Evolved gas analysis with advanced mass spectrometric detection for the molecular description of heavy petroleum fractions

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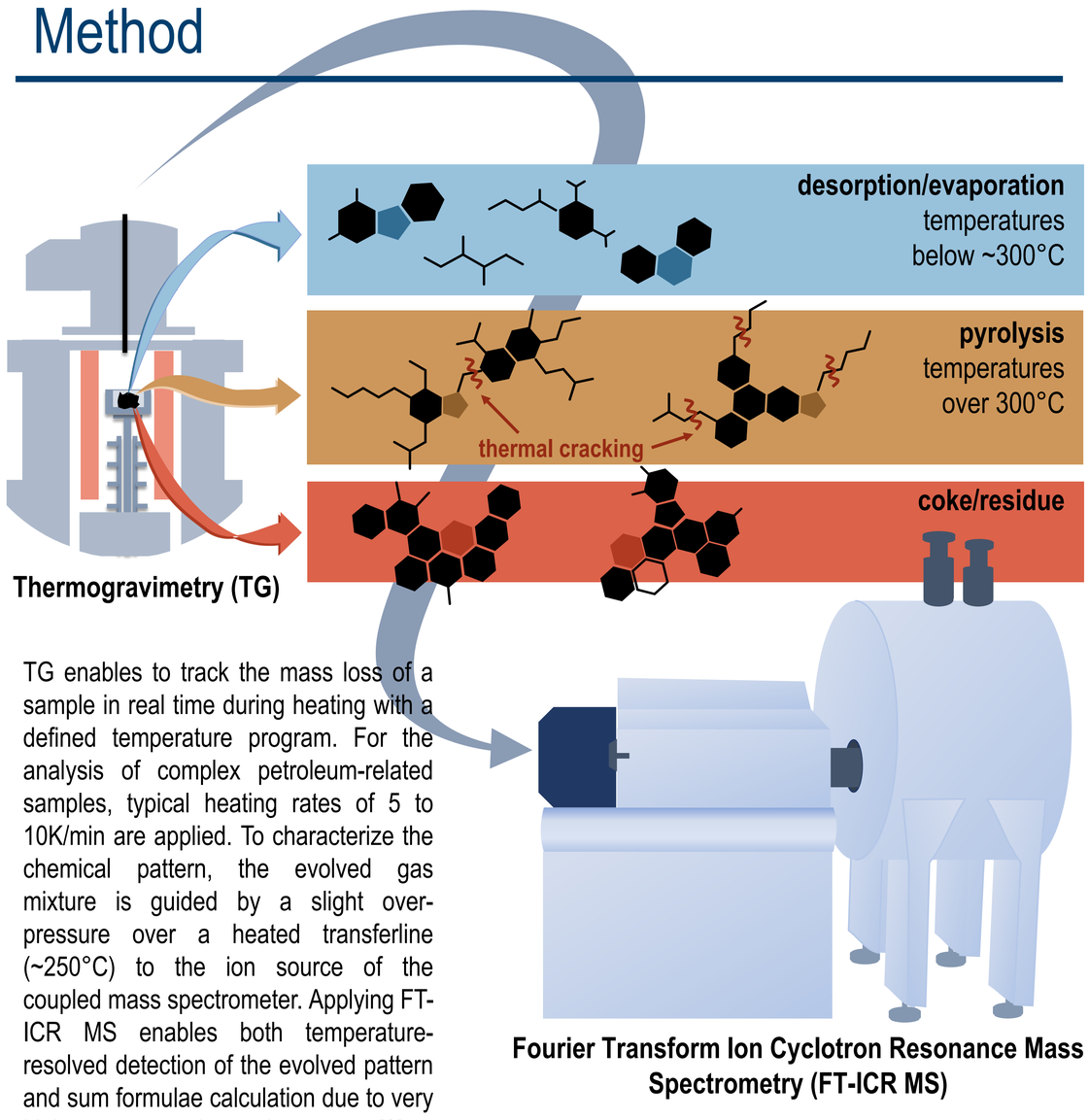
Introduction

Evolved gas analysis (EGA) realized by a thermobalance (TG) or direct inlet probe (DIP) coupled to high resolution FT-ICR mass spectrometry serves as a powerful tool for the description of complex evaporable and pyrolyzable mixtures. Classical direct infusion experiments might suffer from matrix and solubility effects, whereas TG-FT-ICR MS can add a complementary, temperature-resolved dimension. [1]

The objective of the presented work is to establish analytical workflows for the chemical description of heavy petroleum fractions, such as bitumen and asphaltene sample materials, using the high potential of thermal analysis high-resolution mass spectrometry.

Method



TG enables to track the mass loss of a sample in real time during heating with a defined temperature program. For the analysis of complex petroleum-related samples, typical heating rates of 5 to 10K/min are applied. To characterize the chemical pattern, the evolved gas mixture is guided by a slight over-pressure over a heated transferline (~250°C) to the ion source of the coupled mass spectrometer. Applying FT-ICR MS enables both temperature-resolved detection of the evolved pattern and sum formulae calculation due to very high mass resolution and accuracy. [2]

Typical ionization techniques used for the TG-FT-ICR MS coupling are atmospheric pressure chemical ionization (APCI, polar to semipolar compounds) and atmospheric pressure photo ionization (APPI, semi-polar to non-polar compounds). [3]

Conclusion

TG-FT-ICR MS was shown to be a valuable and versatile tool for the description of high complex petroleum samples. Due to the increasing awareness of alternative fuels, recycling and upcycling, new application areas are emerging. Pyrolysis oils from polymers, algae or other biogenic origin require in-depth chemical characterization for efficient refining. Other possible application fields might be the chemical description of biochar production and recycling of composite materials processes.

Literature

[1] Rüger, C. P. et al.; Energy Fuels, 2021, DOI: 10.1021/acs.energyfuels.1c02720
[2] Rüger, C. P. et al.; Analytical chemistry, 2015, DOI: 10.1021/acs.analchem.5b00785
[3] Rüger, C. P. et al.; Energy Fuels, 2018, DOI: 10.1021/acs.energyfuels.7b02762
[4] Neumann, A et al.; Energy Fuels, 2020, DOI: 10.1021/acs.energyfuels.0c01242
[5] Chacón-Patiño, M. L.; Energy Fuels, 2021, DOI:10.1021/acs.energyfuels.1c02107
[6] Neumann, A. et al.; Energy Fuels, 2021, DOI: 10.1021/acs.energyfuels.0c03751

Results

Bitumen, a highly viscous petroleum distillation residue, is often used as binder in asphalt concrete production. During the mixing of binder and mineral aggregates, high temperatures (150-160°C) and the contact with air leads to short-term aging effects, which makes the pavement harder and more brittle. To track the changes during aging, a model bitumen was aged with a modified rotating flask test (RFT) for 0 to 7 days. Samples were investigated by combining TG-APCI-FT-ICR MS and two-dimensional gas chromatography (GCxGC) with EI-HRTOF MS. Both techniques partially support and complement each other (Figure 1). [4]

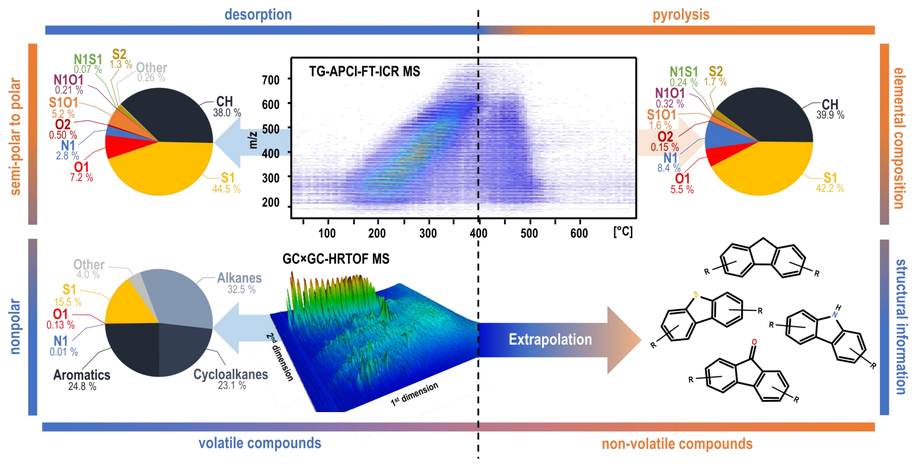


Figure 1: Method integration of TG-FT-ICR MS and GCxGC-HRTOF MS: Temperature-resolved mass spectrum (top) and 2D gas chromatogram (bottom) of 7 days aged bitumen.

Different aging related changes in the model bitumen could be observed on the molecular level:

- CH class turned out to be mostly inert against aging
- Oxygen-containing compounds and especially fluorenones highly increased
- Non-aromatic sulphur compounds (e.g. tetrahydrothiophenes) strongly decreased
- Nitrogen-containing (e.g. carbazoles) strongly decreased, slight increasing trend for N_1O_1 compounds

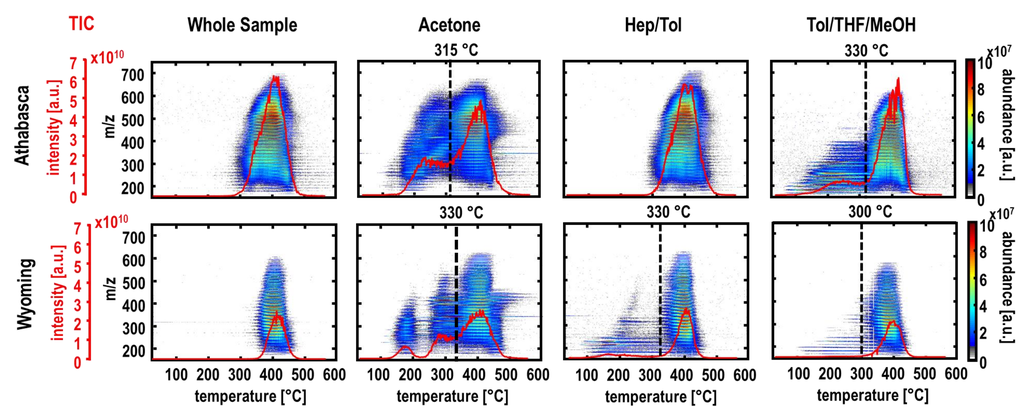


Figure 2: Temperature-resolved TG-FT-ICR MS of island-enriched (Wyoming) and archipelago-enriched (Athabasca) asphaltenes and their solubility fractions.

Asphaltenes are a high complex fraction of petroleum strongly related to problems during oil production and refining. Further fractionation with different solvent mixtures of highly purified asphaltenes (whole sample) reveals the release of smaller occluded material from asphaltene aggregates (Figure 2) during the temperature-resolved measurement.

Two structural motifs are discussed for asphaltenes: island and archipelago molecular architecture (Figure 3). TG-FT-ICR MS reveals a higher formation of residue during TG measurement for island-type asphaltenes. Furthermore, FT-ICR MS spectra exhibit typical pyrolysis products for both structural motifs. Double bond equivalent (DBE) versus carbon number (#C) diagrams in Figure 3 illustrate the occurrence of two typical regions: Island asphaltenes show in particular pyrolysis products with high DBE values and short alkylation (low #C), whereas archipelago asphaltene pyrolysis products reveal a lower DBE range with higher #C (longer alkyl side chains). The proportion of the presence of characteristic pyrolysis products differs between the solubility fractions. [5,6]

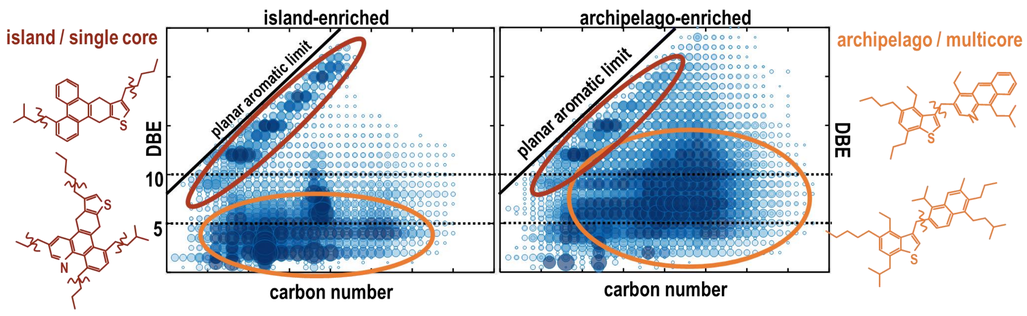


Figure 3: Typical DBE vs. #C regions for pyrolysis products of island- and archipelago-enriched asphaltenes.

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