

Report on the ASMS 2016 workshop for the Energy, Petroleum & Biofuels Interest Group: "Petroleum and Biofuels: Handling the Data"

Lateefah Stanford and Mark P. Barrow presiding
Tuesday (June 7th, 2016), 17:45-19:00, Room 301A, level 3

Format:

- Lateefah Stanford (BP)
 - Welcome
 - Introduction to workshop
- Mark Barrow (University of Warwick, United Kingdom)
 - Overview of available petroleomics software
 - Examples of approaches used by different groups
- Ralf Zimmermann (University of Rostock and Helmholtz Zentrum München, Germany)
 - GCxGC TOF MS, thermogravimetry photoionization MS, GC-APCI-FTICR MS
 - SPI and REMPI; aliphatic and aromatic species
 - Variety of data analysis and visualization methods for different data
 - Questions/Discussion
- Sunghwan Kim (Kyungpook National University, South Korea)
 - Petroinformatics: combining petroleomic data and statistical tools to predict physical and chemical properties
 - Use of multiple methods (MS, LC, IMMS, NMR, IR); need to combine data
 - Proposal for discussion: conversion of DBE information to structures, to be compared with NMR
 - Questions/Discussion

At the beginning of the workshop, over 50 attendees were counted, although more also arrived later. The attendees represented both academic and commercial establishments, and the workshop lasted the full duration of the allocated time. Lateefah Stanford opened the workshop, providing the welcome and introduction. Mark Barrow provided a short presentation, with an overview of different petroleomics software tools available, examples of types of data being produced by different laboratories, and examples of possible topics for discussion, where the workshop should be discussion-led.

Two speakers were invited to highlight potential areas for further discussion. Ralf Zimmermann presented data produced using a range of experimental methods. GCxGC TOF MS data were displayed using multiple dimensions, including m/z or Kendrick mass defect. For thermogravimetry measurements, temperature vs. m/z was plotted and comparisons of ionization methods were made by color coding data points according to whether peaks were observed only by single photon ionization (SPI), resonance-enhanced multiphoton ionization (REMPI), or both methods. Thermal analysis or GC was coupled with FTICR MS, where the data was plotted as retention time or temperature vs. m/z. When GC was used, artifact species from the ionization process could be excluded by ensuring correlation of peaks of interest with appropriate retention times.

Sunghwan Kim discussed the concept of "petroinformatics," using statistical tools to ultimately develop a predictive system for the physical and chemical properties of petroleum. FTICR MS, Orbitrap, 2D GC, LC, and NMR data was shown and there was a question of how to appropriately combine the results from different experiments. Sunghwan presented an idea for combining DBE information with NMR data to determine structures of the components, based upon assumed "basic structures" for different compound classes. The total number of aromatic and non-aromatic carbon atoms could then be calculated, and the calculations were compared with NMR data. The audience was asked to discuss this proposal.

It was clear that there is an increasing diversity of experimental methods for the characterization of petroleum and biofuels, and there is a need to develop better methods for combining and understanding the data. Adding further dimensions to experiments, such as temperature or time, also leads to the acquisition of larger data sets and so creates greater challenges for storage, compression, and analysis. As the outgoing interest group coordinator, Lateefah called for people to put their names forwards if they are interested in being one of the interest group coordinators for next year. By the end of June, one person had contacted the coordinators with an interest in the role.



Petroleum and Biofuels: Handling the Data

Energy, Petroleum & Biofuels
Interest Group

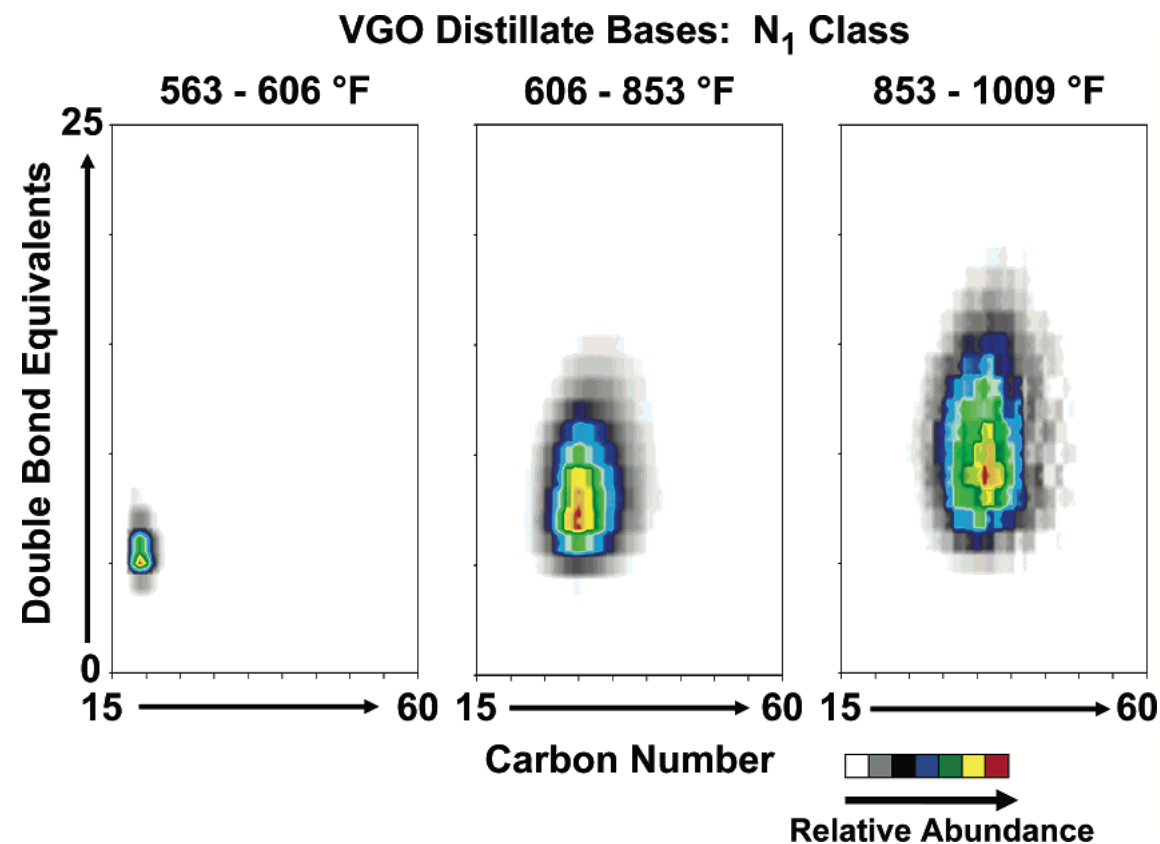
Lateefah Stanford (BP)

Mark P. Barrow (University of Warwick, UK)

Categorization

1. “Heteroatom class” or “Compound class”
2. Carbon number
3. Double bond equivalents (DBE)

$$\text{DBE} = 1 + c - h/2 + n/2$$



Energy Fuels 2006, 20, 1664-1673

Software

1. **Composer**

Sierra Analytics

<http://www.massspec.com/>

2. **PetroOrg**

Florida State University

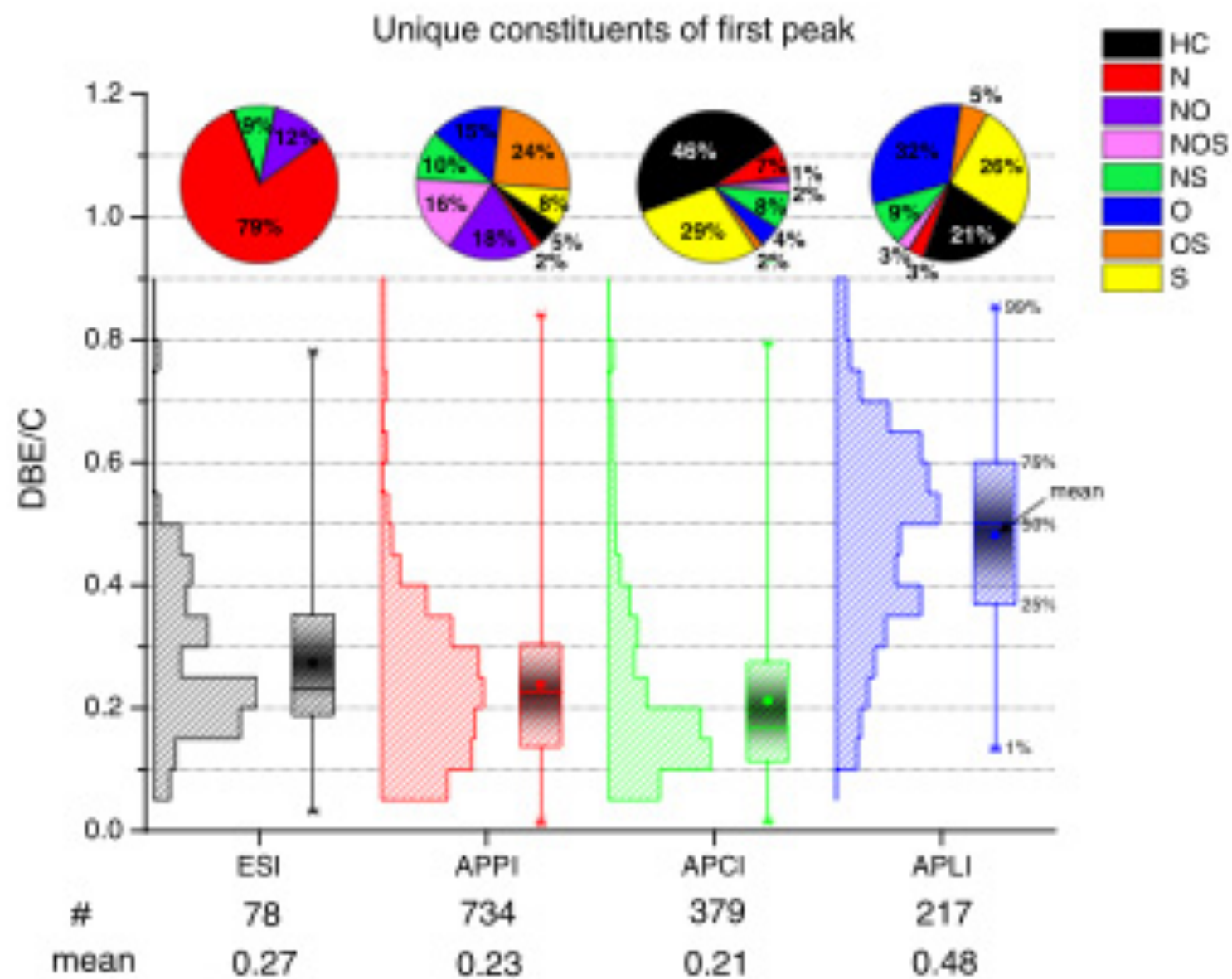
<http://software.petroorg.com>

3. **mzCruiser for Petroleomics**

Manhoi Hur

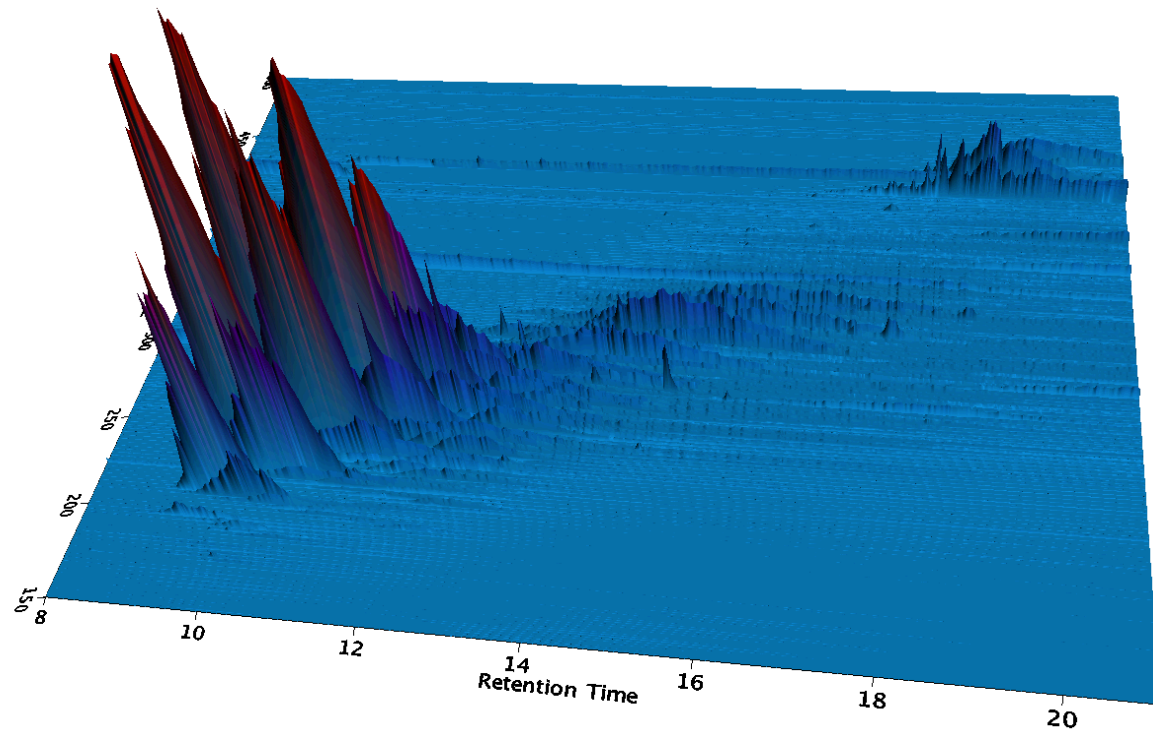
<https://github.com/mhhur/Petroleomics>

Ionization methods

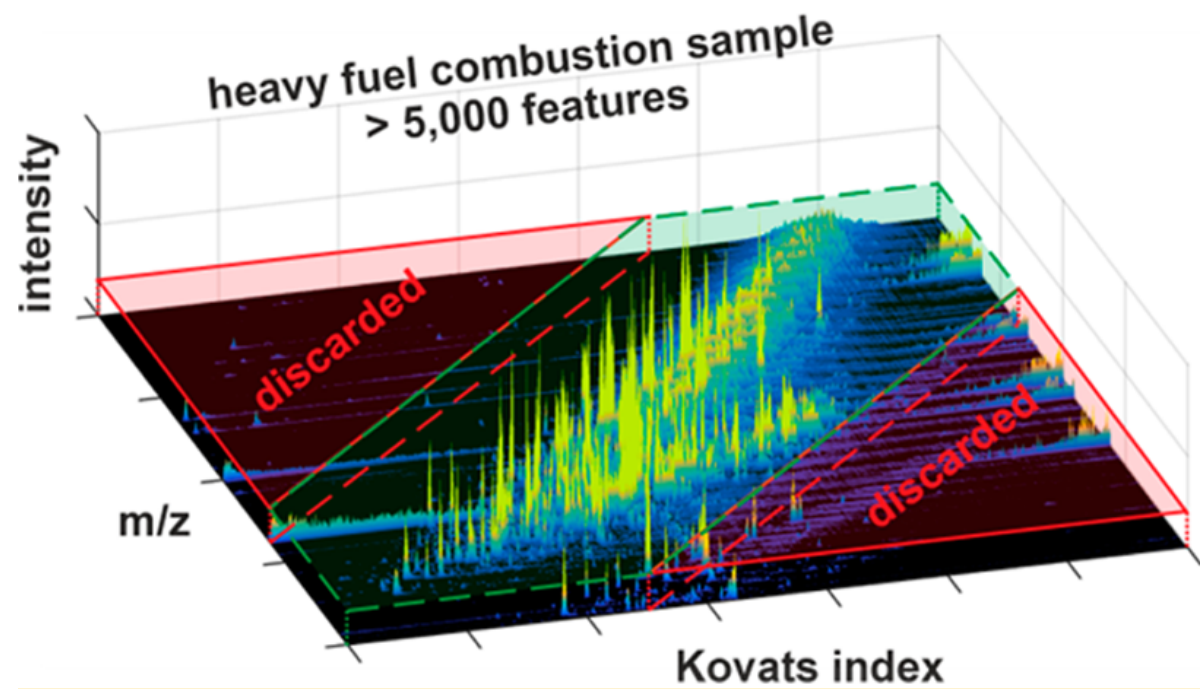


Rapid Commun. Mass Spectrom. **2014**, *28*, 1345-1352

Chromatography

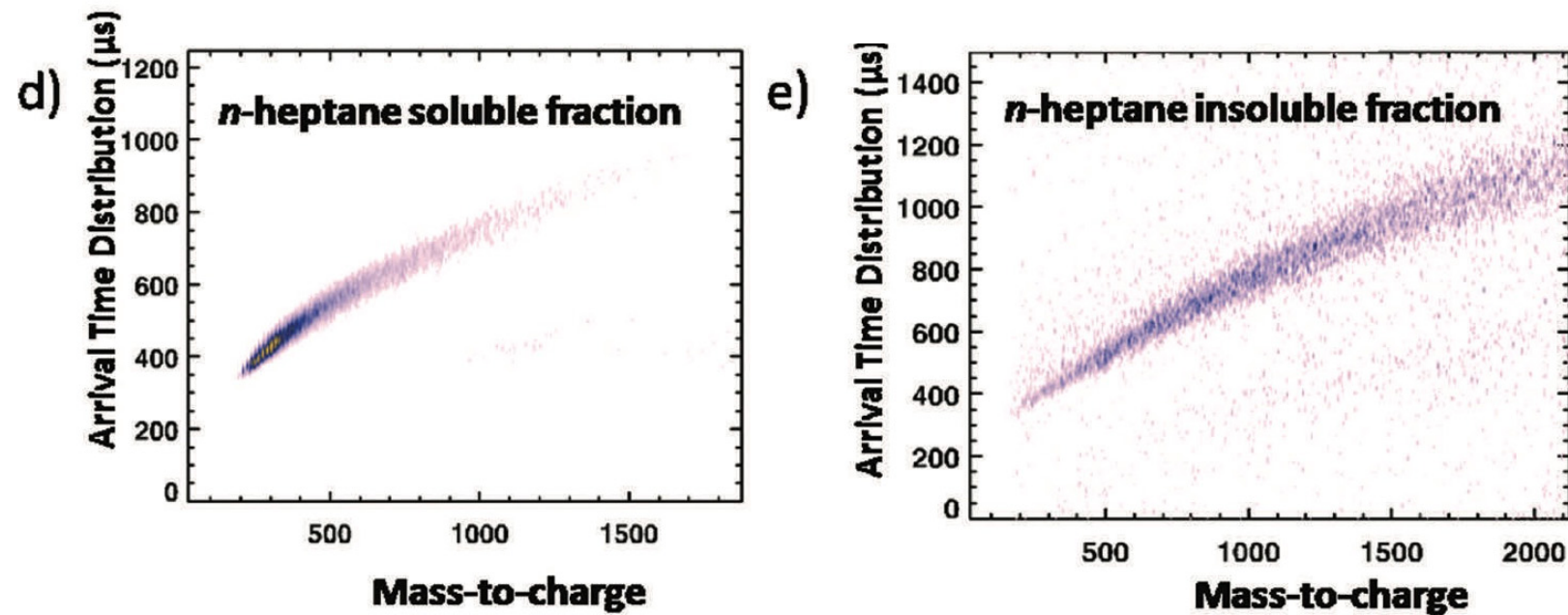


Anal. Chem. **2014**, *86*, 8281-8288

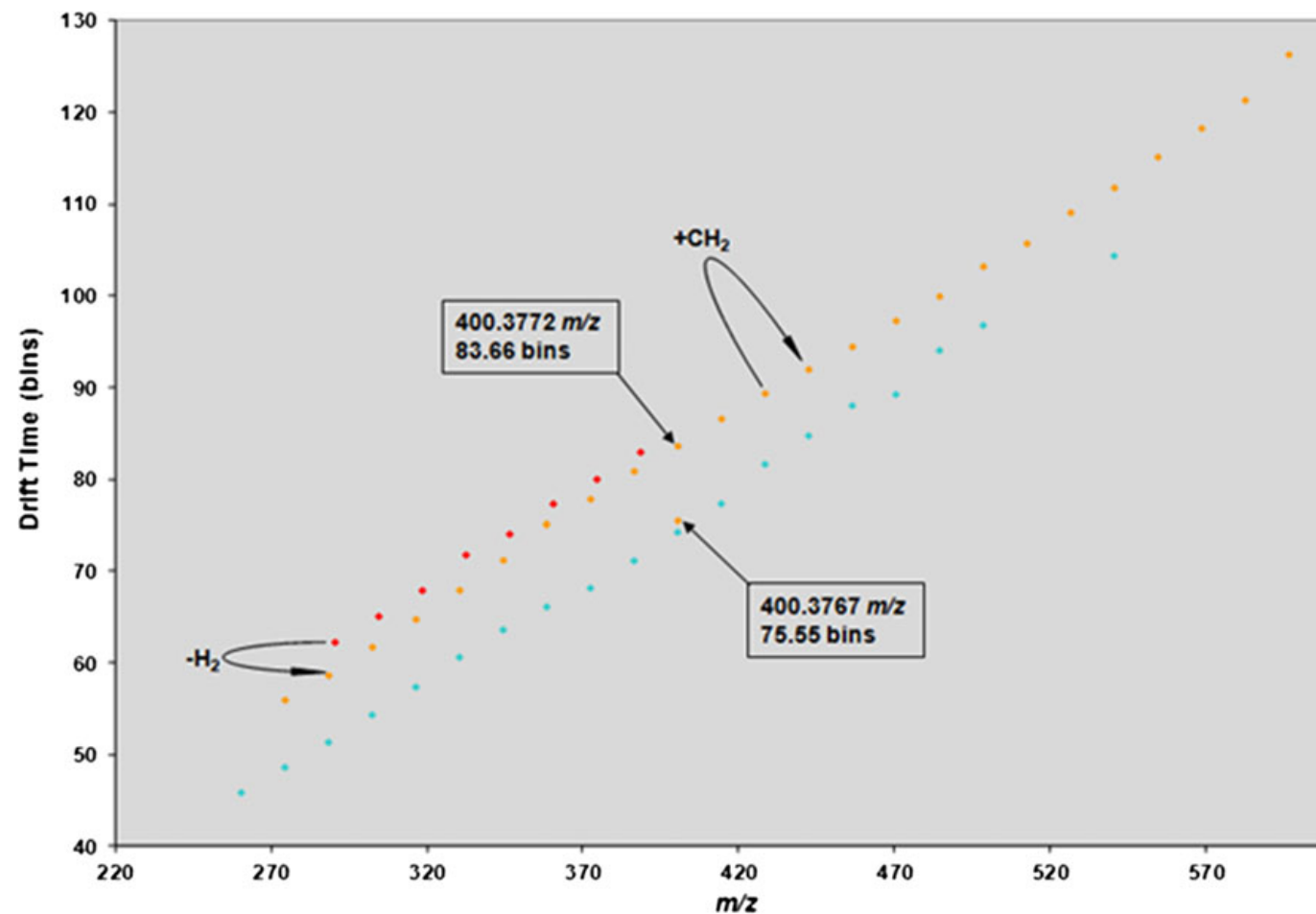


Anal. Chem. **2015**, *87*, 11957-11961

Ion mobility mass spectrometry (IMMS)

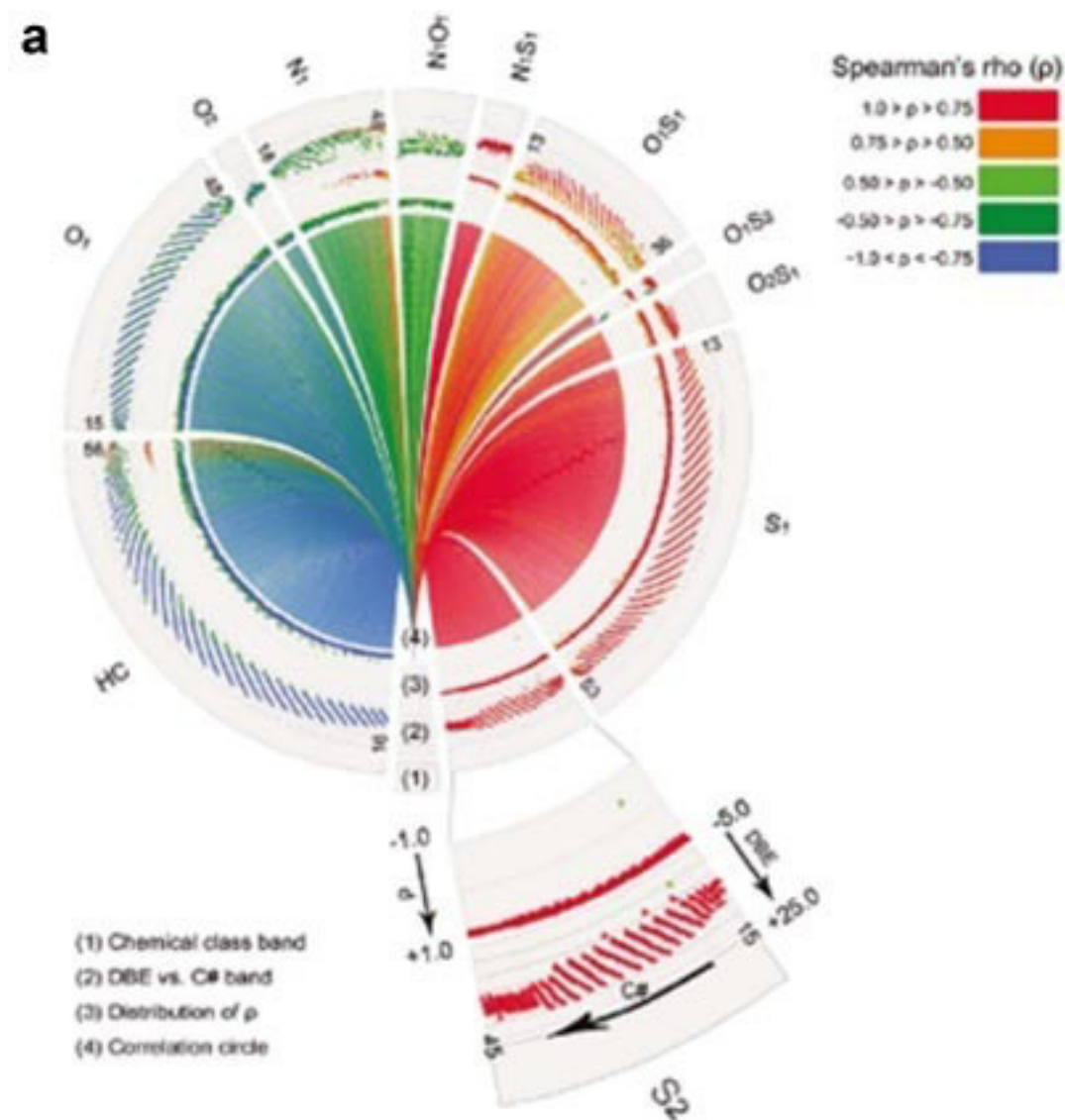
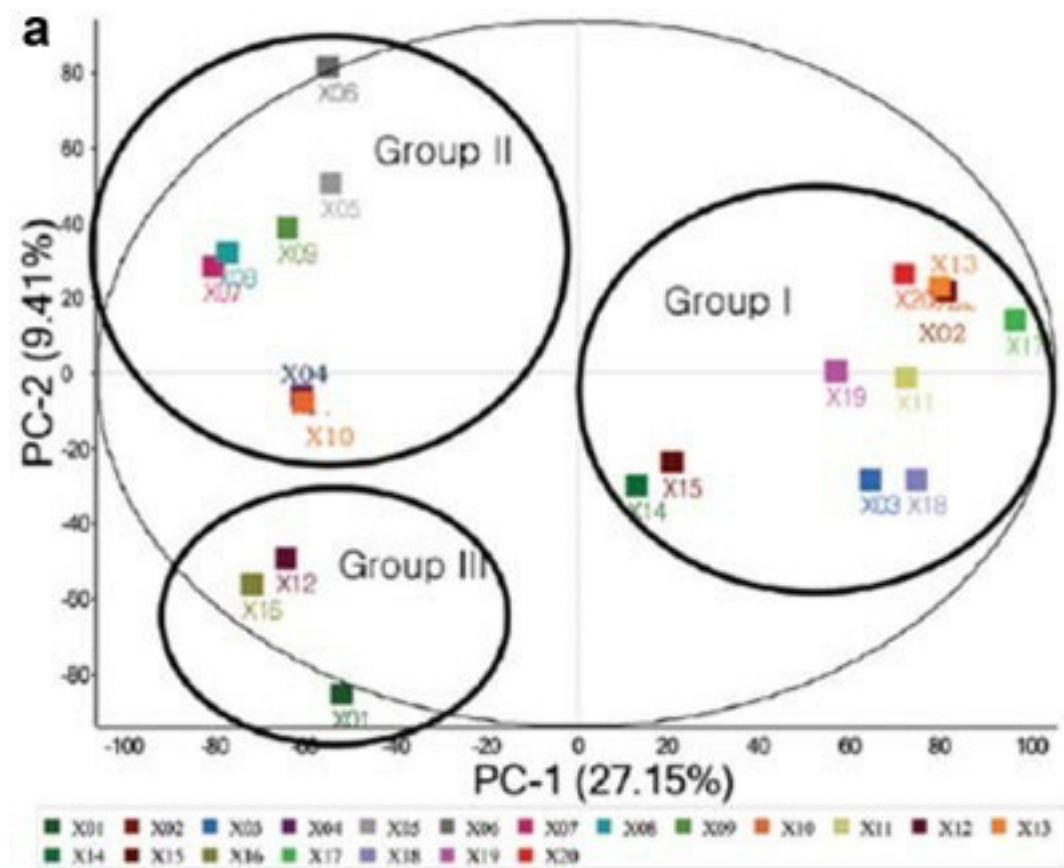


Anal. Chem. **2009**, *81*, 9941-9947



Int. J. Ion Mob. Spect. **2013**, *16*, 95-103

Statistical analysis



Mass Spectrom. Rev. **2014**, *34*, 248-263

Speakers

- Ralf Zimmermann

University of Rostock and Helmholtz Zentrum München, Germany

- Sunghwan Kim

Kyungpook National University, Republic of Korea

Example topics

- Data analysis and visualization
- Additional dimension to data (e.g. temperature, time, etc.);
hyphenated techniques
- Large data sets
- Comparison of different instrumentation and methods
- Statistics, chemometrics

Workshop will be discussion-led

Multiple novel techniques for petrochemical analyses require multiple data analysis approaches

Ralf Zimmermann, Martin Sklorz, Theo Schwemer, Christopher Ruger, Thorsten Streibel, Mohammad Saraji-Bozorgzad, Andreas Walte, Thomas Groger

Joint Mass Spectrometry Centre

University of Rostock, Chair of Analytical Chemistry, Inst. of Chemistry, Germany and Helmholtz-Zentrum Munchen, CMA, Germany (ralf.zimmermann@helmholtz-muenchen.de)



*Photonion GmbH
Schwerin, Germany*

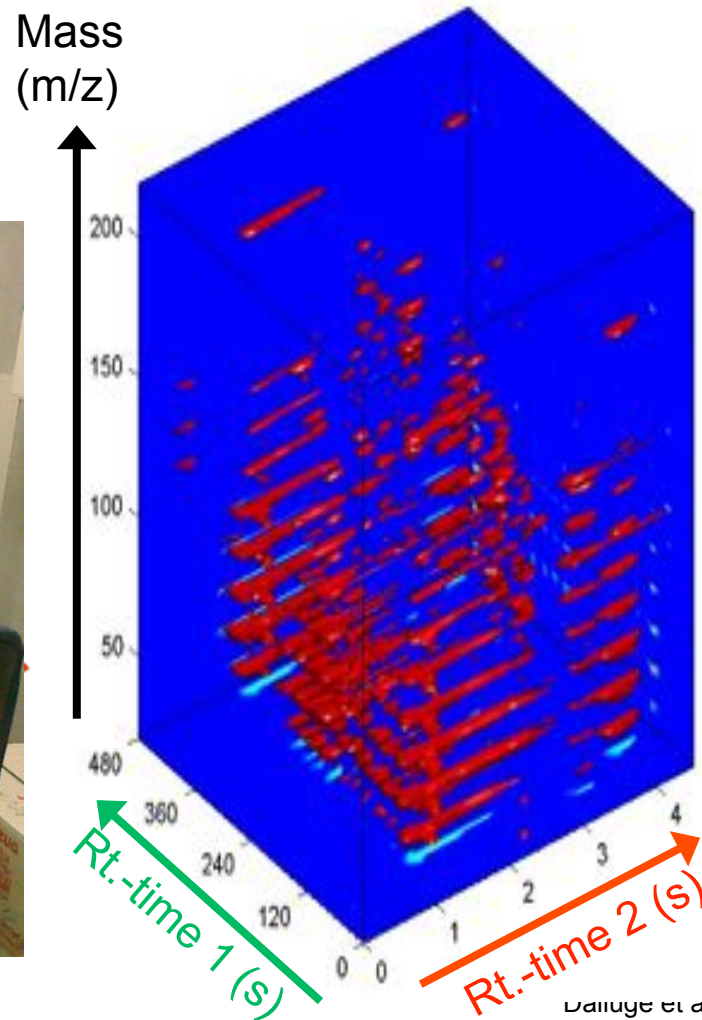


Petrochemical Analyses: Resolution, resolution, resolution ... (mass, chromatographic, process time ...)

Addressing complex petrochemical molecular mixtures:

Enhanced selectivity by chromatographic separation

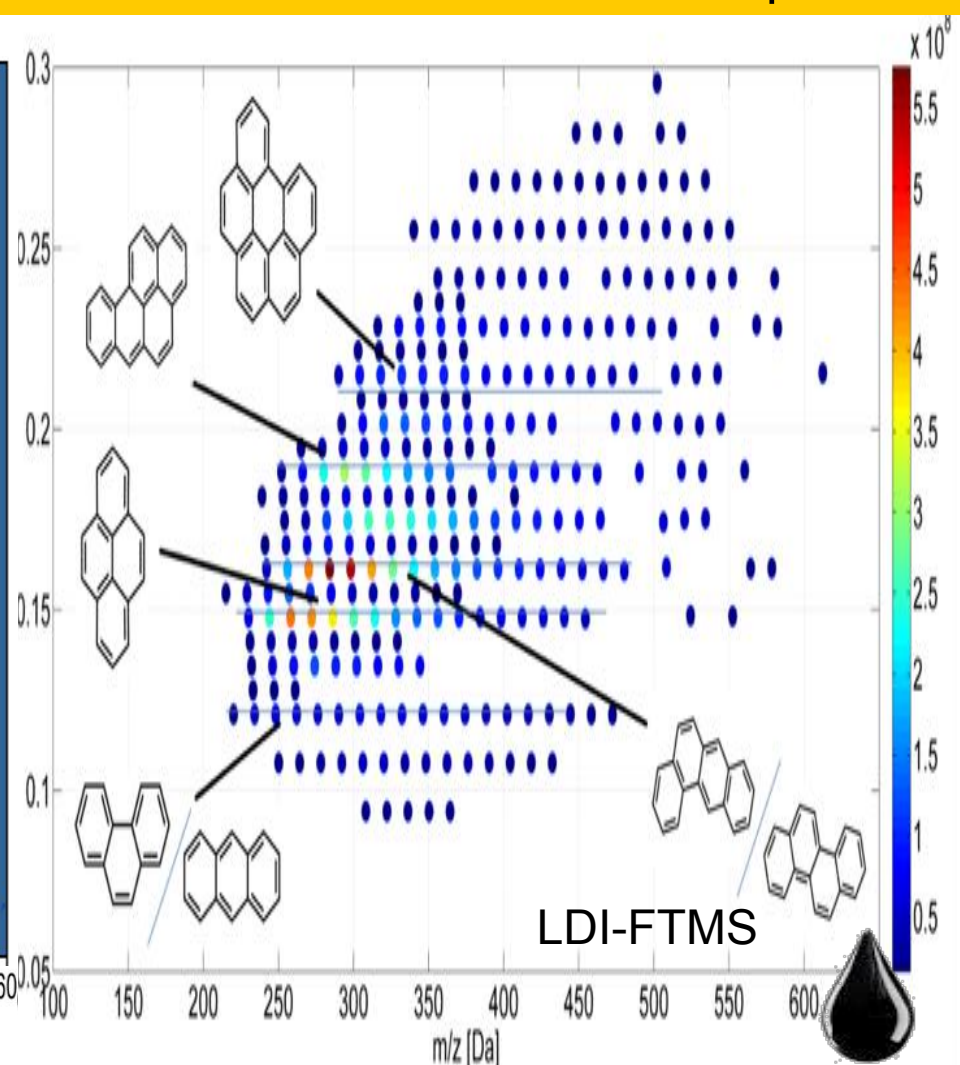
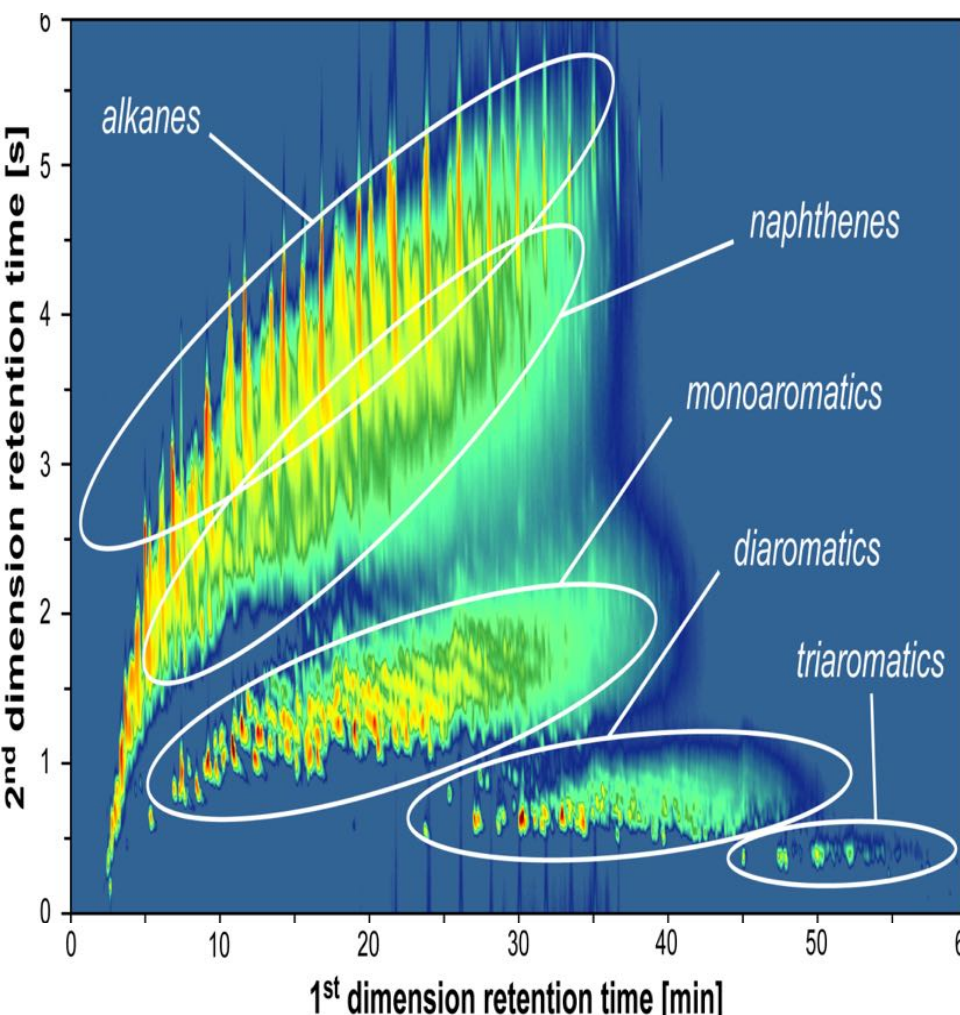
→ Comprehensive gas chromatography
(GCxGC)-TOF mass spectrometry



Comprehensive high resolution 2D GC (GCxGC) and high resolution mass TOF spectrometry

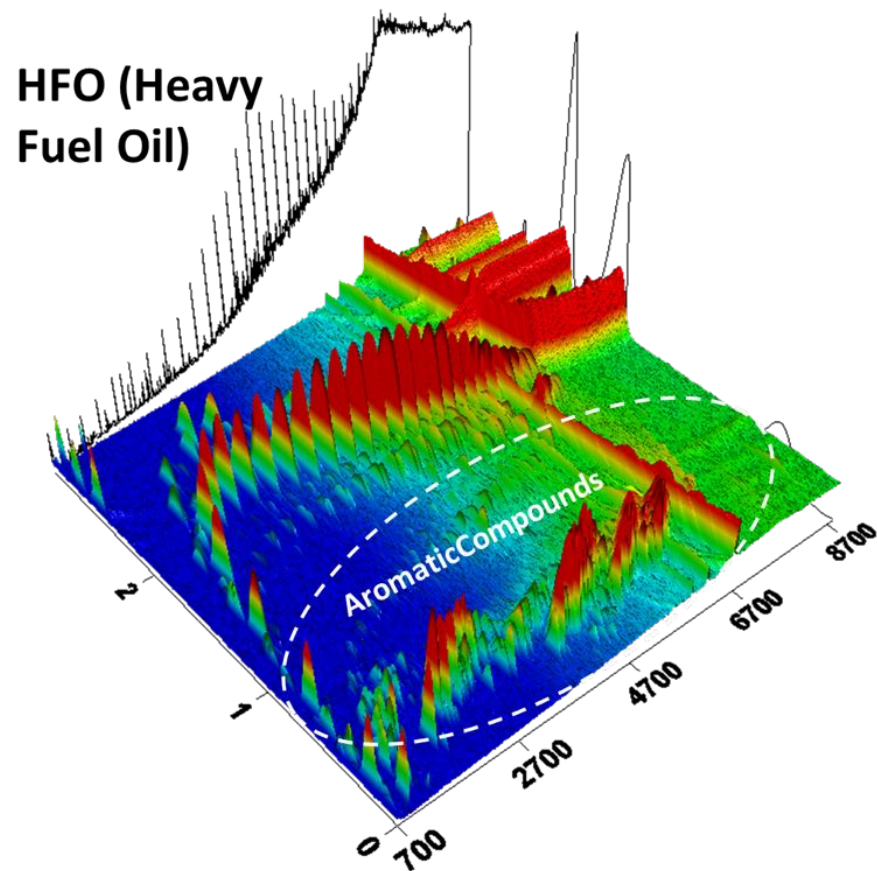
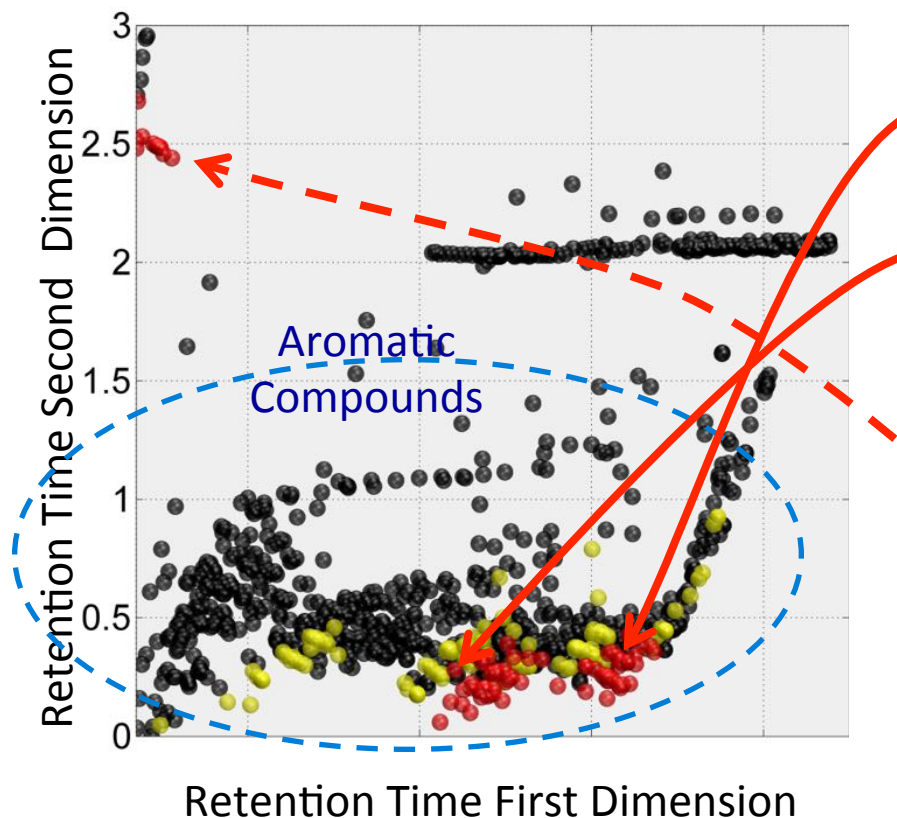
GCxGC chromatogram plot:
➔ Visualizes enhanced GC separation

Kendrick mass defect plot (PAH class)
➔ Visualizes enhanced mass separation



Analysis of the aromatic composition of heavy fuel oil by GCxGC-HRTOFMS

Accurate mass information could be used to calculate elemental composition and Kendrick mass defects from verified M^+ peaks

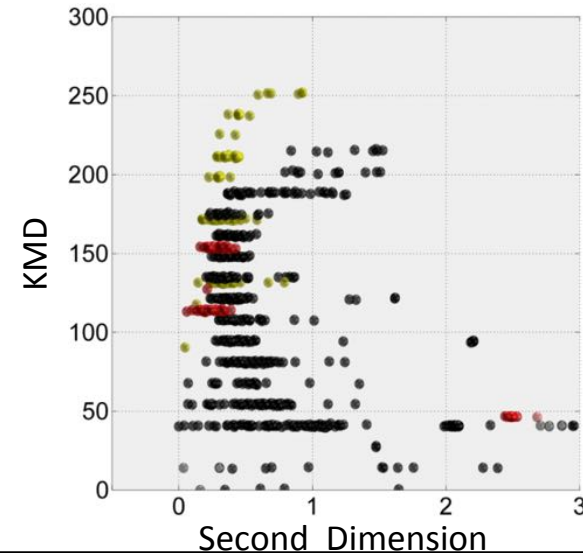
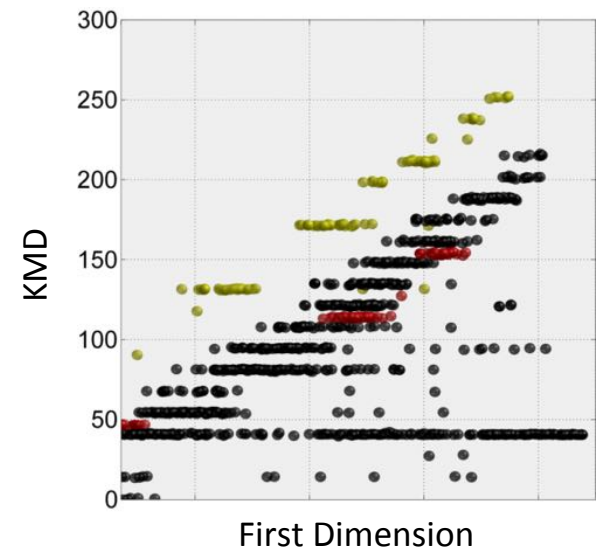
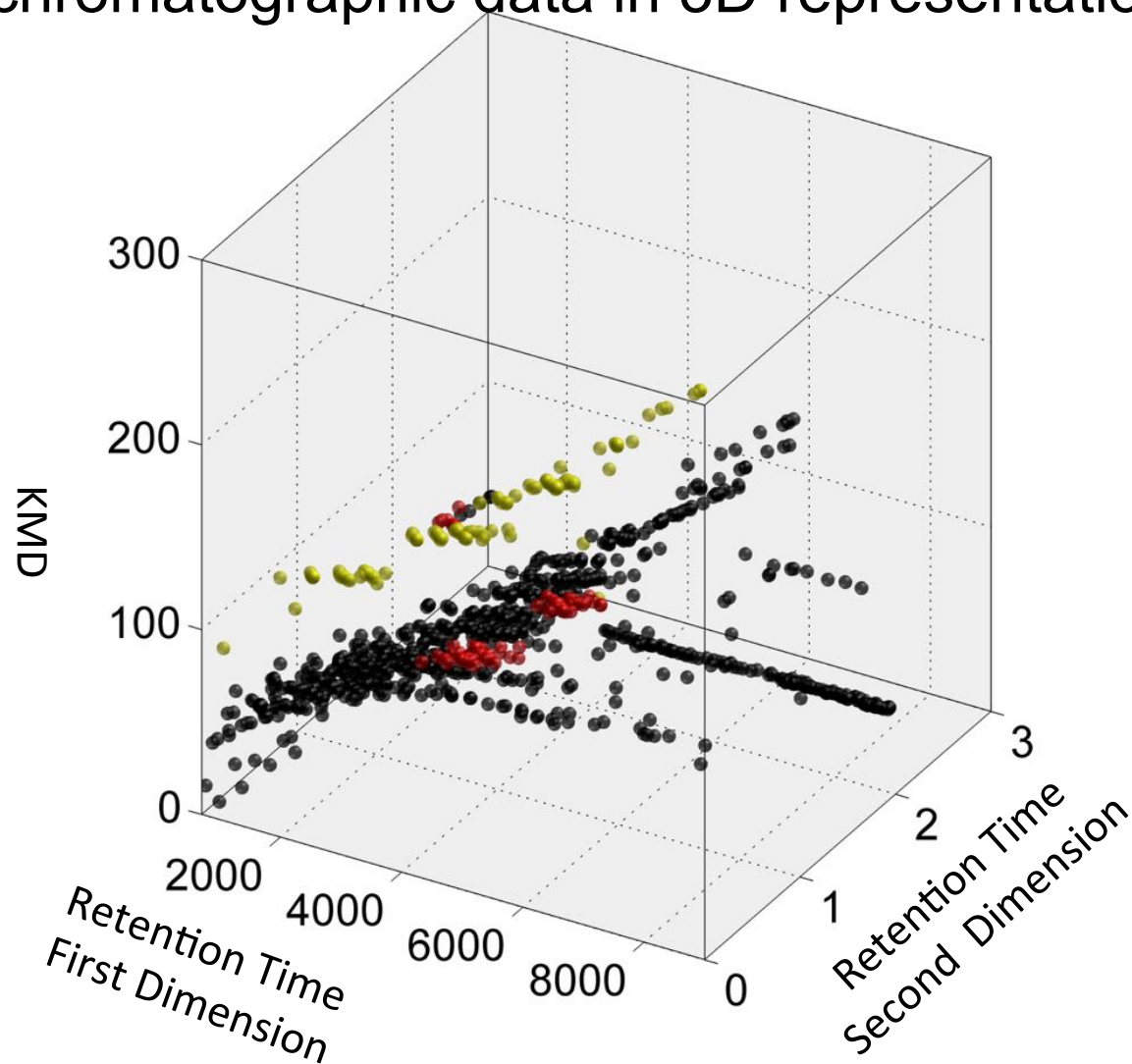


● Pure Hydrocarbons ● One or more sulfur ● One or more nitrogen

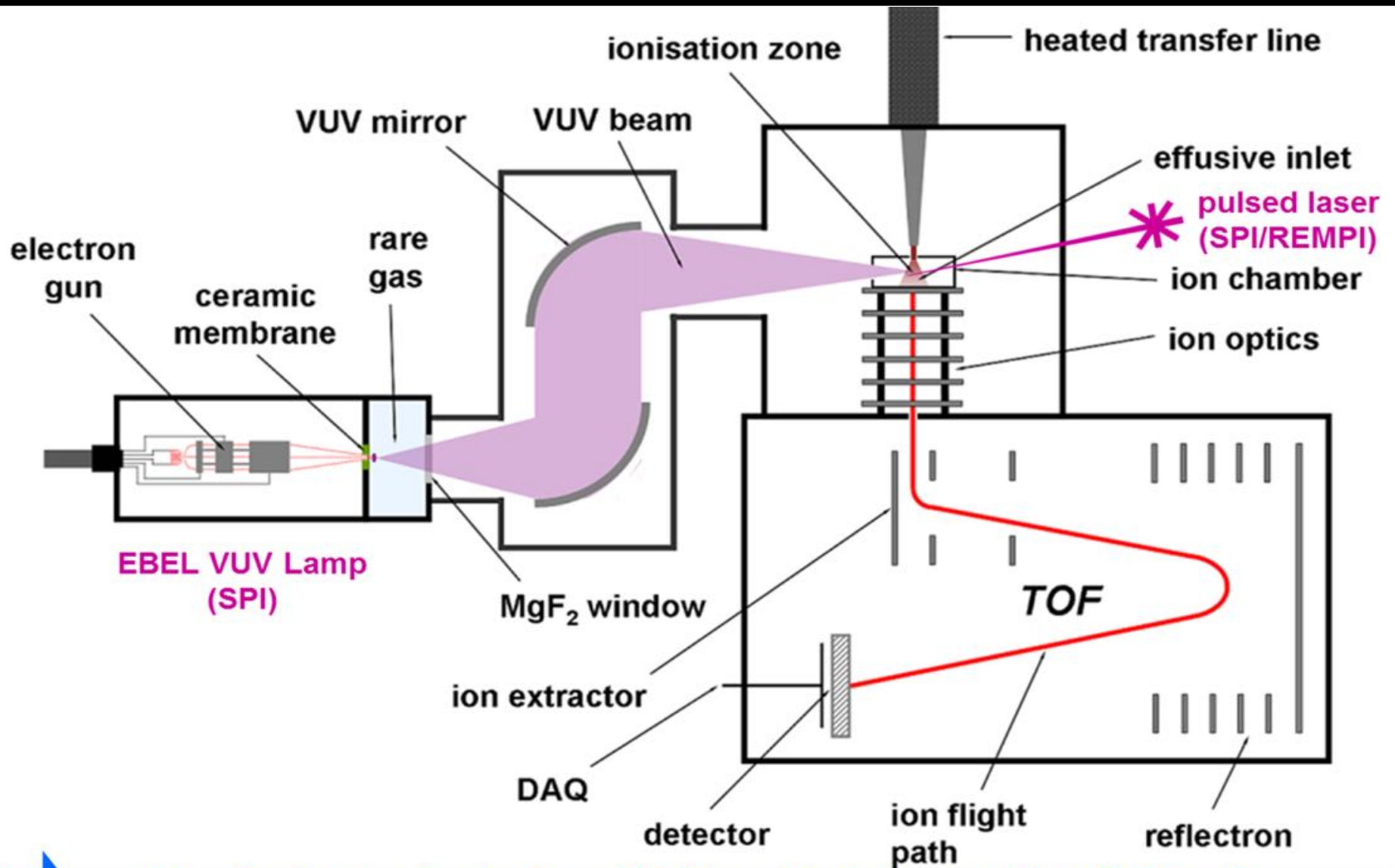
LECO GCxGC-HRTOF (Pegasus HRT, $R \sim 38.000$, < 1 ppm)

Analysis of the aromatic composition of heavy fuel oil by GCxGC-HRTOFMS

Mass defect information could be also be integrated with the 2 D chromatographic data in 3D representation



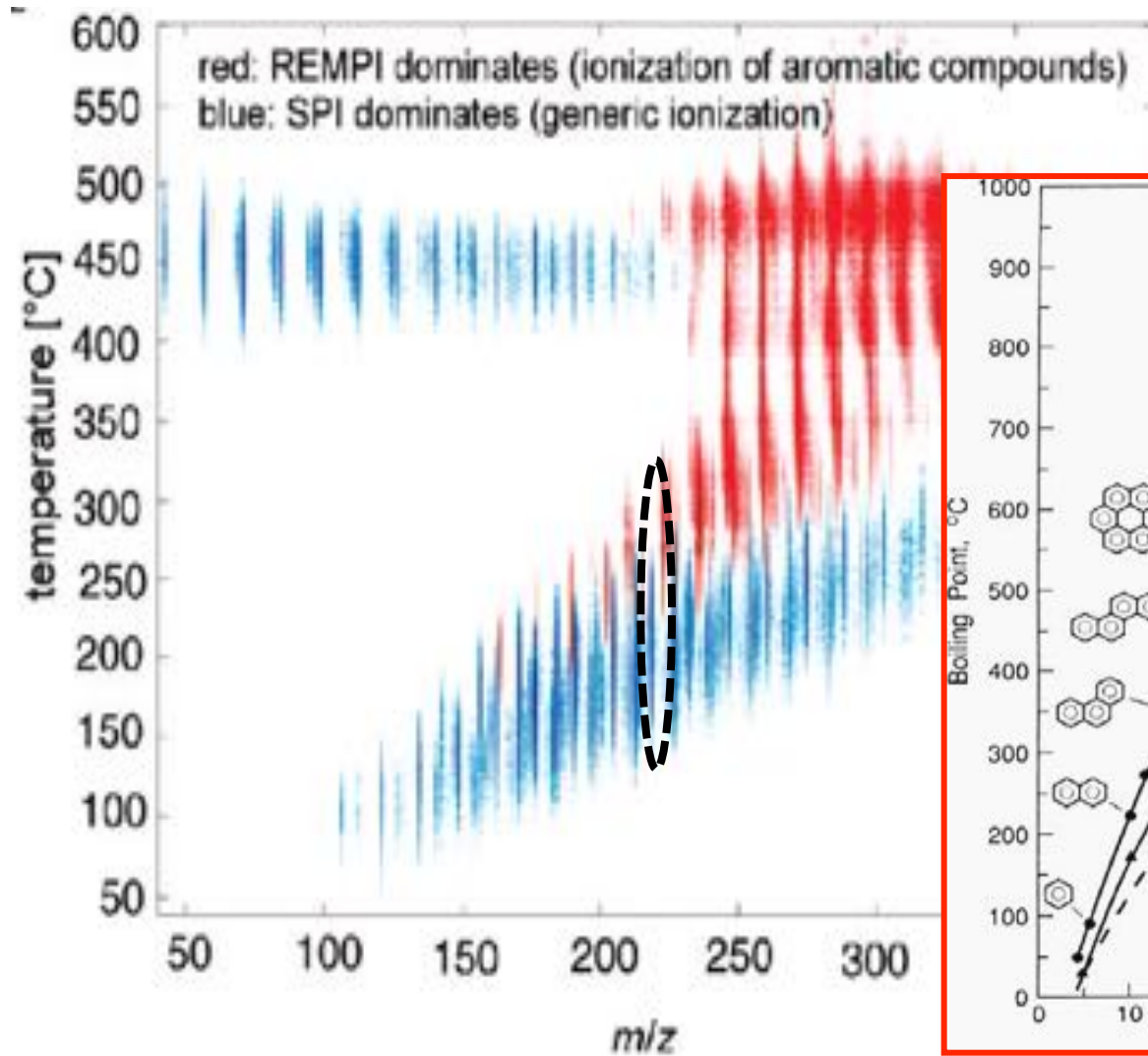
Thermogravimetry - Photo Ionization-Mass Spectrometry: Including soft ionisation MS and thermal process resolution in the analysis



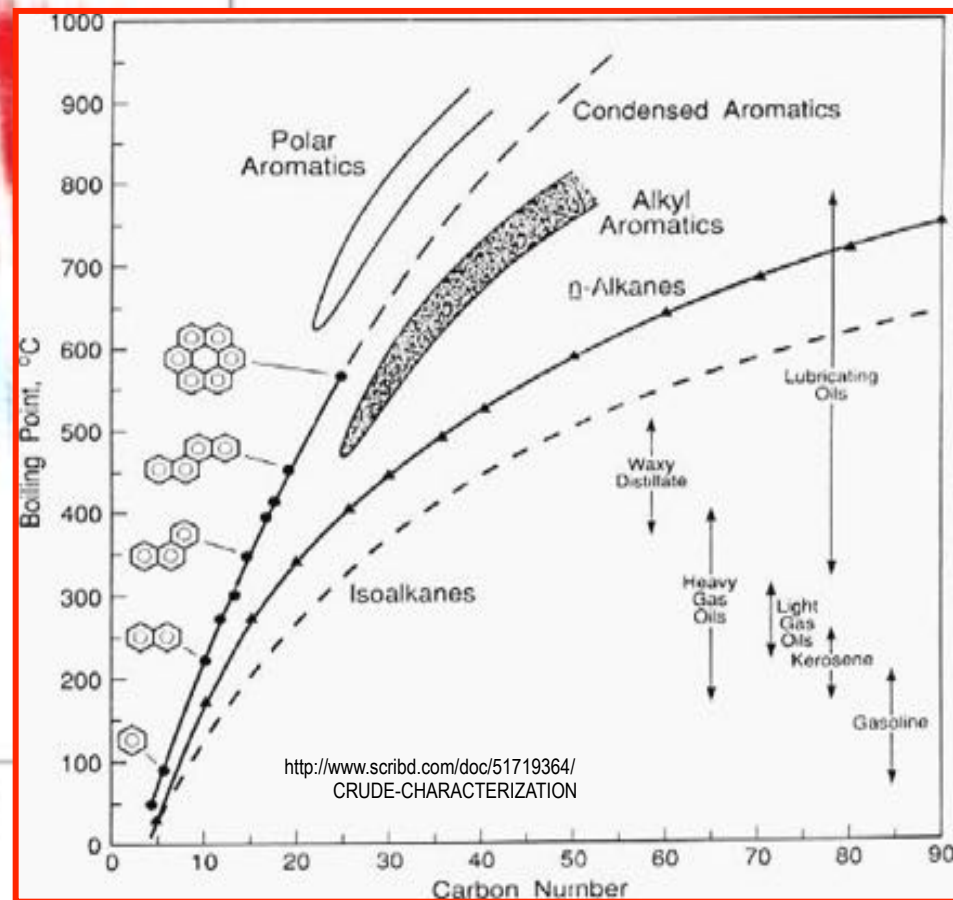
Single photon ionisation (SPI): easily interpretable MS (soft), adjustable energies (semi-specific), masking of background signals

Thermogravimetry - Photo Ionization-Mass Spectrometry: Including soft ionisation MS and thermal process resolution in the analysis

TG-SPI-MS and TG-REMPI-MS (selective “aromatic” ionization) results plotted together

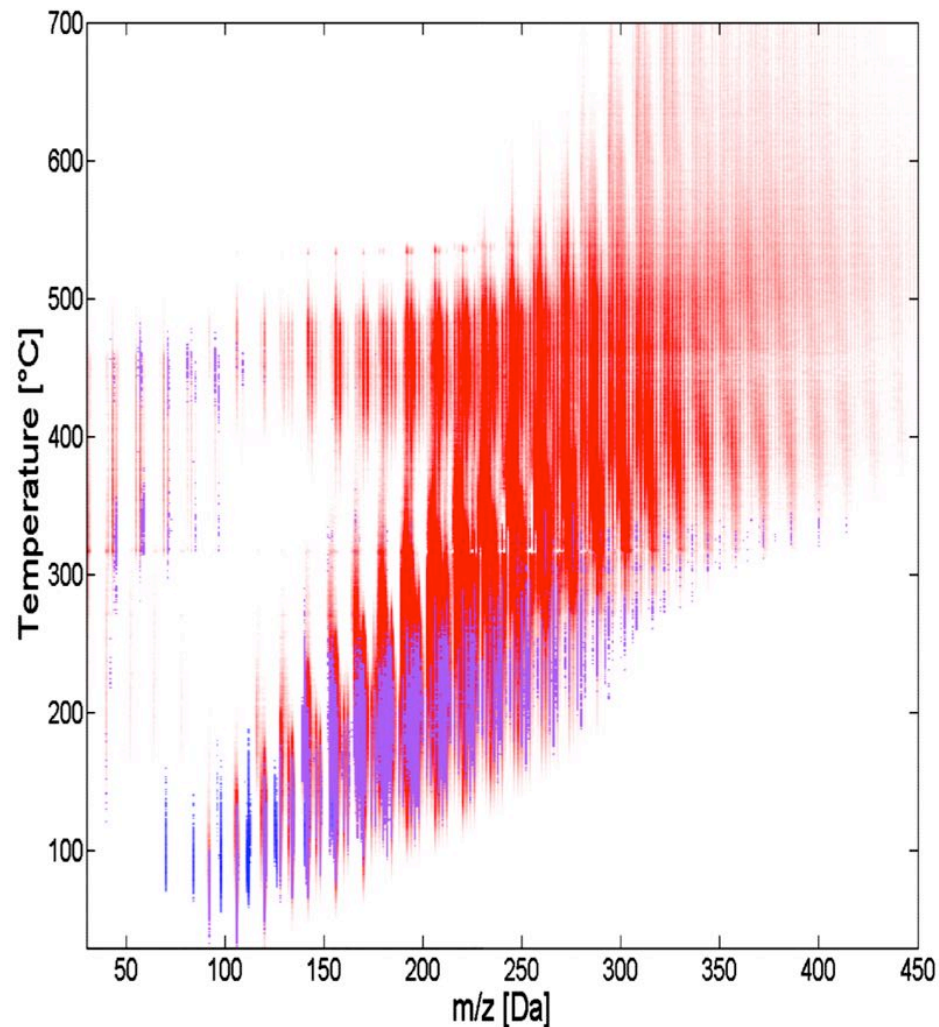


After Mietek Boduszynski

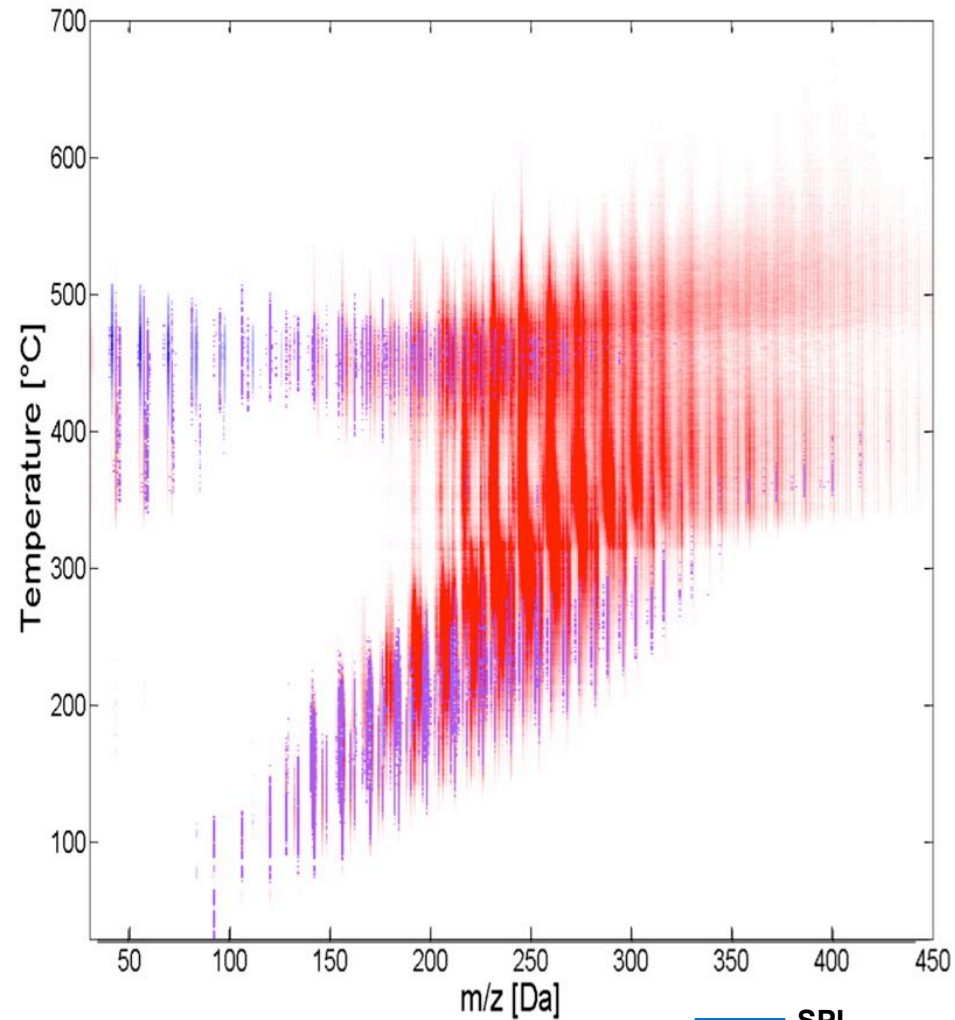


Thermogravimetry - Photo Ionization-Mass Spectrometry: Including soft ionisation MS and thermal process resolution in the analysis

Crude oil 1

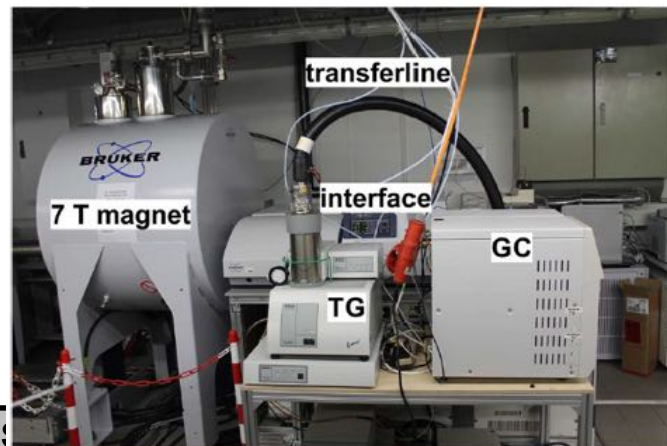
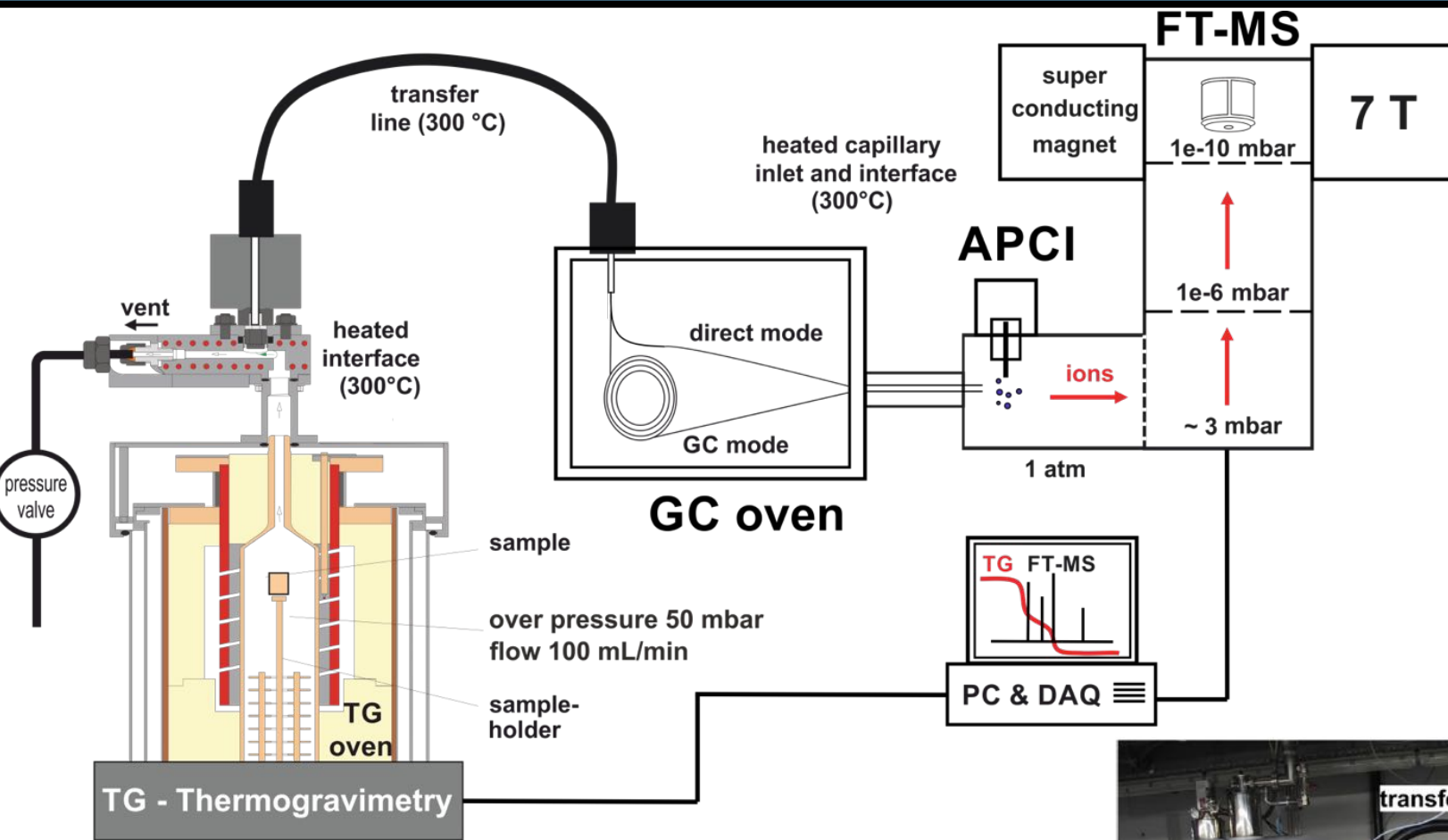


Crude oil 2



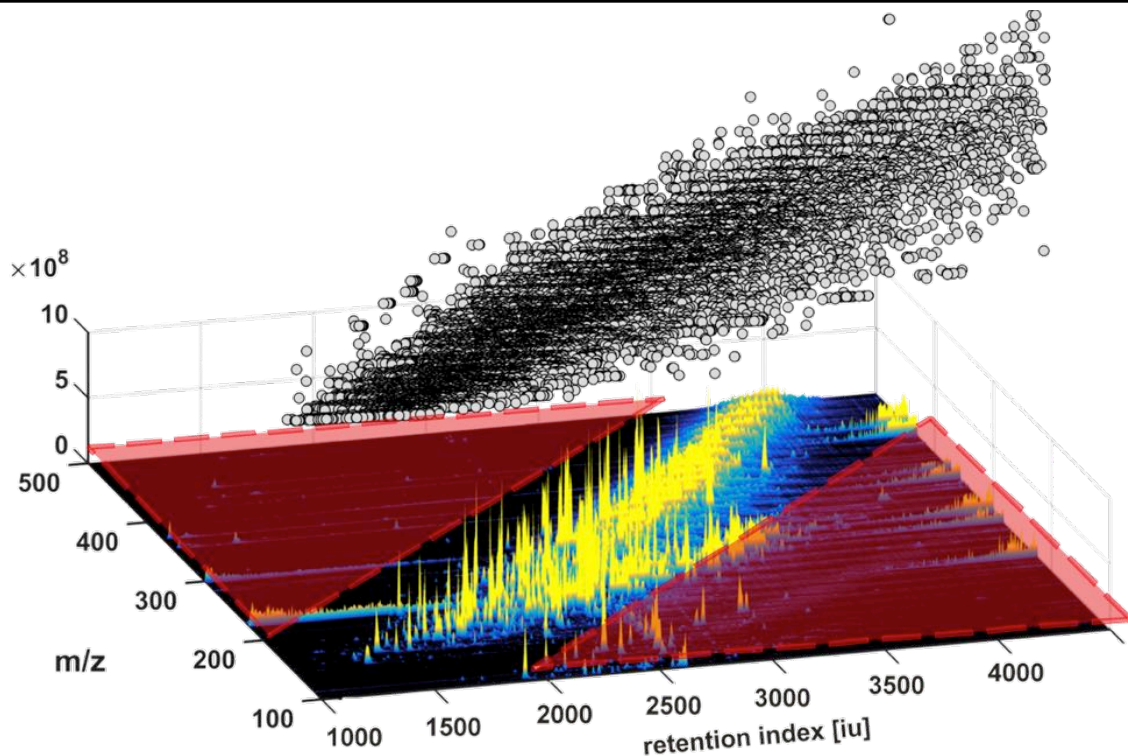
— SPI
— REMPI
— overlap

Thermal analysis (TA) or gas chromatography (GC) coupled to APCI-FTICR: Adding the time dimension to UHR-MS

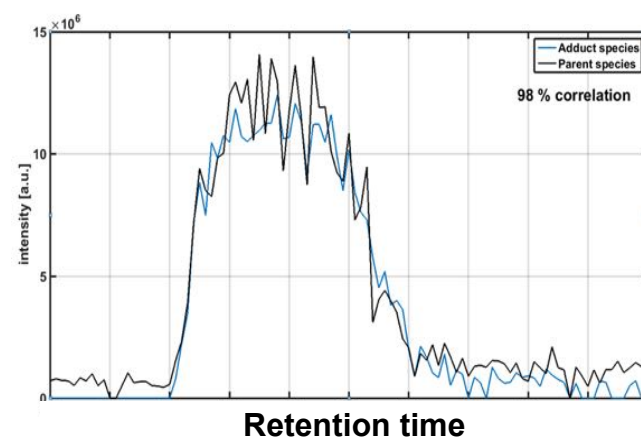
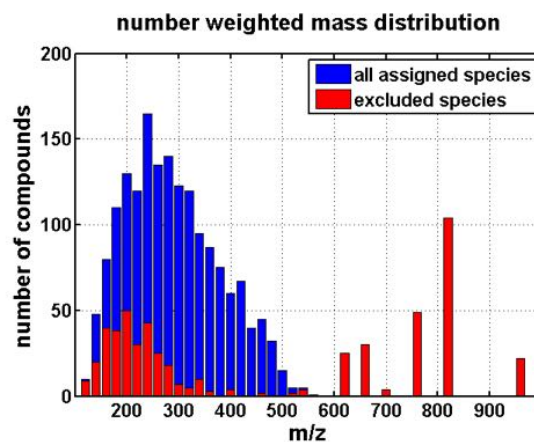
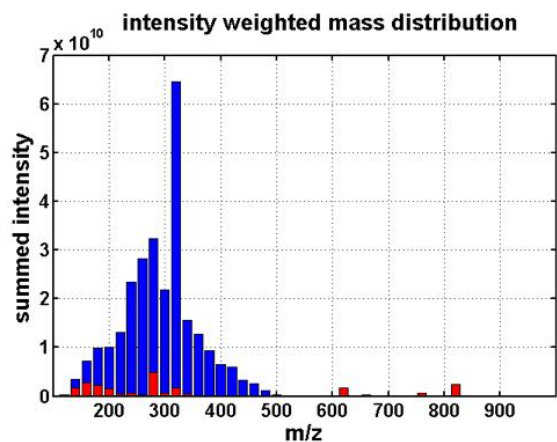


• APCI-FTICR easily switchable between GC- and TG-mode

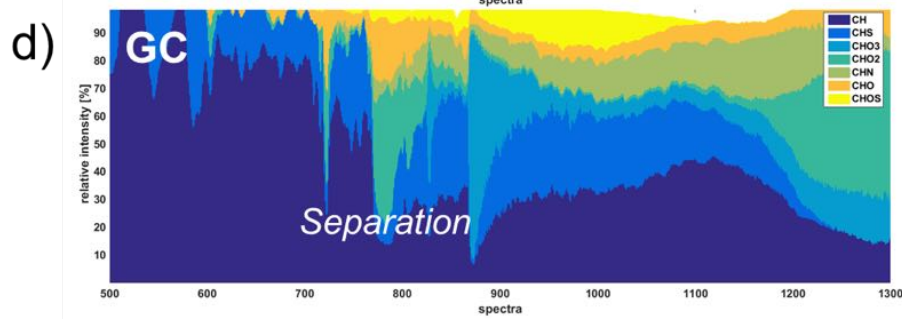
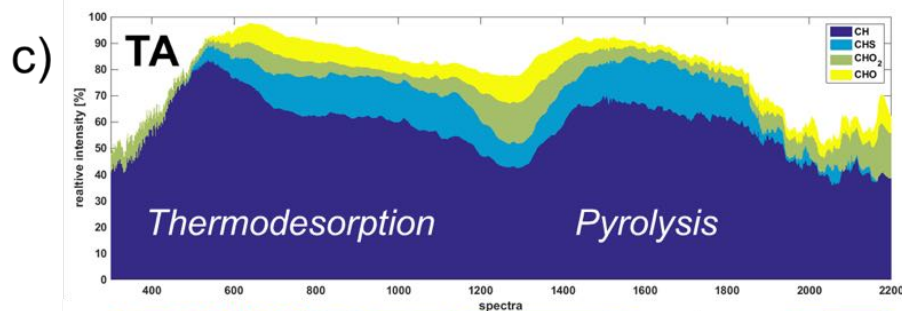
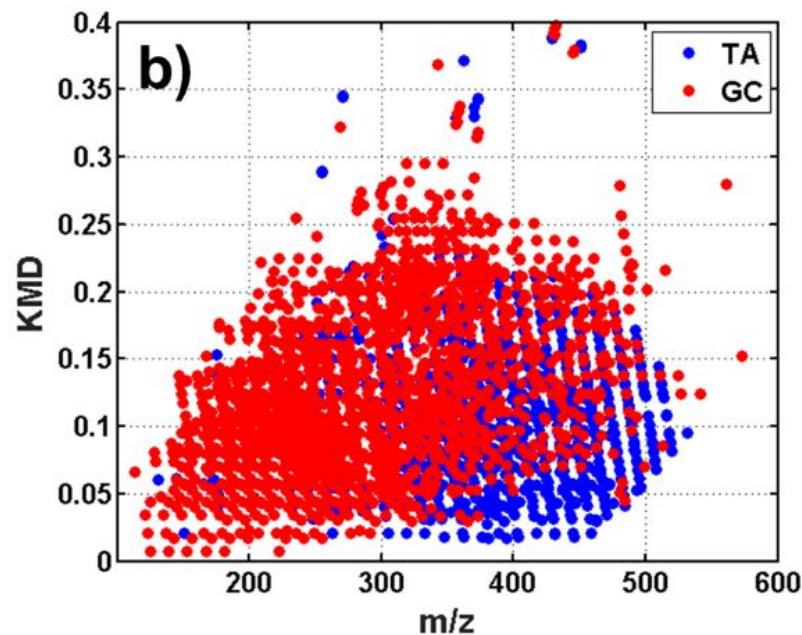
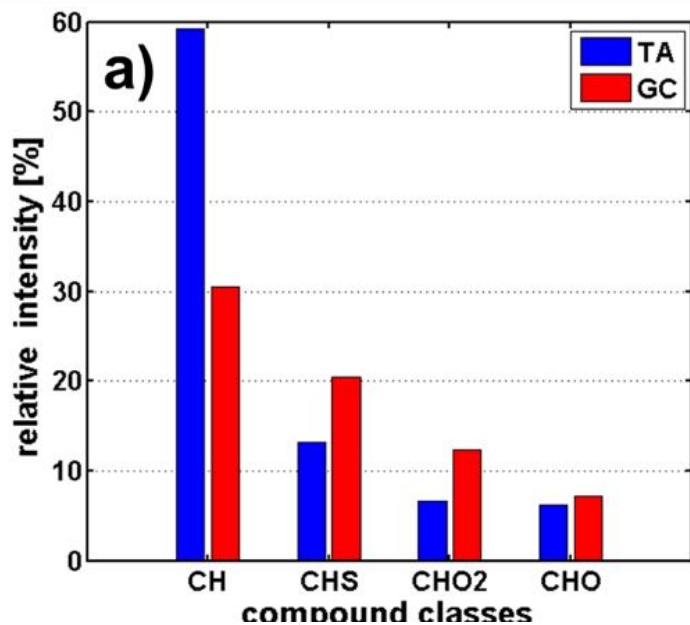
Gas chromatography (GC) coupled to APCI-FTICR: Adding the GC retention time dimension to UHR-MS



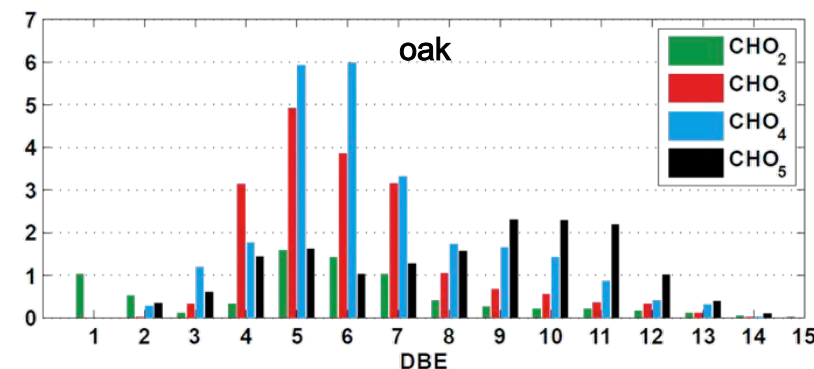
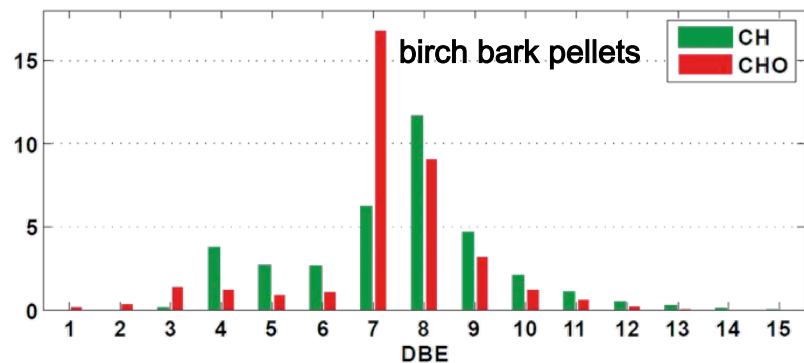
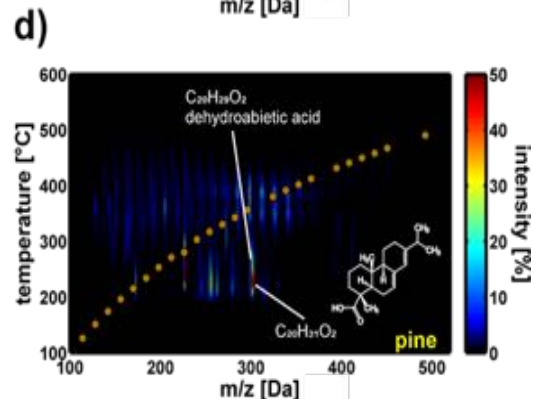
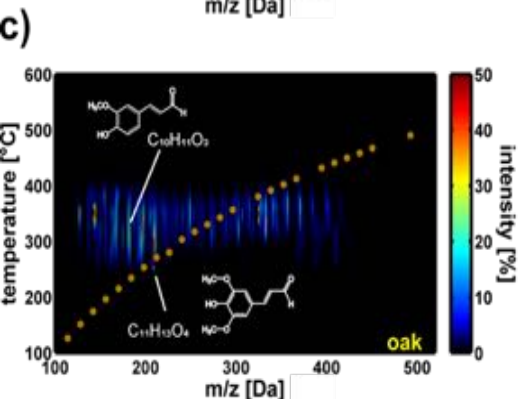
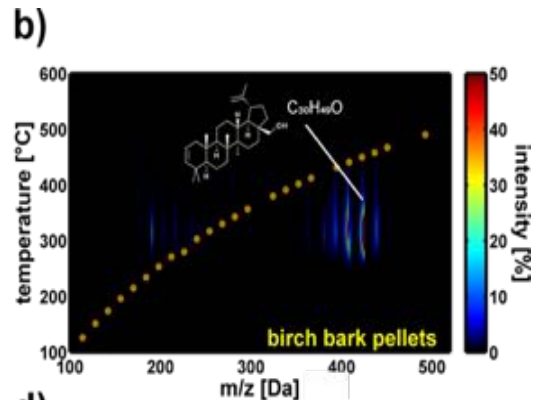
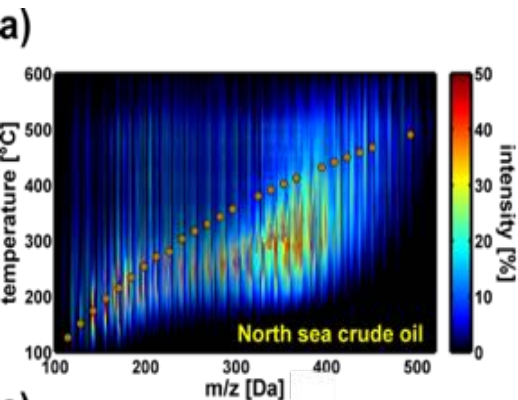
Filter steps	Heavy fuel oil
Detected signals	2776
Compounds removed by applying routine filters	1064
Compounds identified as known adducts and fragments	51
Compounds removed by retention time window correlation	281
Remaining compounds (number of different elemental compositions)	1380 (1003)



Comparison of thermal analysis- and gas chromatographic separation-APCI-FTICR results (Heavy Fuel Oil)

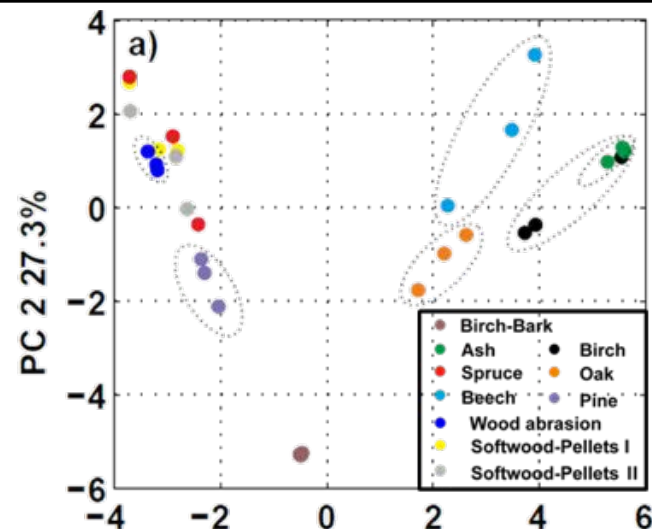
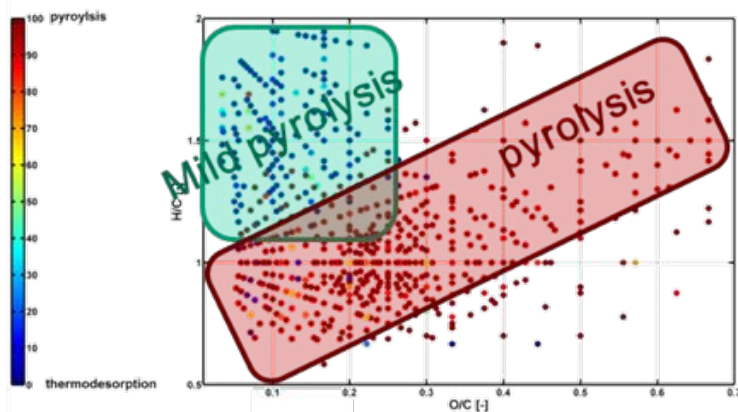
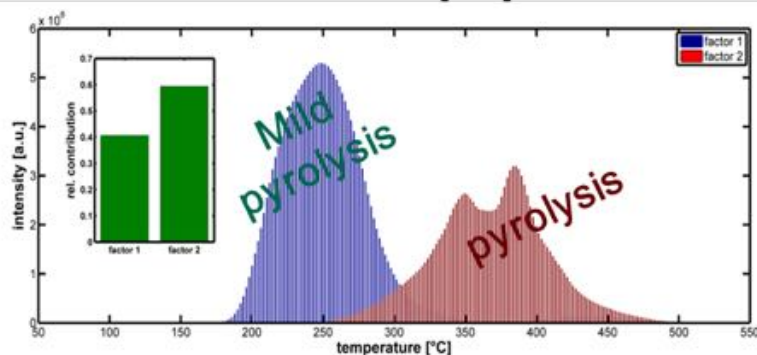
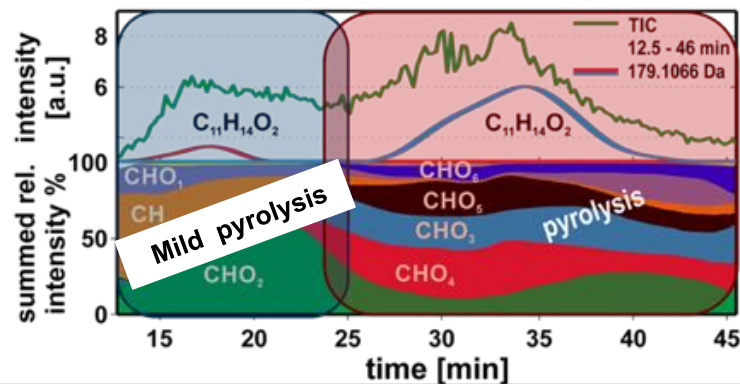


Thermal analysis (TA) coupled to APCI-FTICR: Adding the process time/temperature dimension to UHR-MS

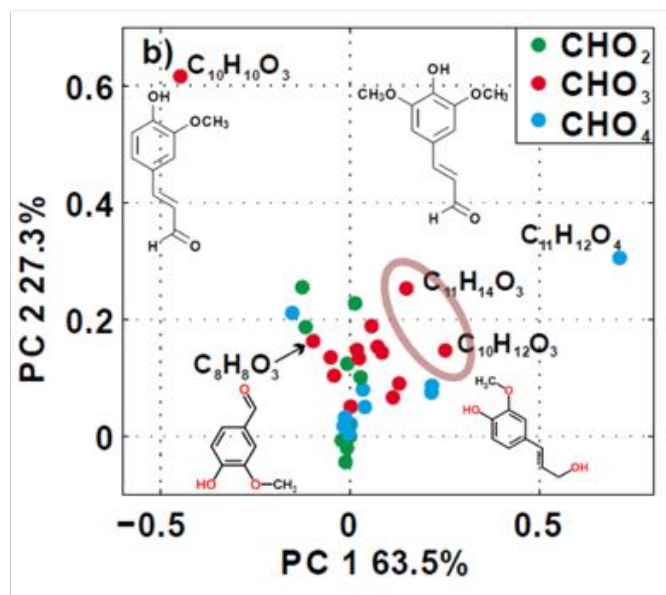


Thermal analysis (TA) coupled to APCI-FTICR: Adding the process time/temperature dimension to UHR-MS

Non negative matrix factorization (NMF)

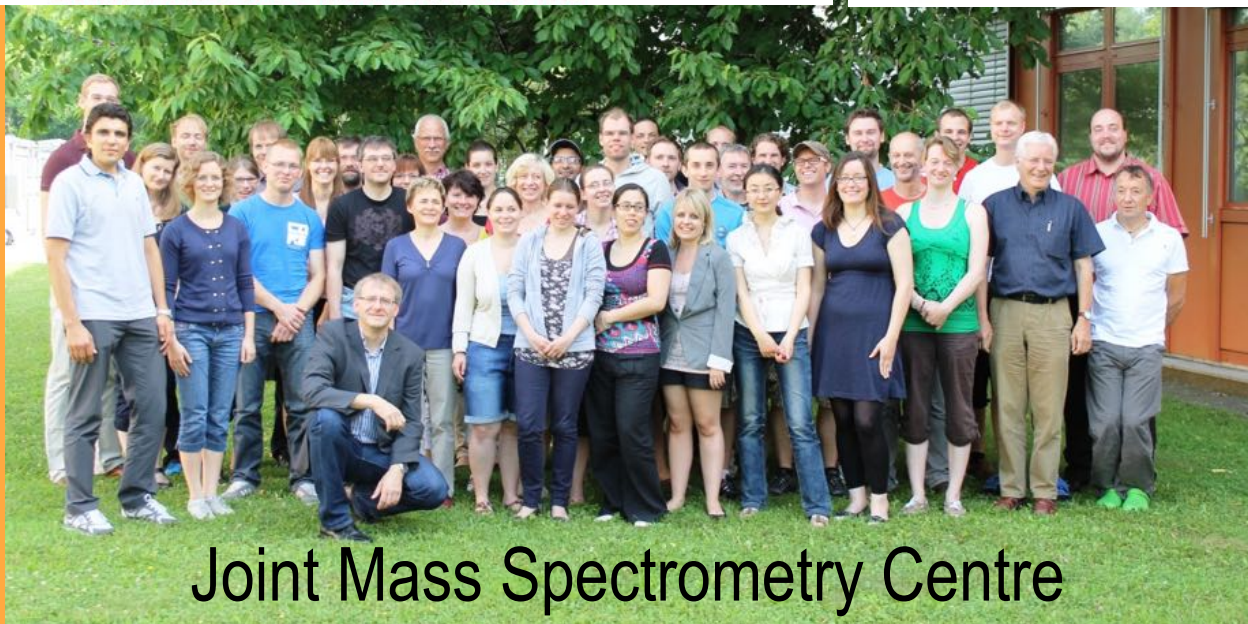


Principal Component Analysis (PCA)



Dr. J. Maguhn	S. Erdmann
Dr. T. Streibel	B. Weggler
Dr. J. Schnelle-Kreis	P. Sattler
Dr. M. Sklorz	G. Abbazade
Dr. J. Lintelmann	M. Oster
Dr. E. Feicht	E. Karg
Dr. M. Kirchner	B. Gruber
Dr. J. Passig	M. Jennerwein
Dr. G. Jakobi	F. Li
Dr. S. Smita	L. Müller
Dr. J. Orasche	A. Rheda
Dr. G Ferron	X. Wu
Dr. S. Haack	L. Müller
Dr. S. Ehlert	K. Lau
Dr. S. Öder	M. Hahn
E. Hübner	Y. Huang
T. Gröger	J. Varga
T. Miersch	S. Scholtes
A. Sutherland	C. Kühl
C. Rüger	R. Reiss
T. Schwemer	A. Hoffmann
G. Dragan	A. Ulbrich
H. Czech	C. Grimmer
V. Kohlmeier	
J. Sanchez	





Joint Mass Spectrometry Centre

Funding:

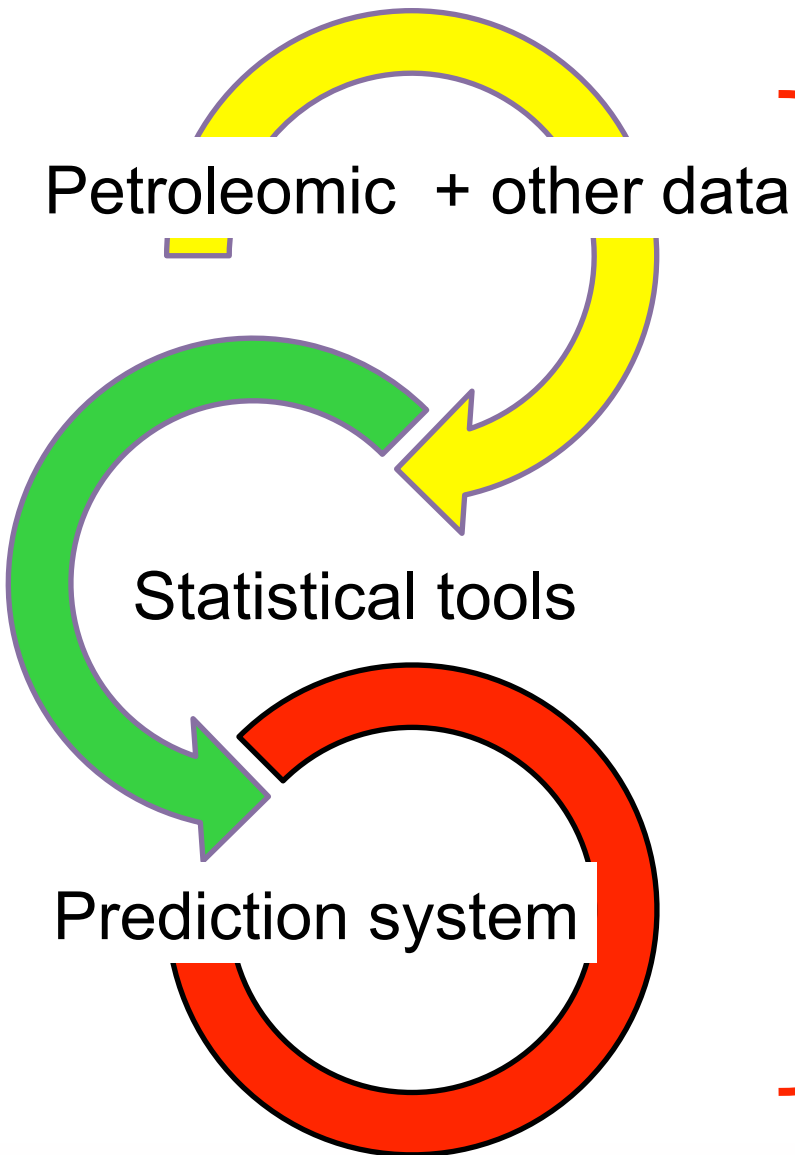
- Uni Rostock and State of Mecklenburg Vorpommern
- Helmholtz Zentrum München
- **Deutsche Forschungsgemeinschaft (DFG)**
- Bundesministerien für Bildung & Forschung/Wirtschaft (BMBF, BWM)
- **Bayerische Forschungstiftung (BFS)**
- Deutsche Gesetzl. Unfallversich. (DGUV)
- Bundeskriminalamt (BKA)
- Companies (SASOL Ltd., Netzsch GmbH, Photonion GmbH, LECO, Airsense GmbH, Borgwaldt KC, SABIC Inc., Shimadzu etc.)
- Helmholtz-Impulse and Networking- Fonds (Virtual Helmholtz Institute - HICE)

Combining Data and Data Mining in Petroleomics

Sunghwan Kim

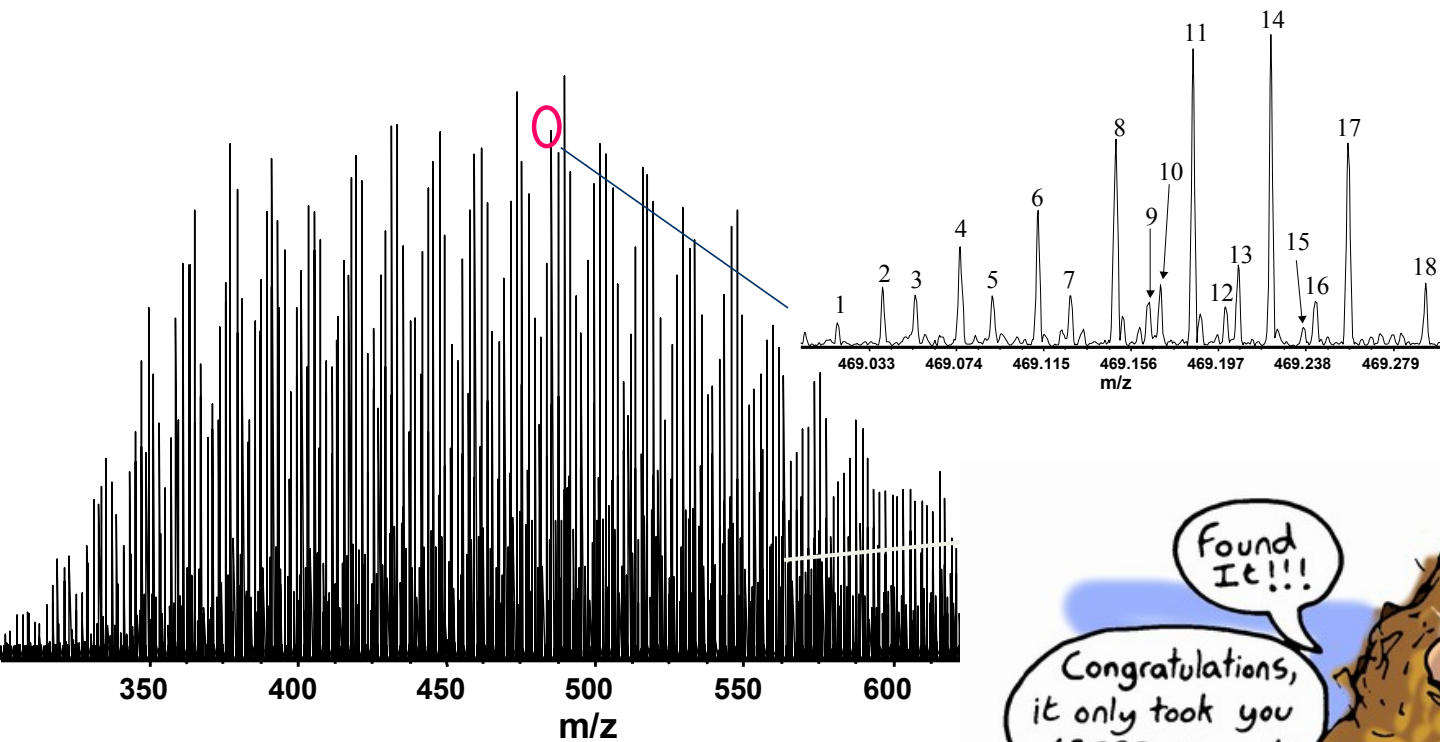
**EEMSLab
Kyungpook National University
Department of Chemistry**

Petroinformatics



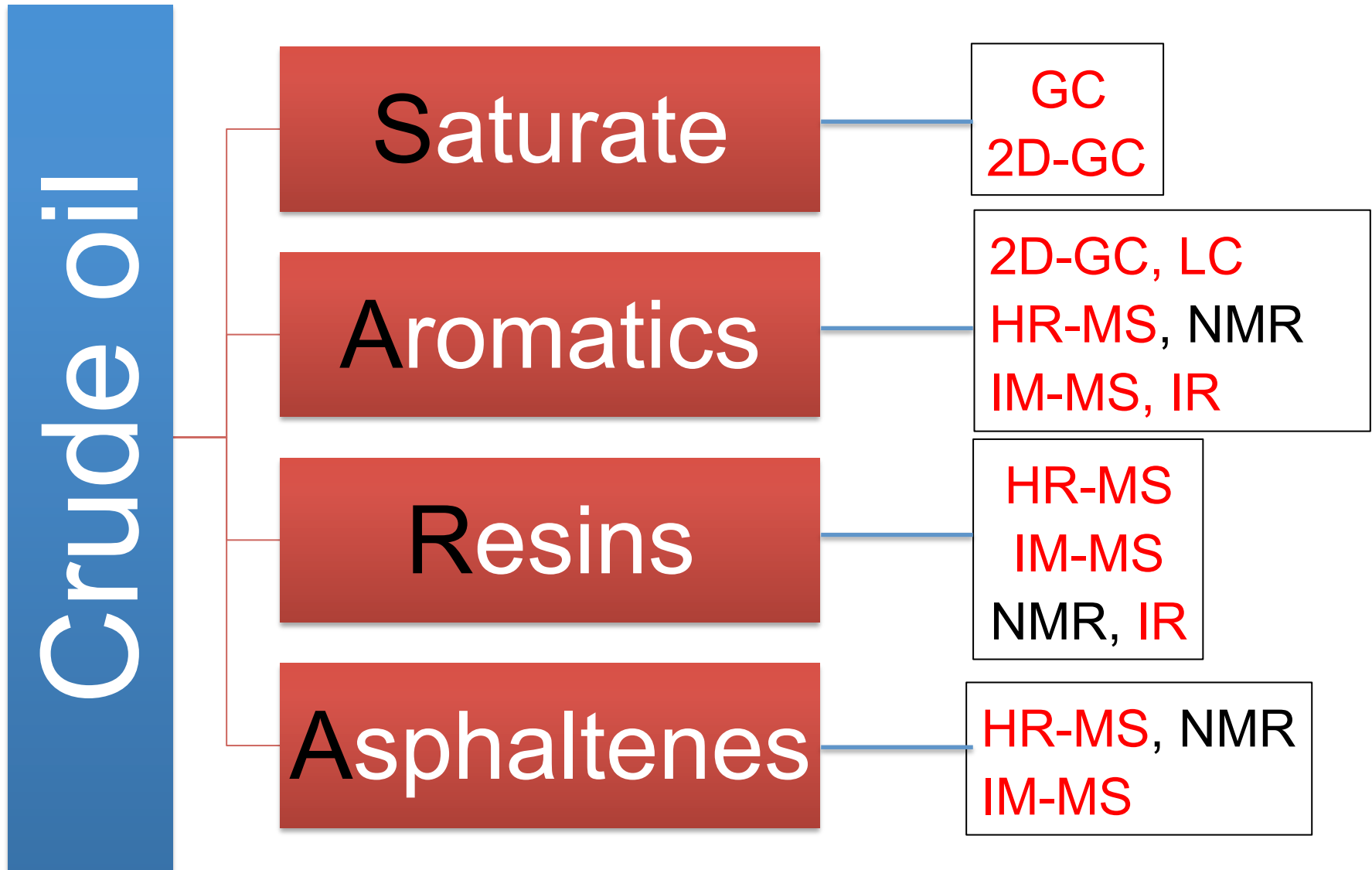
“It should be possible to predict the chemical and physical properties of crude oils from the chemical compositions determined using FT-ICR MS.”

Petroinformatics



Finding a needle in a haystack!!!





Atmospheric Pressure Photoionization Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry To Characterize Asphaltene Deposit Solubility Fractions: Comparison to Bulk Properties

Energy Fuels 2016, 30, 915–923

Estrella Rogel^{*,†} and Matthias Witt[‡]

$$\rho = -0.064H + 1.6793$$

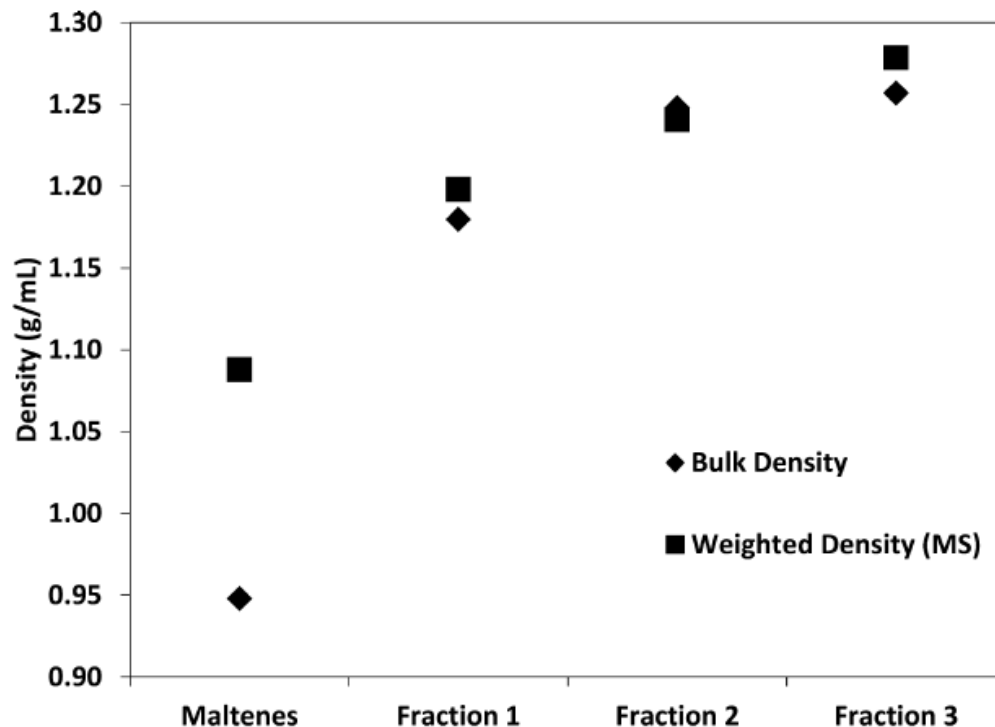


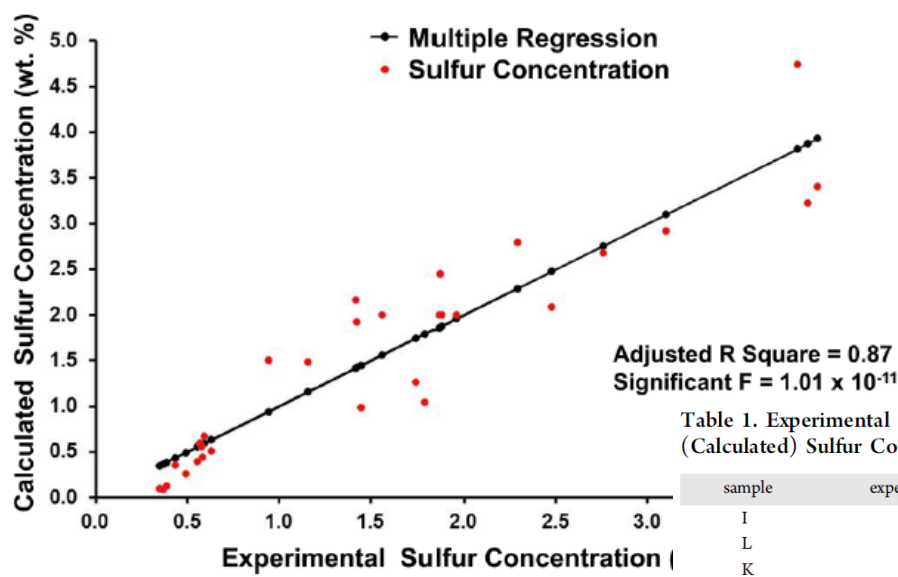
Figure 13. Comparison of average density values calculated on the basis of MS data and experimental bulk values determined previously.¹⁵

Calculation of the Total Sulfur Content in Crude Oils by Positive-Ion Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Yuri E. Corilo,^{*,†} Steven M. Rowland,[‡] and Ryan P. Rodgers^{*,†,§}

[†]National High Magnetic Field Laboratory, and [‡]Future Fuels Institute, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310-4005, United States

[§]Department of Chemistry and Biochemistry, Florida State University, 95 Chieftain Way, Tallahassee, Florida 32306, United States



shows the calculated sulfur concentration plotted against the experimental sulfur concentration obtained from bulk elemental analysis. A linear trend confirms that the model explains the sulfur content with good accuracy and precision.

$$\%S = 0.94 \left(\frac{S_1}{HC} \right) + 0.06 \left(\frac{S_2}{HC} \right) + 4.21 \left(\frac{S_3}{HC} \right) + 0.31 \quad (1)$$

Table 1. Experimental Sulfur Concentration, Ratio of the Relative Abundances for S₁/HC, S₂/HC, and S₃/HC, and Predicted (Calculated) Sulfur Concentration

sample	experimental %S	S ₁ /HC	S ₂ /HC	S ₃ /HC	calculated %S	error
I	3.79	3.48	1.77	0.14	4.03	0.24
L	2.34	1.88	0.63	0.02	2.12	-0.23
K	2.00	1.41	0.54	0.07	1.89	-0.11
J	1.74	1.22	0.32	0.00	1.43	-0.31
A	0.97	0.21	0.00	0.00	0.50	-0.47
D	0.94	0.66	0.13	0.00	0.91	-0.03
B	0.90	0.25	0.00	0.00	0.54	-0.36
G	0.61	0.65	0.12	0.01	0.93	0.32
F	0.60	0.24	0.00	0.00	0.53	-0.07
E	0.56	0.59	0.10	0.00	0.85	0.29
H	0.28	0.26	0.00	0.00	0.55	0.27

-0.04 ± 0.36

Figure 4. Results of the calculated sulfur concentration against the experimental sulfur concentration.

Laser desorption ionization FT-ICR mass spectrometry and CARSPLS for predicting basic nitrogen and aromatics contents in crude oils

Luciana A. Terra^a, Paulo R. Filgueiras^a, Lílian V. Tose^b, Wanderson Romão^{b,c}, Eustáquio V.R. de Castro^b, Lize M.S.L. de Oliveira^d, Júlio C.M. Dias^d, Boniek G. Vaz^{b,e}, Ronei J. Poppi^{a,*}

^aInstitute of Chemistry, State University of Campinas, Campinas, SP, Brazil

^bPetroleomic and Forensic Chemistry Laboratory, Department of Chemistry, Federal University of Espírito Santo, 20075-910 Vitória, ES, Brazil

^cFederal Institute of Education, Science and Technology of

^dCENPES/PETROBRAS, Rio de Janeiro, RJ, Brazil

^eChemistry Institute, Federal University of Goiás, Goiânia,

L.A. Terra et al. / Fuel 160 (2015) 274–281

Table 1
Variables selected by CARS for the basic nitrogen and aromatic compounds.

Basic nitrogen				Aromatics	
C ₂₈ H ₂₄	C ₃₇ H ₄₄	C ₄₇ H ₇₀	C ₂₈ H ₂₉ N	C ₂₃ H ₂₁ N + H	C ₃₇ H ₅₂
C ₂₃ H ₂₆	C ₄₁ H ₅₀	C ₅₂ H ₇₀	C ₂₈ H ₃₃ N	C ₂₆ H ₂₁ N + H	C ₄₀ H ₅₆
C ₂₅ H ₂₈	C ₄₂ H ₅₂	C ₅₄ H ₇₄	C ₃₈ H ₅₃ N	C ₂₉ H ₃₃ N + H	C ₄₇ H ₆₈
C ₂₆ H ₃₀	C ₄₃ H ₅₄	C ₅₂ H ₇₆	C ₃₉ H ₄₉ N	C ₃₇ H ₂₄ O ₂ + H	C ₃₇ H ₃₅ N
C ₂₉ H ₃₀	C ₄₃ H ₅₆	C ₅₇ H ₈₀	C ₃₉ H ₅₁ N	C ₃₈ H ₂₆ O ₂ + H	C ₃₉ H ₃₇ N
C ₂₇ H ₃₂	C ₄₄ H ₅₆	C ₁₇ H ₁₉ N	C ₄₀ H ₄₇ N	C ₃₉ H ₂₆ O ₂ + H	C ₄₉ H ₅₃ N
C ₃₂ H ₃₄	C ₄₅ H ₆₂	C ₂₀ H ₂₁ N	C ₄₀ H ₅₁ N	C ₃₉ H ₂₈ O ₂ + H	C ₅₄ H ₈₁ N
C ₃₂ H ₃₆	C ₄₈ H ₆₄	C ₂₁ H ₂₃ N	C ₄₈ H ₆₅ N	C ₄₀ H ₂₈ O ₂ + H	C ₅₄ H ₈₁ N
C ₃₄ H ₄₀	C ₅₀ H ₆₆	C ₂₂ H ₂₁ N	C ₆₃ H ₉₃ N		C ₁₆ H ₃₃ N ₃ O ₂ S
C ₃₅ H ₄₀	C ₄₆ H ₆₈	C ₂₅ H ₂₇ N	C ₆₆ H ₉₇ N		C ₂₆ H ₄₅ N ₃ O ₂ S + H

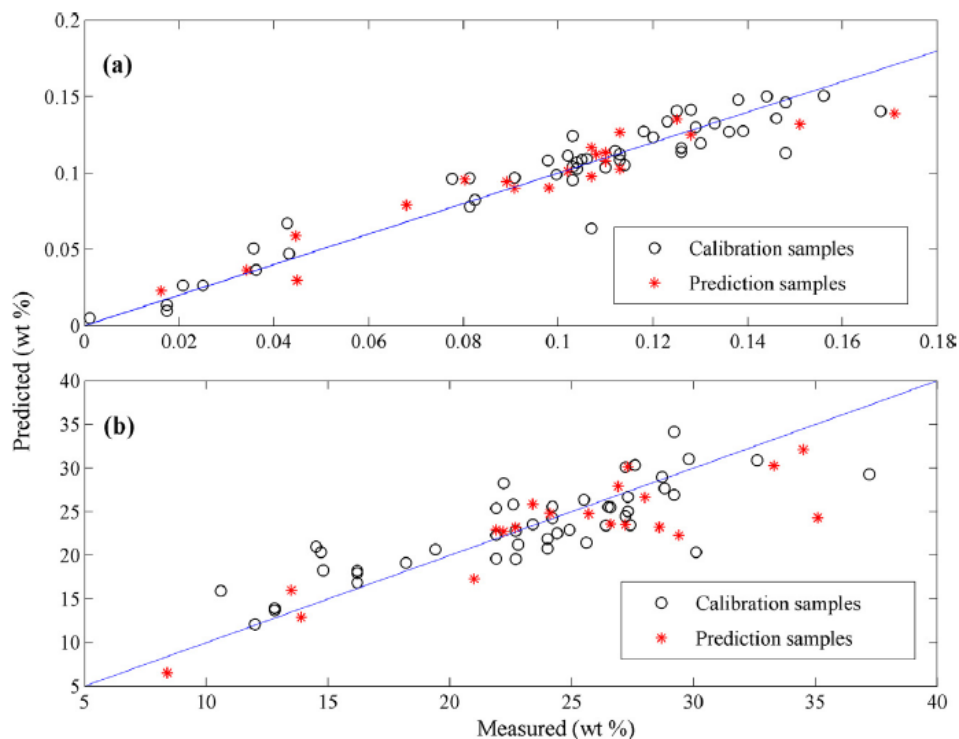


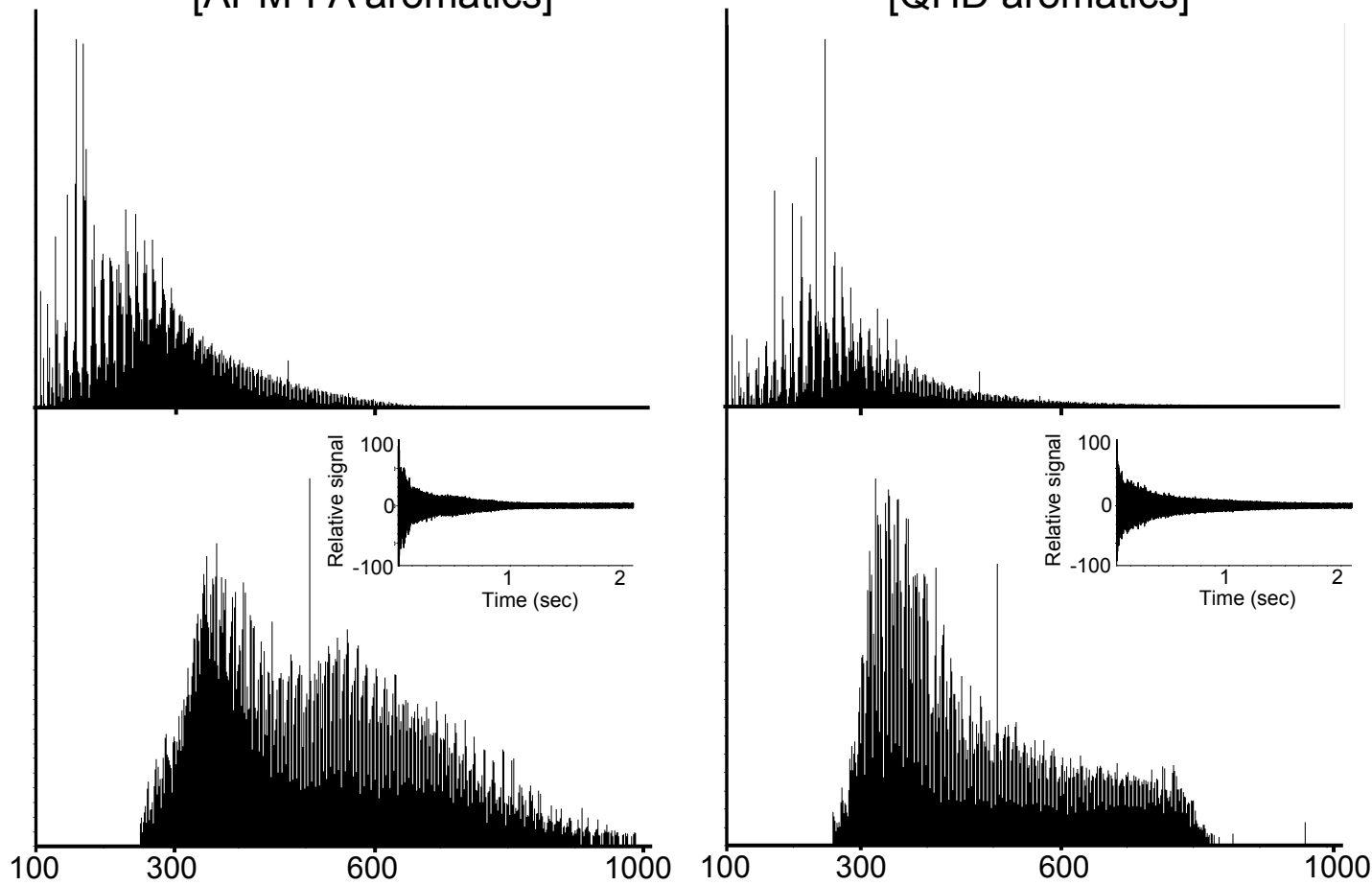
Fig. 8. Plot of values predicted by CARSPLS against those measured by a reference method. (a) Basic nitrogen and (b) aromatics properties prediction.

DBE vs #C plot as a basis for combining data

(a) Orbitrap MS

[APM-FA aromatics]

[QHD aromatics]

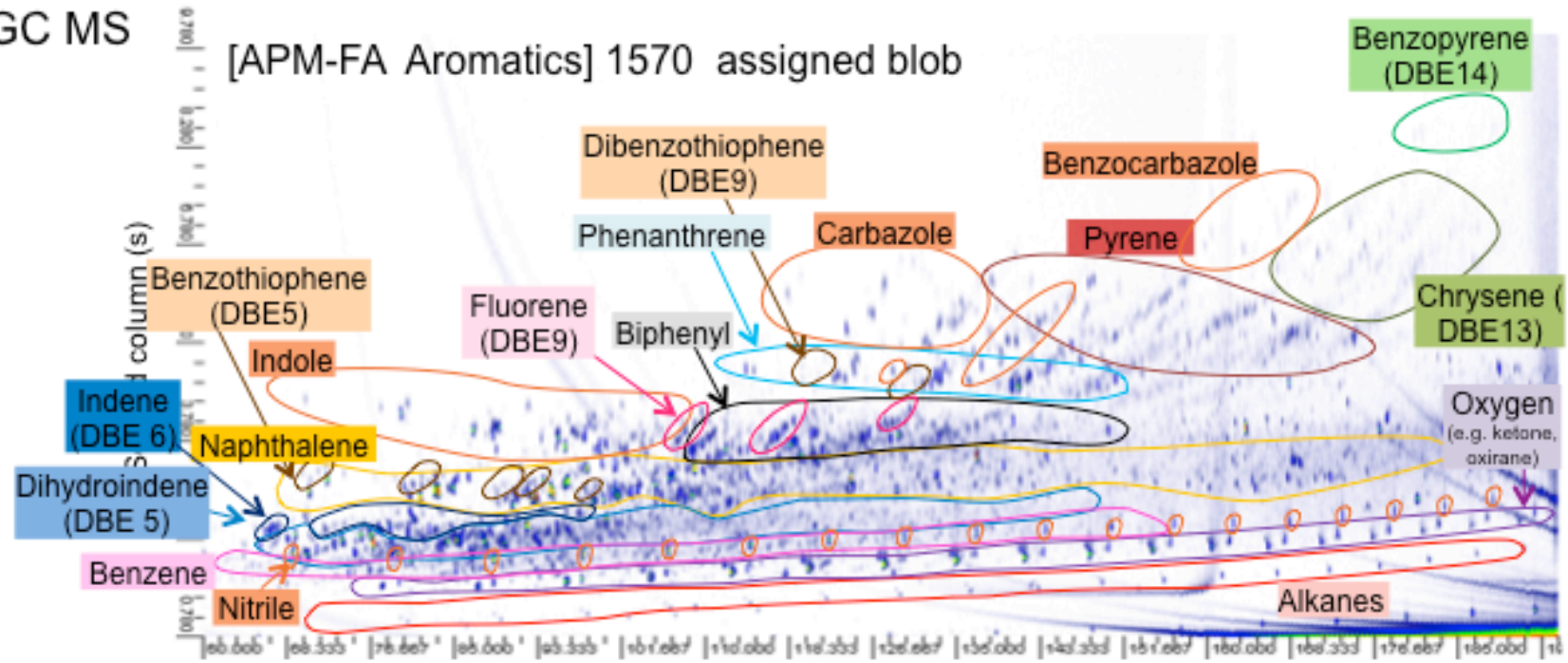


(b) FT-ICR MS

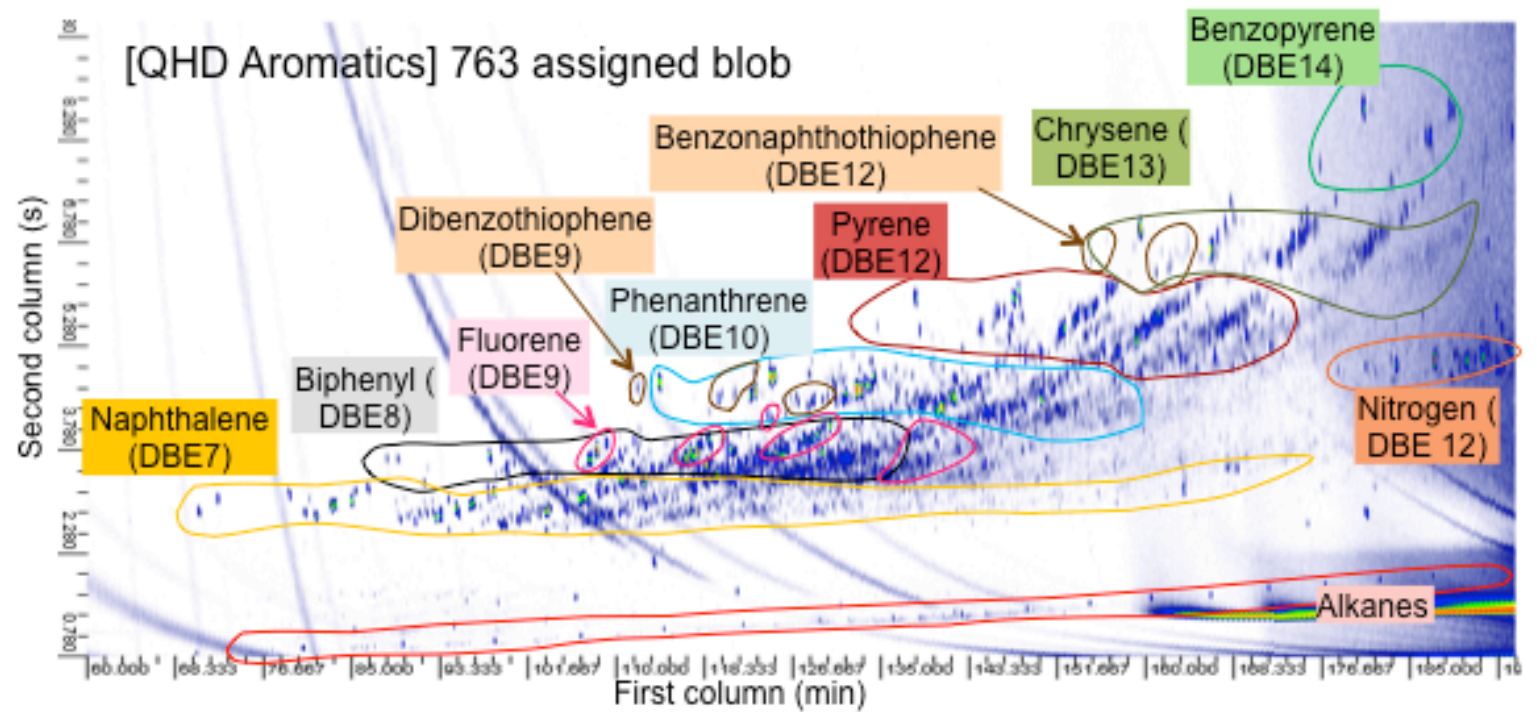


(c) 2D GC MS

[APM-FA Aromatics] 1570 assigned blob



[QHD Aromatics] 763 assigned blob



b

Chrysene

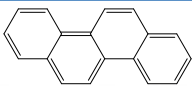
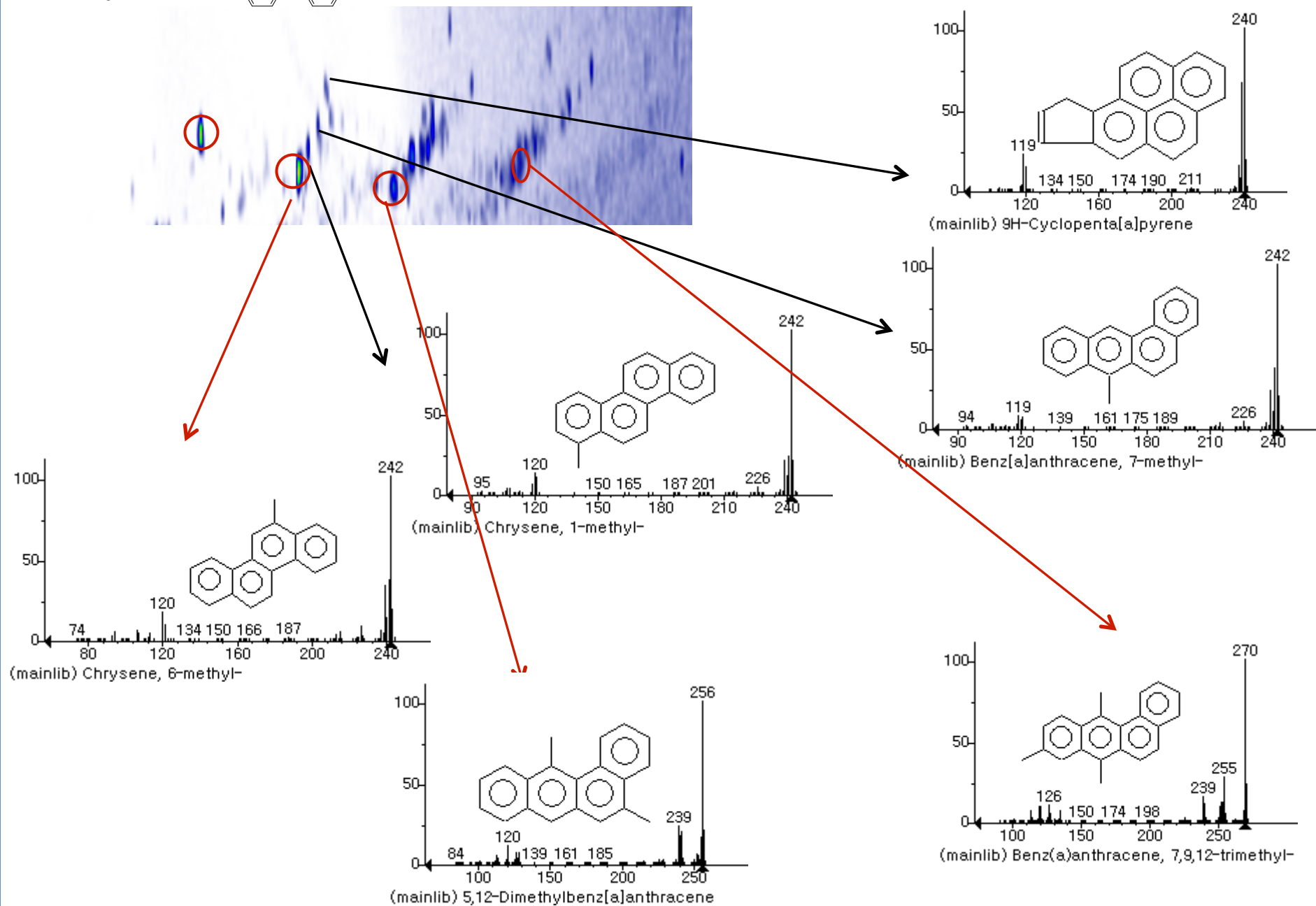
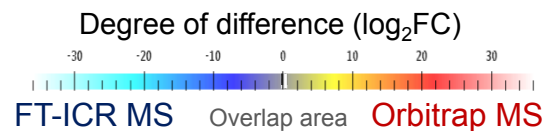


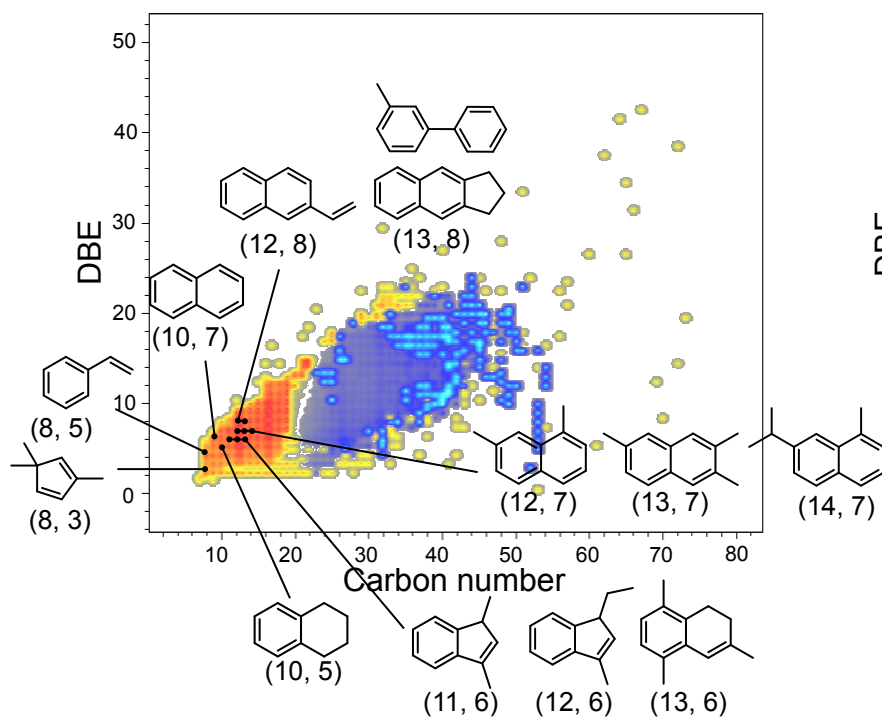
Figure S1.



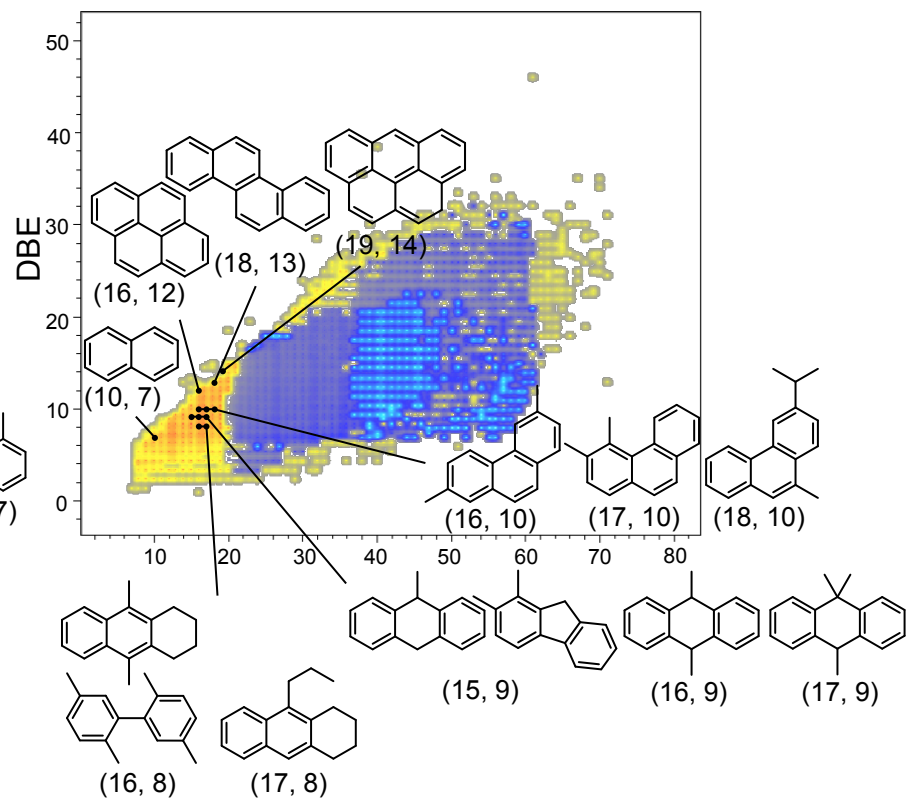
(a) HC class



[APM-FA aromatics]



[QHD aromatics]



Converting DBE to structures and comparison with NMR data

Manuscript in preparation

a flow rate of 25 mL/min
 0.1~0.3 g of sample loaded

Time(min) \ Solvent(%)	0.00	7.00	14.00	21.00	28.00	35.00	42.00	49.00
Toluene(%)	0	5	30	100	0	0	0	0
Ethyl acetate(%)	0	0	0	0	100	0	0	0
Methanol(%)	0	0	0	0	0	100	0	0
Hexane(%)	100	95	70	0	0	0	100	100

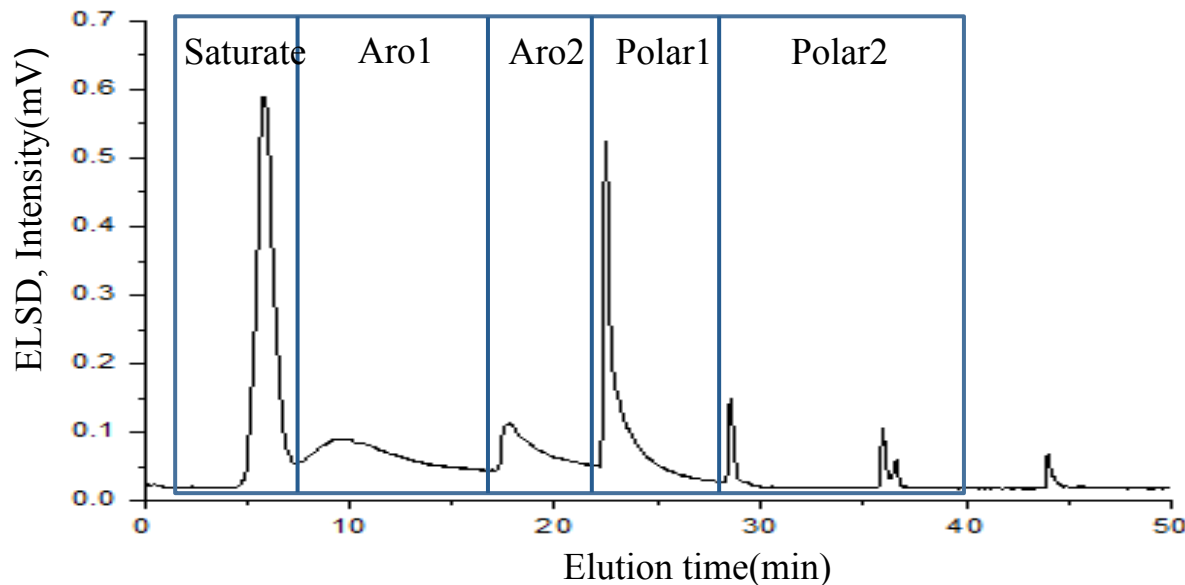
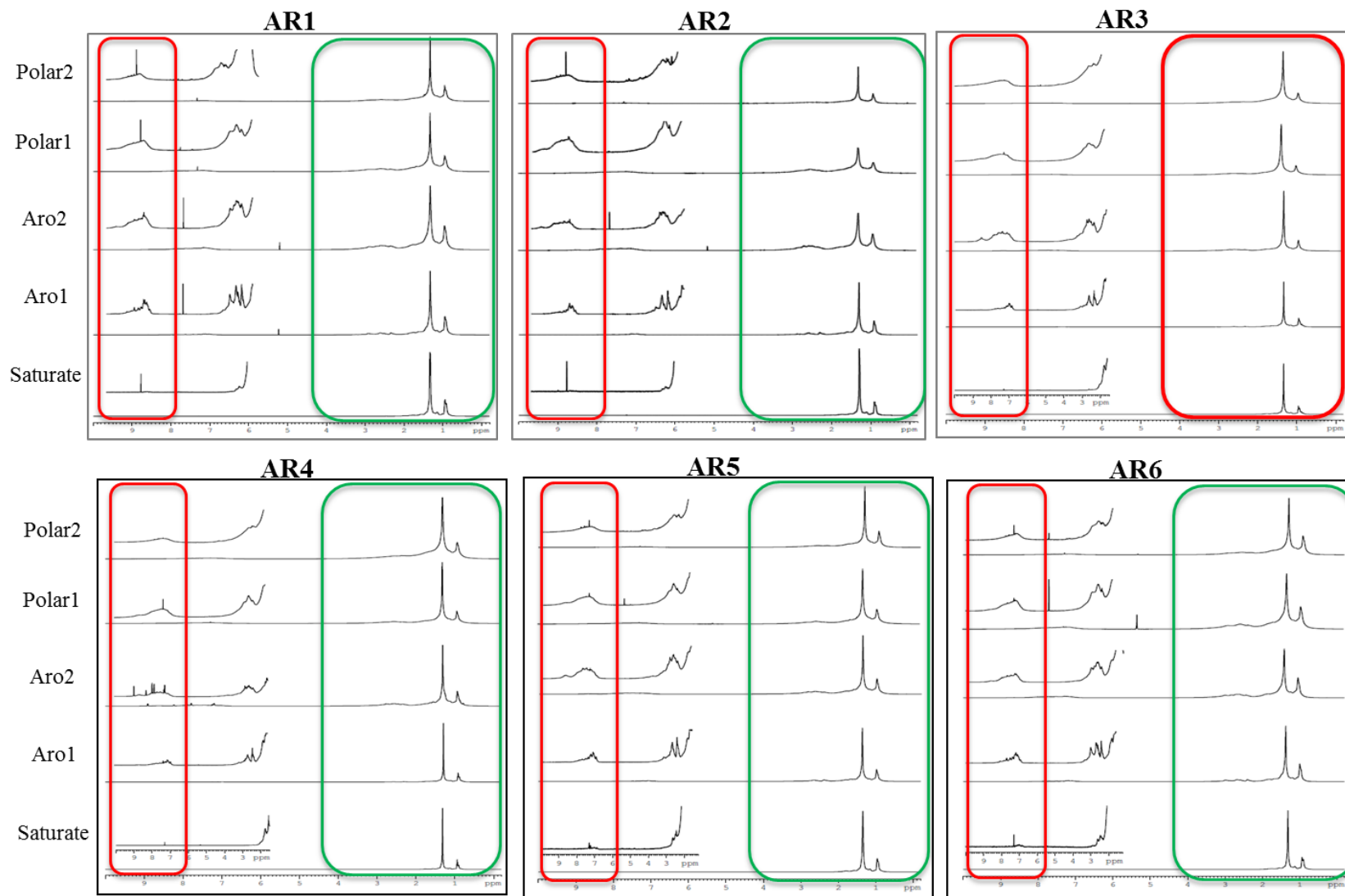


Figure 1. MPLC-ELSD spectrum of an AR maltene.



— aromatic region — Non-aromatic region

Converting DBE to # of aromatic carbons

1. All the compounds with DBE values smaller than the ones of the basic structures are considered non-aromatic.
2. Linear polyaromatic hydrocarbon structure is dominant. Therefore, an increase of 3 in the DBE value is equivalent to addition of an aromatic ring to the basic structure.
3. Increase of 1 and 2 in the DBE value from the aromatic structured obtained from assumption 1 and 2 is not caused by increased number of aromatic ring.

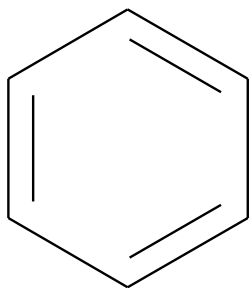
◆ Basic structures

Class of compounds	Assumed basic structure	DBE
HC	benzene	4
S ₁	Thiophene	3
S ₂	Thienothiophene	6
N ₁ in Polar 1 fraction	Pyrrole	3
N ₁ in Polar 2 fraction	Pyridine	4
O ₁	Phenol	4
N ₁ O ₁	Hydroxyl pyridine	4
S ₁ O ₁	Hydroxyl thiophene	3

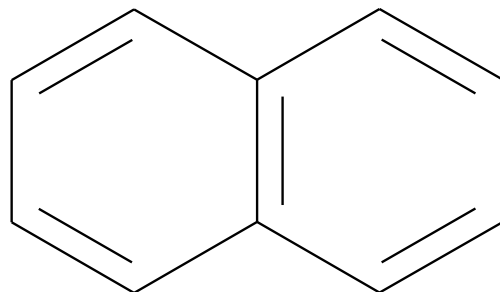
HC class

DBE	Total #C	Aromatic #C	%C _{non-aro}
7	15	10	$(15-10)/15$
8	16	10	$(16-10)/16$
12	20	12	$(20-12)/20$

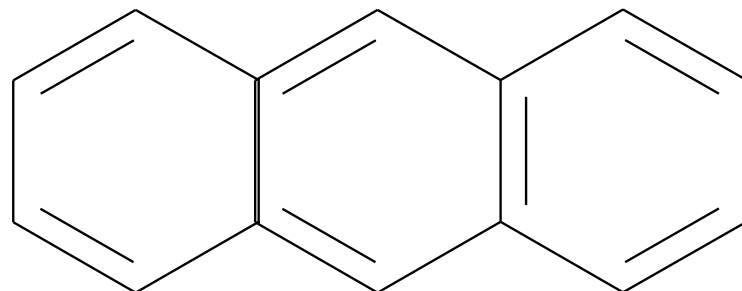
DBE=4



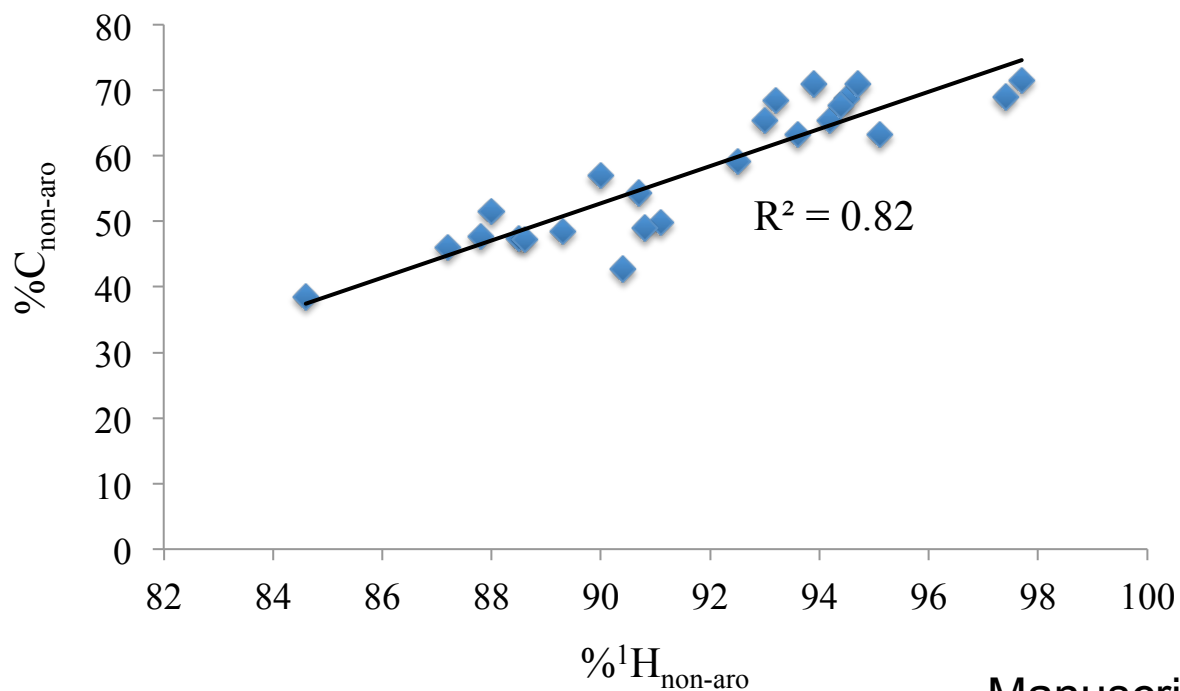
DBE=7



DBE=10



DBE \rightarrow # aromatic ring in a given formulae \rightarrow # aromatic carbon in the formulae
 \rightarrow (total # of carbon - # aromatic carbon) = total # of carbon



Manuscript Submitted

Summary and remarks

- Development of a good algorithm and sub
sequent development of software
- Any comment is welcome!!!