Universität Rostock Traditio et Innovatio

HelmholtzZentrum münchen
Deutsches Forschungszentrum für Gesundheit und Umwelt

JOINT MASS SPECTROMETRY CENTRE

Comprehensive mass spectrometric evolved gas analysis in the context of Petroleomics

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&

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Outline

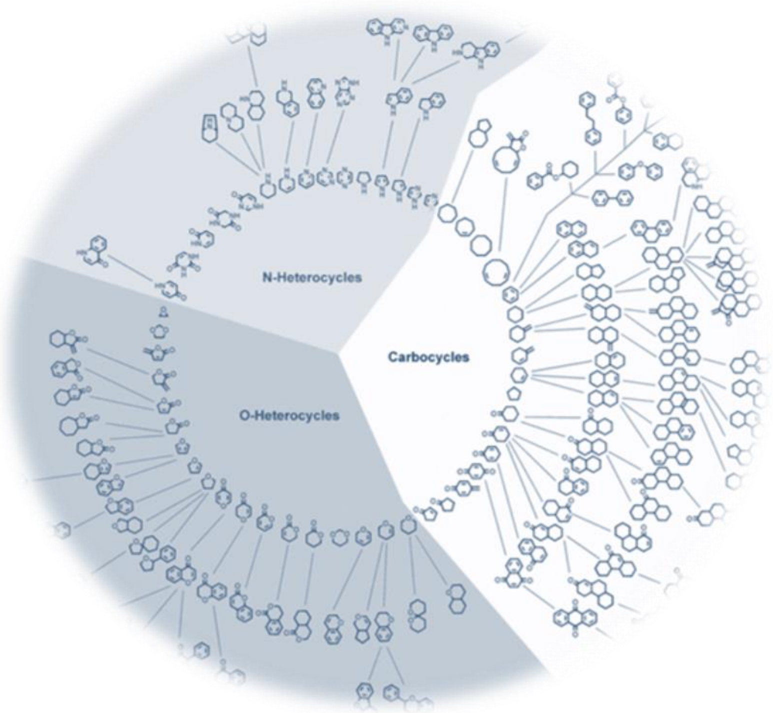
1) Motivation and Introduction

2) Instrumental Setup and Sample Material

3) Results and Discussion

4) Summary and Outlook

Motivation and Introduction 1

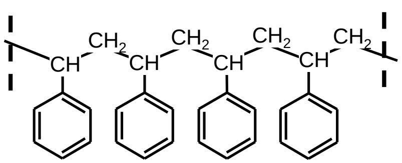


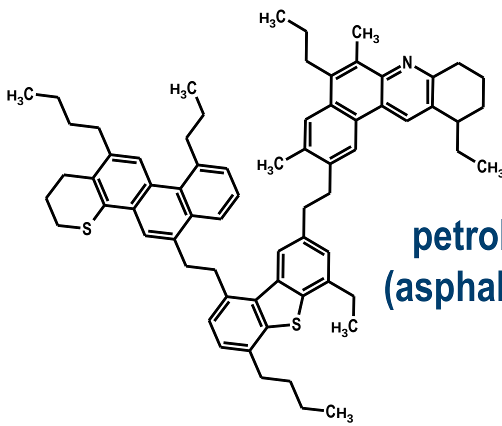
Motivation and Introduction

Macromolecules

synthetic polymeres

polystyrene

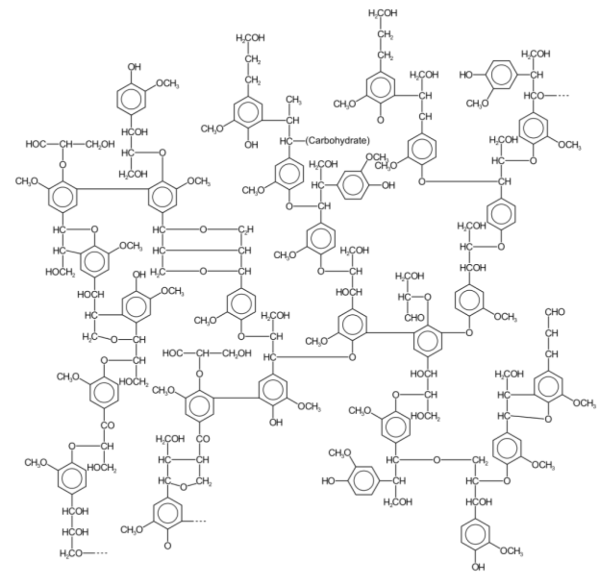




petroleum (asphaltenes)

natural macromolecules

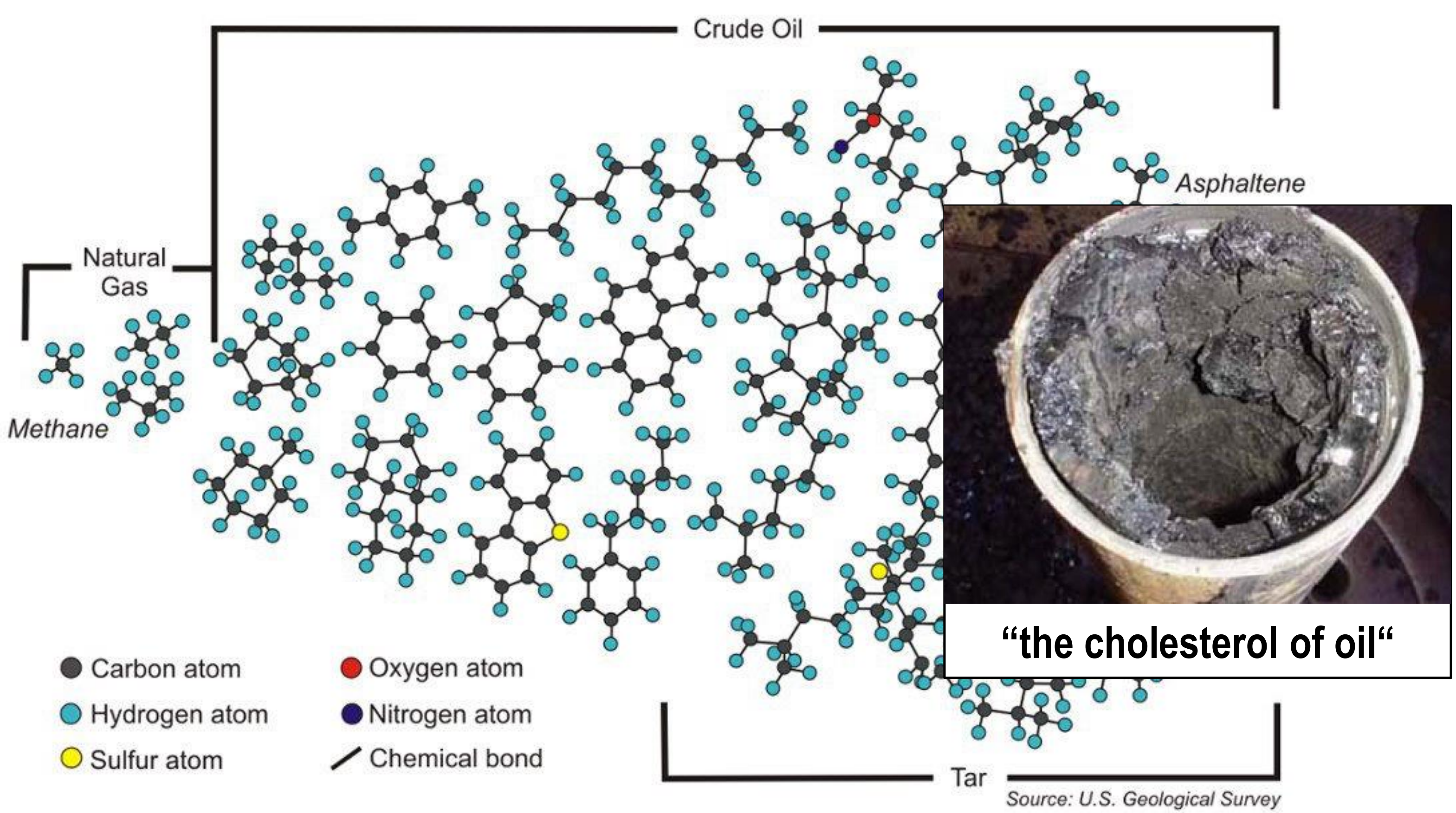
wood (lignin)



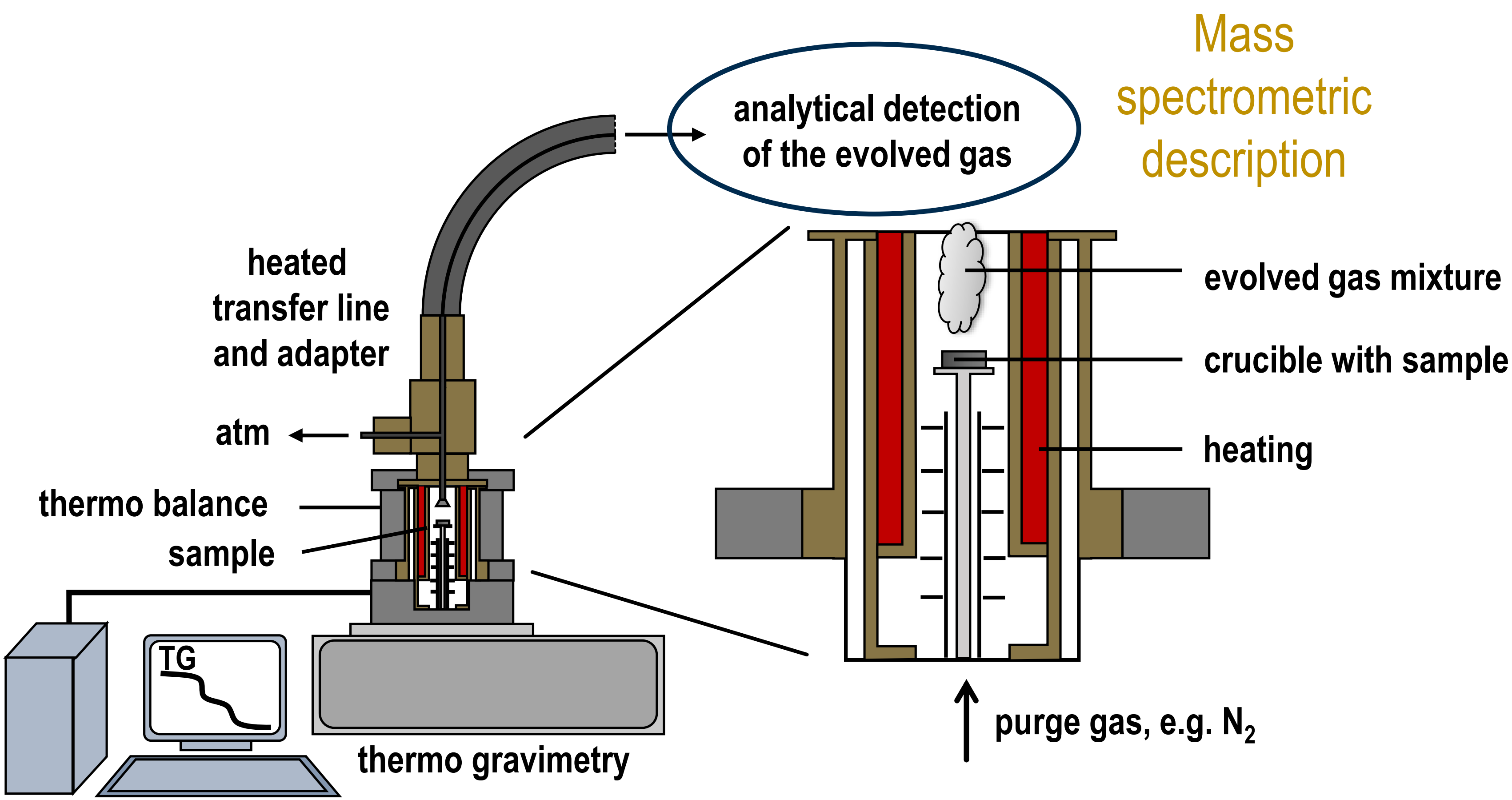
How to access the chemical nature of these macromolecules?

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

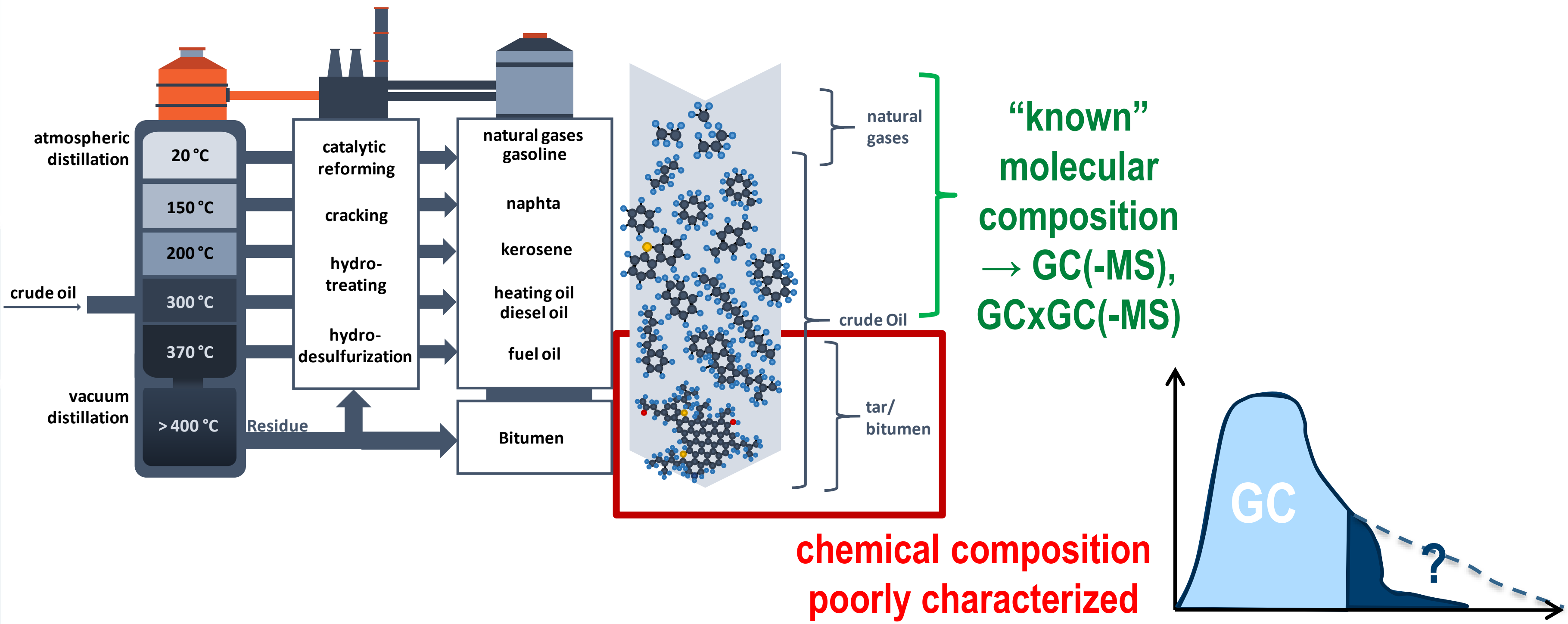
Mass spectrometric petroleum analysis – Petroleomics



Basic concept of evolved gas analysis (EGA)



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

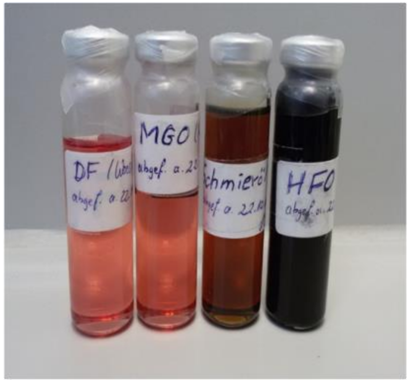
Material and Method 2

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

Mass separation

TG-APPI/APCI-FTMS

DIP-EI-HRTOF

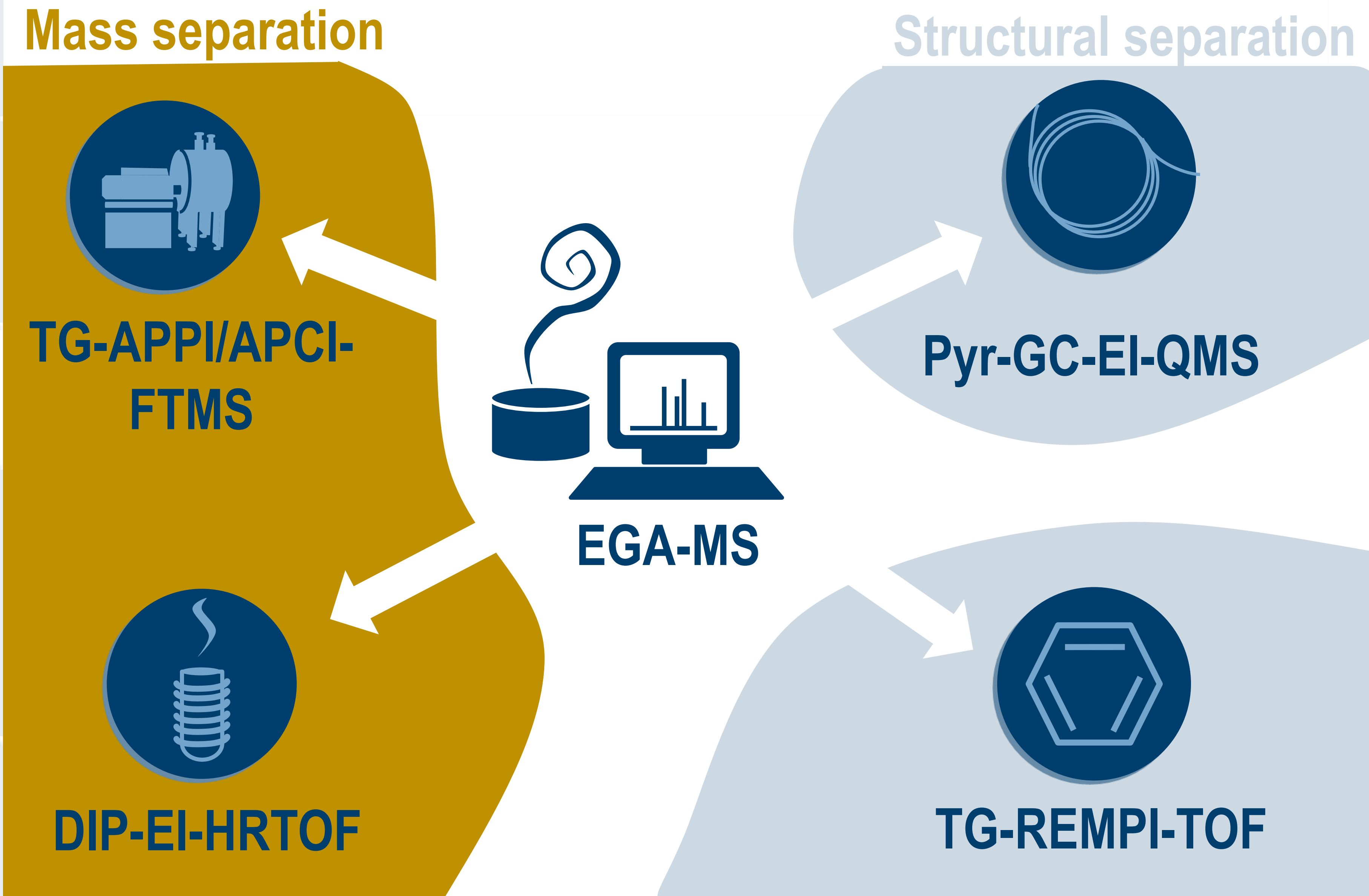
EGA-MS

Structural separation

Pyr-GC-EI-QMS

TG-REMPI-TOF

Material and Method



Thermal analysis coupled to Fourier-Transform MS

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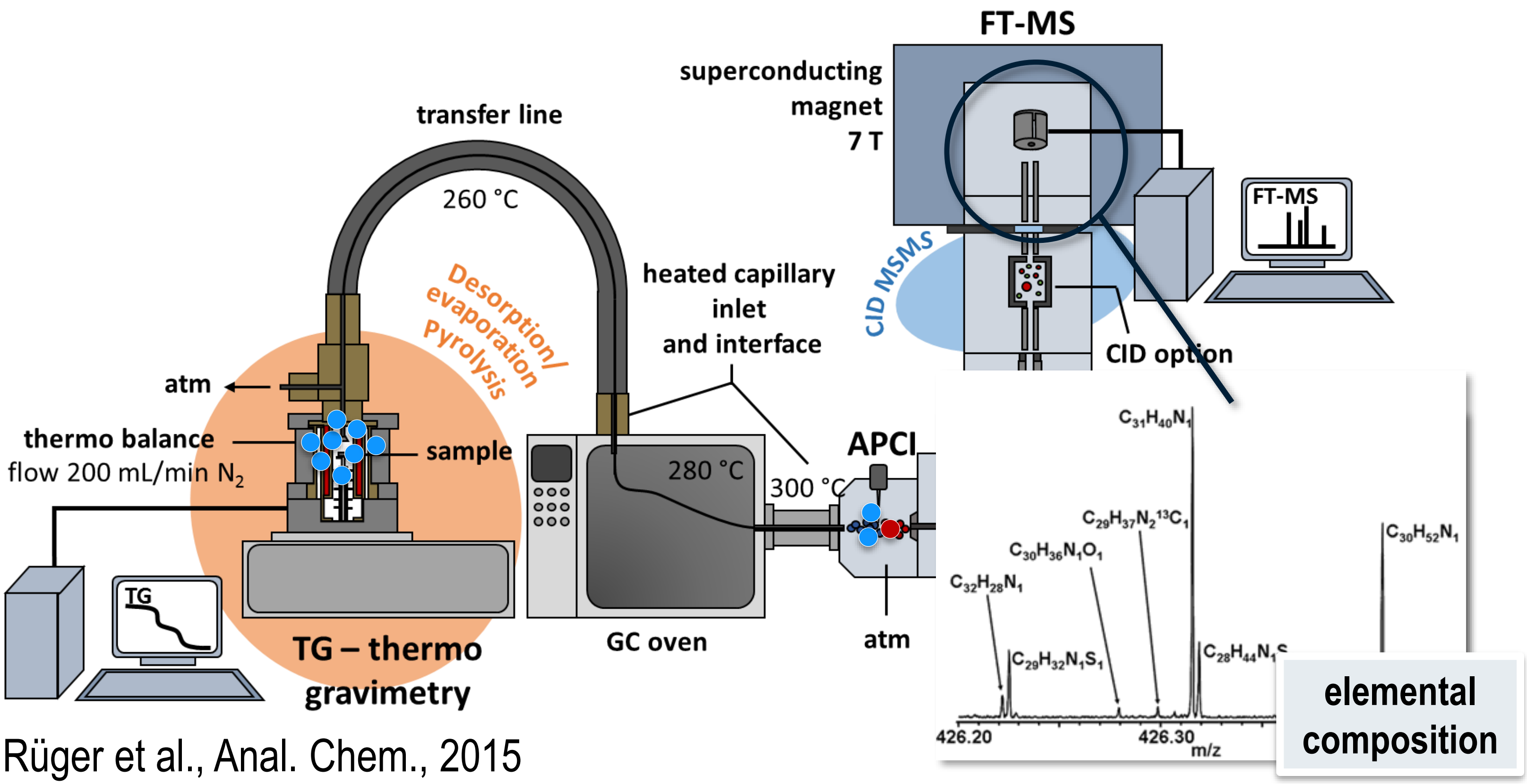

Rüger et al., Anal. Chem., 2015

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

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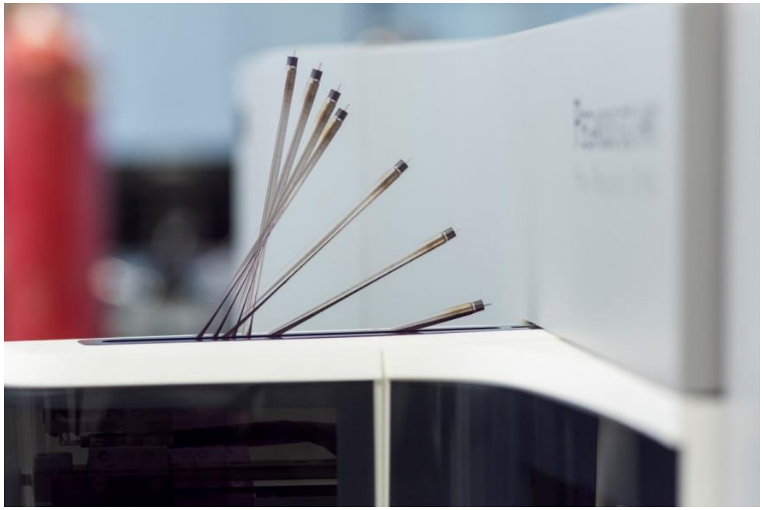
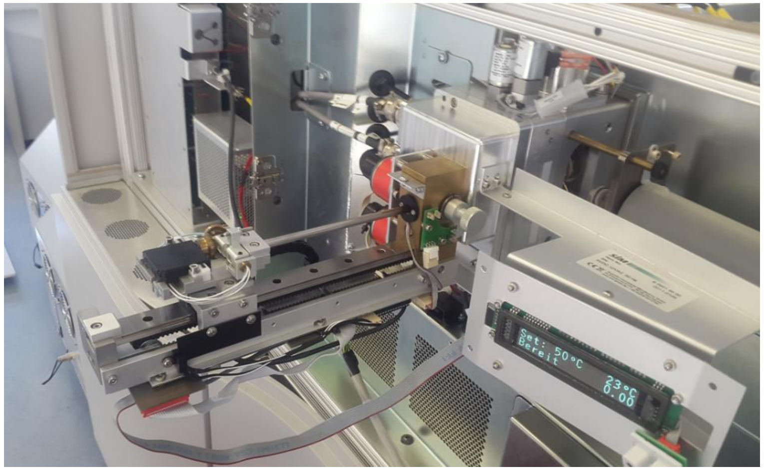
Direct inlet probe (DIP) high resolution time-of-flight MS



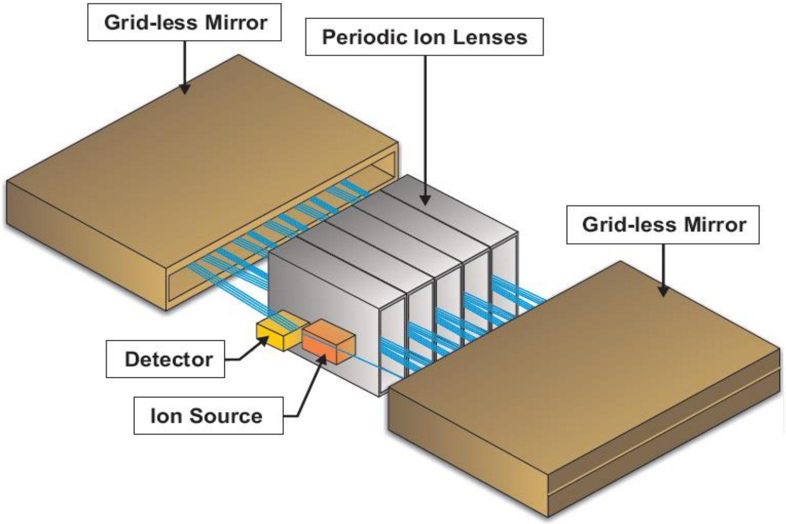


Instrument

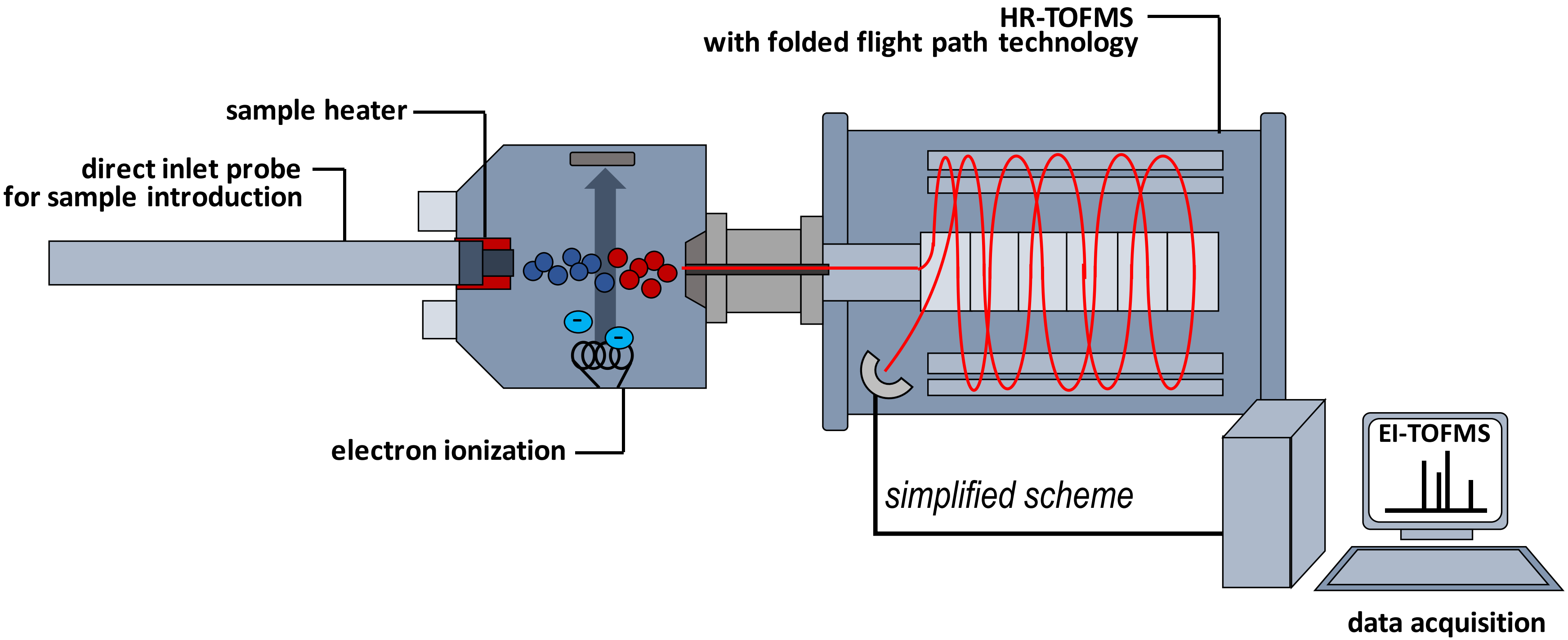
- modified LECO Pegasus GC×GC-HRT
- multi-reflection TOF-MS

MS Parameter (HRT MS):

- acquisition frequency: 200 Hz
- resolution: 25,000-50,000
- mass accuracy < 2 ppm

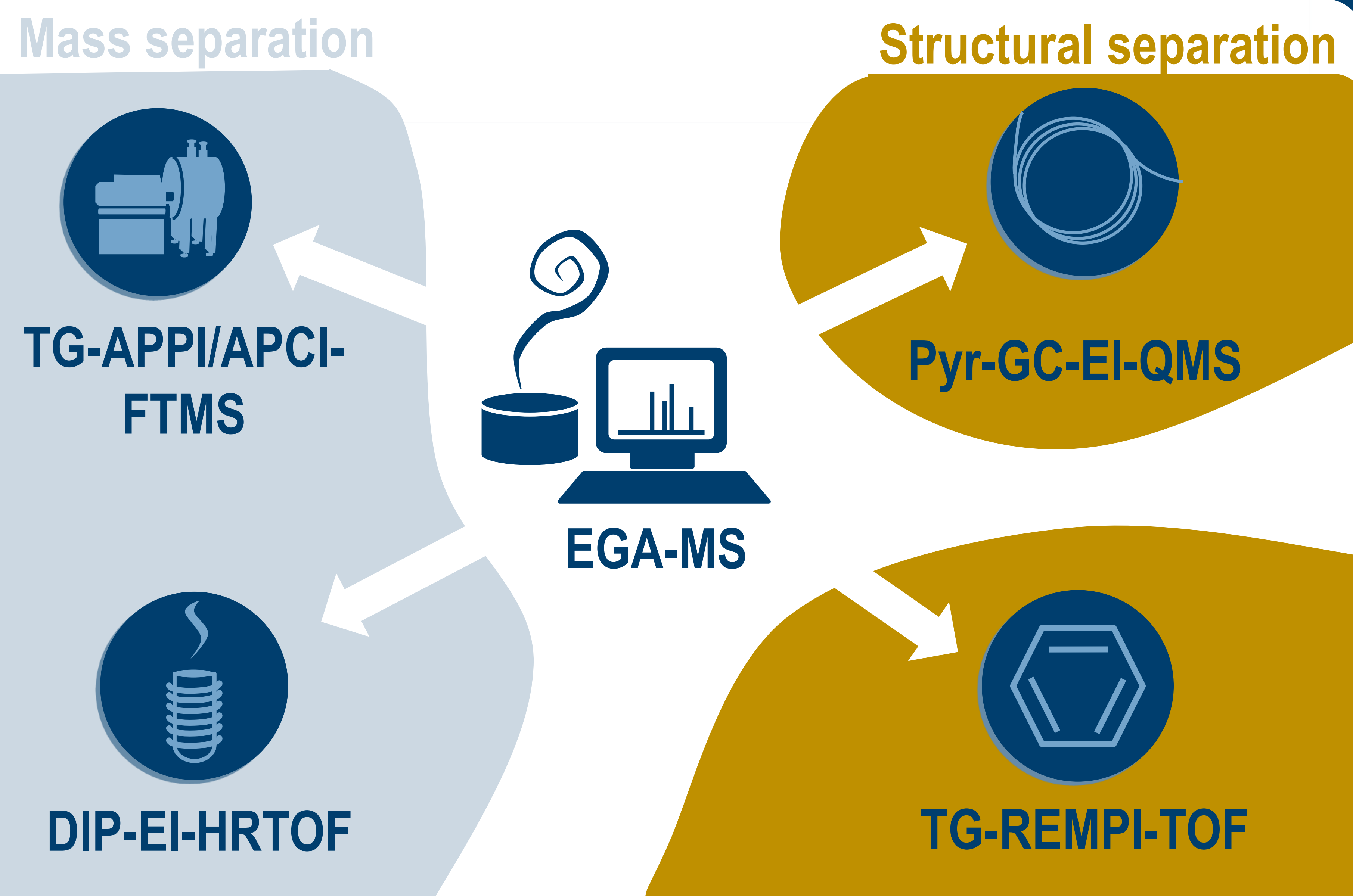


Direct inlet probe (DIP) high resolution time-of-flight MS

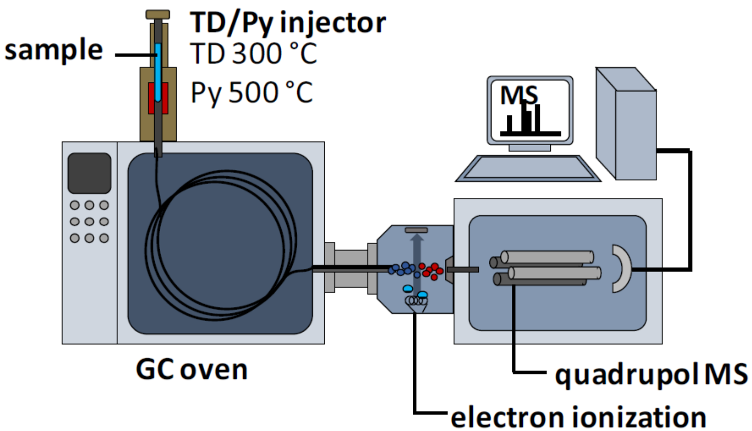


→ heating at reduced pressure to intactly evaporate larger constituents
+ EI as universal ionization technique

Material and Method

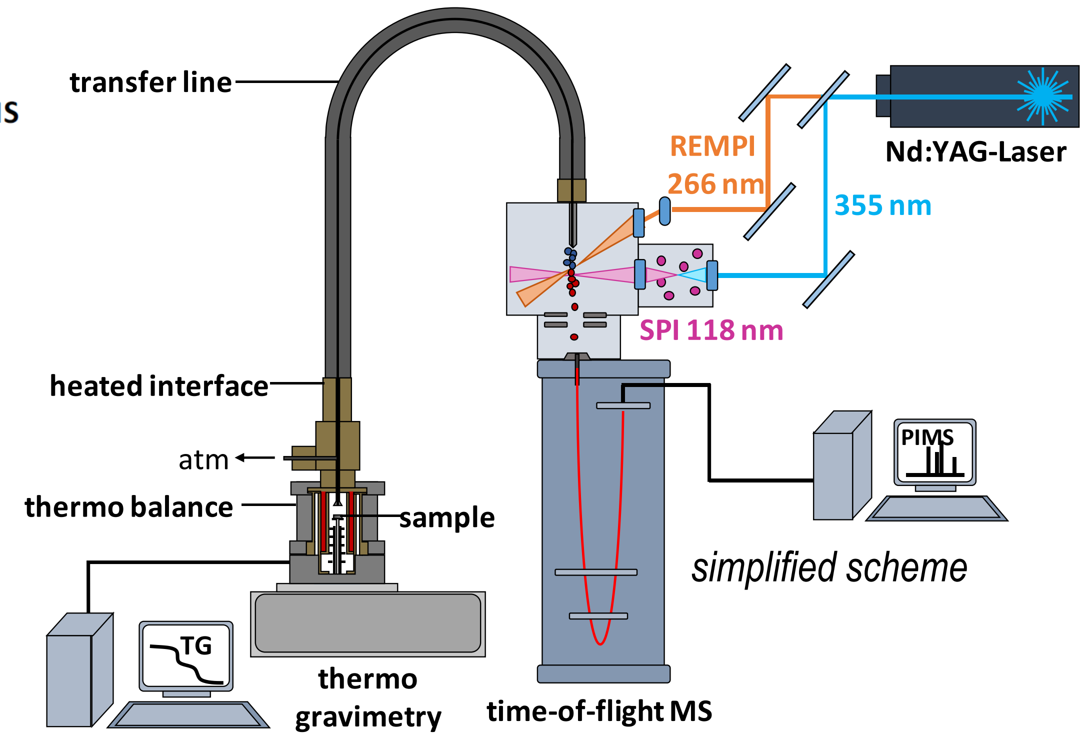


Pyrolysis-GC EI-MS and photo ionization TOF-MS

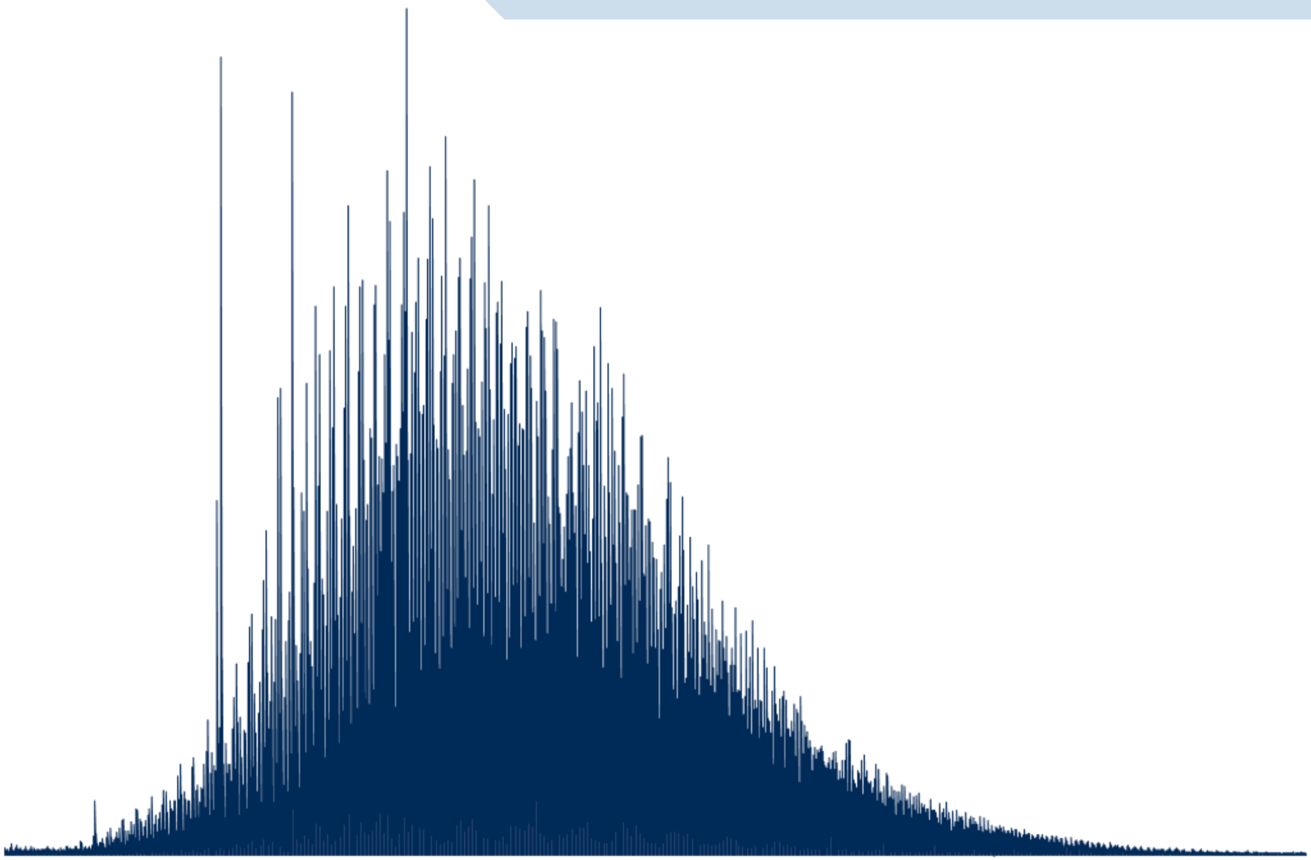


→ structural information via retention index and EI-fragment spectra

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

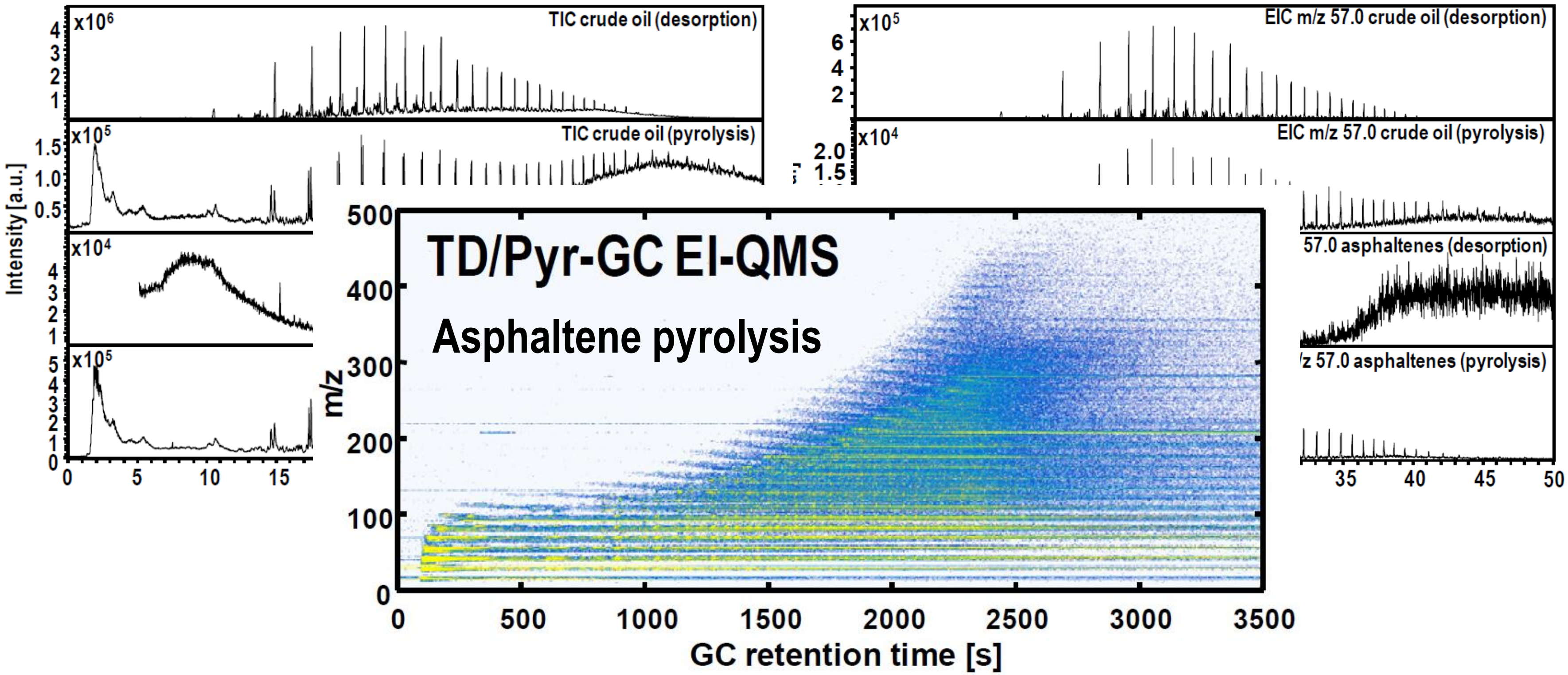


Results and Discussion 3



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**



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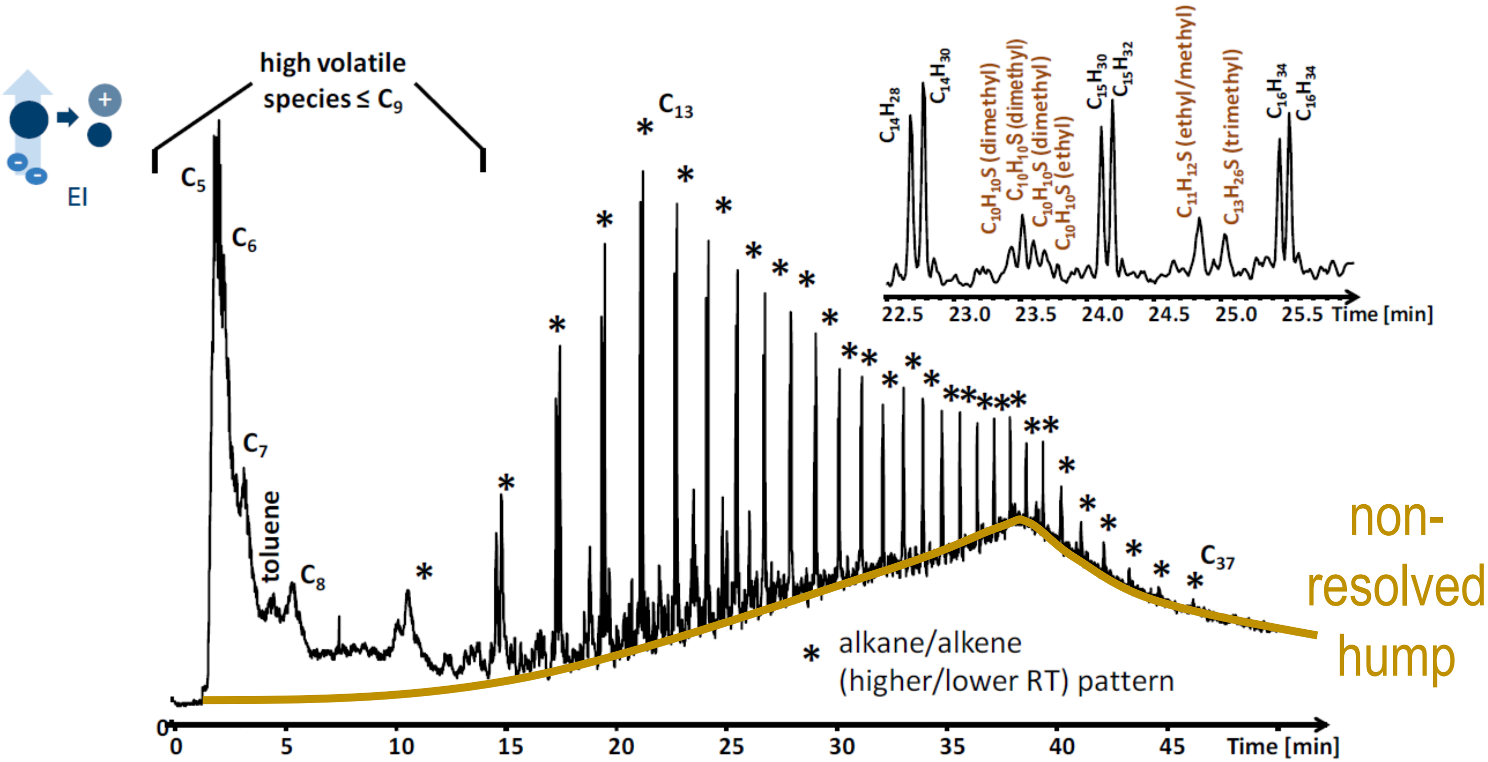
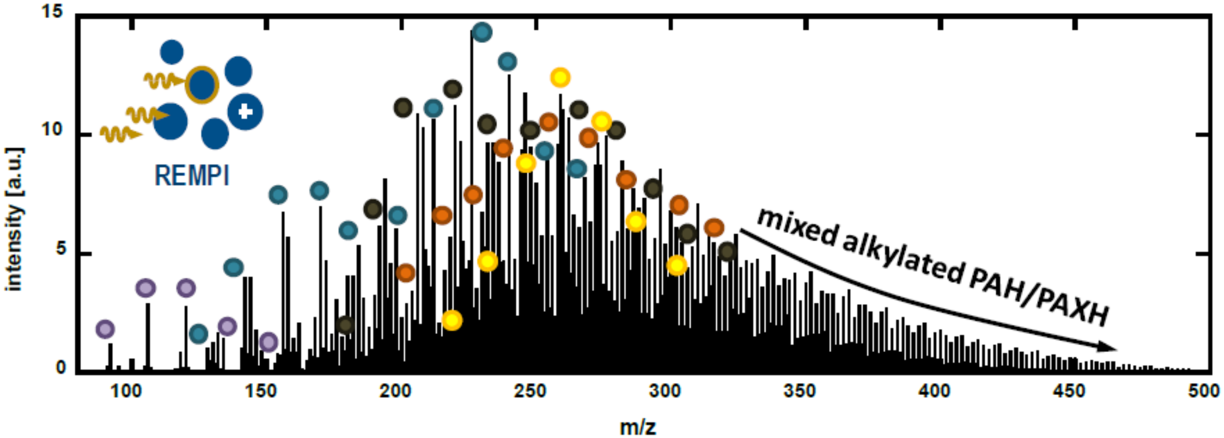
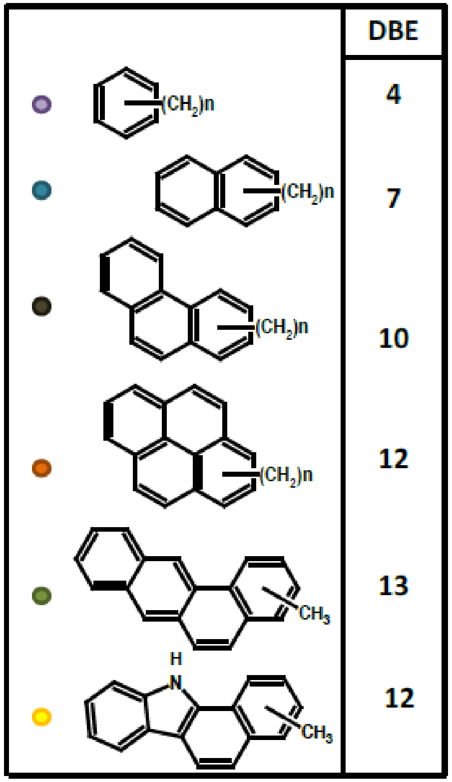


Resonance-enhanced multiphoton ionization

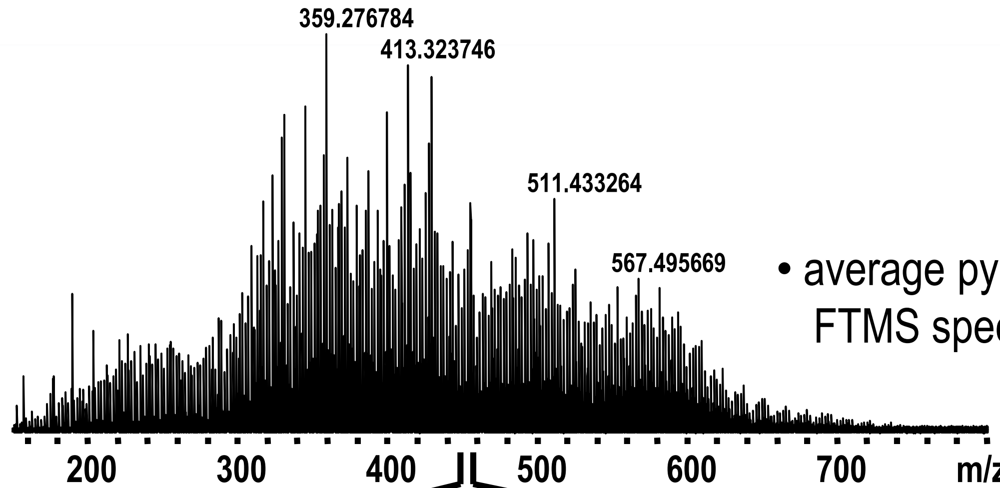
- **selective and sensitive** ionization approach for **aromatic** constituents



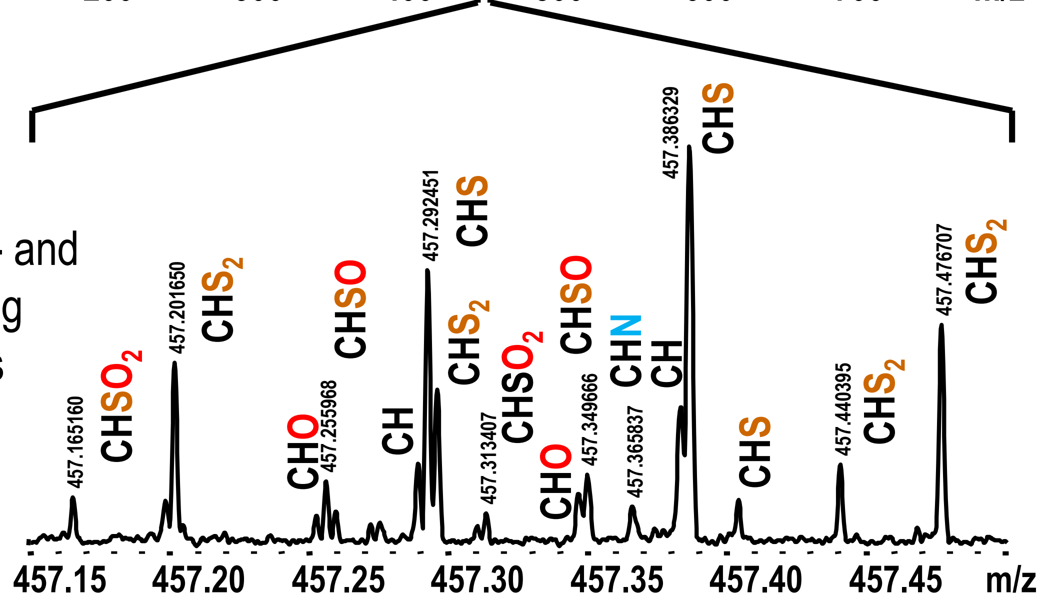


- intense and **complex** mass spectrometric pattern
- **broad** m/z range from benzene up to > m/z 500
- even-numbered homologue series indicating **Nitrogen-** containing poly-aromatic core structures
- two- to four-ring aromatic alkylated rows dominate

General API-MS response for Asphaltene pyrolysis

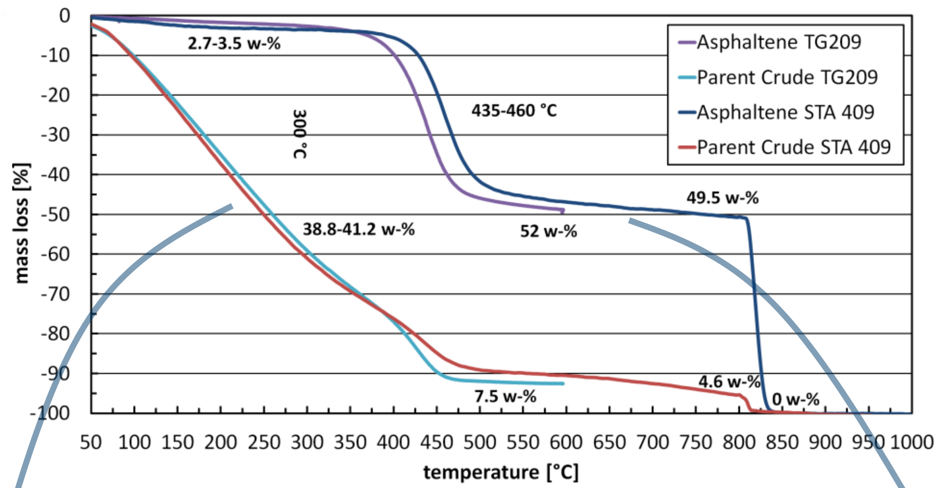


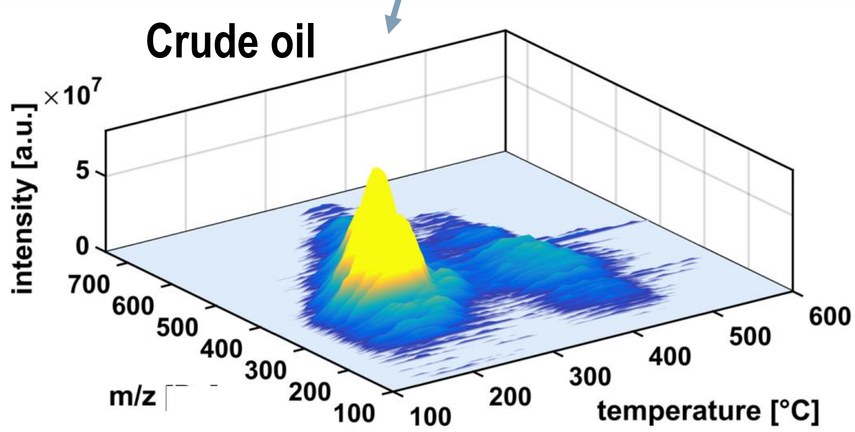
- average pyrolysis APCI-FTMS spectrum



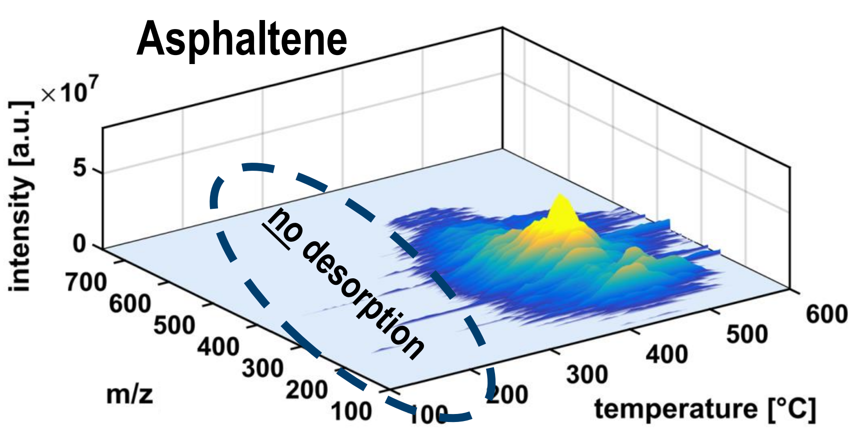
- CHS-, CHS_2-, $CHSO_x$- and CH-species dominating
- > 3,500 distinct peaks

Mass loss and API mass spectrometric response



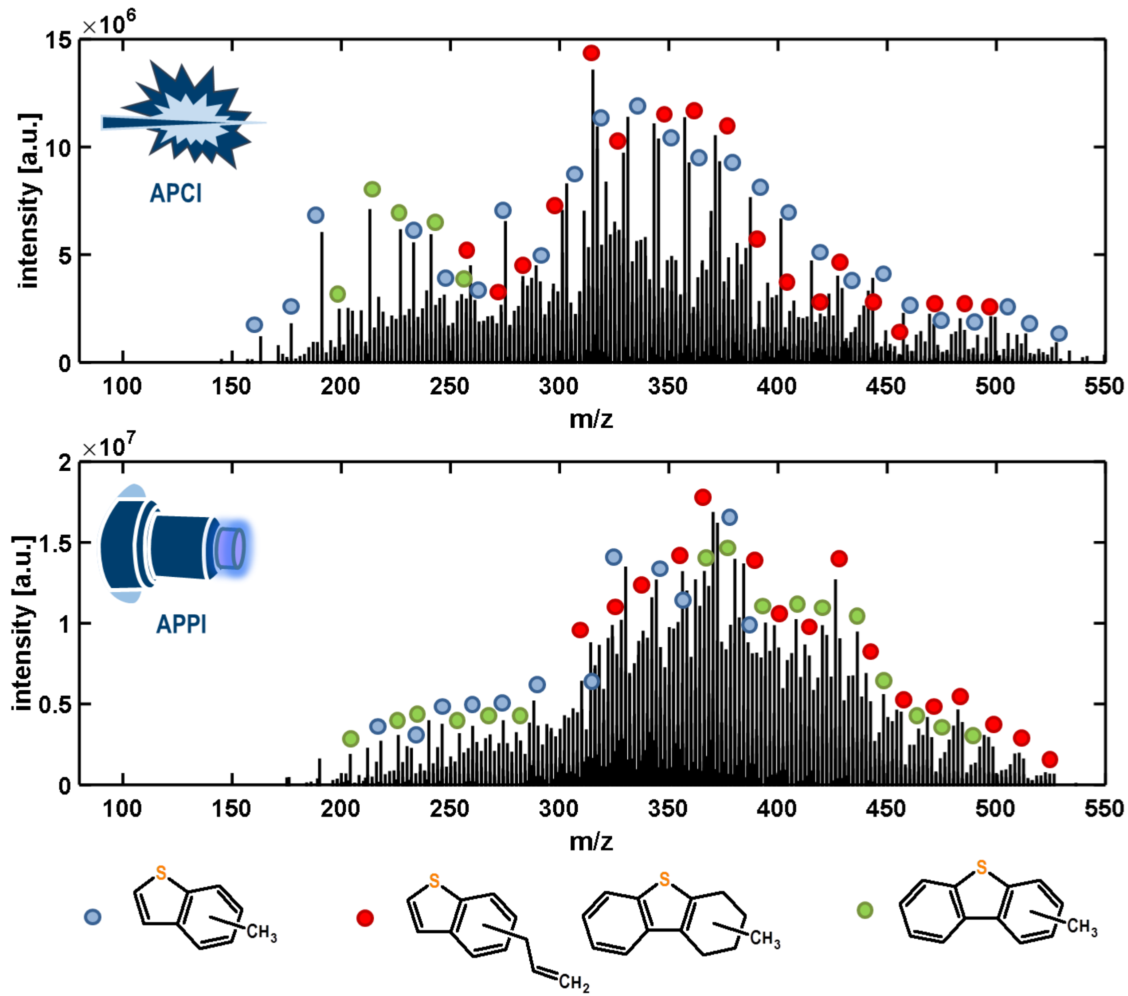


FT-MS APCI



FT-MS APCI

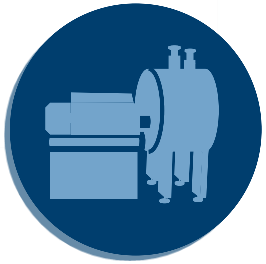
Averaged asphaltene pyrolysis molecular pattern

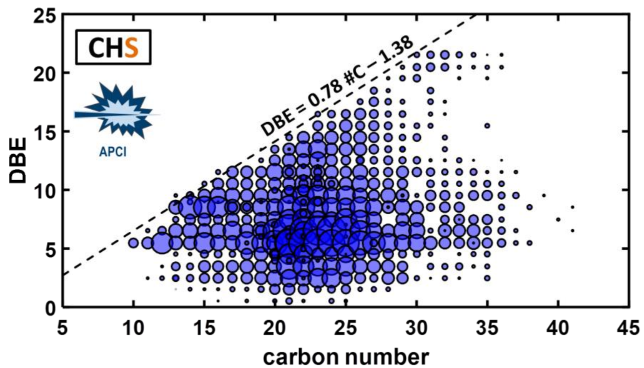


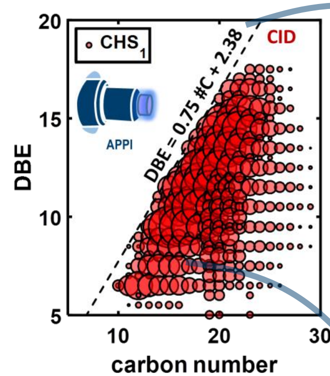
- alkylated aromatic structures with 2-4 rings as major motive
- CH- and CHS-species as major contributor to APCI and APPI

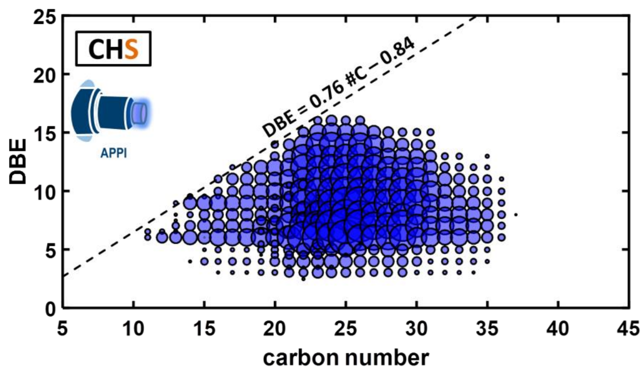
core structural motives?

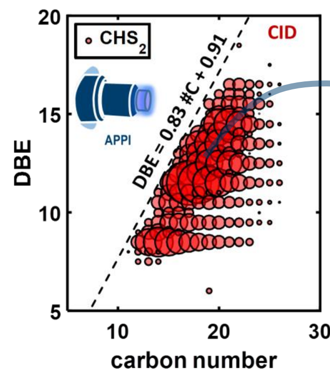
Collision induced dissociation data assessment







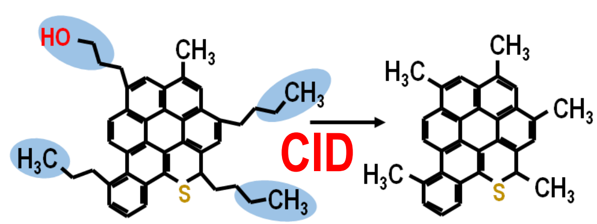




- slope of the left-side DBE versus #C carbon distribution reveals information on ring attachment
  → mainly **cata-condensed** benzene (minor amount of peri-condensed)

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

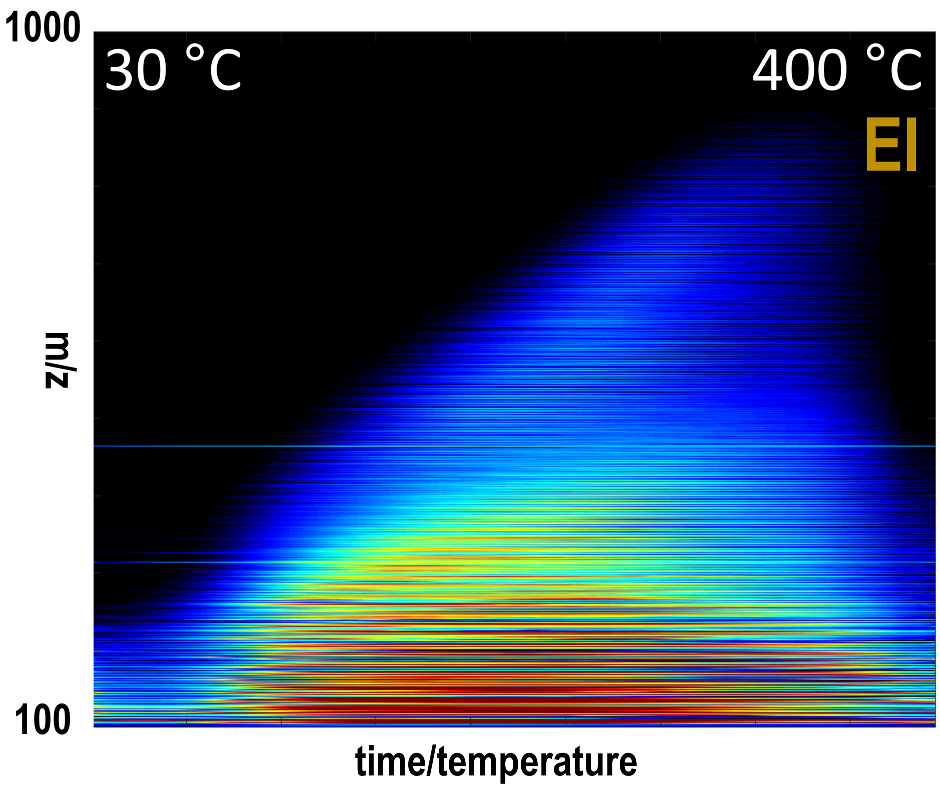
aromatic description of the CHS pyrolysis pattern **thermal fragments**



core structure analysis **MS-fragments**

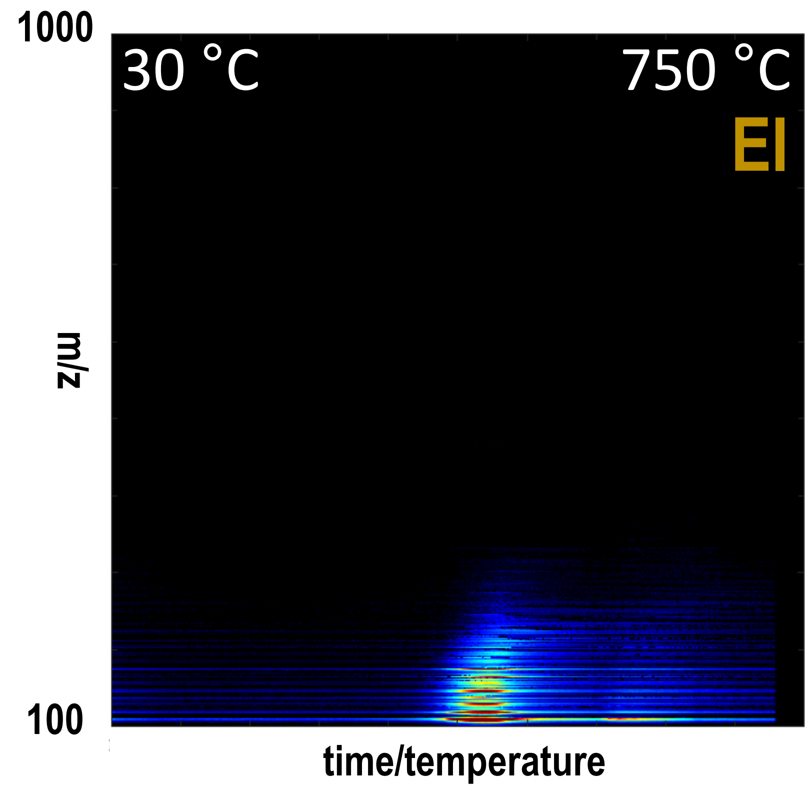
Going further – DIP reduced pressure evaporation

DIP (10^{-6} mbar)



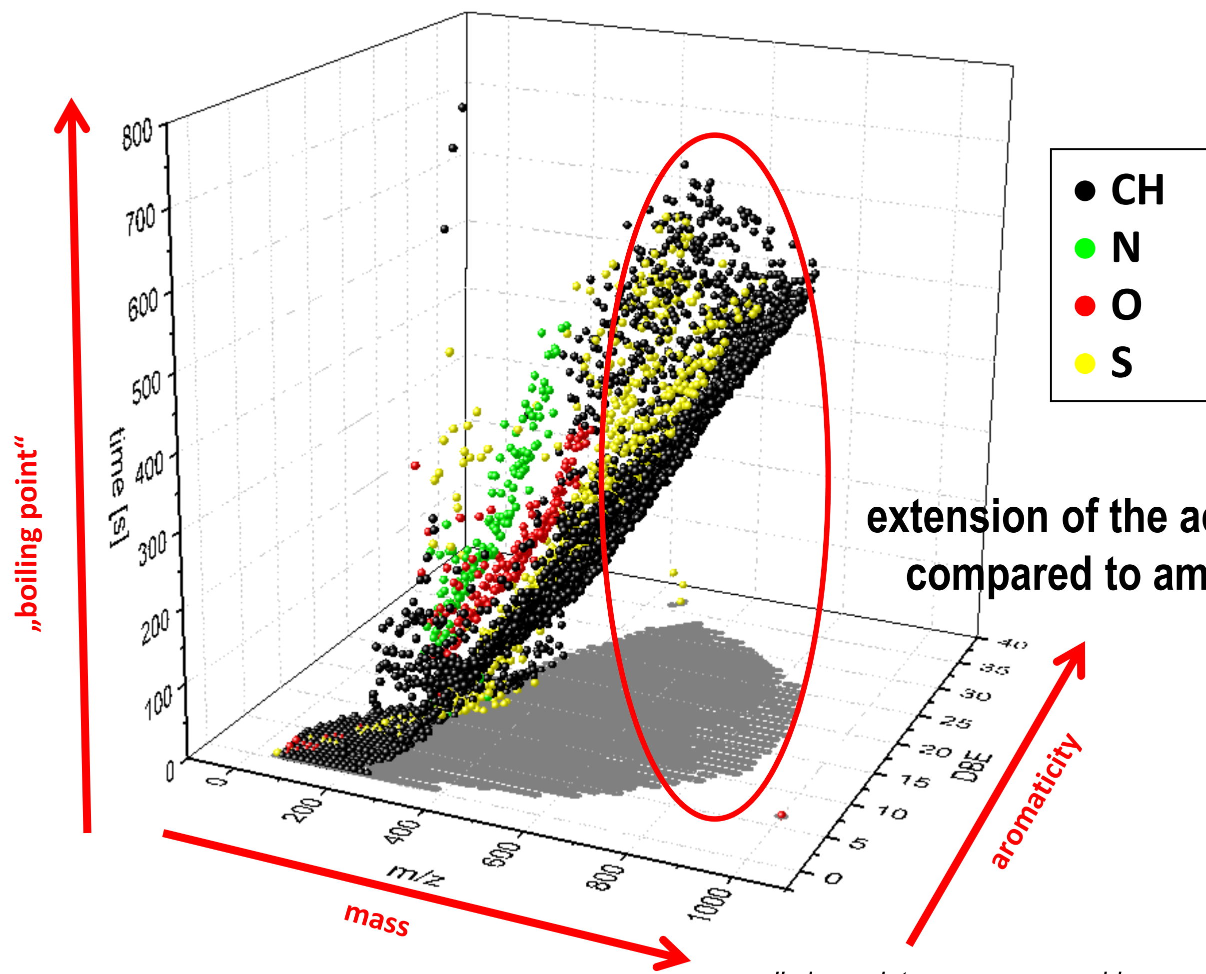
destruction free volatilization

TGA (Atmospheric pressure)



thermal fragments (pyrolysis)

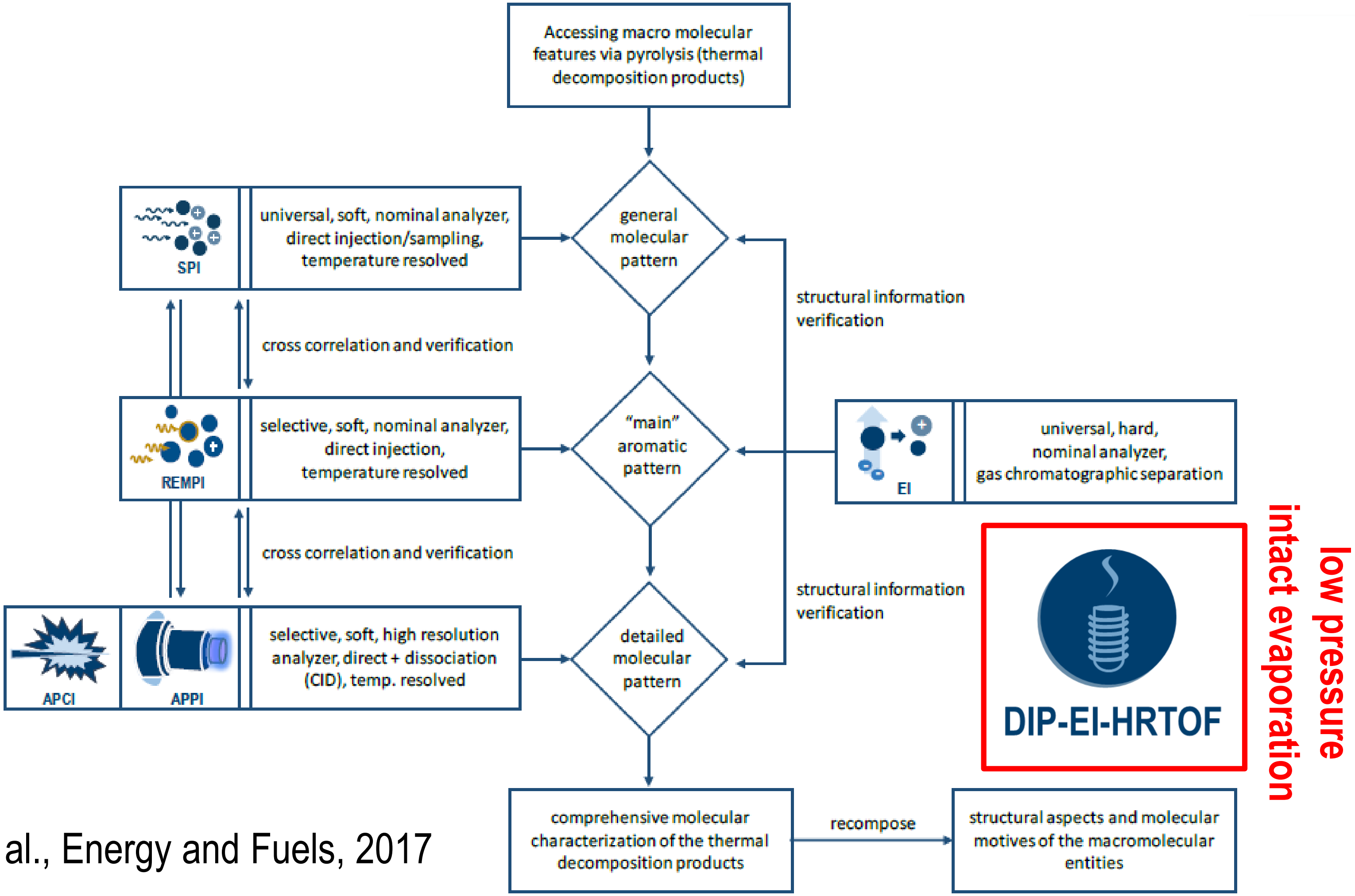
Reduced pressure evaporation utilizing the DIP



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

preliminary data on vacuum residues

Outlook - Data combination and integration



Rüger et al., Energy and Fuels, 2017

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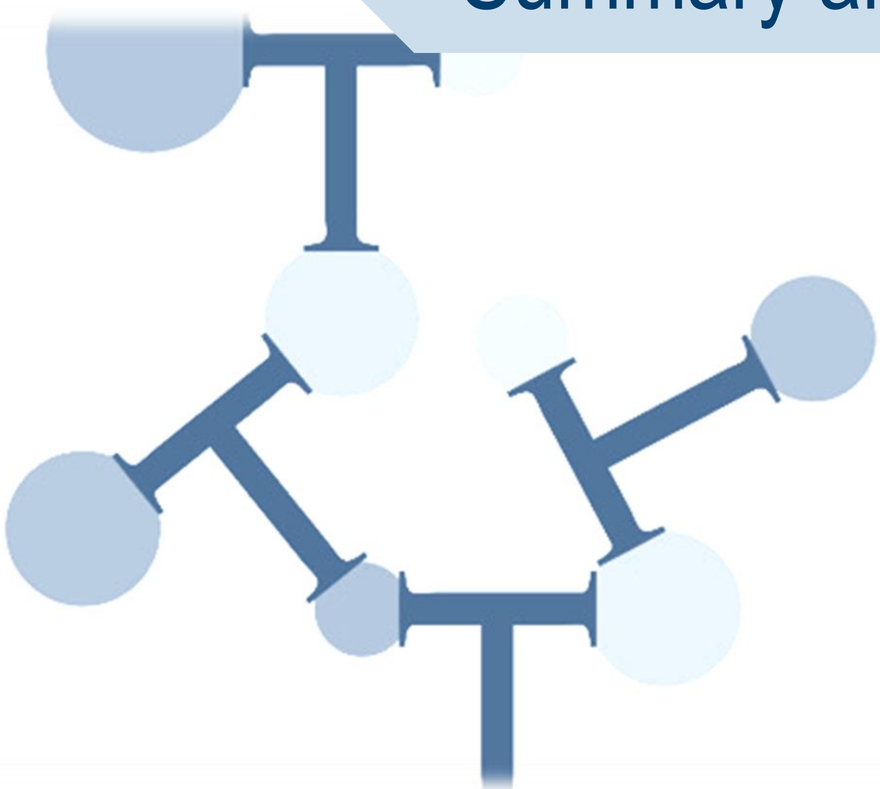
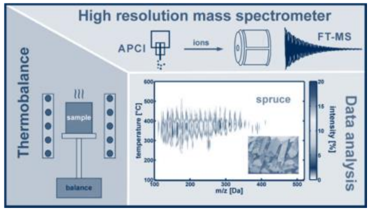


Summary and Outlook

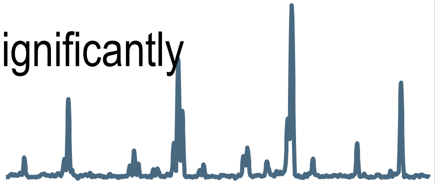
Introduction of thermal analysis high resolution mass spectrometry

- **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



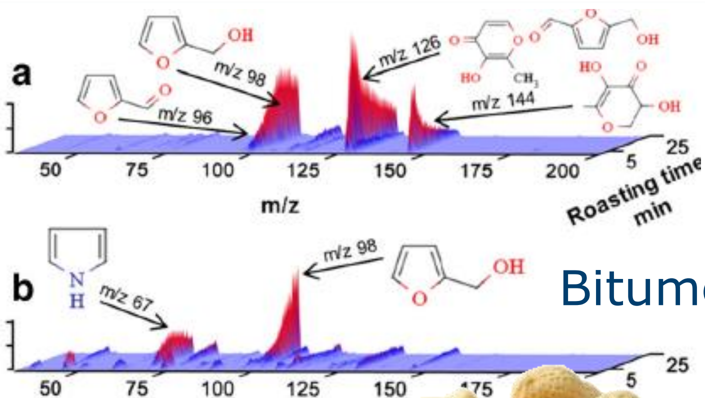
Combination of thermal analysis approaches for asphaltene pyrolysis

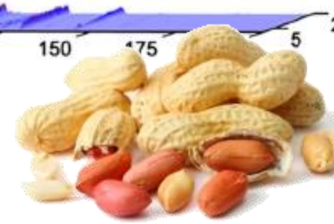
- Interlaboratory study on a **purified** asphaltene
- **multi-methodological** thermal analysis mass spectrometry approach
- data combination for structural elucidation of the dominant **asphaltene architecture**

Other Application Fields of EGA-MS

Biomass pyrolysis

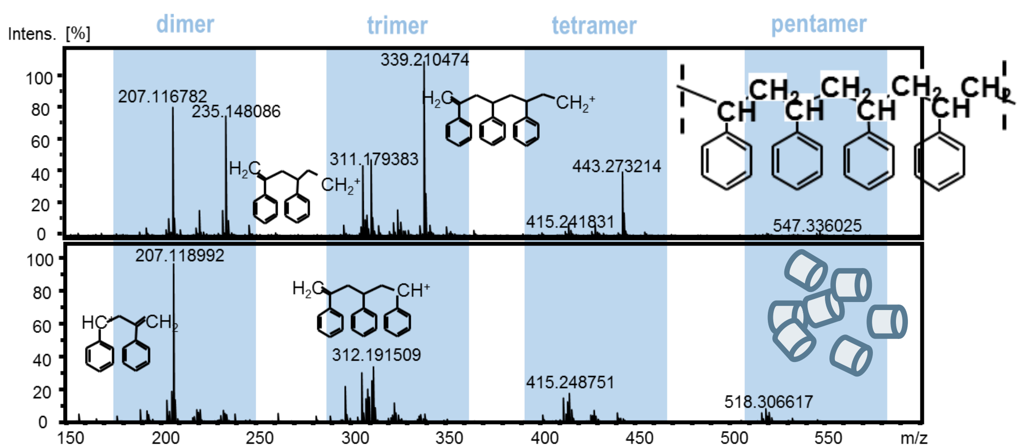
Food processing (coffee/nut roasting)



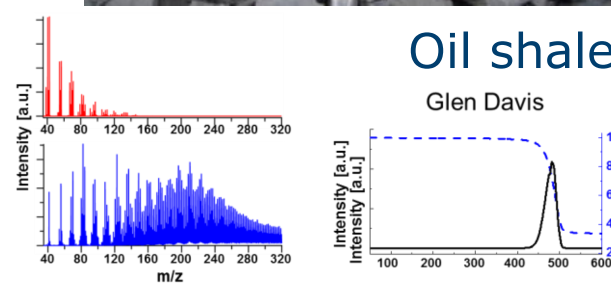


Bitumen and Bitumen ageing

Polymers and oligomeric samples



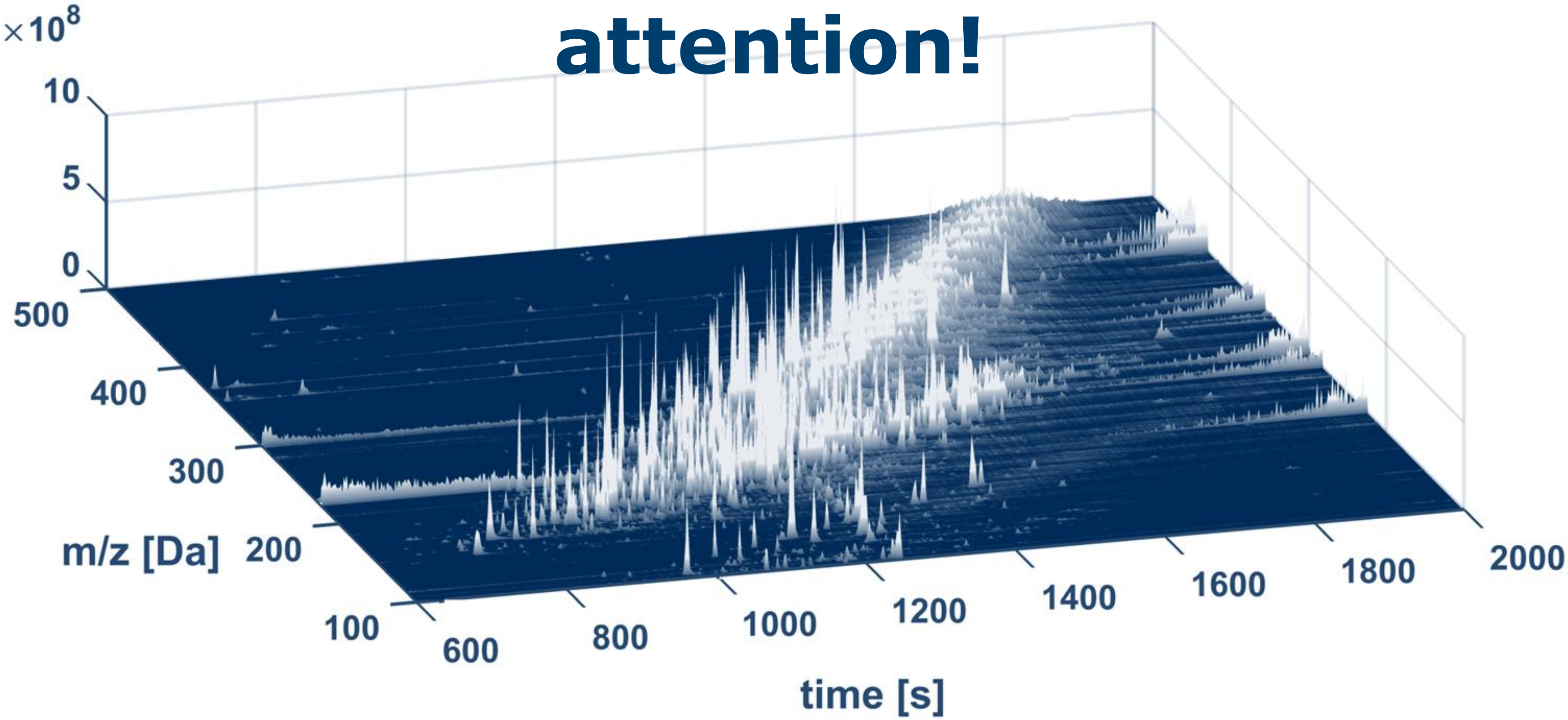
Oil shale



Acknowledgment

Zimmermann Group – September 2017

Thank you for your kind attention!



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