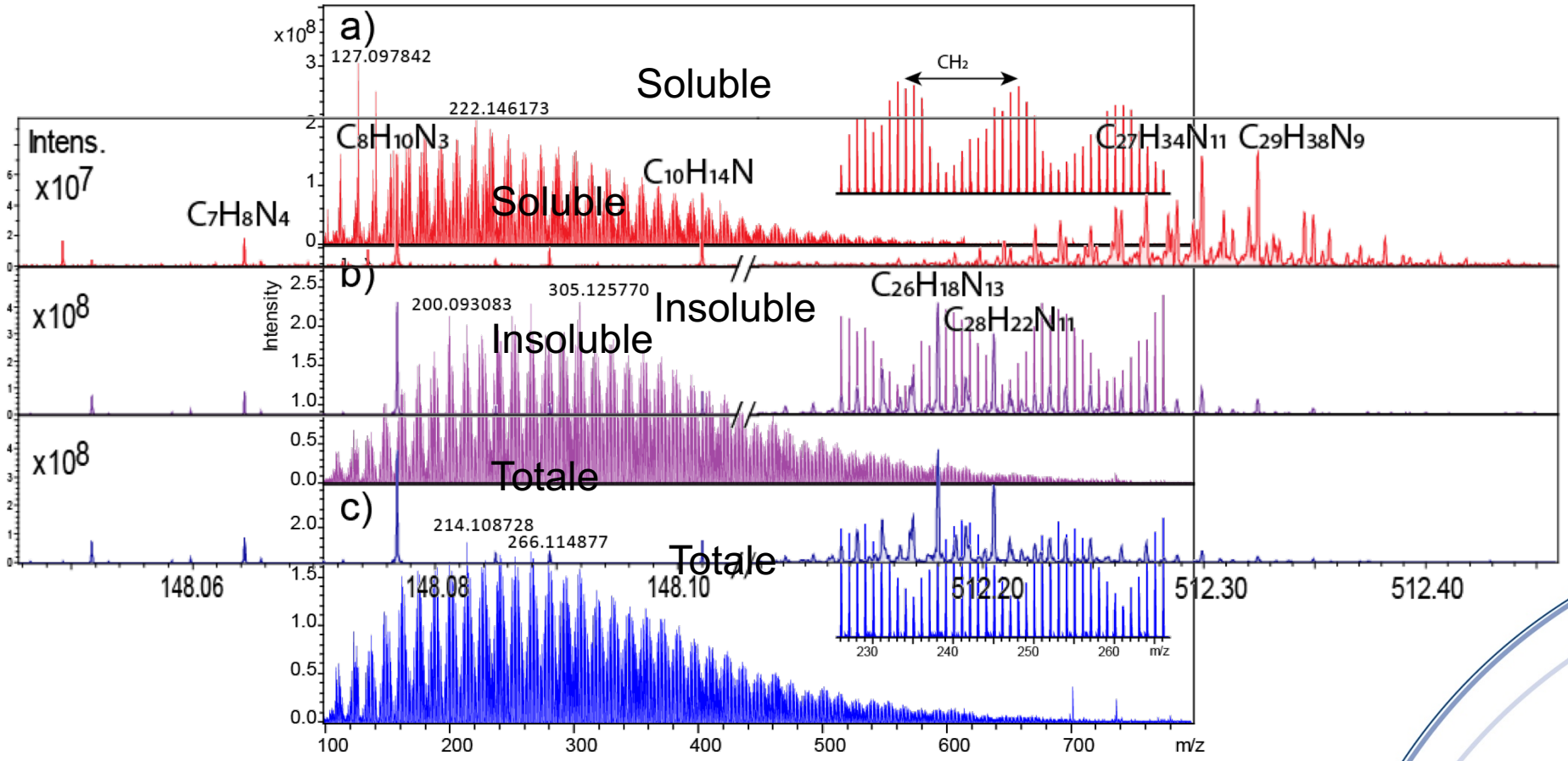
What do we know?

- **Physical properties of tholins (Carrasco et al. 2009) :**
  Elemental analysis,
  Solubility,
  (35% of tholins prepared with 5% of methane are soluble in methanol)
  Absorption IR,
  (Soluble and non soluble have nearly identical IR spectra)

- **Analysis of soluble fraction by ESI-Orbitrap (Gautier et al. 2014):**
  Polymers: CH_2 and HCN repeat units

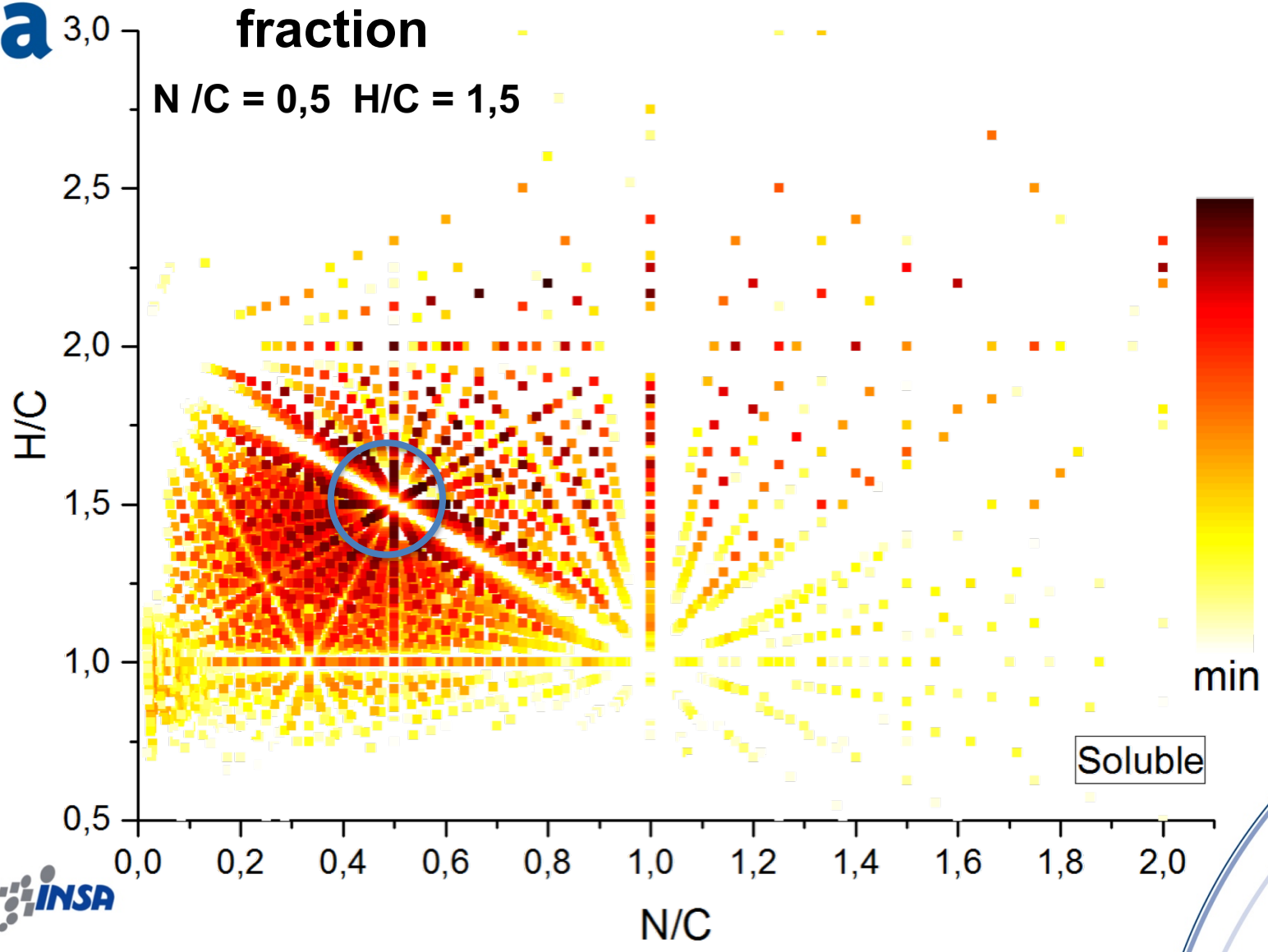
  Hypothesis: soluble and non soluble fraction are similar

Laser desorption analysis of soluble and non-soluble fractions



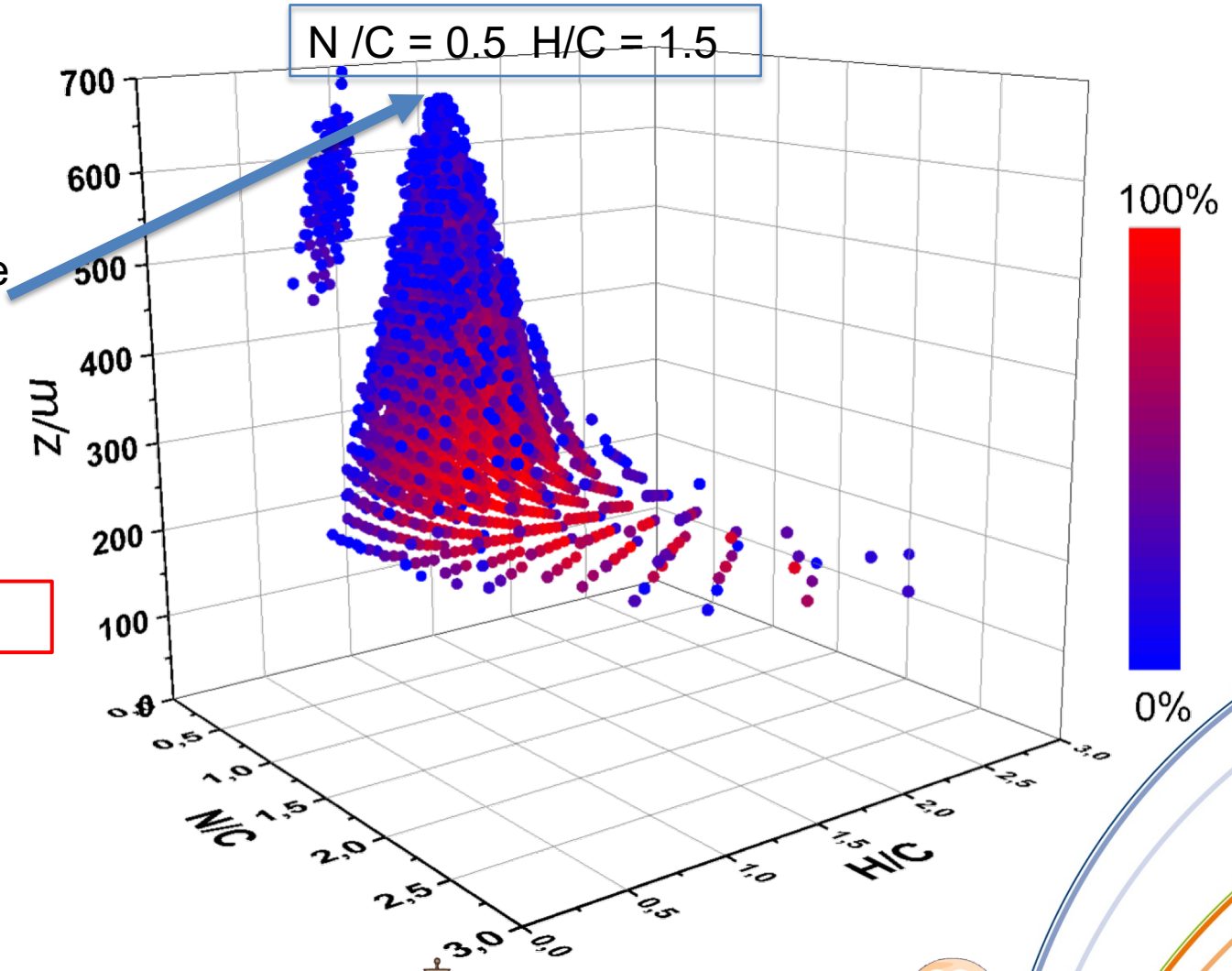
Maillard J, Carrasco N, Schmitz-Afonso I, et al. Comparison of soluble and insoluble organic matter in analogues of Titan's aerosols. Earth Planet Sci Lett 2018; 495: 185-191.

Van Krevelen diagram of the soluble fraction



3D Van Krevelen with x = N/C, y = H/C et z = m/z

- Soluble fraction
- Convergence of the species

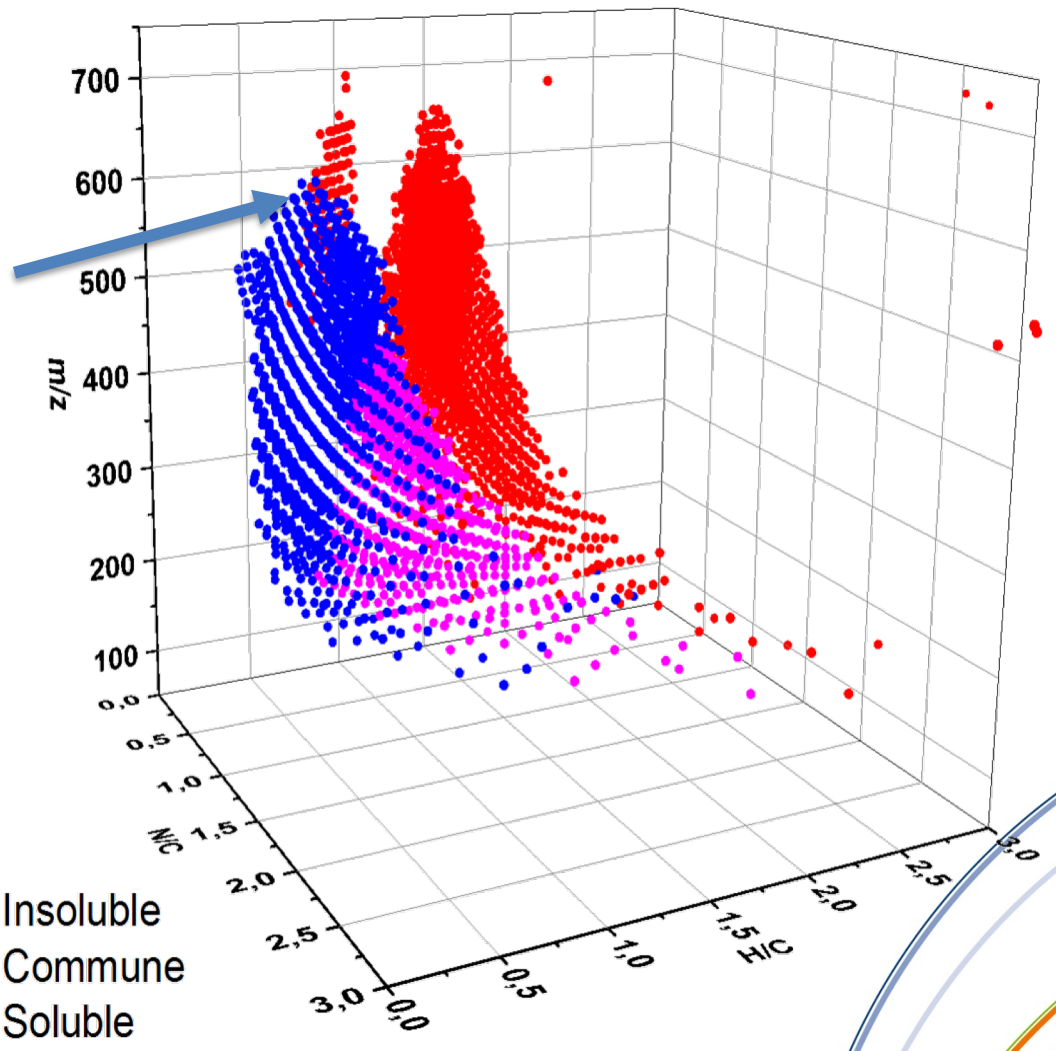


$-C_2H_3N-$ repeat unit

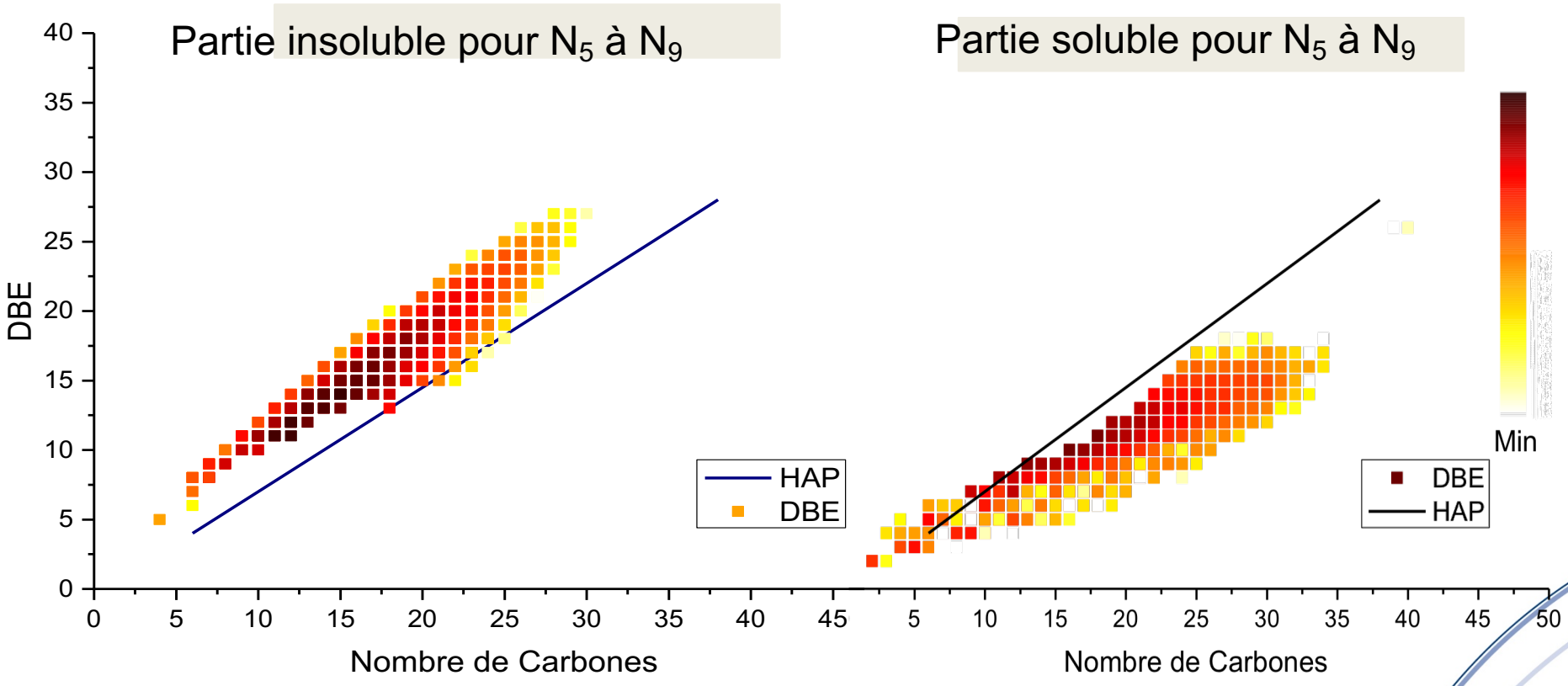
Diagrammes de Van Krevelen de la fraction insoluble

- Other distribution with of ther convergence point

N/C = 0.5; H/C = 0.75
Motif: $C_4H_3N_2$

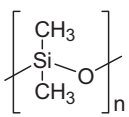


Comparison of soluble and non soluble fractions unsaturation

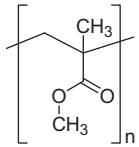


Polymers and MS

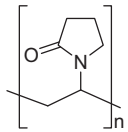
- Polymers
  - Repeat unit
  - End-groups
  - Average mass



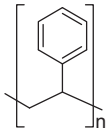
PDMS **1**



PMMA **2**

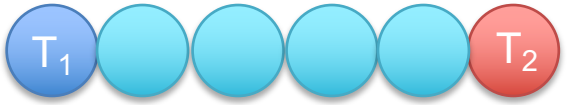


PVP **3**



PS **7**

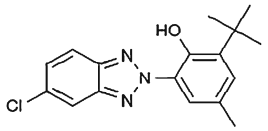
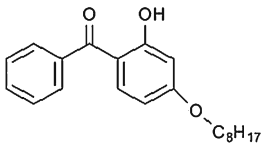
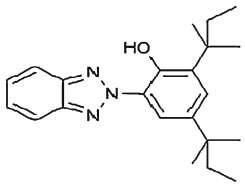
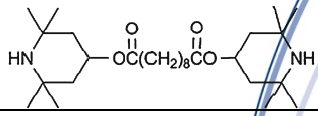
- Additives
  - Anti-UV
  - Antioxidants
    - HALS (hindered amine light stabilizants)
  - …



$M_N = \Sigma M_i N_i / \Sigma N_i$

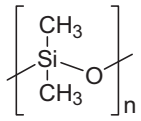
$M_W = \Sigma(M_i)\, N_i / \Sigma M_i N_i$

polydispersité $D = M_W / M_N$

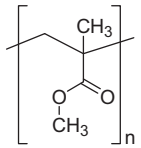
Substance	Formula	[M+H]+ calculated
Chimassorb 81		316.1211
Tinuvin 326		327.1955
Tinuvin 328		352.2383
Tinuvin 770		481.4000

Ionization of Polymers

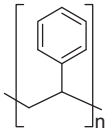
- Ionization
  - $M^{+\bullet}$
  - $[M+H]^+$, $[M+Na]^+$, $[M+Met]^+$
- Polymers : large molecular diversity
  - Heteroatoms (PEG, PMMA…)
  - Unsaturated (PB)
  - Aromatics (PS)
  - Saturated (PE, PP…)
- Solubility
  - In MS most ionization imply that the sample is soluble



PDMS **1**



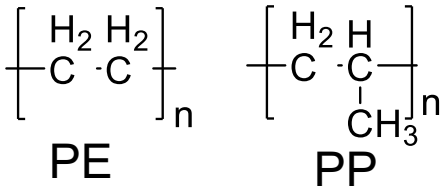
PMMA **2**

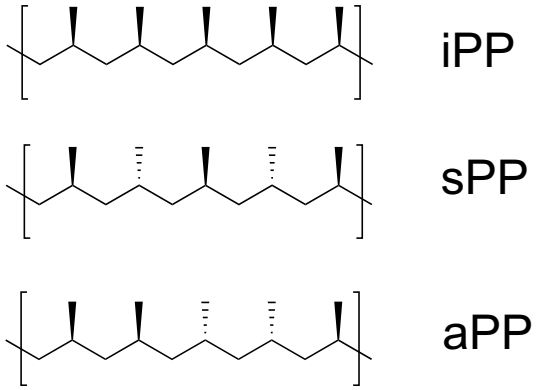


PS **7**

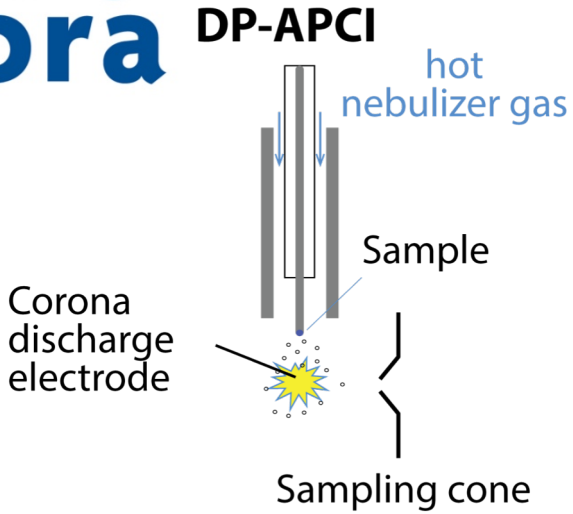
Polyolefins

- 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 ?





ASAP or DIP-APCI: a complex ionization process



Ionization
By charge exchange

e^-

N_2 $N_2^{+\bullet}$

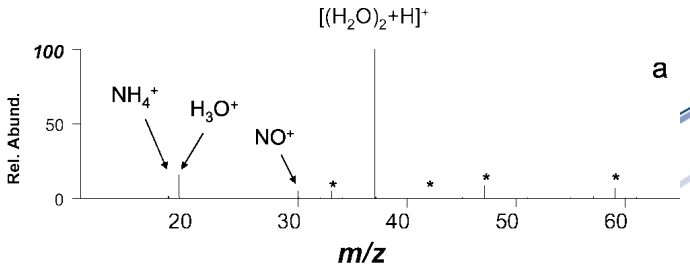
pyrolysis

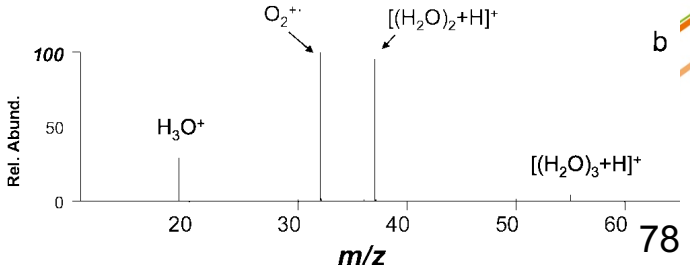
PP

Pyrolysis products

Traces of O_2 and H_2O

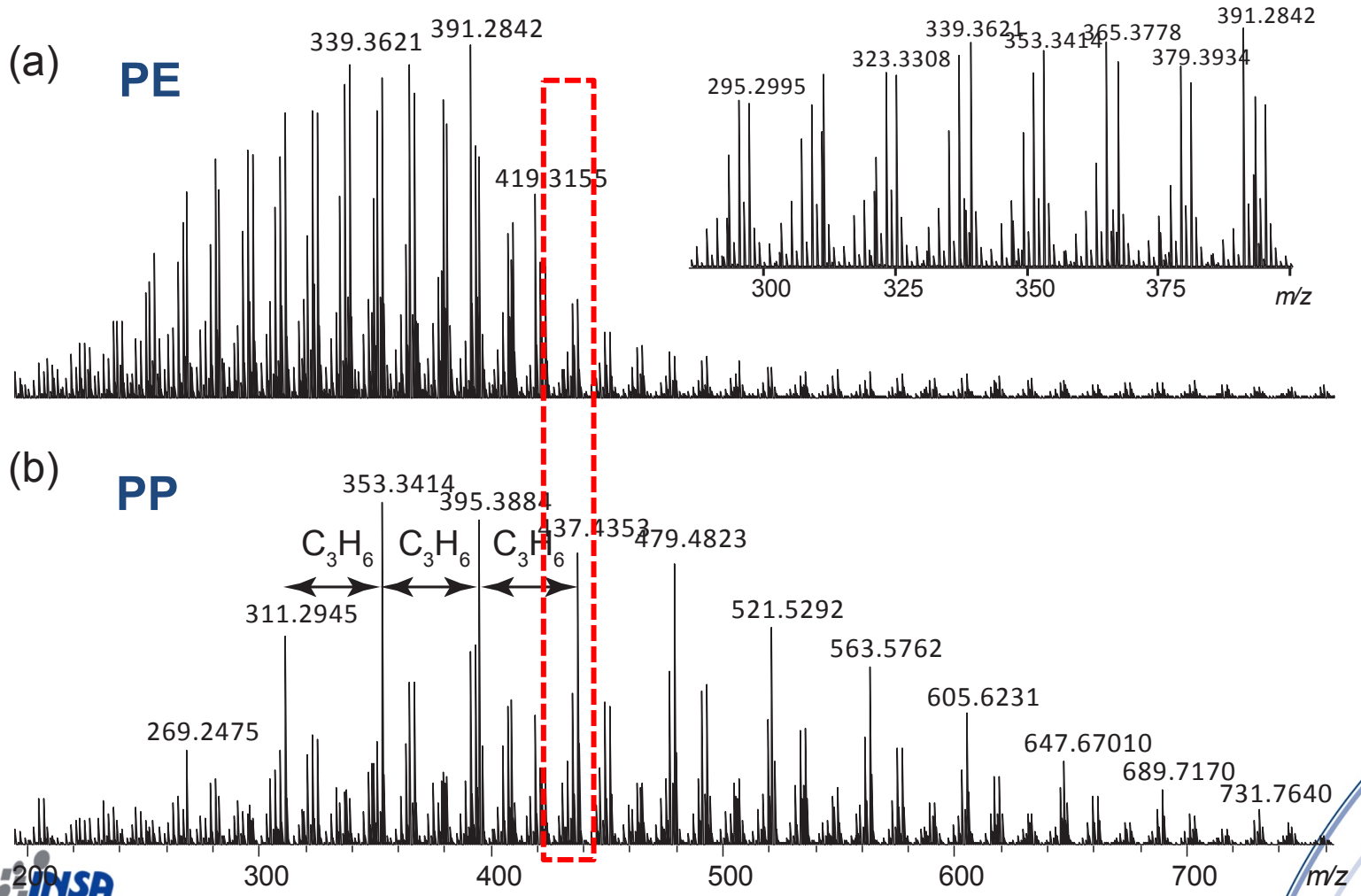
?





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

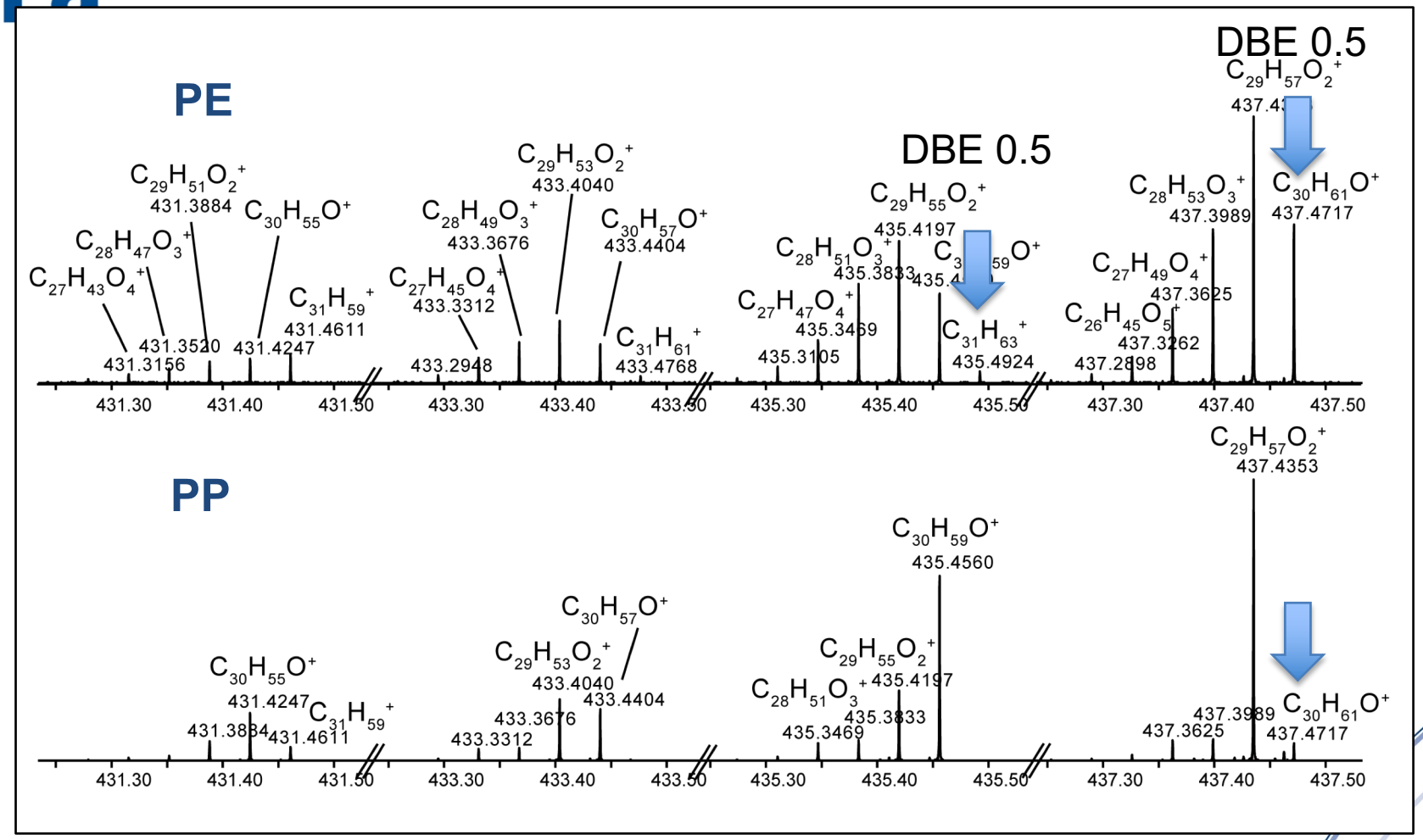
FTICR analysis



Differentiation of PP and PE

RP=900000

FT-ICR Analysis

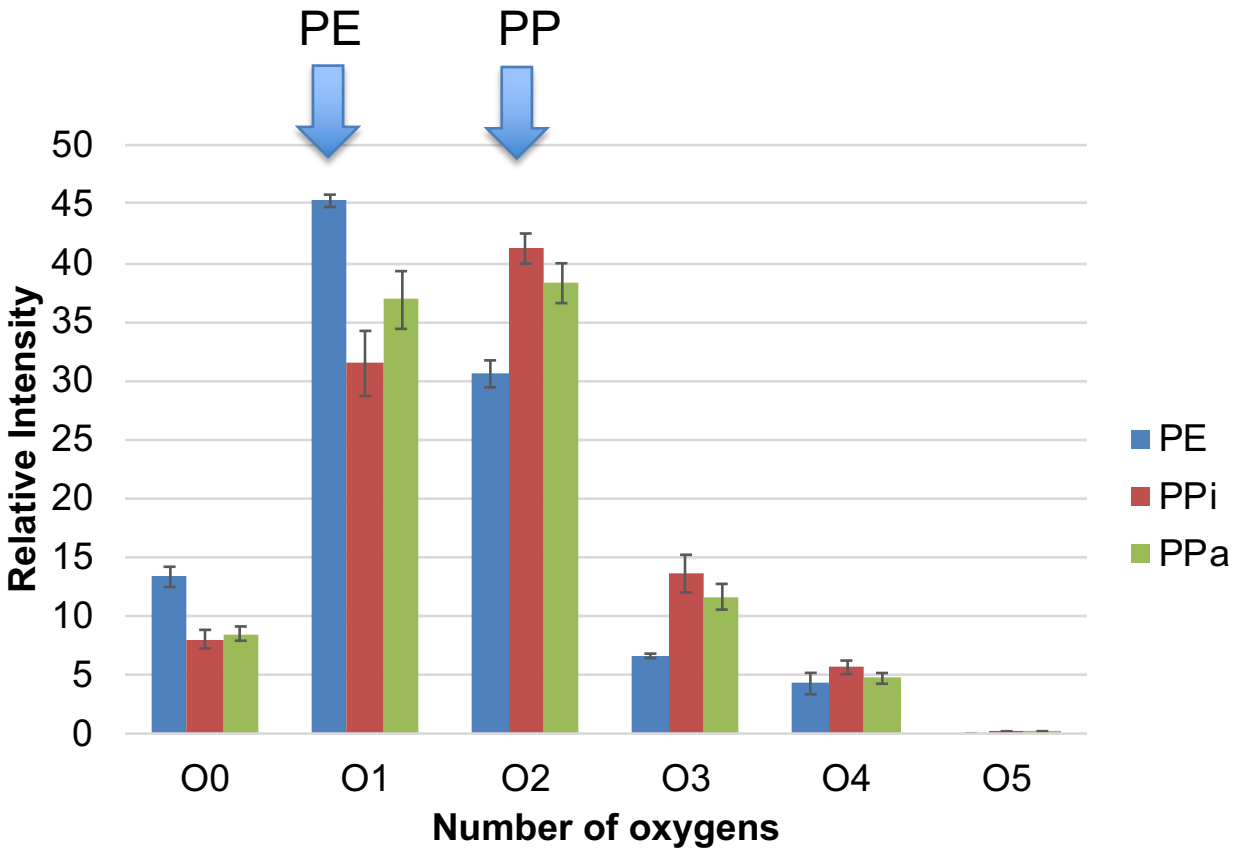


Oxygen containing species for PE and PP

Low DBE species detected for PE not for PP

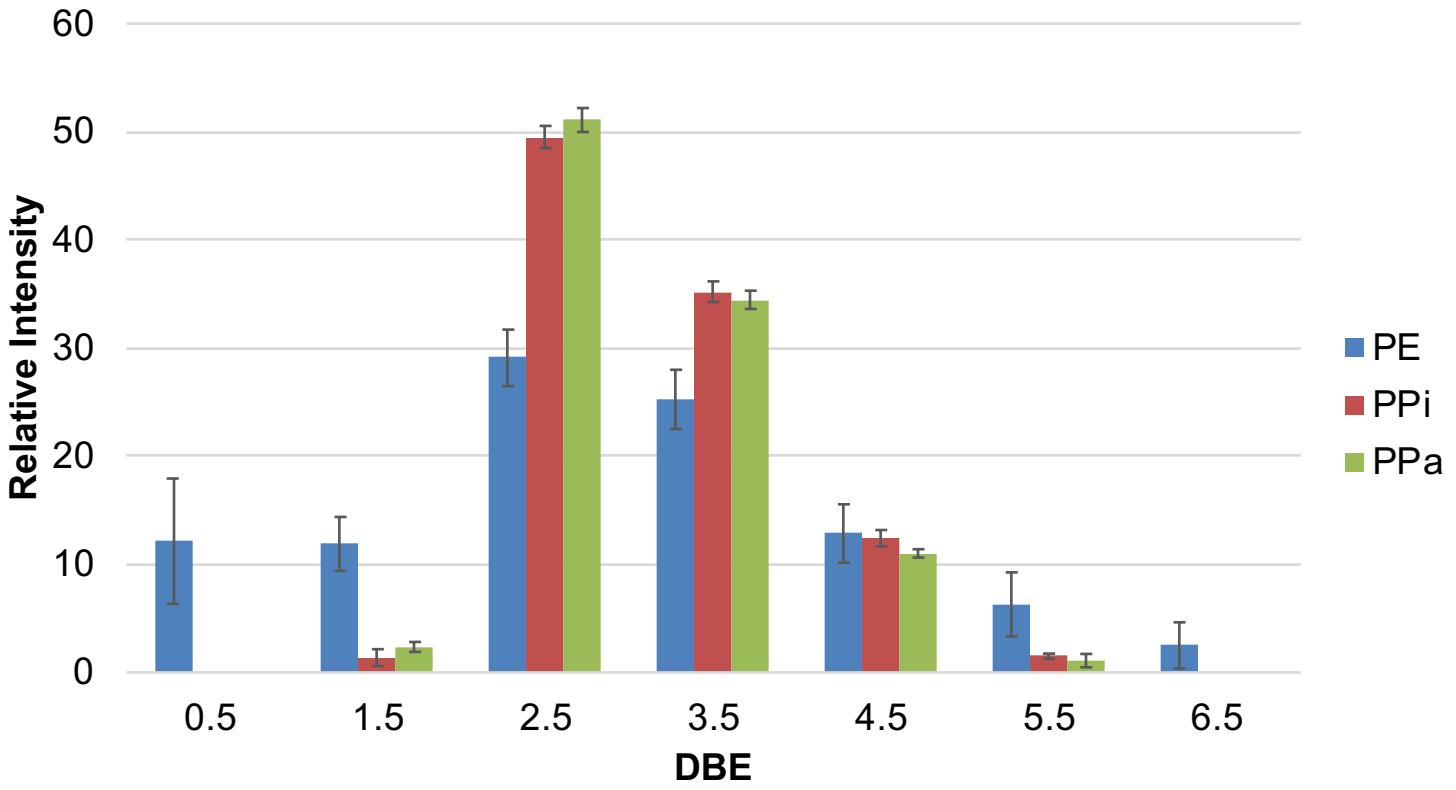
M. Farenc, M. Witt, K. Craven, C. Barrere-Mangote, C. Afonso, P. Giusti. Characterization of Polyolefin Pyrolysis Species Produced Under Ambient Conditions by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry and Ion Mobility-Mass Spectrometry. *J Am Soc Mass Spectrom* **2017**, *28*, 507.

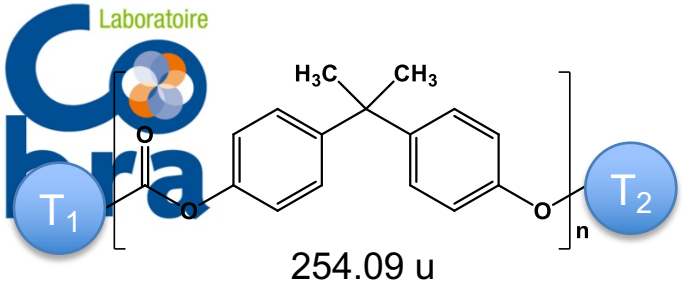
Oxygen number distribution (FT-ICR)



Higher number of oxygens for PP related to ramifications ?

DBE distribution C_xH_y (no oxygen) (FTICR)





254.09 u

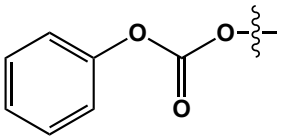
polybisphenol A carbonate (PC)

2270 = T1+T2+n×254.09+23

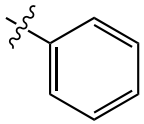
$n \leq 2247/254=8.8$

n=8 254.09 x 8 = 2032.7

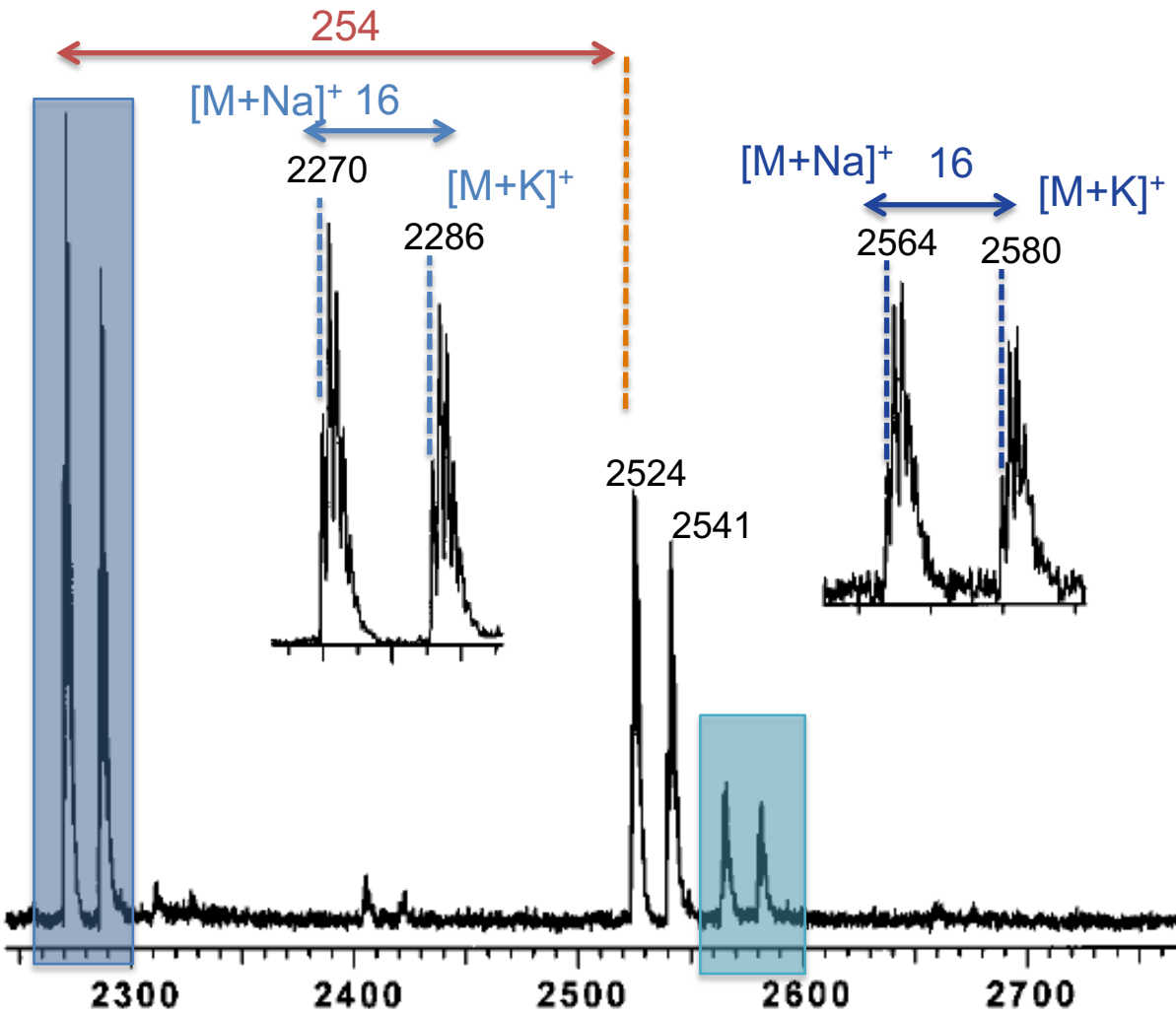
T1+T2 = 214.3



137.02



77.04



2564 = T1+T2+n×254.09+23

$n \leq 2541/254.09=10.00$

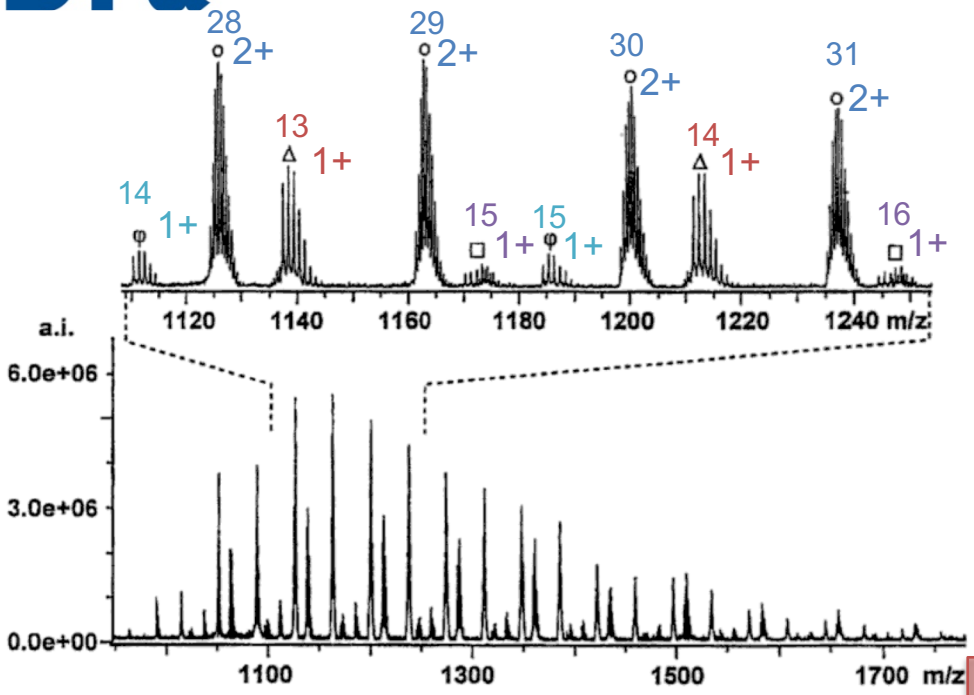
T1+T2=0

polymère cyclique

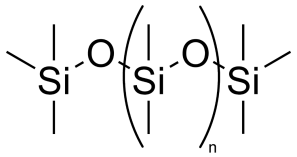
DE ROUEN

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	$H_3NC_3H_6$–[Si(CH$_3$)$_2$–O]$_n$–Si(CH$_3$)$_2$–$C_3H_6NH_2$	13	1137.4067	1137.4121	4.7
○	$H_3NC_3H_6$–[Si(CH$_3$)$_2$–O]$_n$–Si(CH$_3$)$_2$–$C_3H_6NH_3^+$	29	2322.7152	2322.7144	0.3
φ	$H_3NC_3H_6$–[Si(CH$_3$)$_2$–O]$_n$–CH$_3$	14	1110.3595	1110.3599	0.4
□	$H_3NC_3H_6$–[Si(CH$_3$)$_2$–O]$_n$–H	15	1170.3626	1170.3588	3.2

[a] Degree of polymerization

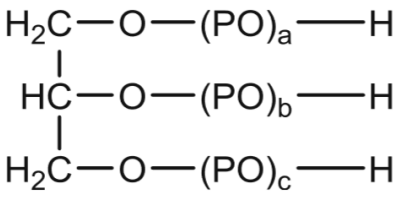
Maziarz et al. *Macromolecules*,1999,32,4411

Polymer mix

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

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

PPO-triol

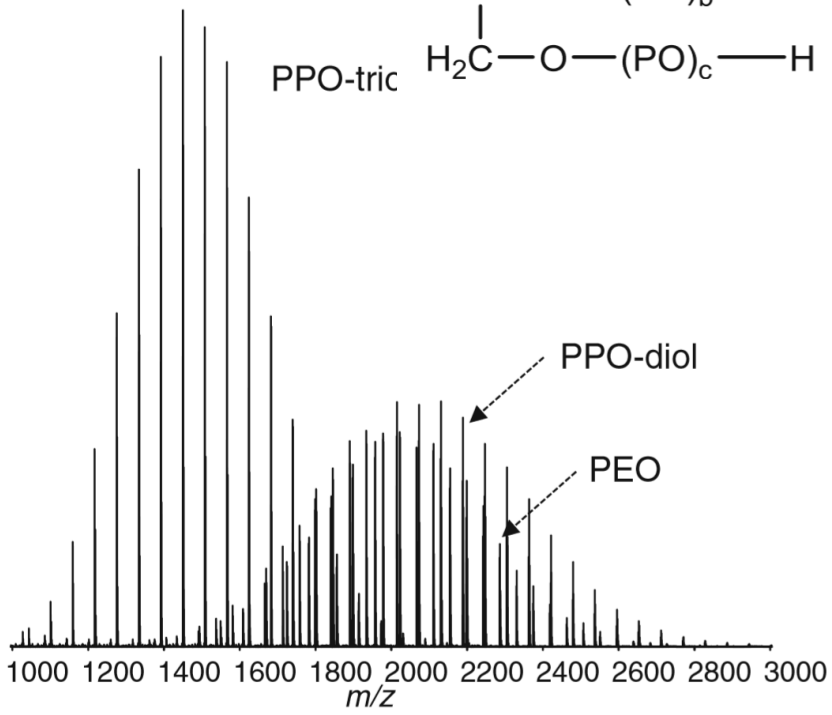


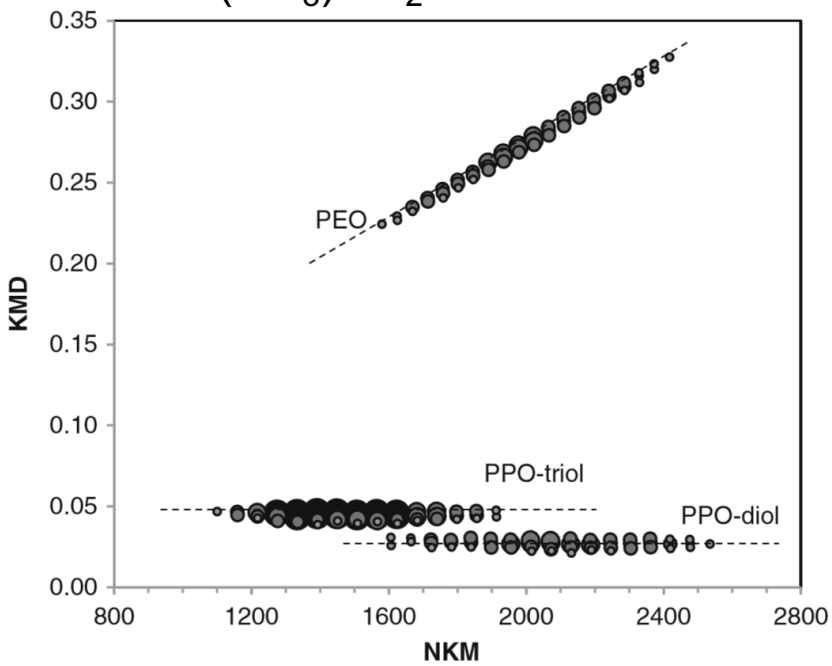
PPO-tric

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

mass scale based on PO units

$-CH(CH_3)CH_2O$

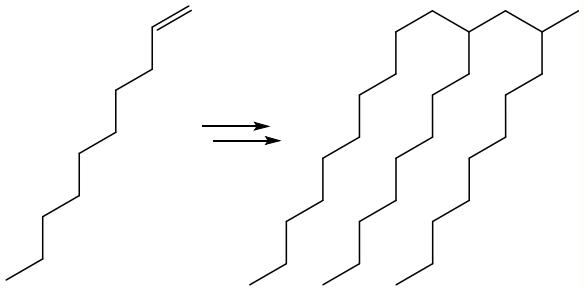




H. Sato, S. Nakamura, K. Teramoto, T. Sato. Structural characterization of polymers by MALDI spiral-TOF mass spectrometry combined with Kendrick mass defect analysis. *J Am Soc Mass Spectrom* **2014**, *25*, 1346.

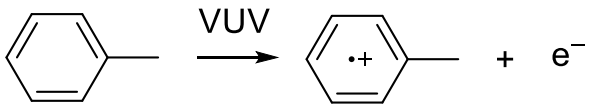
Alkanes: halide attachment

lubrifiants



Alpha-olefin poly-alpha-olefin

photoionization

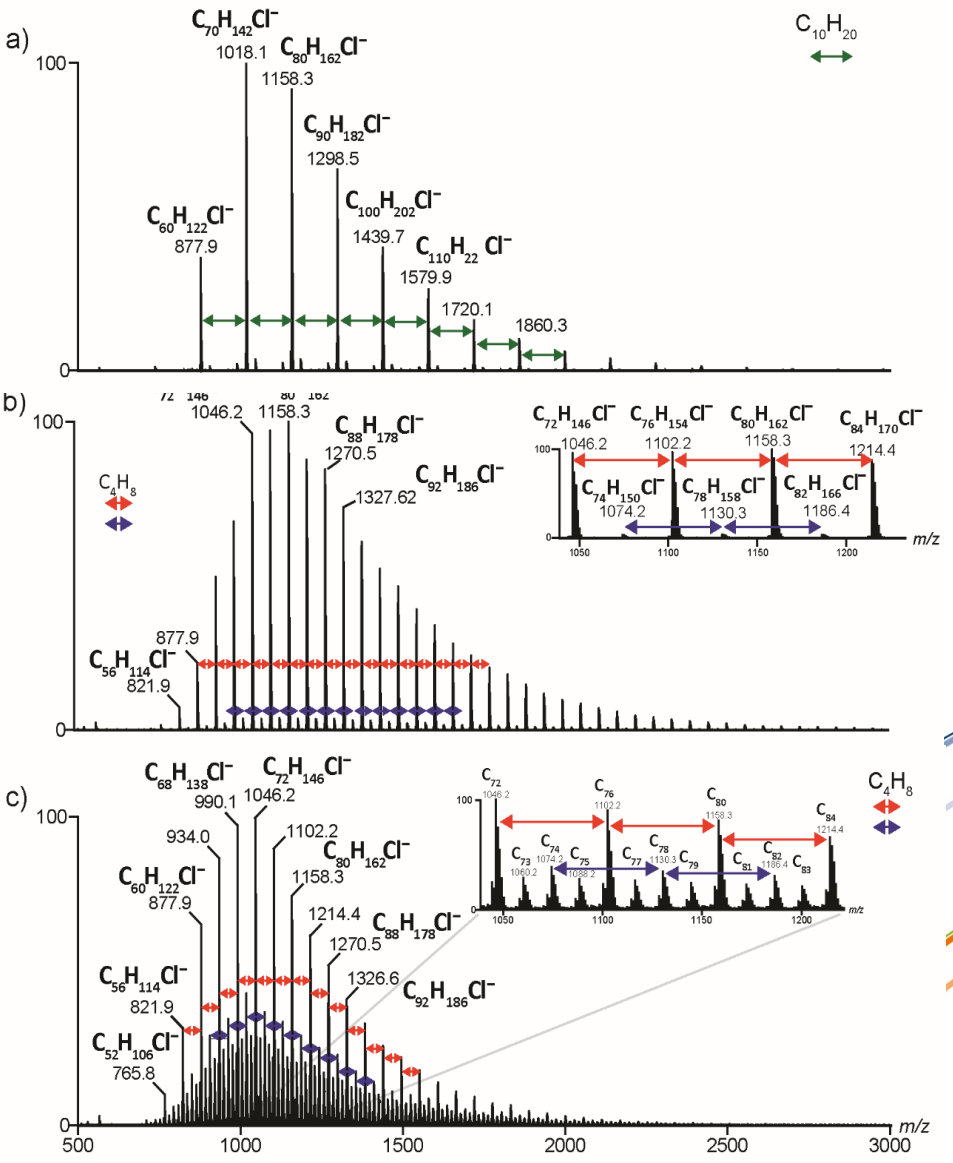


Electron capture dissociation

$e^- + CH_2Cl_2 \longrightarrow Cl^- + CH_2Cl^{\cdot}$

Anion attachment

$Alcane + Cl^- \longrightarrow [Alcane+Cl]^-$



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