Universität Rostock Traditio et Innovatio

HelmholtzZentrum münchen
Deutsches Forschungszentrum für Gesundheit und Umwelt

JOINT MASS SPECTROMETRY CENTRE

EU FT-ICR MS

Comprehensive high resolution mass spectrometric evolved gas analysis in the context of Petroleomics: Analysis of bitumen, heavy crude oils and asphaltenes

Christopher P. Rüger, Anika Neumann, Christoph Grimmer, Uwe Käfer, Thomas Gröger, Thorsten Streibel, Martin Sklorz, Ralf Zimmermann

Joint Mass Spectrometry Centre:

Chair of Analytical Chemistry, University of Rostock, 18059 Rostock, Germany

&

Cooperation Group Comprehensive Molecular Analytics, Helmholtz Zentrum München, 85764 Neuherberg, Germany

13th European Fourier Transform Mass Spectrometry Workshop,

Freising (Germany), 23.-27.04.2018

Universität Rostock Traditio et Innovatio | HelmholtzZentrum münchen Deutsches Forschungszentrum für Gesundheit und Umwelt

EU FT-ICR MS

JOINT MASS SPECTROMETRY CENTRE

Chair for Analytical Chemistry

Universität Rostock Traditio et Innovatio

Thermal Analysis / Photionization MS	Aerosol and Laser-MS	Ultra-high Resolution MS
		
Thorsten Streibel	Johannes Passig	Marin Sklorz

Aerosol Chemistry	Aerosol Toxicology	Aerosol Physics	Bio-monitoring	Comprehensive Separation
				
Jürgen Schnelle-Kreis	Sebastian Öder	Thomas Adam	(Jutta Lintelmann)	Thomas Gröger

Ralf Zimmermann
University Rostock
Chair for Analytical Chemistry and Head of the Cooperation Group Complex Molecular Analysis

HICE › Aerosols and Health
Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health

Aerosol & Health

Enabling Technologies

CMA Cooperation Group Comprehensive Molecular Analytics

HelmholtzZentrum münchen
German Research Center for Environmental Health

Universität der Bundeswehr München

Chair for Chemistry, Environmental- & Energy process technology

photonion

Spin-off Company
Photoionization mass spectrometry and online process analytics

(Staff: about 50 people)

Outline

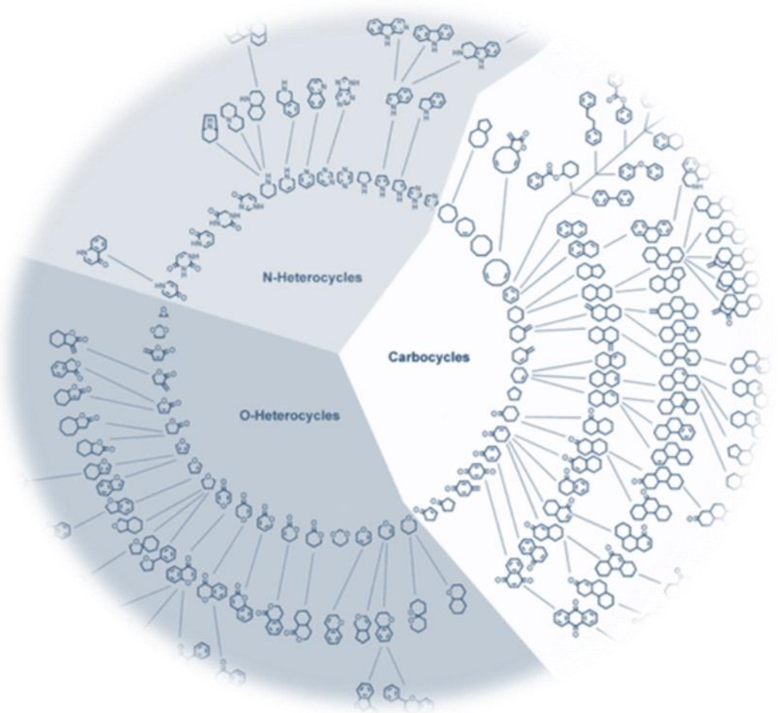
1) Motivation and Introduction

2) Instrumental Setup and Sample Material

3) Results and Discussion

4) Summary and Outlook

Motivation and Introduction 1

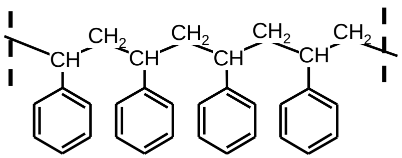


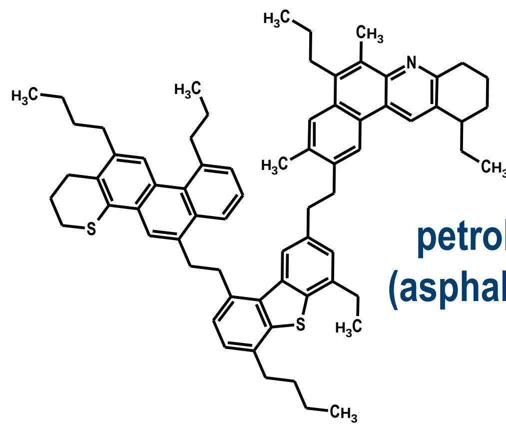
Motivation and Introduction

Macromolecules

synthetic polymeres

polystyrene

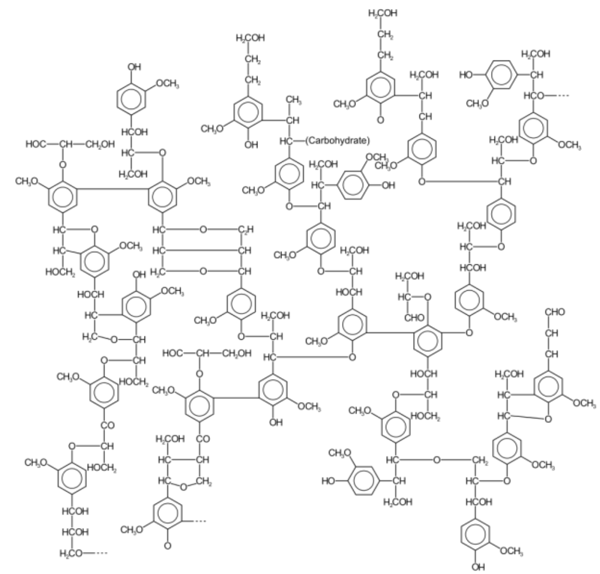




petroleum (asphaltenes)

natural macromolecules

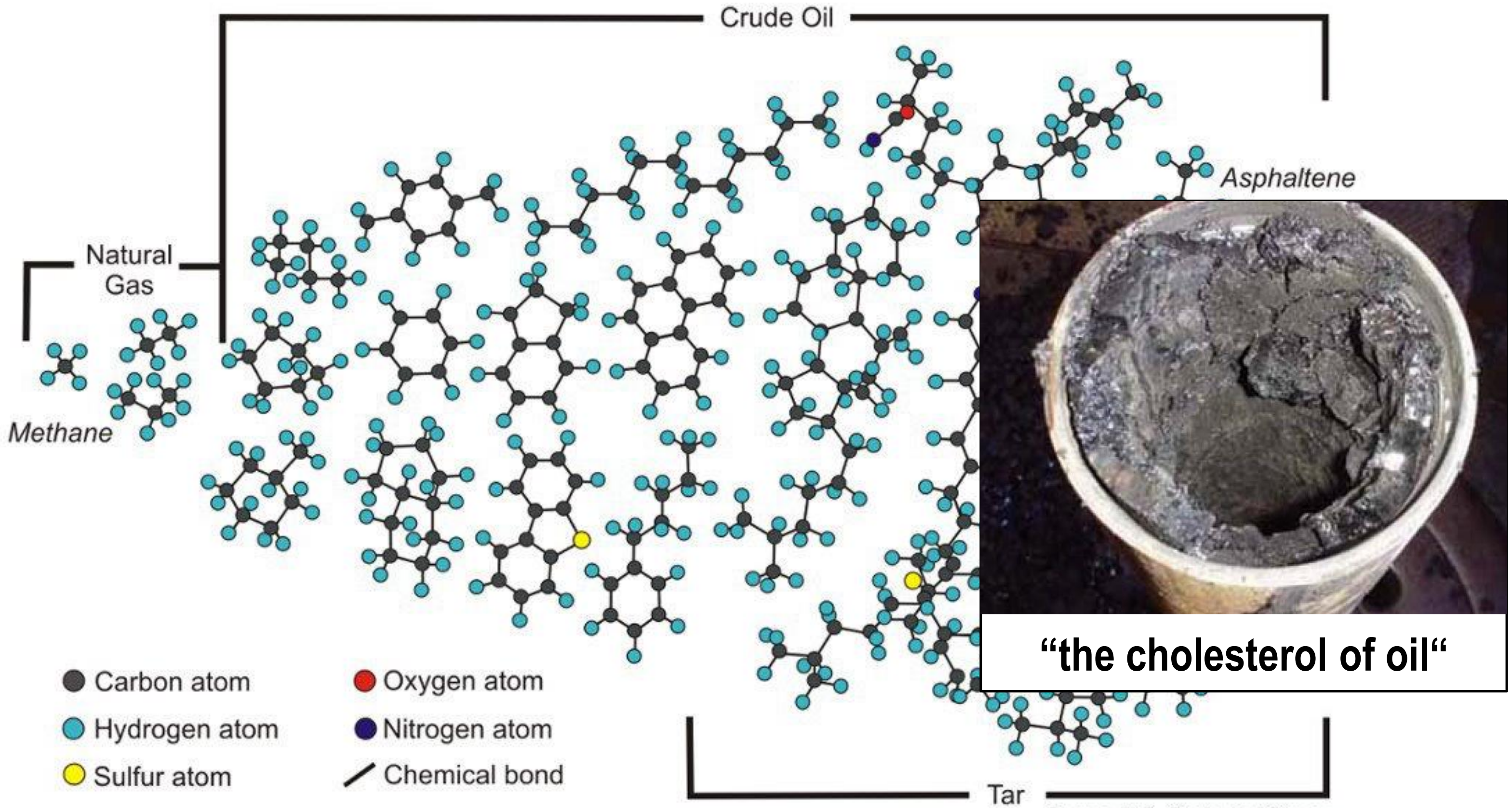
wood (lignin)



How to access the chemical nature of these macromolecules?

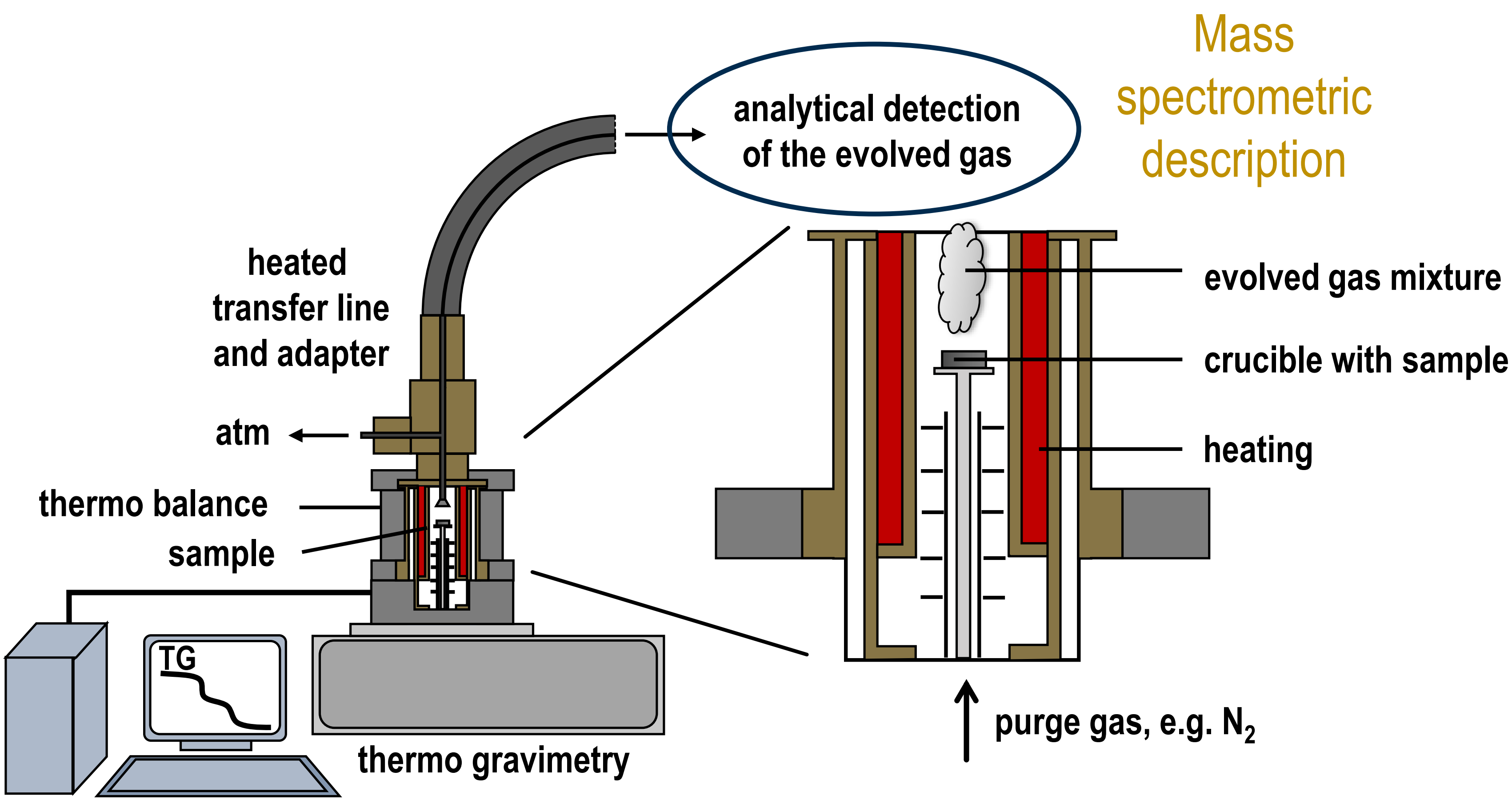
→ **thermal decomposition into smaller sub-units by pyrolysis**

Mass spectrometric petroleum analysis – Petroleomics

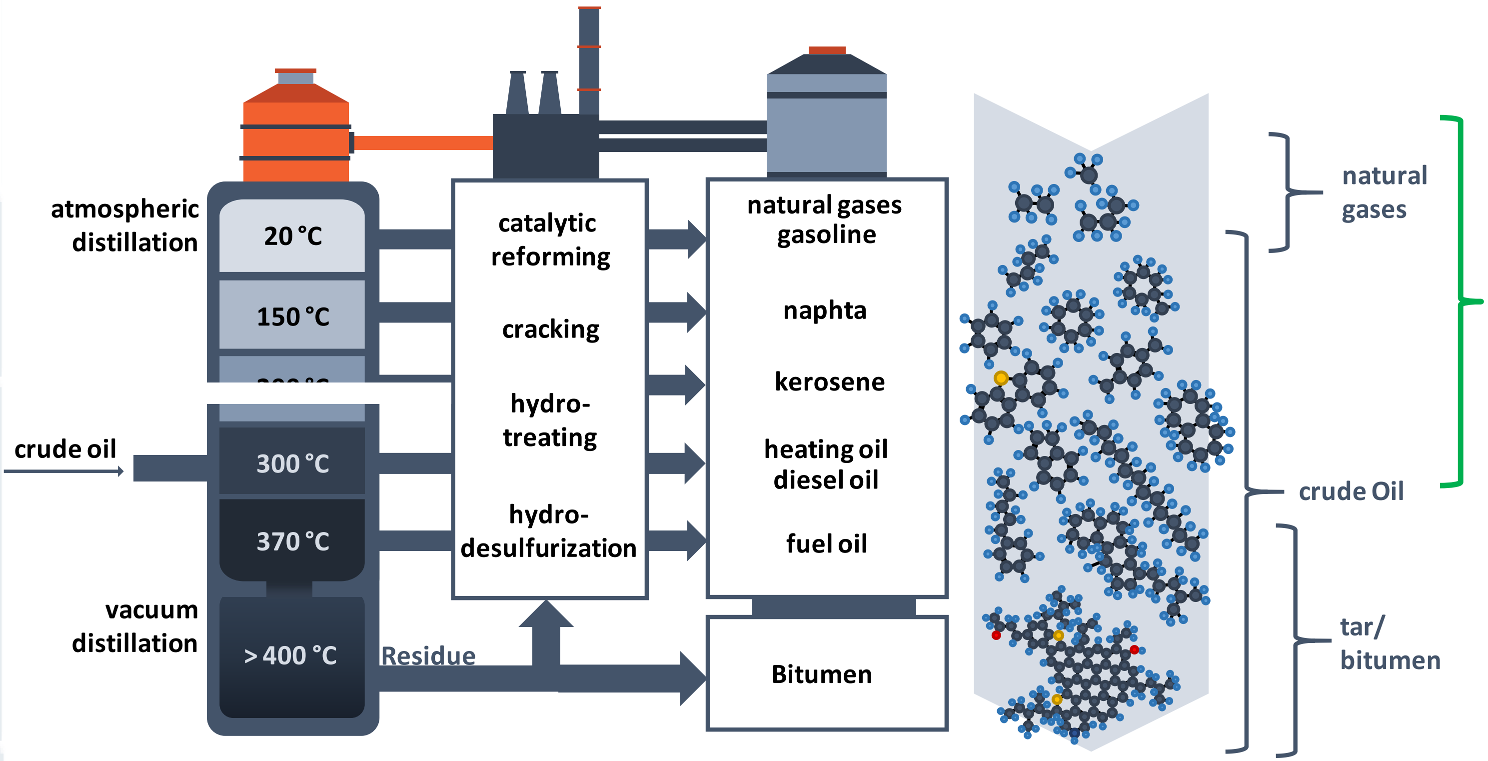


Source: U.S. Geological Survey

Basic concept of evolved gas analysis (EGA)

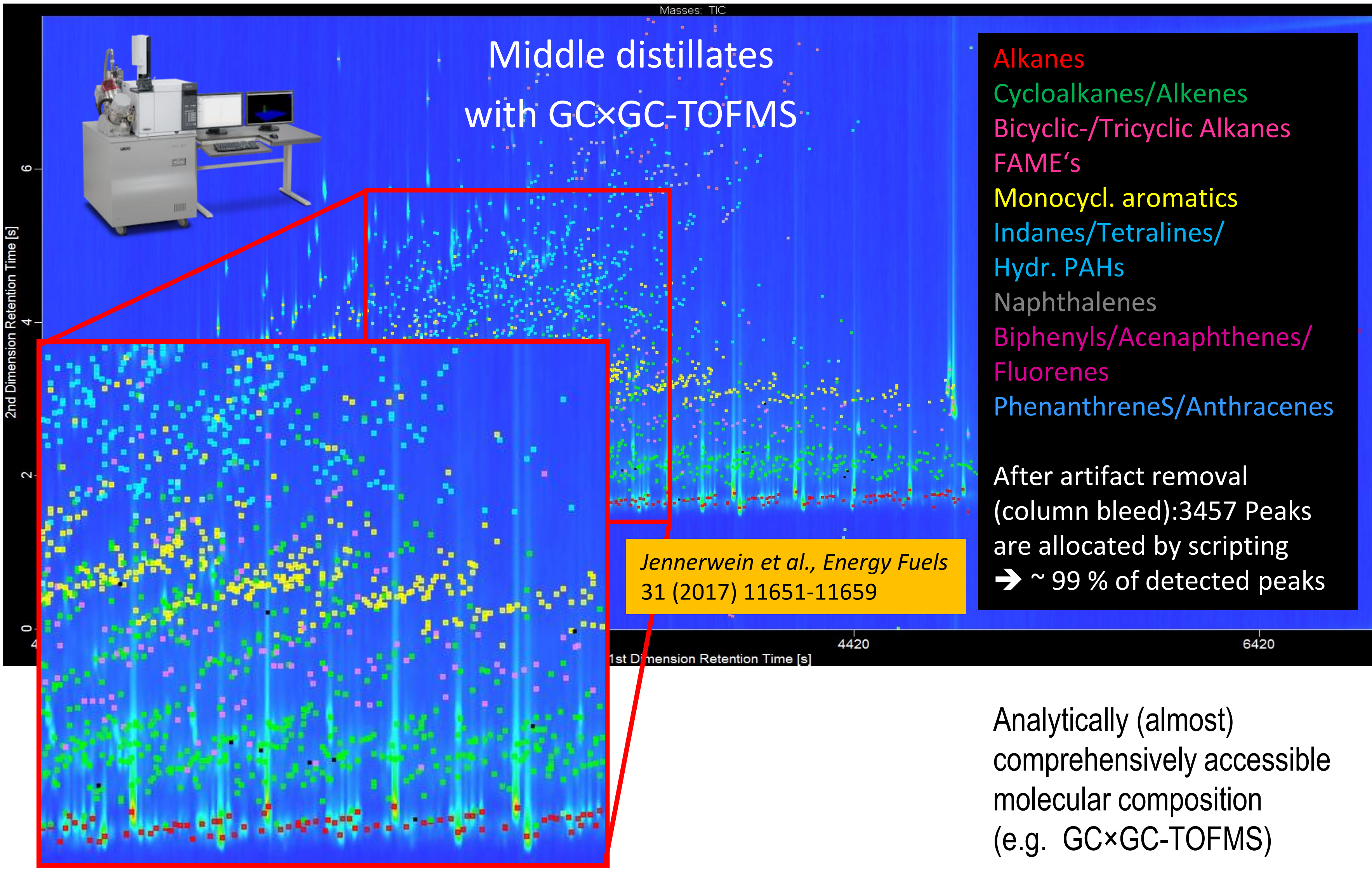


Why can thermal analysis be beneficial for Petroleomics?



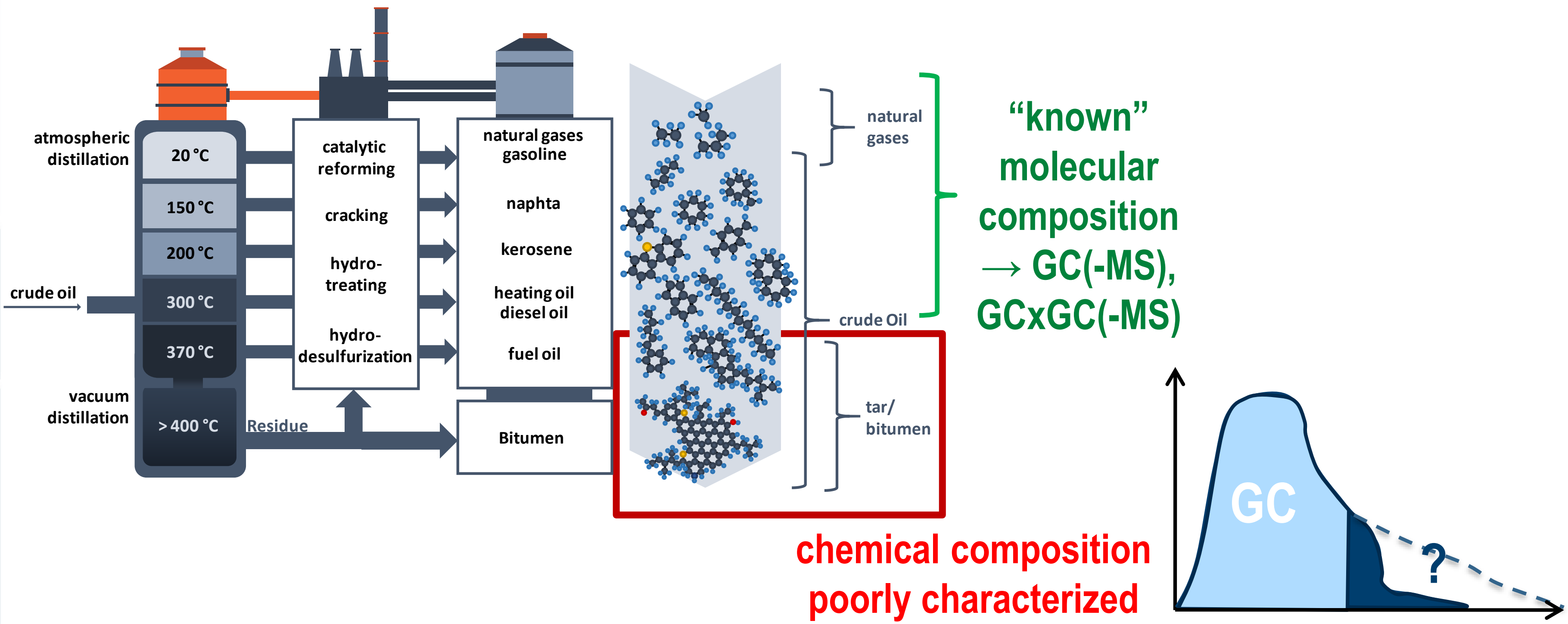
“known” molecular composition → GC(-MS), GCxGC(-MS)

Motivation and Introduction



Analytically (almost) comprehensively accessible molecular composition (e.g. GC×GC-TOFMS)

Why can thermal analysis be beneficial for Petroleomics?



- gas chromatography is **limited** on the volatility **and stability** of the analytes
- **intended pyrolysis** of larger macromolecules in thermal analysis to study the **building blocks** and diagnostic thermal fragments

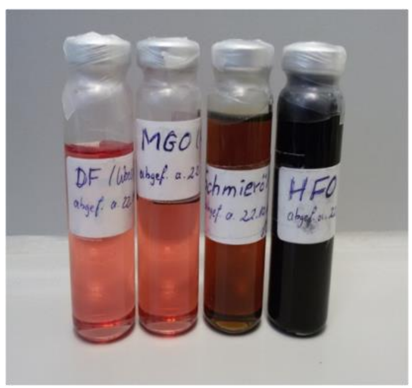
Material and Method 2

Sample material

- **standards**, e.g., polymers, fatty acid methyl ester mixture, PAHs for validation
- various petroleum samples (diesel, gas oil, heavy oil) and lignocellulosic biomass for evaluation regarding **complex samples**
- different **asphaltenes and heavy oils** for applicative interest

Diesel fuels

Marine fuels

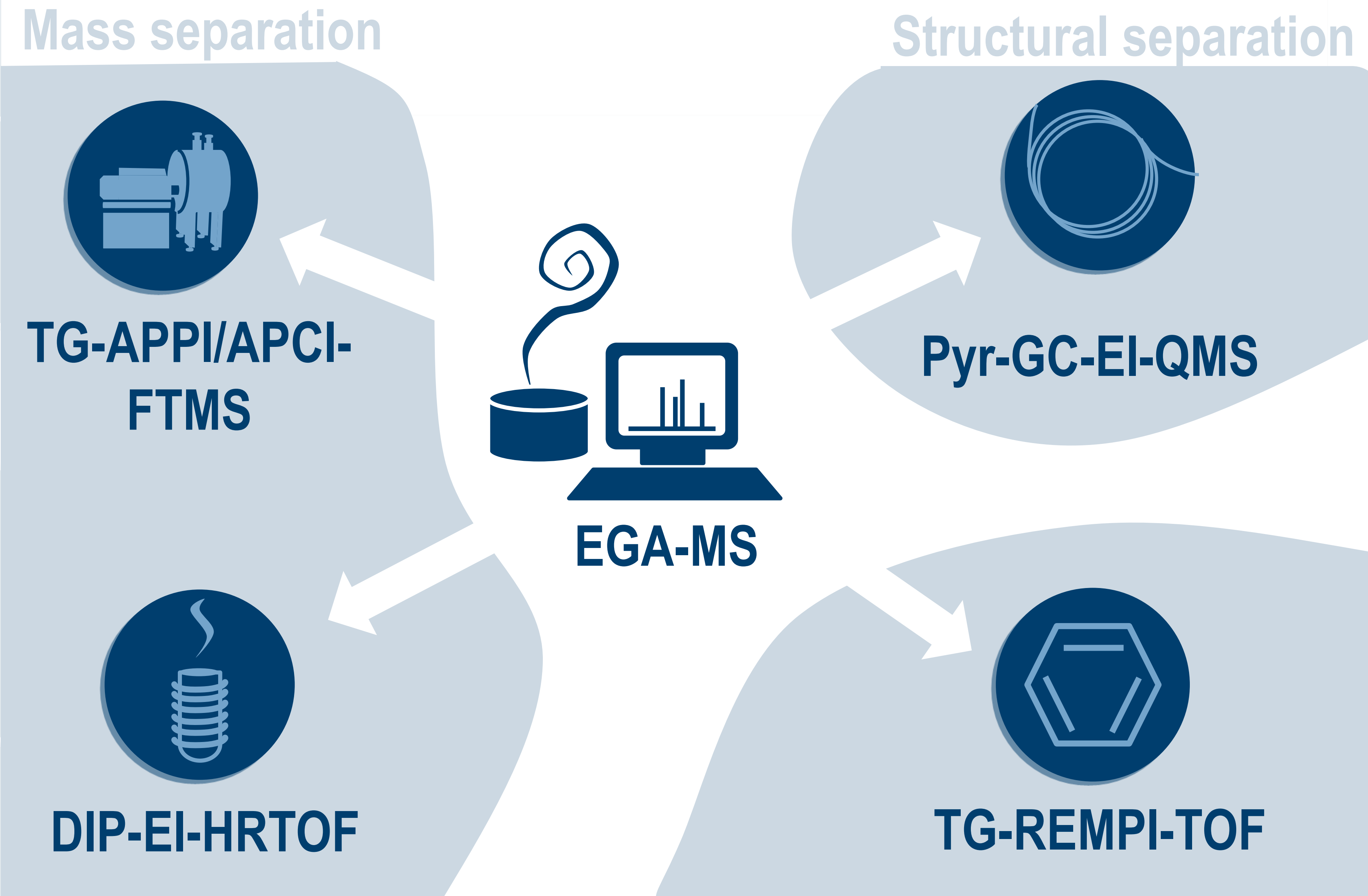


Crude oil

Asphaltenes

complexity

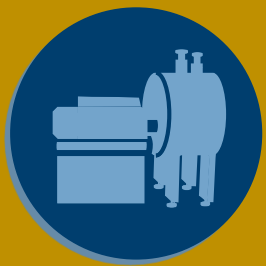
Material and Method



Material and Method

Mass separation

Structural separation



TG-APPI/APCI-FTMS

EGA-MS

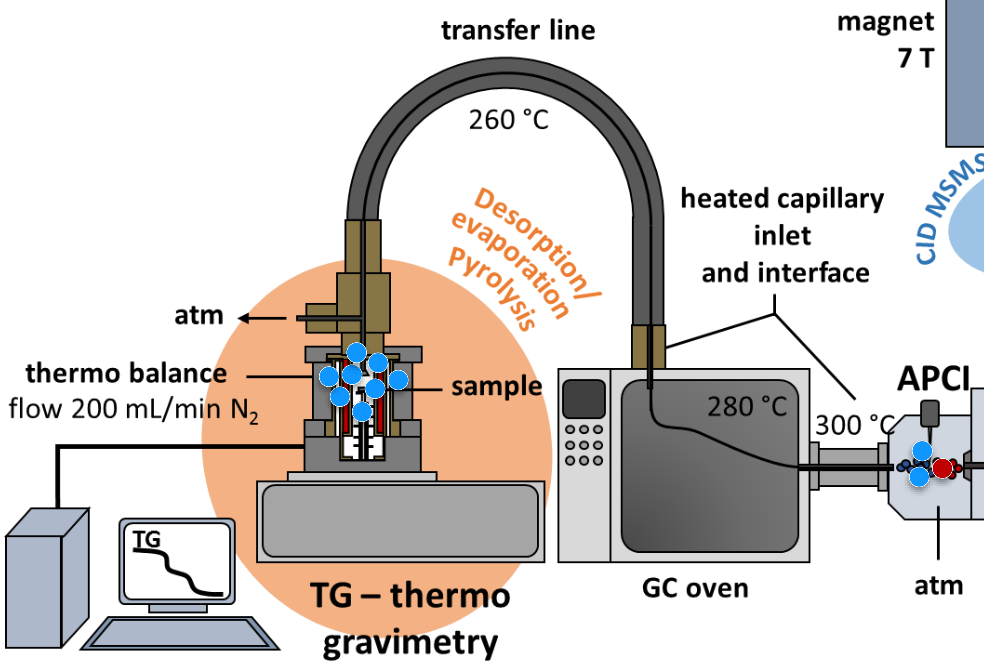
Pyr-GC-EI-QMS

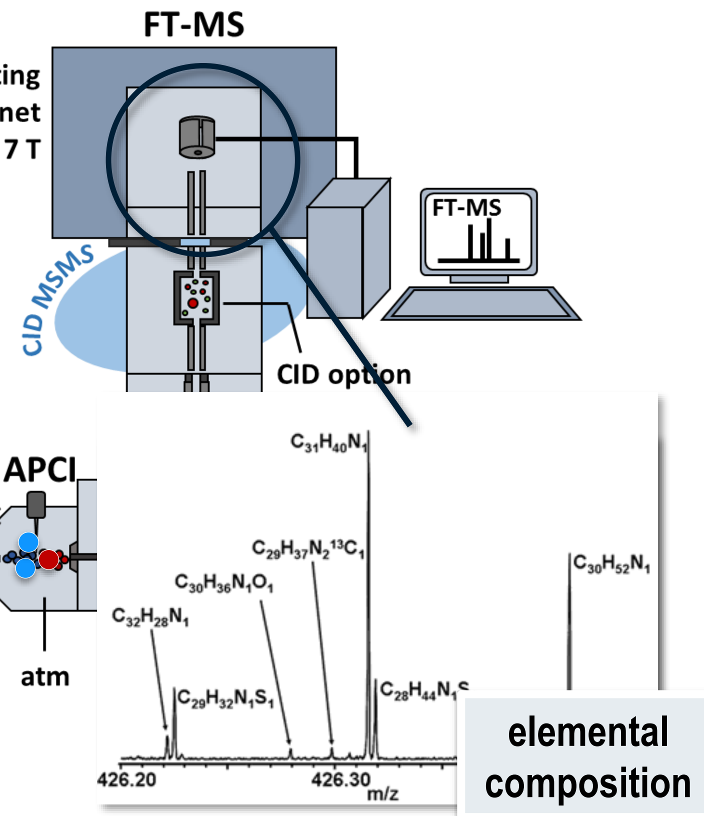
DIP-EI-HRTOF

TG-REMPI-TOF

Thermal analysis coupled to Fourier-Transform MS

Thermal analysis coupled to Fourier-Transform MS

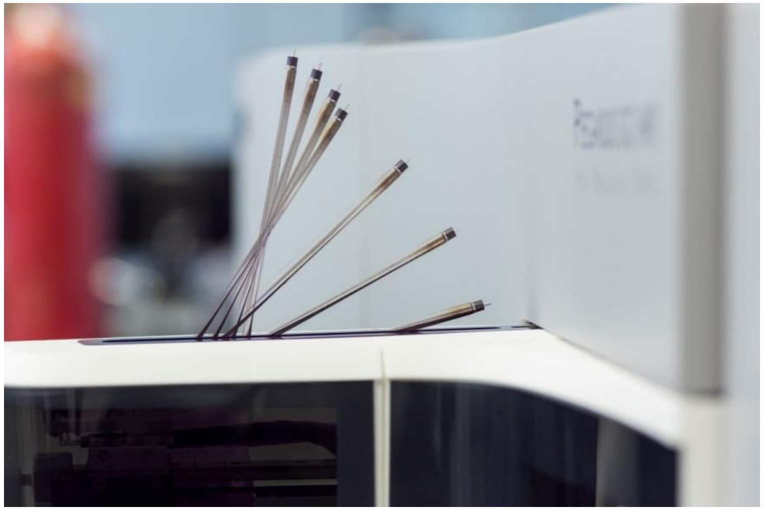




Rüger et al., Anal. Chem., 2015

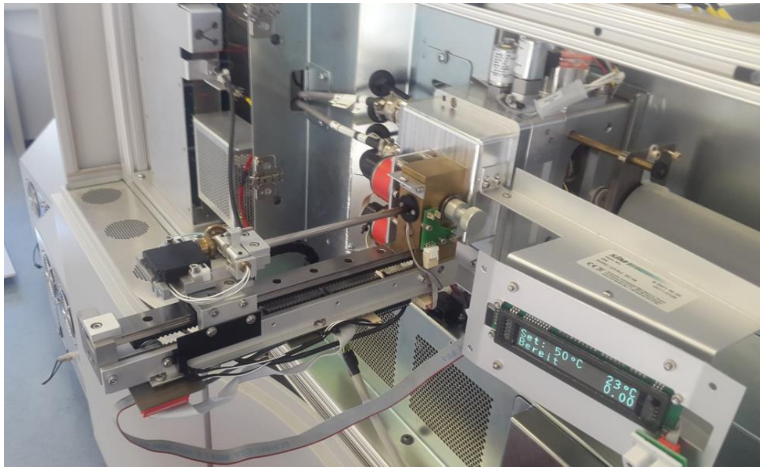
→ high resolving power and mass accuracy + APPI/APCI-selectivity

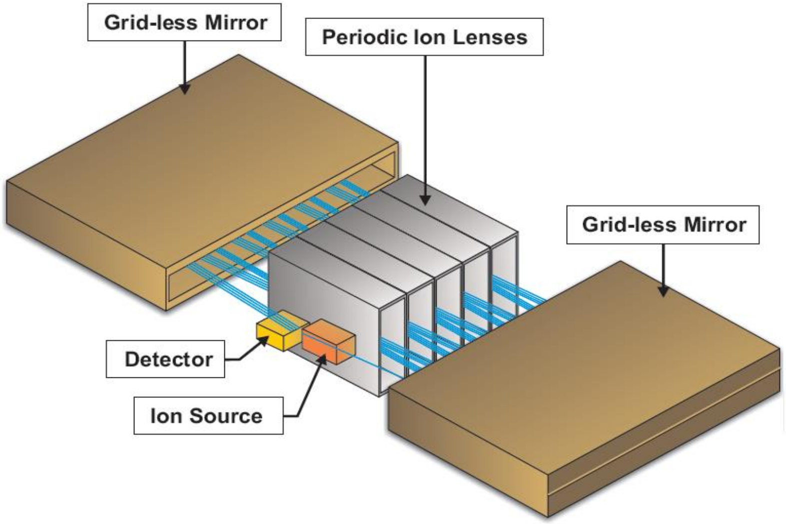
Direct inlet probe (DIP) high resolution time-of-flight MS



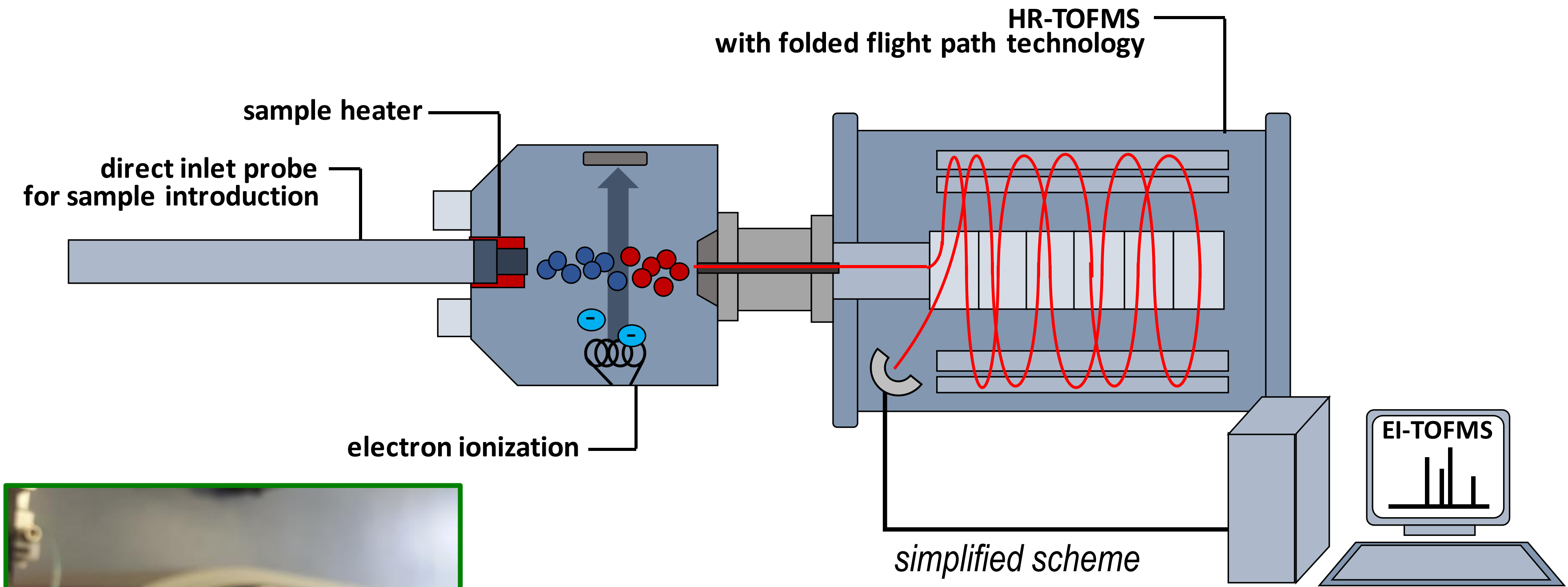
Instrument
- modified LECO Pegasus GC×GC-HRT
- multi-reflection TOF-MS

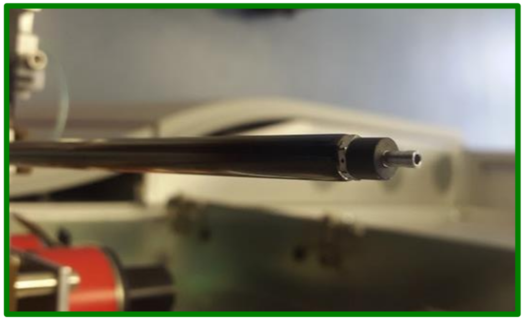
MS Parameter (HRT MS):
- acquisition frequency: 200 Hz
- resolution: 25,000-50,000
- mass accuracy < 2 ppm





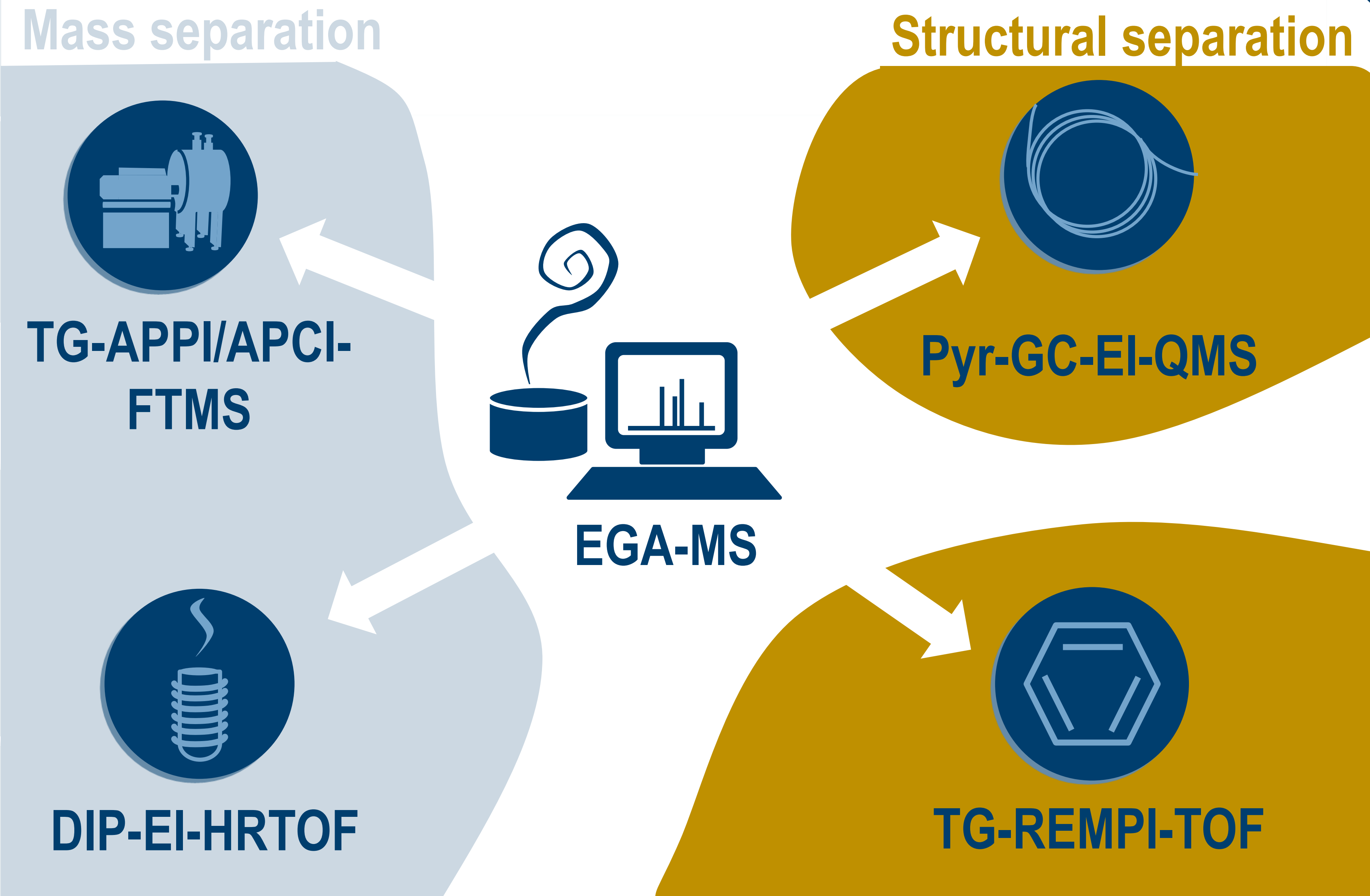
Direct inlet probe (DIP) high resolution time-of-flight MS





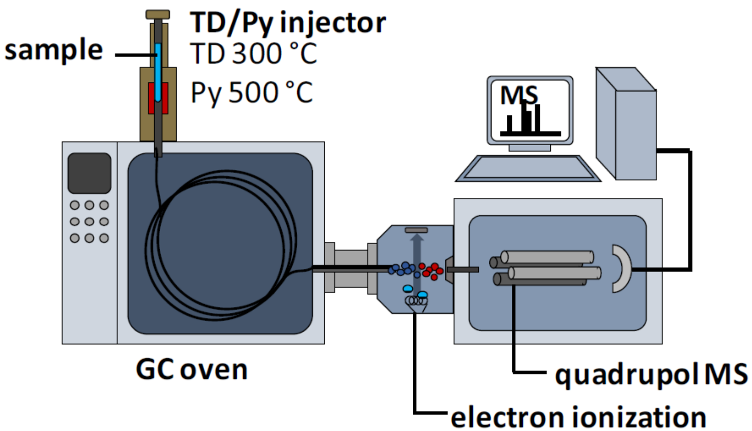
→ heating at reduced pressure to intactly evaporate larger constituents + EI as universal ionization technique (CI/PI possible and under evaluation)

Material and Method



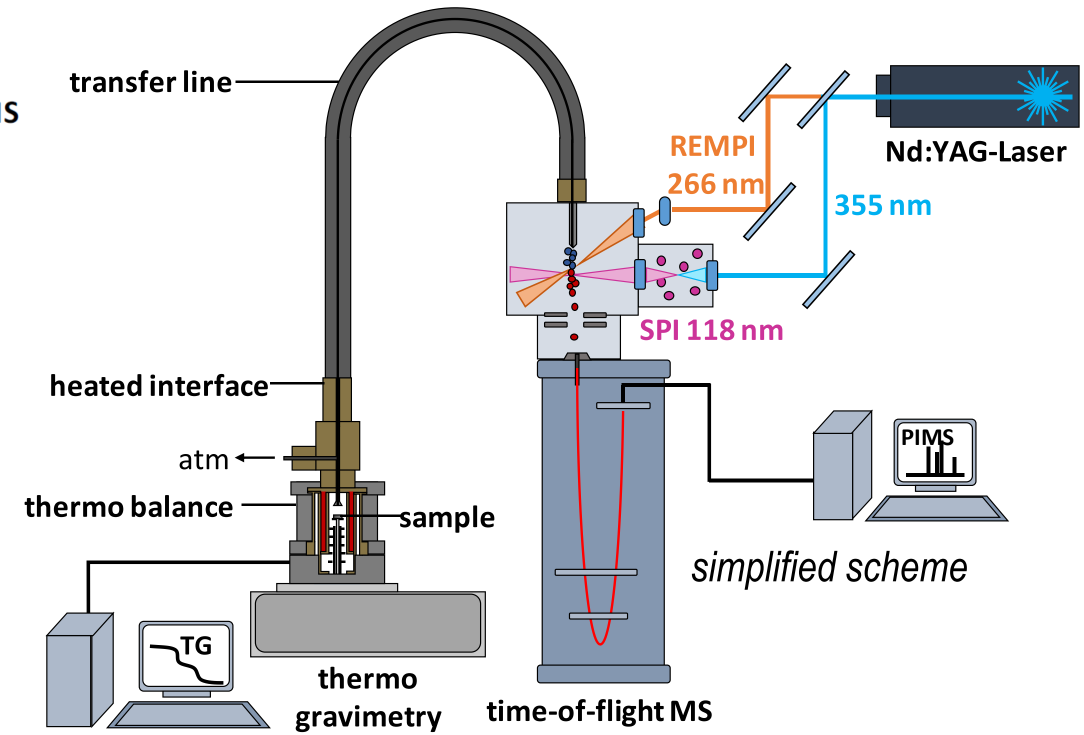
Outline
Introduction
M&M
Results/Discussion
Summary

Pyrolysis-GC EI-MS and photo ionization TOF-MS

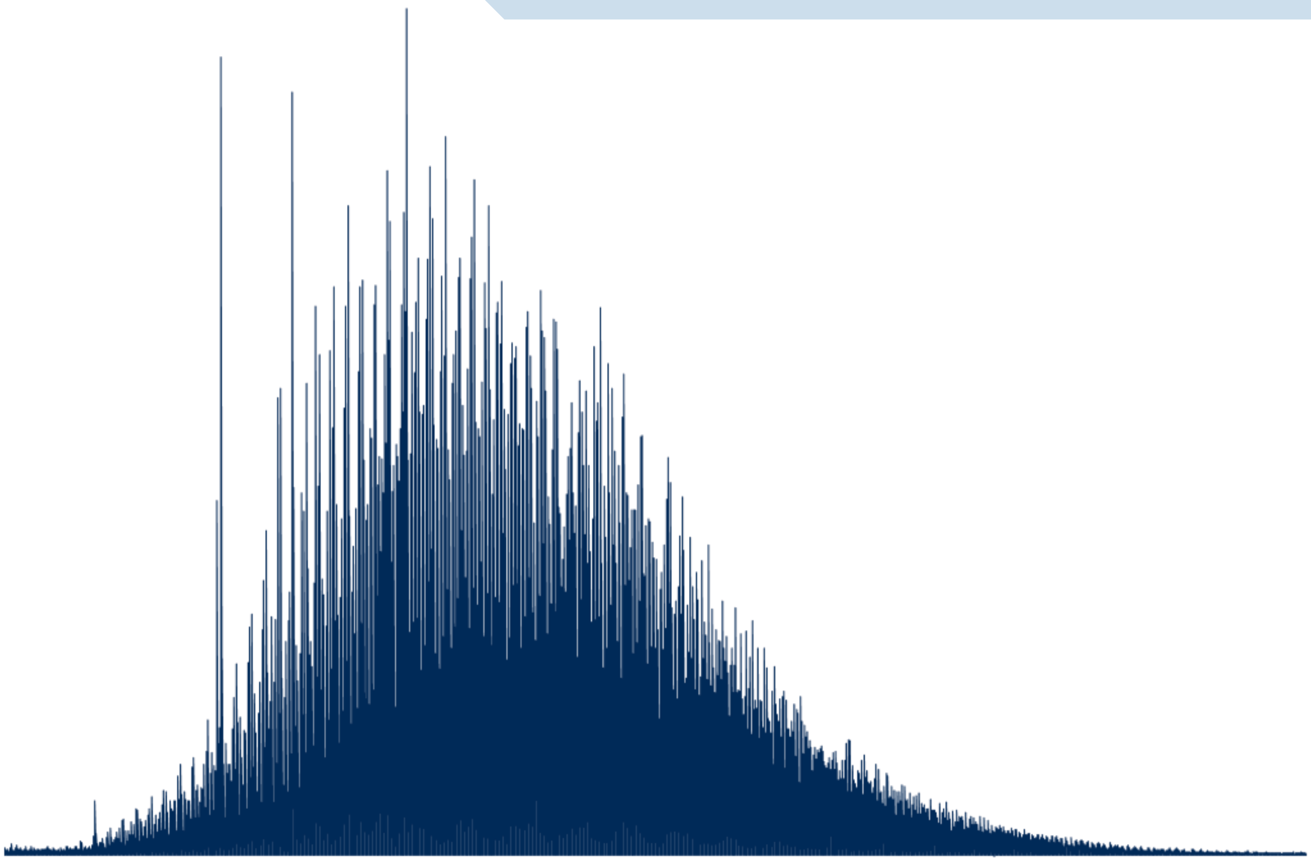


→ structural information via retention index and EI-fragment spectra

→ photo ionization introducing selectivity, e.g. REMPI for aromatic constituents

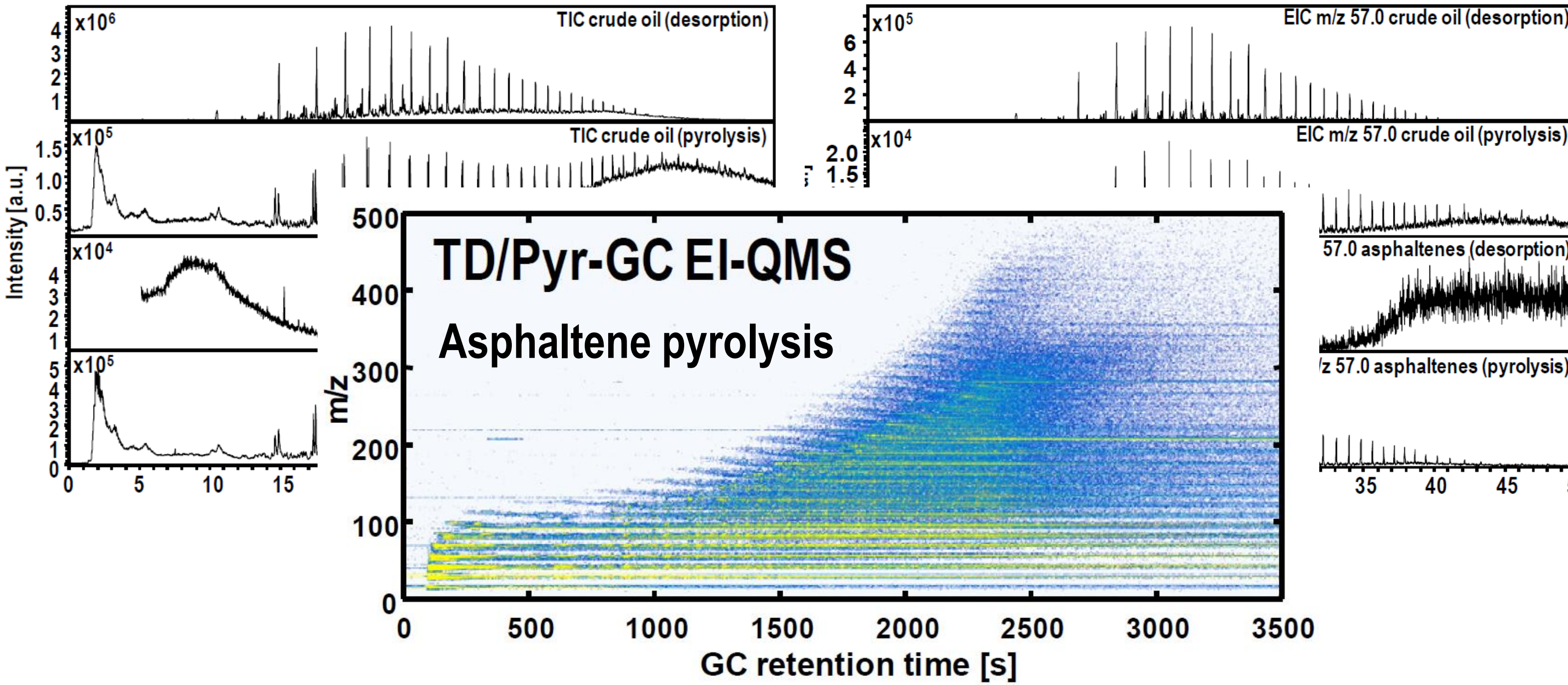


Results and Discussion 3



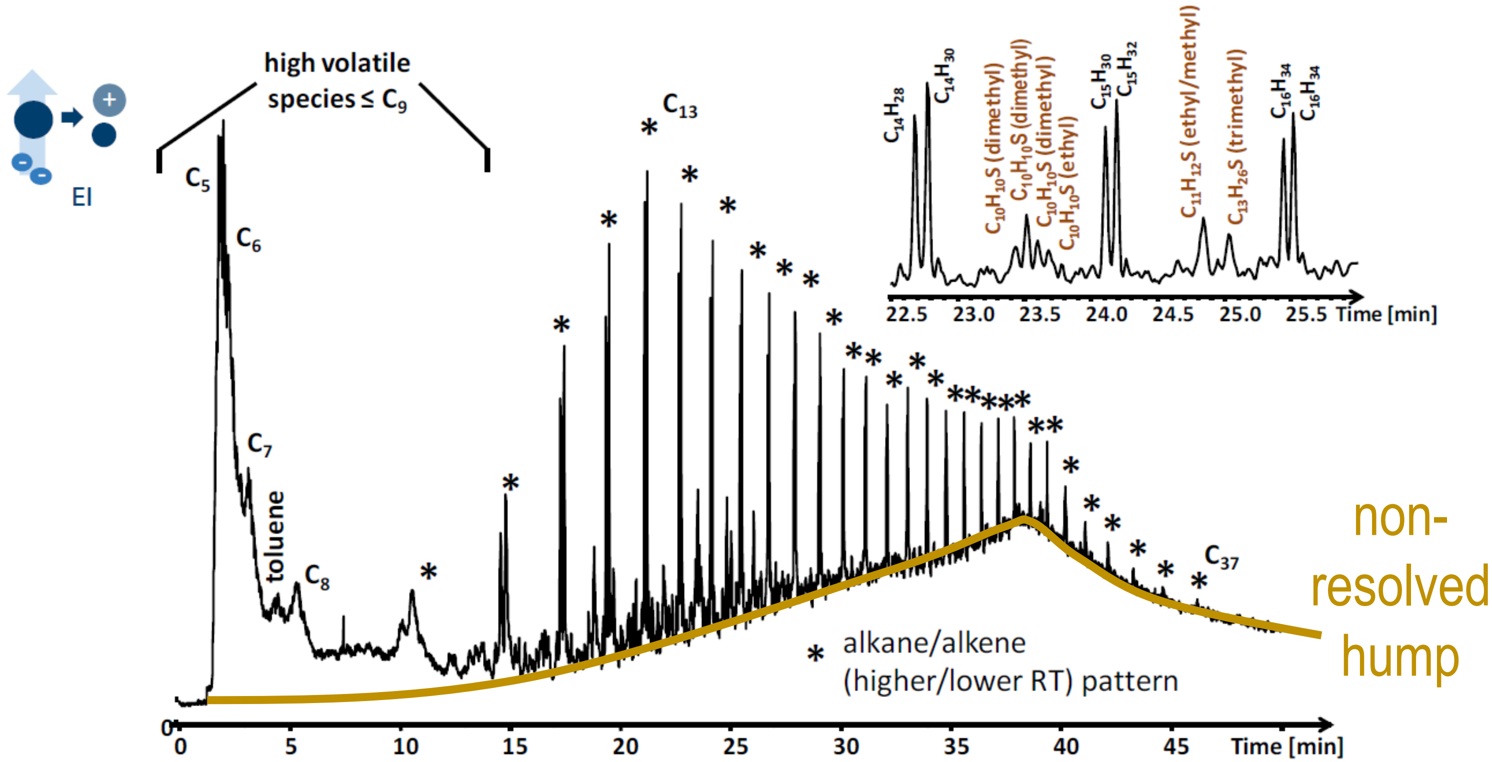
TD/Pyrolysis GC EI-QMS of Asphaltenes

- **no** thermal desorbed components for purified Asphaltenes at 300 °C
- second step (500 °C pyrolysis) induce **complex thermal decomposition pattern**



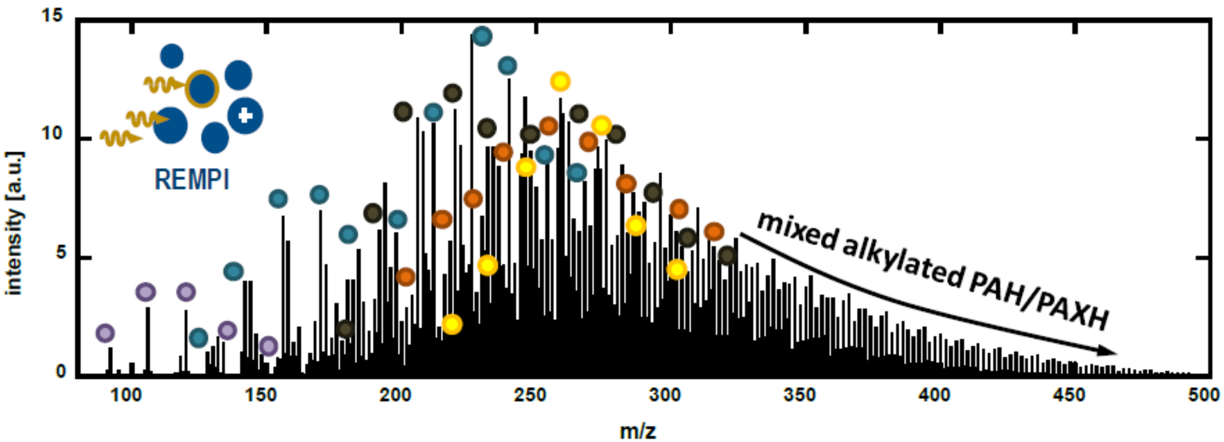
TD/Pyrolysis GC EI-QMS of Asphaltenes

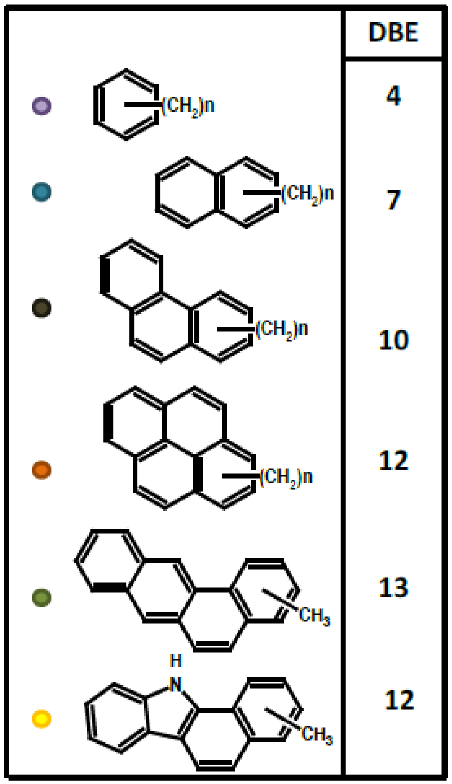
- **no** thermal desorbed components for purified Asphaltenes at 300 °C
- second step (500 °C pyrolysis) induce **complex thermal decomposition pattern**



Resonance-enhanced multiphoton ionization

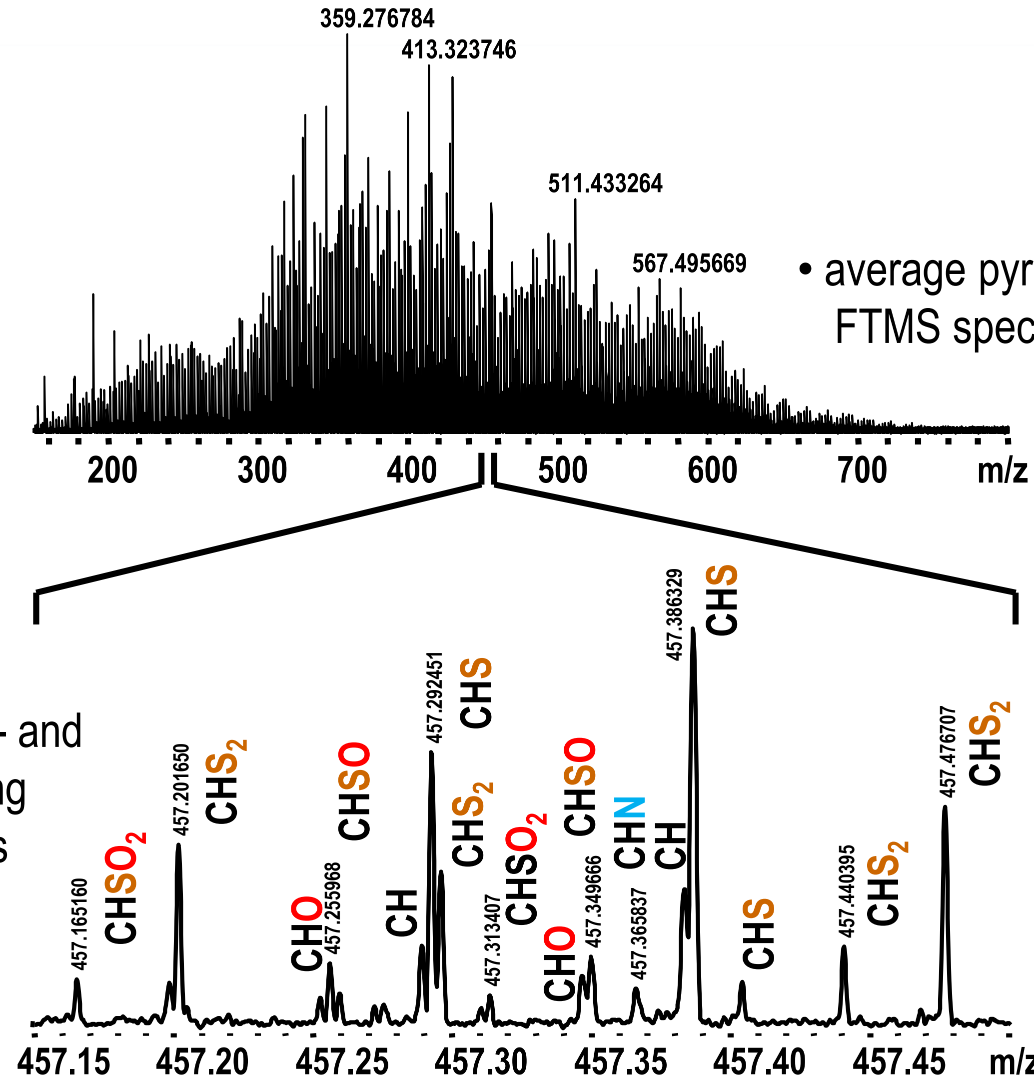
- **selective and sensitive** ionization approach for **aromatic** constituents





- intense and **complex** mass spectrometric pattern
- **broad** m/z range from benzene up to > m/z 500
- even-numbered homologue series indicating **Nitrogen-** containing poly-aromatic core structures
- two- to four-ring aromatic alkylated rows dominate

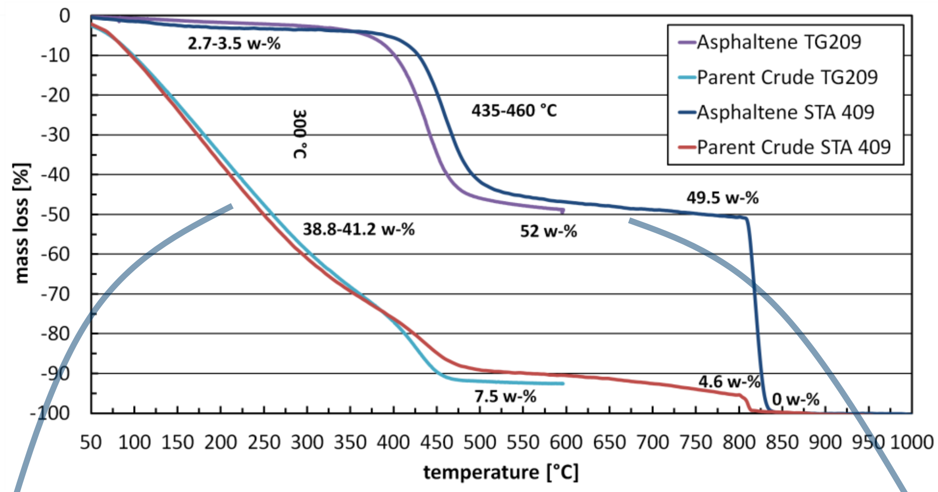
General API-MS response for Asphaltene pyrolysis

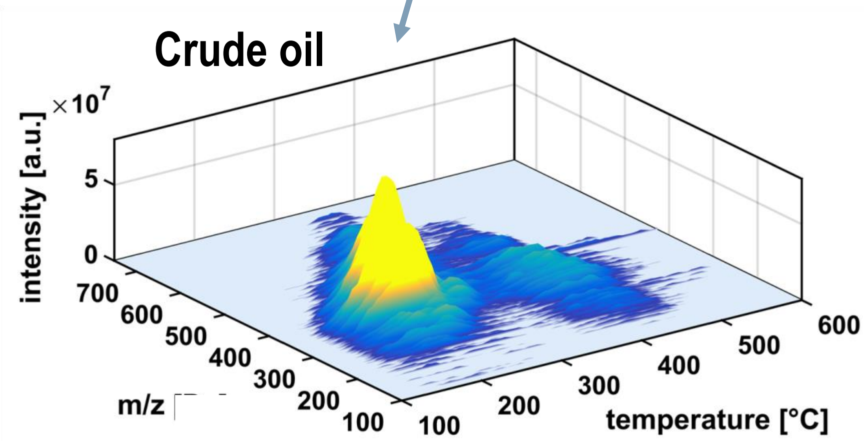


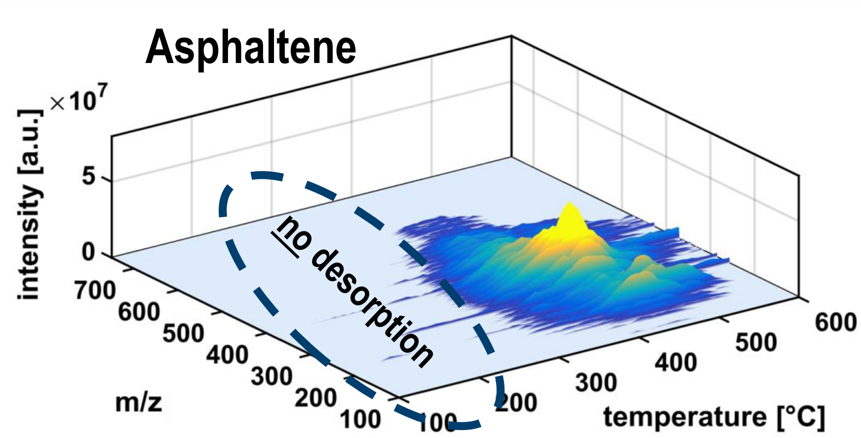
- average pyrolysis APCI-FTMS spectrum

- CHS-, CHS_2-, $CHSO_x$- and CH-species dominating
- > 3,500 distinct peaks

Mass loss and API mass spectrometric response

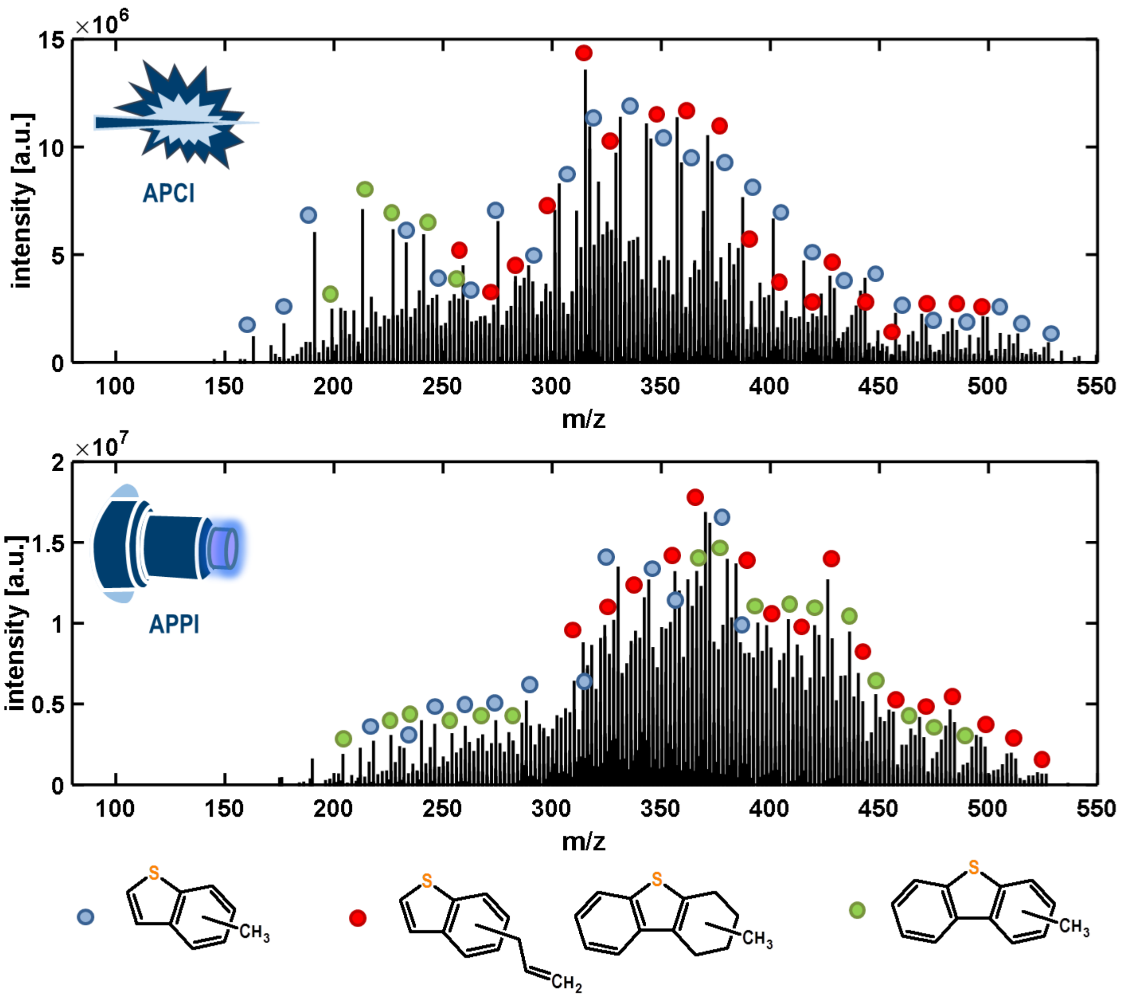






Outline
Introduction
M&M
Results/Discussion
Summary

Averaged asphaltene pyrolysis molecular pattern

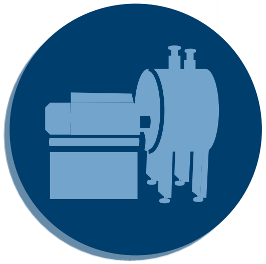


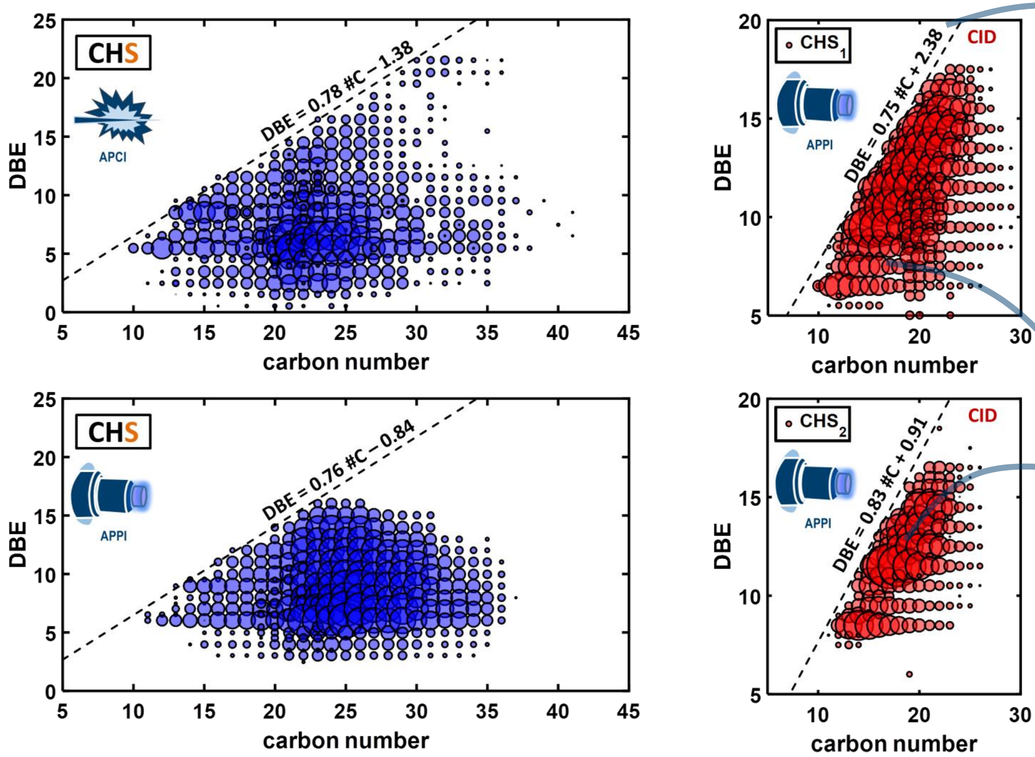
- alkylated aromatic structures with 2-4 rings as major motive
- CH- and CHS-species as major contributor to APCI and APPI

core structural motives?

Outline
Introduction
M&M
Results/Discussion
Summary

Collision induced dissociation data assessment

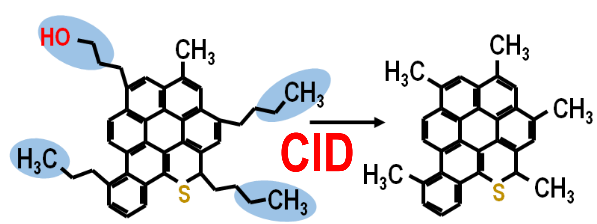




- slope of the left-side DBE versus #C carbon distribution reveals information on ring attachment
  → mainly **cata-condensed** benzene (minor amount of peri-condensed)

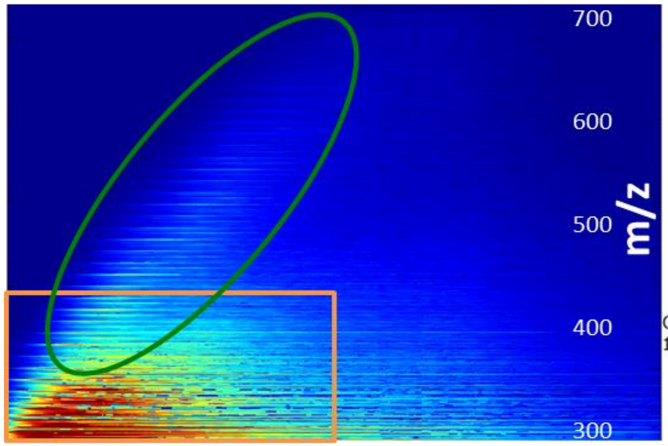
- thiophenic CHS-class species with up to **6 annulated rings**
- CHS_2-class reveals higher DBE
- **no** indication for **thiols**

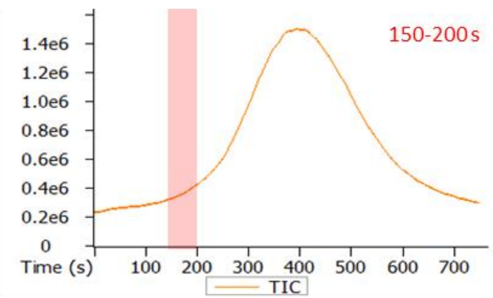
aromatic description of the CHS pyrolysis pattern
thermal fragments

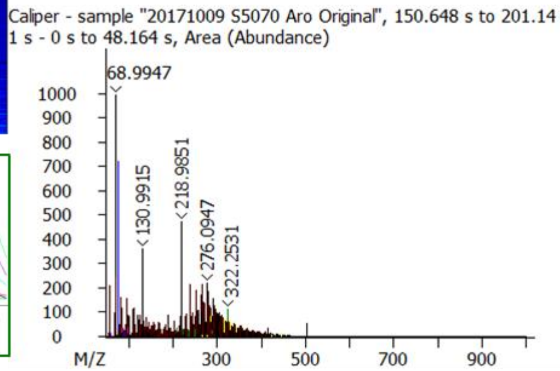


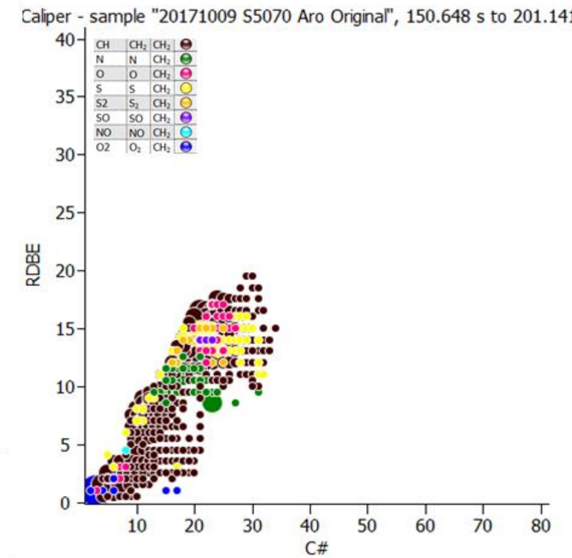
core structure analysis
MS-fragments

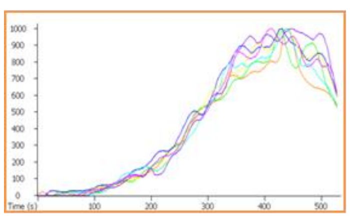
Can we go further with evolved gas analysis HRMS: DIP reduced pressure evaporation of a vacuum gas oil

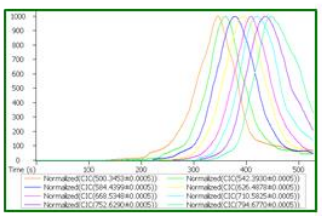












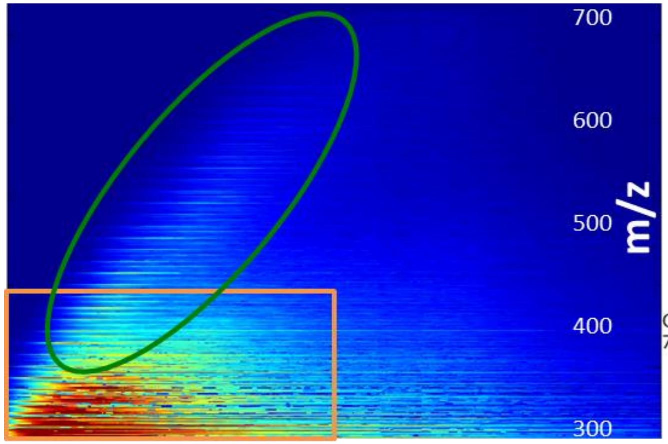
Non specific Fragmentation

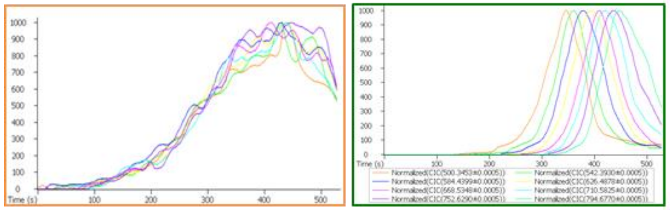
Molecular Information

Boiling behavior

Class Information

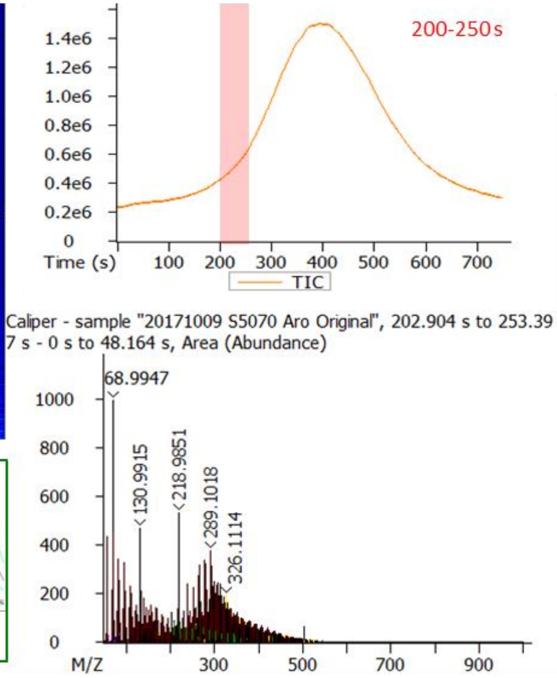
Can we go further with evolved gas analysis HRMS: DIP reduced pressure evaporation of a vacuum gas oil



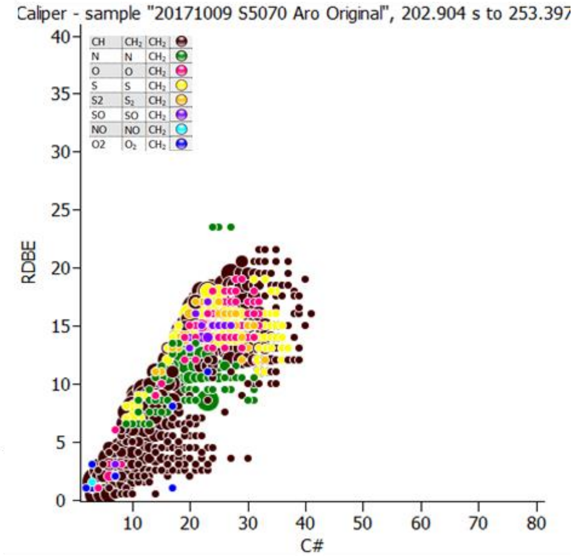


Non specific Fragmentation

Molecular Information

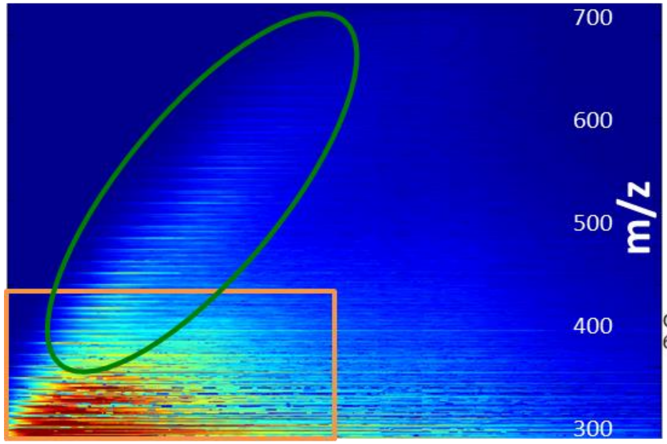


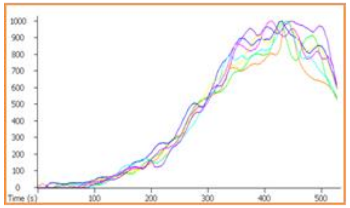
Boiling behavior



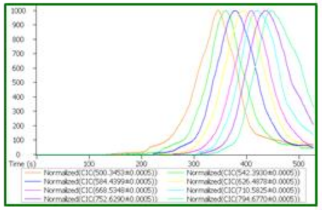
Class Information

Can we go further with evolved gas analysis HRMS: DIP reduced pressure evaporation of a vacuum gas oil

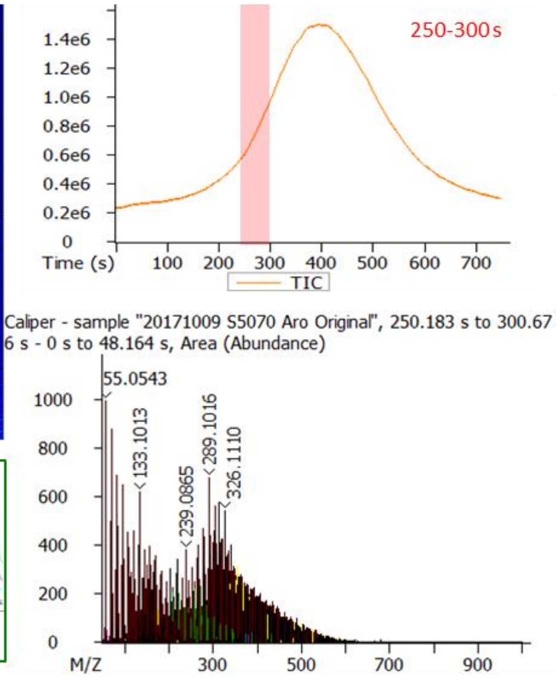




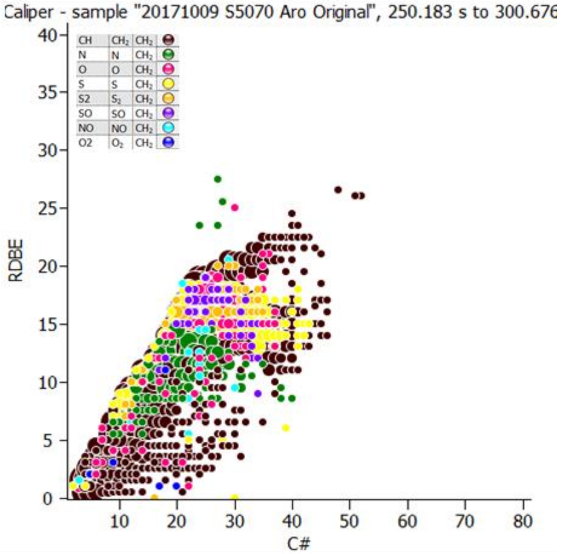
Non specific Fragmentation



Molecular Information

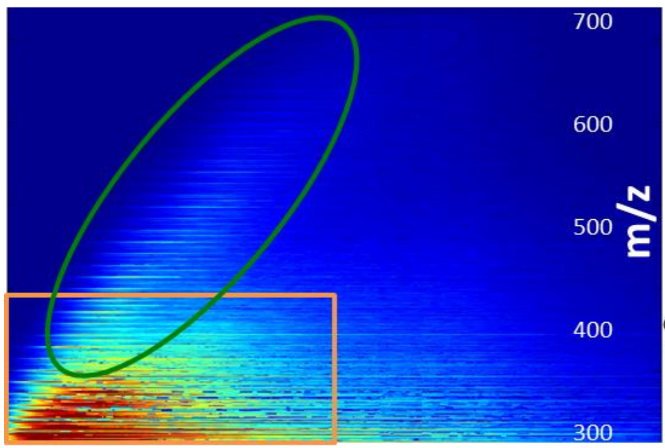


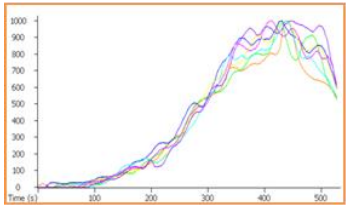
Boiling behavior



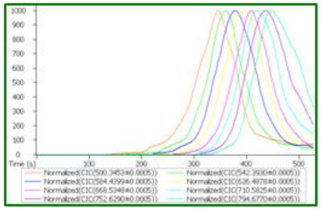
Class Information

Can we go further with evolved gas analysis HRMS: DIP reduced pressure evaporation of a vacuum gas oil

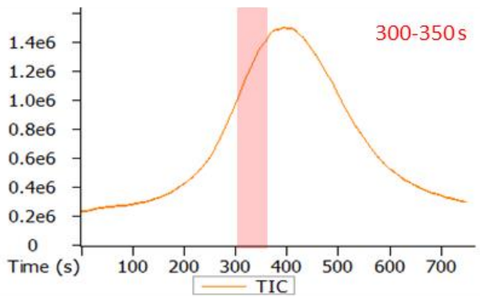


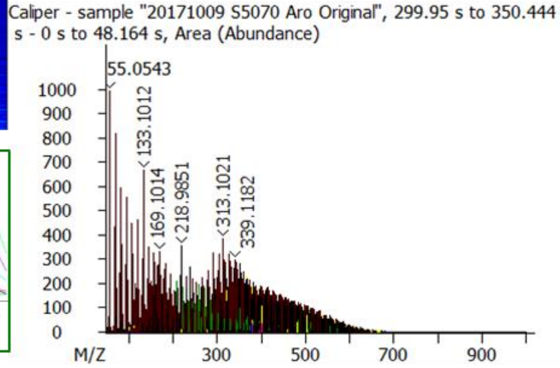


Non specific Fragmentation

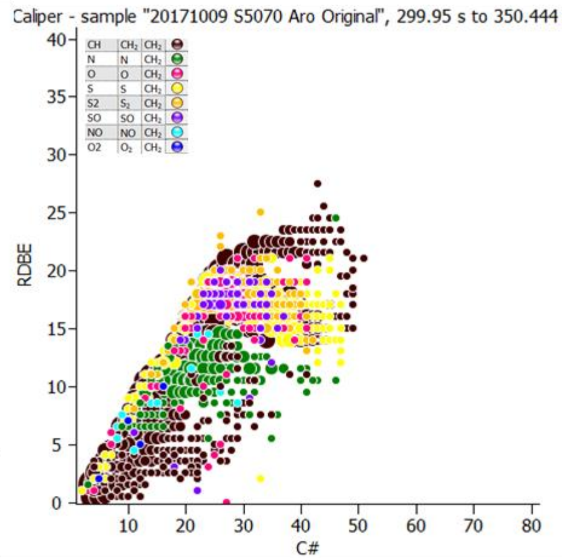


Molecular Information



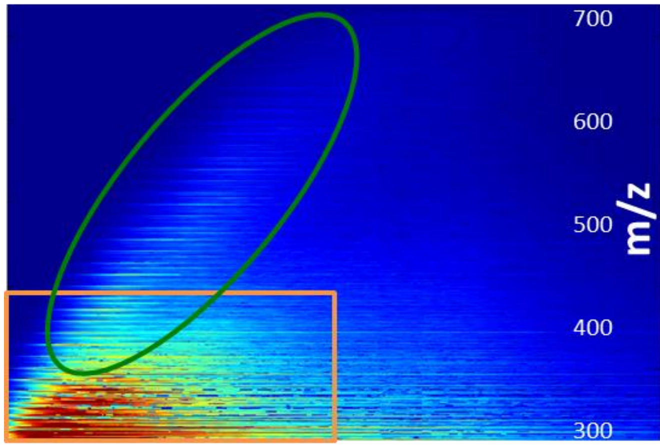


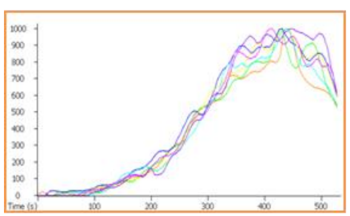
Boiling behavior

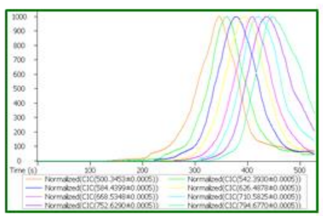


Class Information

Can we go further with evolved gas analysis HRMS: DIP reduced pressure evaporation of a vacuum gas oil

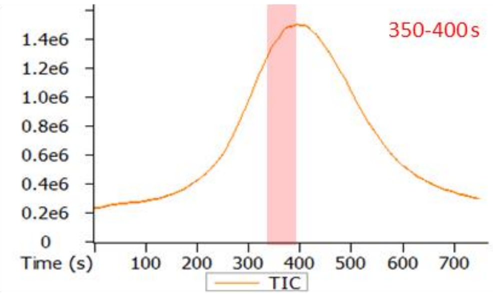


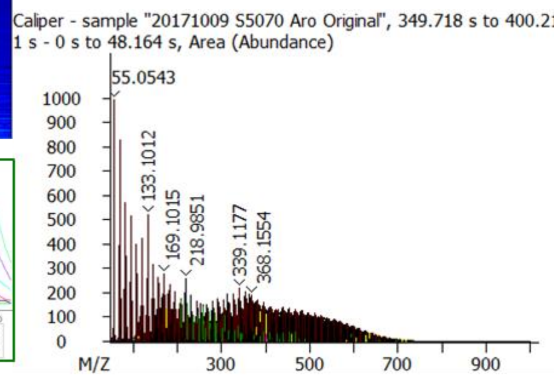




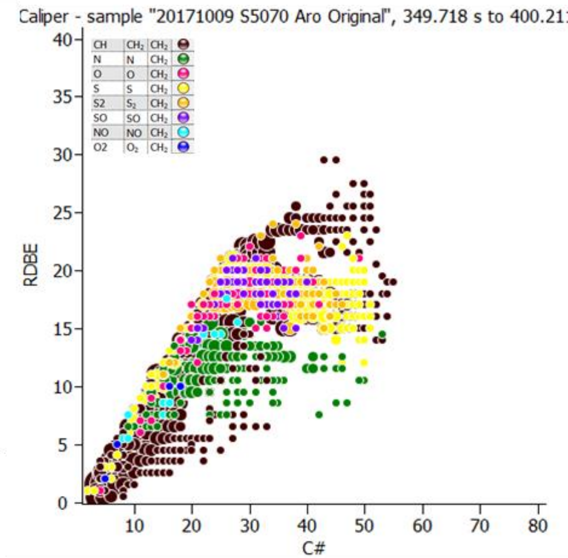
Non specific Fragmentation

Molecular Information



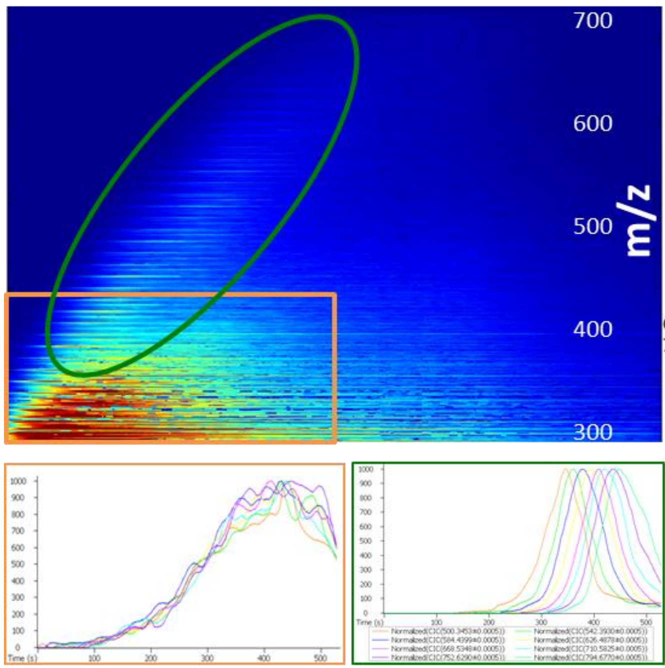


Boiling behavior



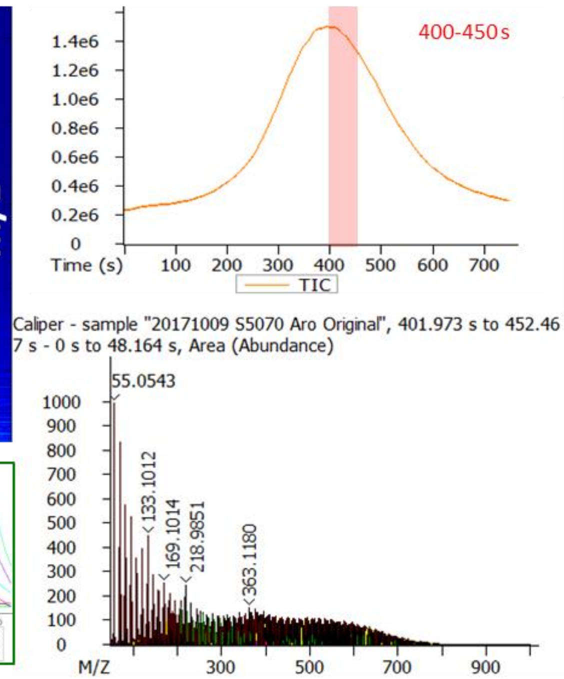
Class Information

Can we go further with evolved gas analysis HRMS: DIP reduced pressure evaporation of a vacuum gas oil

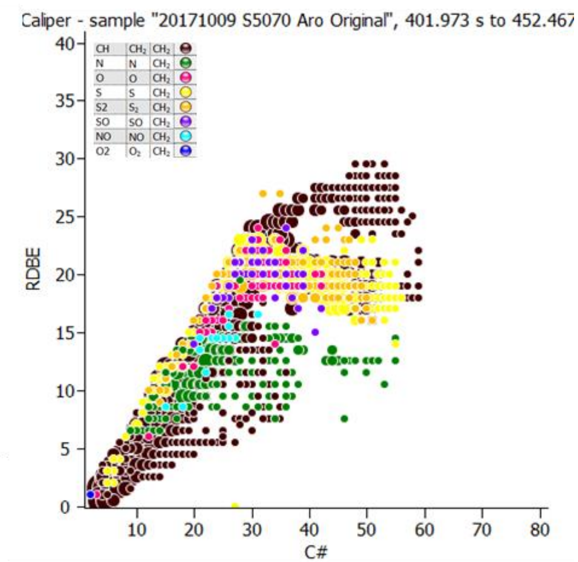


Non specific Fragmentation

Molecular Information

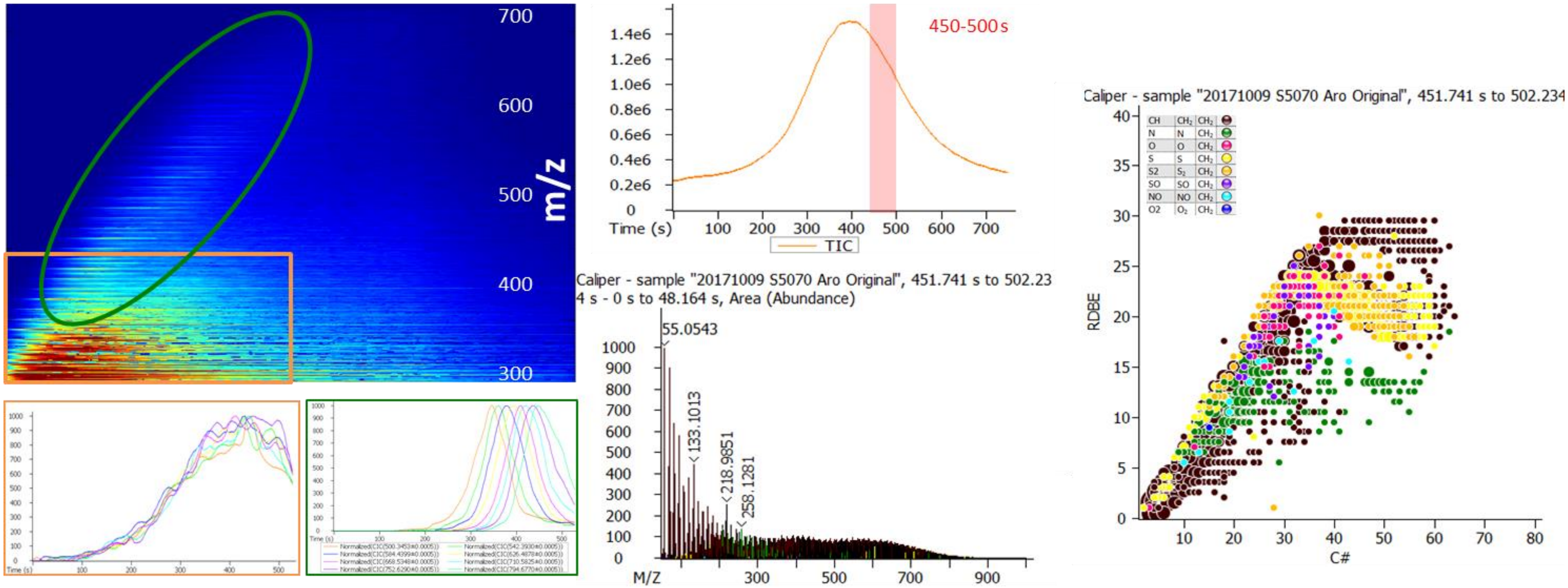


Boiling behavior



Class Information

Can we go further with evolved gas analysis HRMS: DIP reduced pressure evaporation of a vacuum gas oil



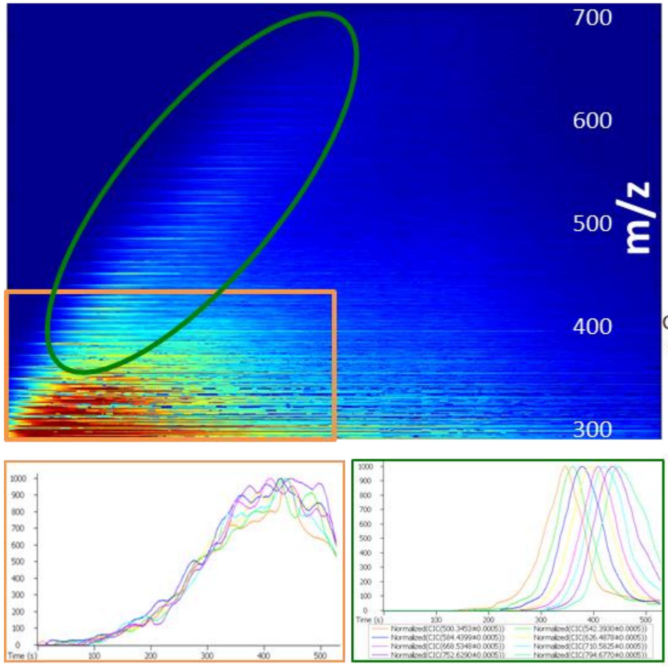
Non specific Fragmentation

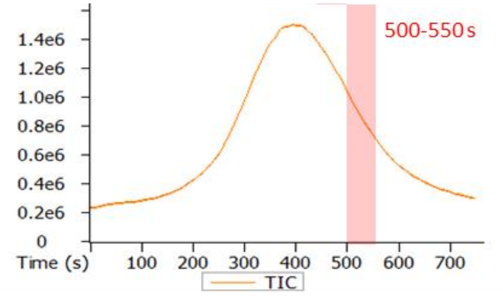
Molecular Information

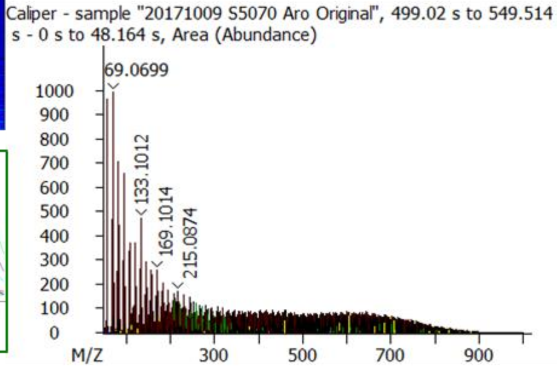
Boiling behavior

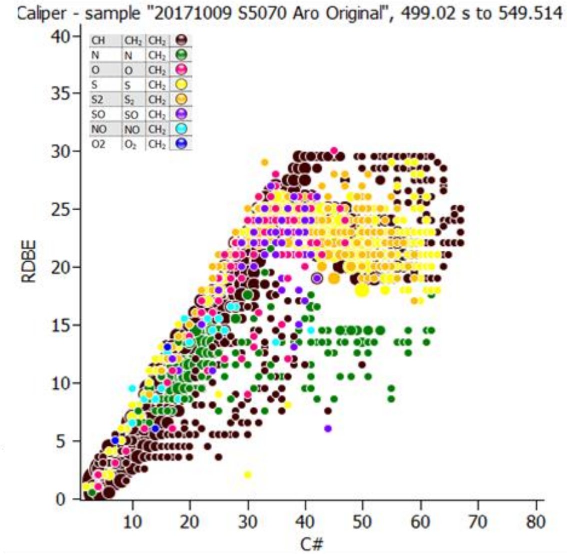
Class Information

Can we go further with evolved gas analysis HRMS: DIP reduced pressure evaporation of a vacuum gas oil









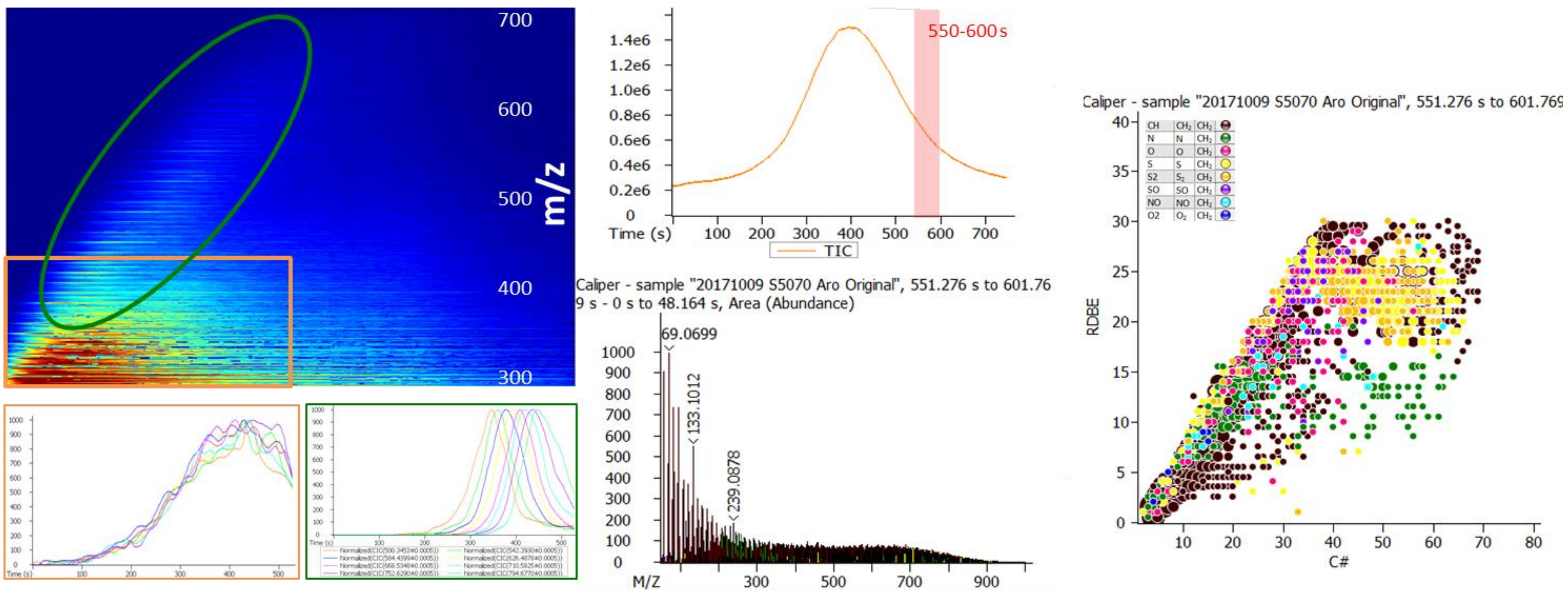
Non specific Fragmentation

Molecular Information

Boiling behavior

Class Information

Can we go further with evolved gas analysis HRMS: DIP reduced pressure evaporation of a vacuum gas oil



Non specific Fragmentation

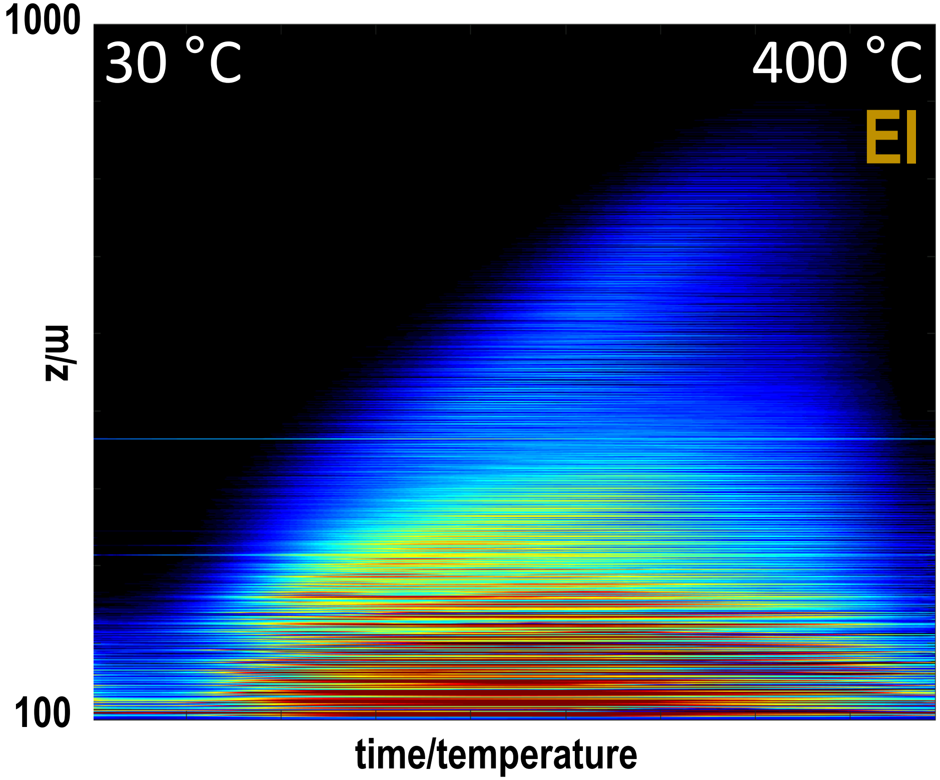
Molecular Information

Boiling behavior

Class Information

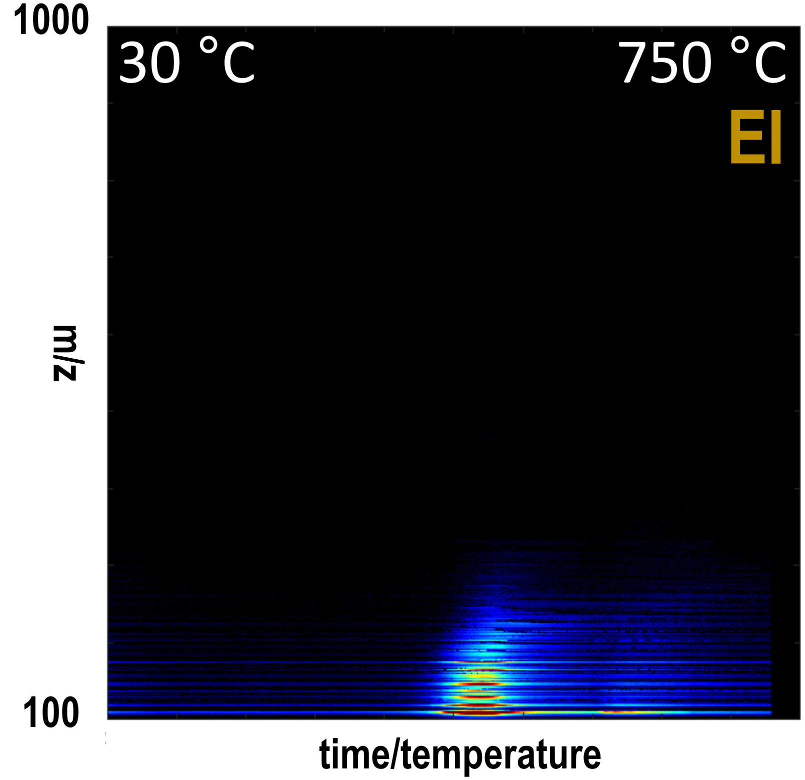
Going further – DIP reduced pressure evaporation

DIP (10^{-6} mbar)



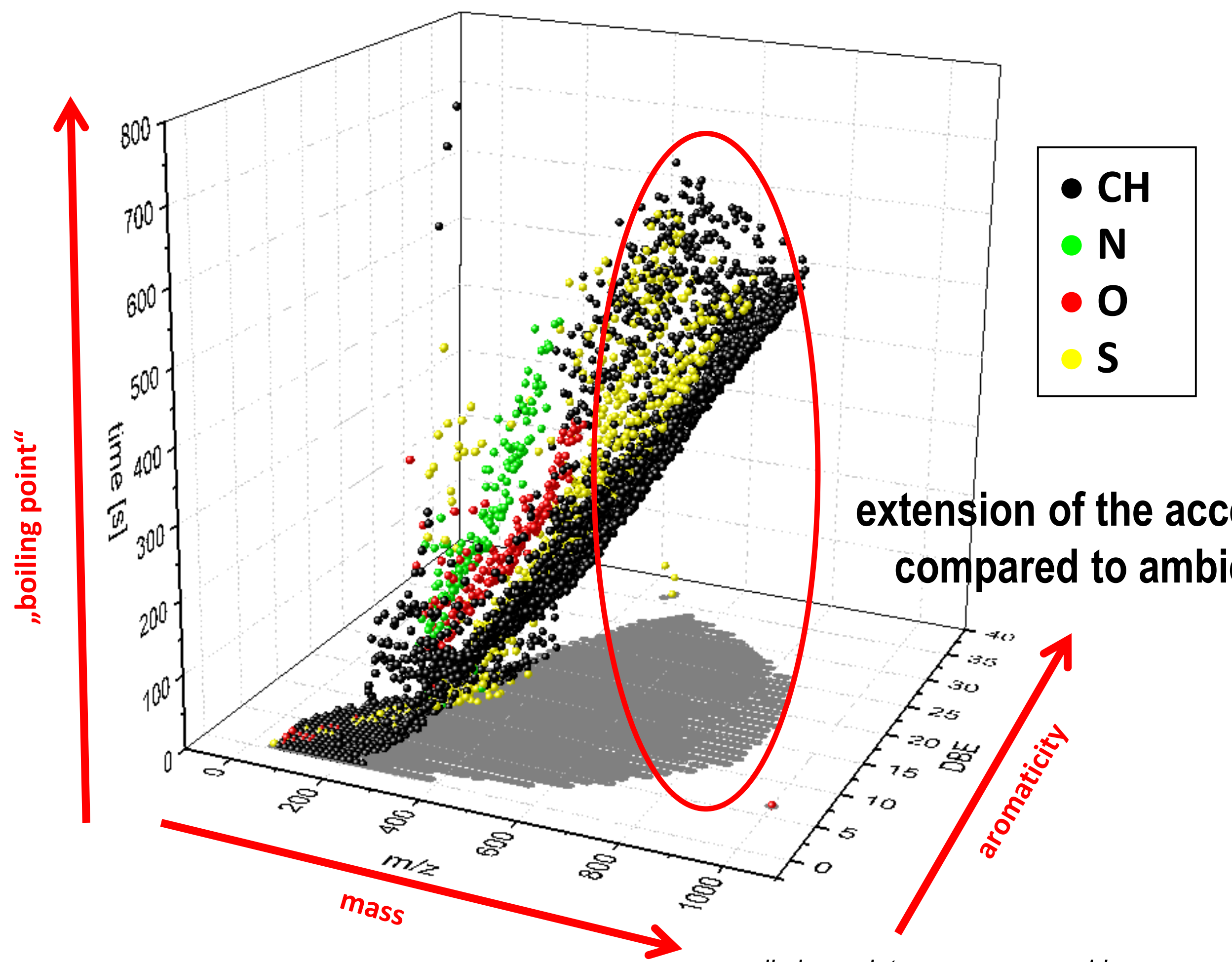
destruction free volatilization

TGA (Atmospheric pressure)



thermal fragments (pyrolysis)

Reduced pressure evaporation utilizing the DIP



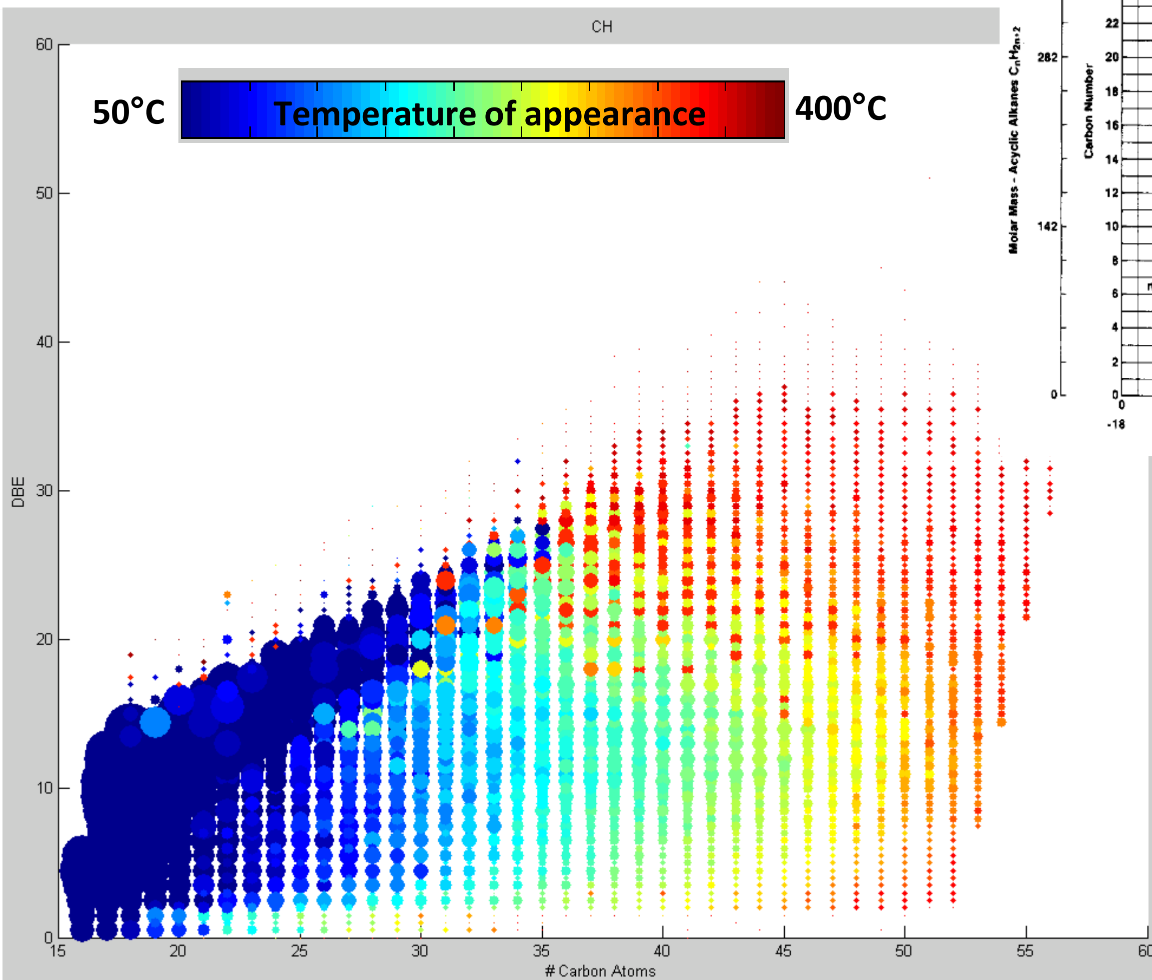
extension of the accessible m/z-range compared to ambient evaporation

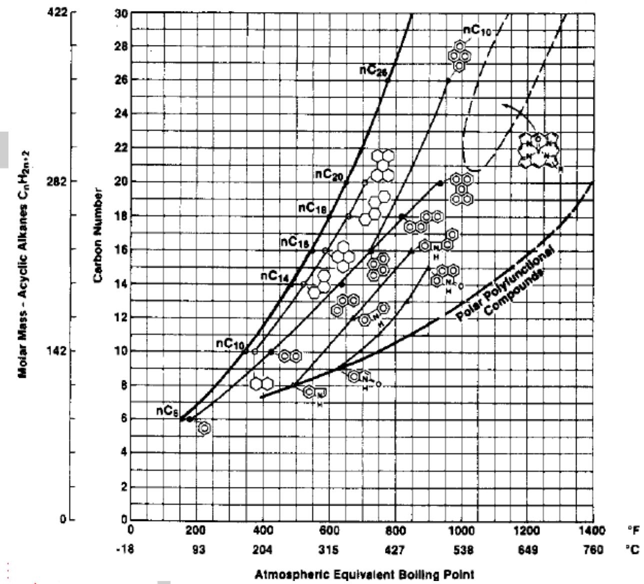
preliminary data on vacuum residues

Results and Discussion

Evidence of the Boduszynsky model

Aromaticity



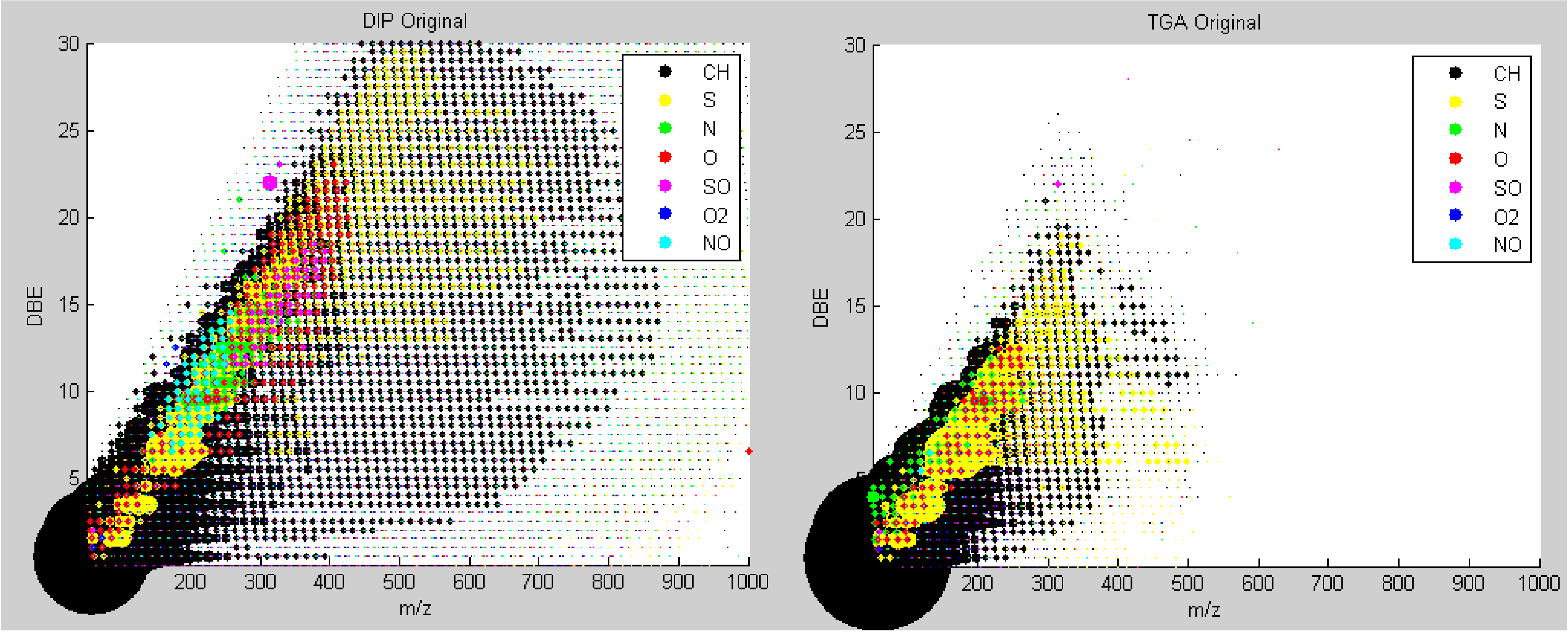


Increasing „boiling point“ for higher Aromaticity

Increasing „boiling point“ for higher #C

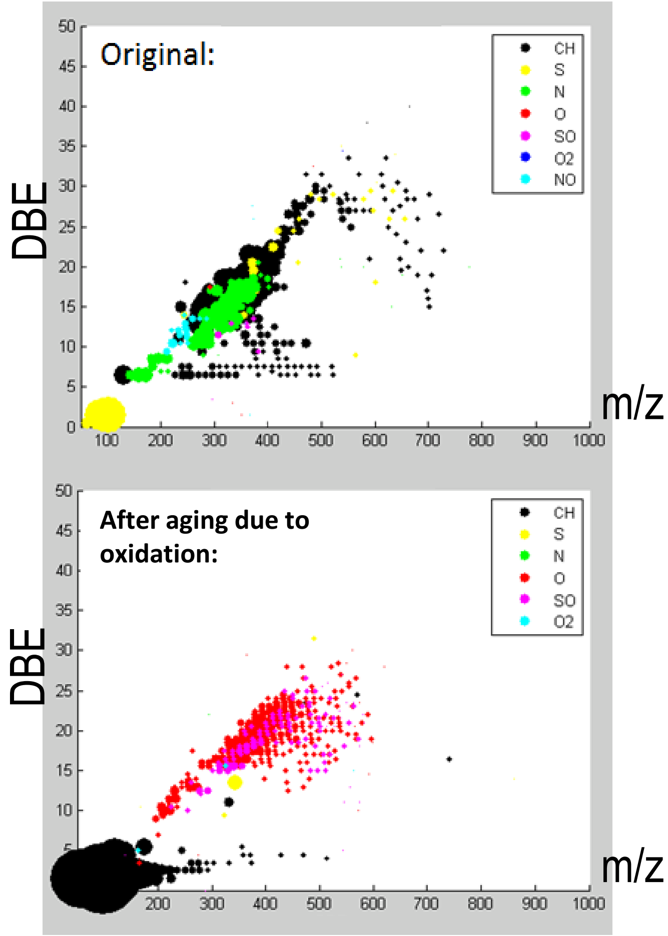
DIP – HRT vs TG – HRT (desorption profile)

DIP (10^{-6} mbar) **TGA (Atmospheric pressure)**

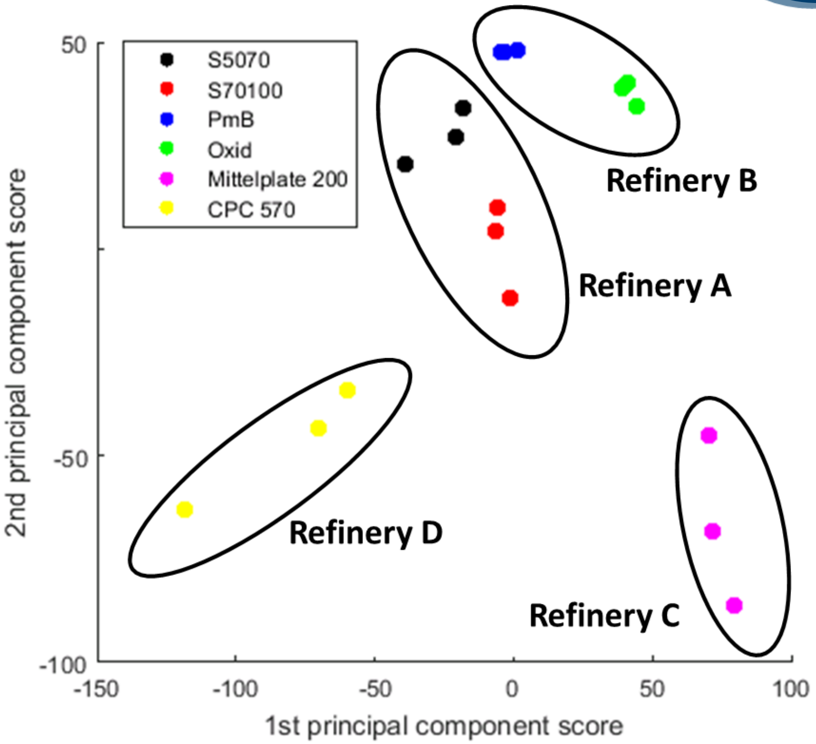


Differentiation of Bitumen and Bitumen aging

Bitumen aging



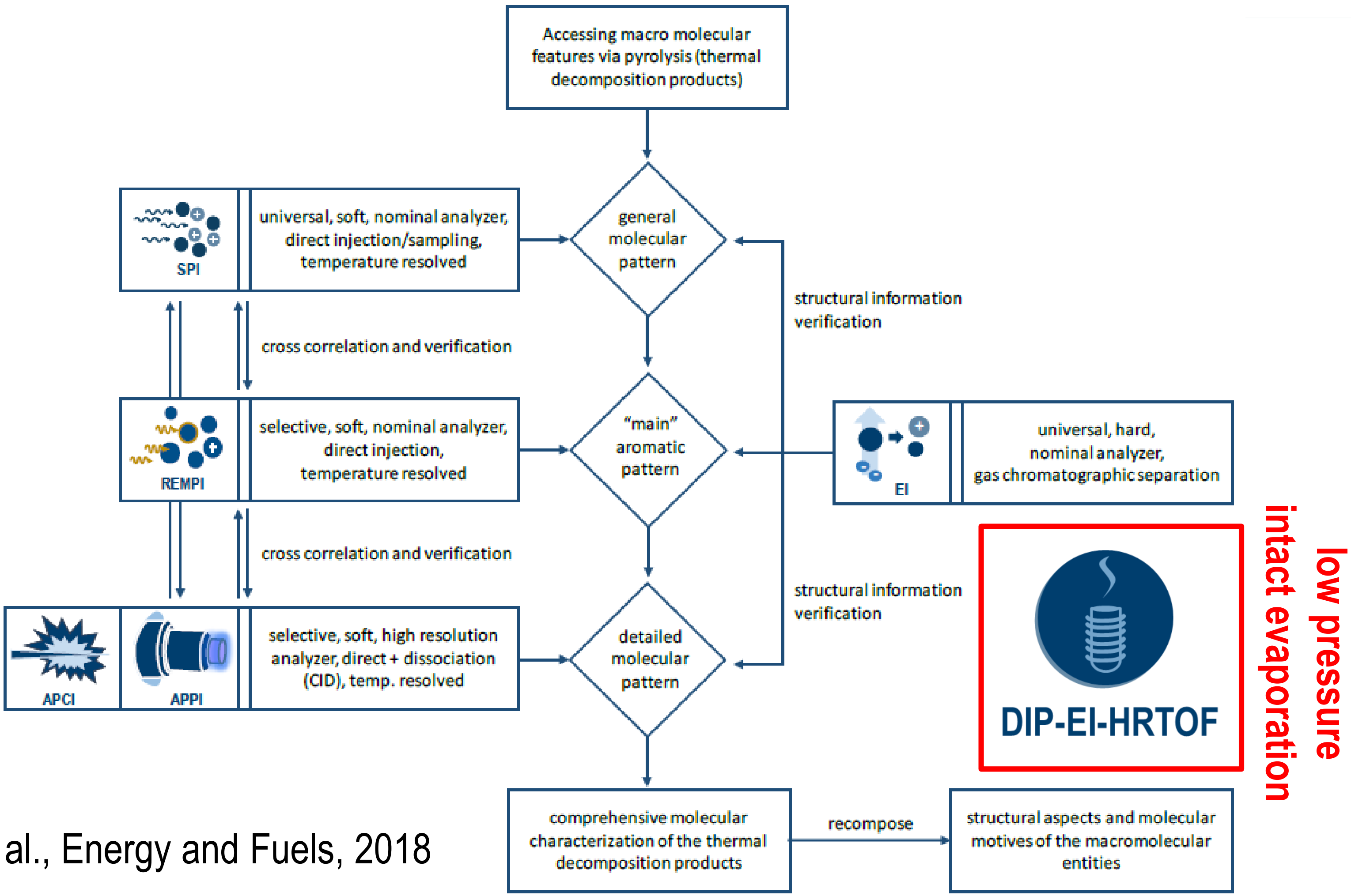
Bitumen origin



<u>Fingerprinting</u>

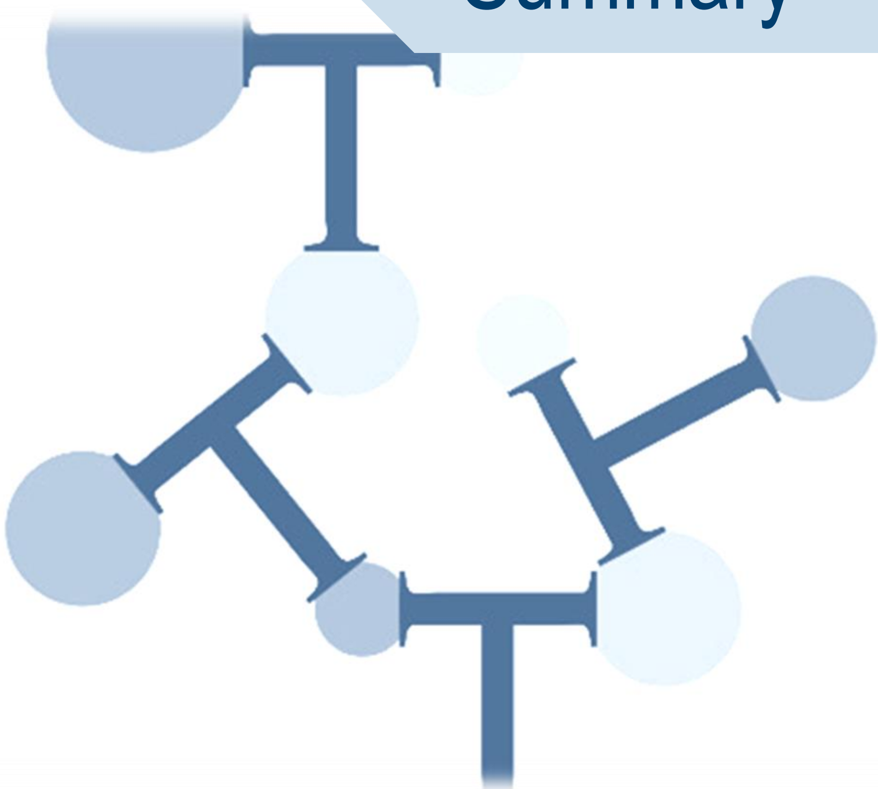
- Principal component analysis with 6 bitumen samples (á 3 replicates) from 4 refineries
- ≈ 25.000 mass traces (variables) used for discrimination

Outlook - Data combination and integration



Rüger et al., Energy and Fuels, 2018

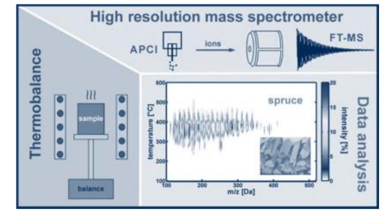
Summary 4



Summary

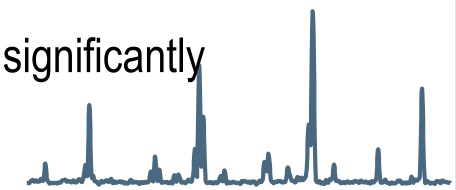
Introduction of thermal analysis high resolution mass spectrometry

- **powerful tool** for chemical characterisation - macromolecular structures decompose
- temperature **emission profile** of individual elemental compositions traceable
- no solvent effects, sample material **directly useable**, minimum sample amount



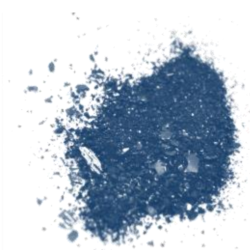
Application towards heavy oils and asphaltenes

- asphaltenes reveal **ultra-complex spectra** dominated by CH- and CHS_x-signals (APCI/APPI)
- **DIP** at reduced pressure allows to **extent the accessible chemical space** significantly



Combination of thermal analysis approaches for asphaltene pyrolysis

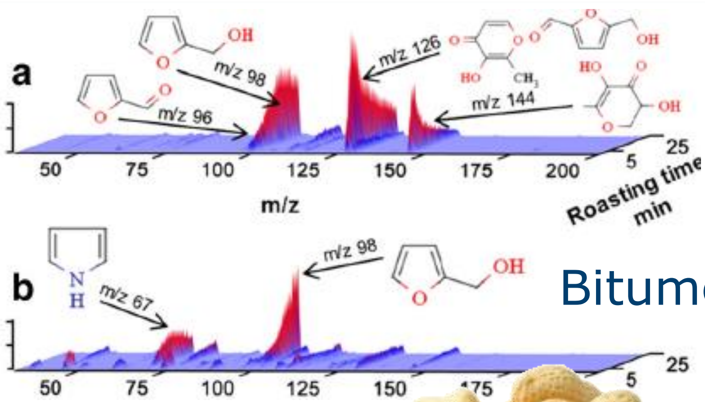
- Interlaboratory study on a **purified** asphaltene
- **multi-methodological** thermal analysis mass spectrometry approach
- data combination for elucidation of the dominant **structural motives**

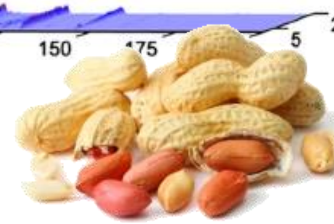


Other Application Fields of EGA-MS

Biomass pyrolysis

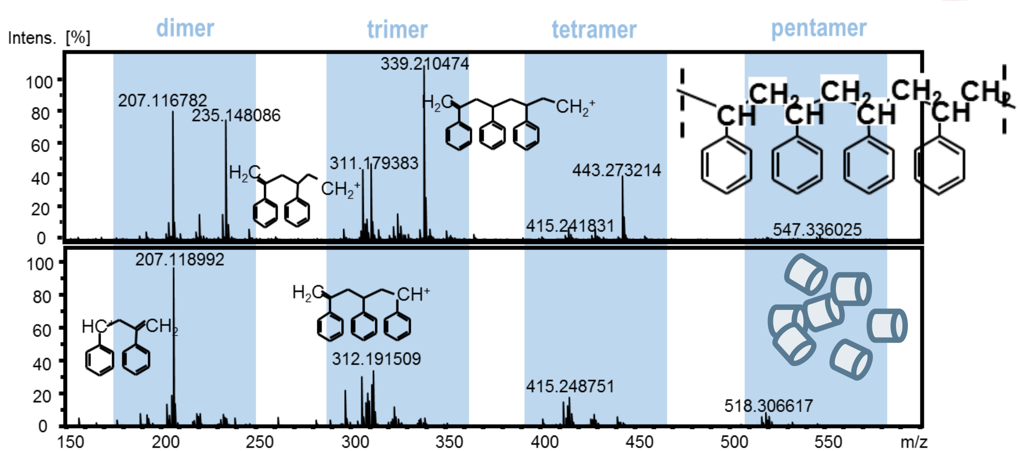
Food processing (coffee/nut roasting)





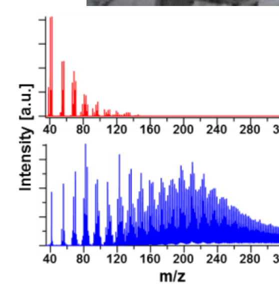
Bitumen and Bitumen ageing

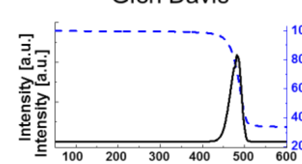
Polymers and oligomeric samples



Oil shale

Glen Davis

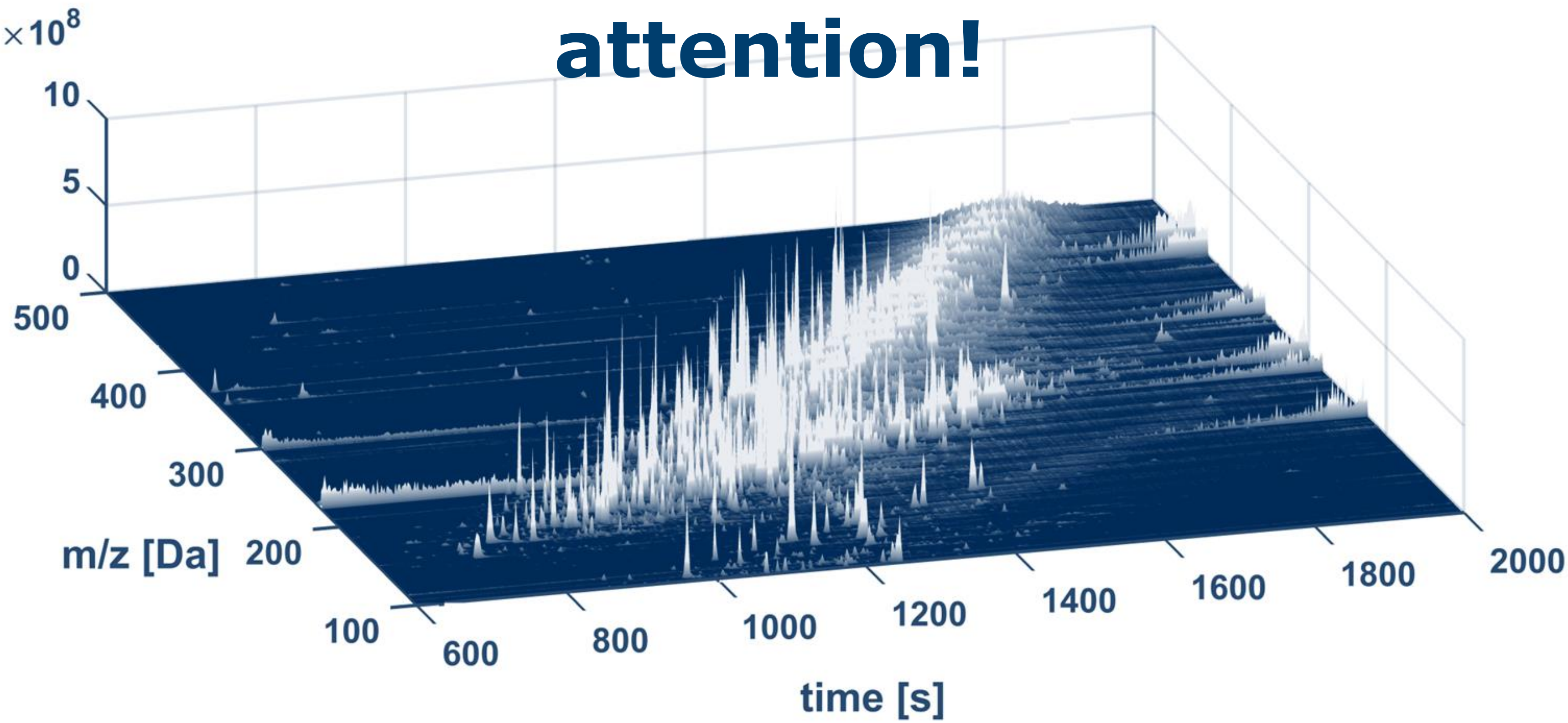




Acknowledgment

Zimmermann Group – September 2017

Thank you for your kind attention!



christopher.rueger@uni-rostock.de