Isomer-Level Description of Complex Bio-Oils Enabled by gTIMS Hyphenated to 18 T FTICR MS

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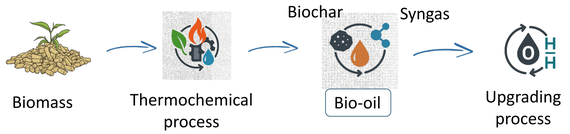
Introduction



- Highly **complex** organic mixtures, usually analyzed by Direct introduction into a Fourier Transform Ion Cyclotron Resonance Mass spectrometer (Di-FTICR MS).[1]
- This method does not separate isomers and requires additional **separative method.**
- Here we evaluate the advantage of **ion mobility** coupled to **FTICR MS** equipped with a **18 teslas** superconducting magnet for the characterization of different upgraded bio-oils.[2]

Materials and methods

- Bio-oils from fast pyrolysis (bio-oil 1), pyrolysis stabilized (bio-oil 2) and hydrothermal liquefaction (bio-oil 3) were dissolved in methanol at 10 mg/mL.
- The gTIMS 18 T FTICR MS was used with an electrospray source in positive mode, with a transient length of 1.3 seconds and a resolution of 1.2 10^6 at *m/z* 200.

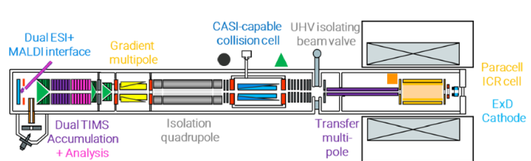


Figure 1: Overview of TIMS-FTICR MS instrument[2]

1. gTIMS coupled to 18 T FTICR MS

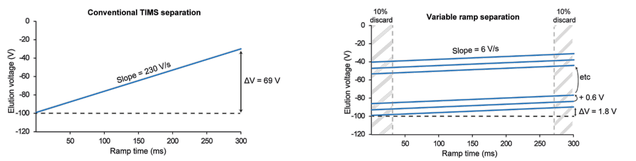


Figure 2. Separation principle of "sweeping ramp" gTIMS compared to a conventional TIMS analyzer

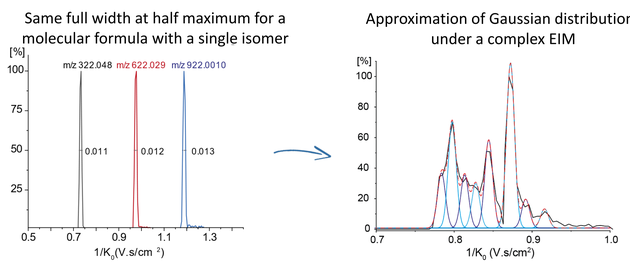


Figure 3. Use of single-isomer standards for Gaussian fit approximation (gTIMS, sweeping ramp)

2. Region of interest in gTIMS FTICR MS

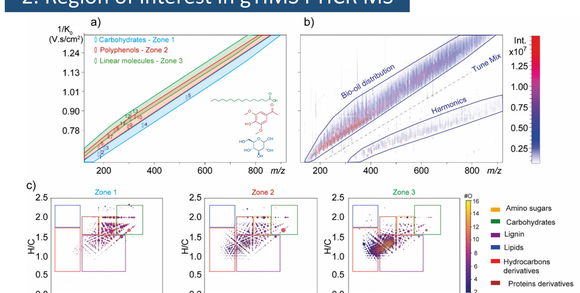


Figure 4. Definition of regions of interest for **different molecular families** in gTIMS-FTICR MS heatmaps (a: **standard** solution, b: bio-oil 1, c: **van Krevelen** of specific zones for bio-oil 1)

3. Compounds families analysis

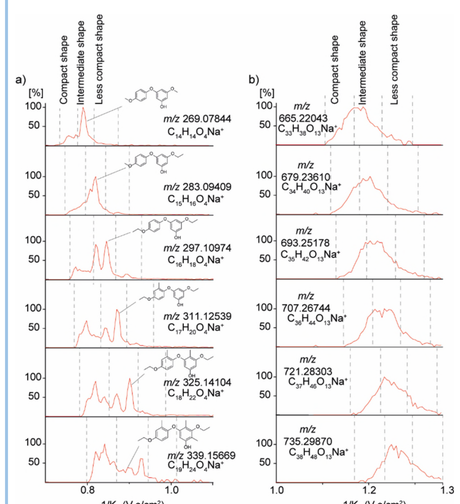


Figure 5. **Isomeric profiles** of an evolution of CH_2 series **aromatic compounds** with low-mass compounds (a) and high-mass compounds (b)

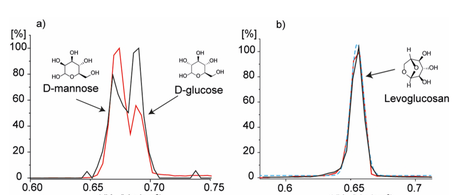
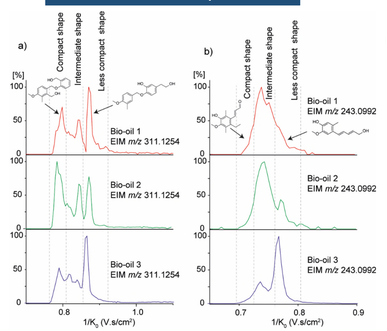


Figure 6. Isomeric profiles of **monosaccharides and derivatives** a) Mannose/glucose standards and bio-oil 1 ($C_6H_{12}O_6Na^+$, m/z 203.05261). b) Levoglucosan standard, bio-oil 1, and single-isomer Gaussian fit ($C_6H_{10}O_5Na^+$, *m/z* 185.04204).

4. Bio-oils comparison



The three bio-oils have **some** molecular formula in common

- But **different isomers**

→ Fast pyrolysis bio-oil

→ Stabilized fast pyrolysis bio-oil

→ Hydrothermal liquefaction bio-oil

Figure 7. Comparison of $1/K_0$ **profiles** for 2 different low-mass compounds (*m/z* 311.1254 and *m/z* 243.0992) **in three bio-oils**

5. Conclusion

- Coupling TIMS with FTICR MS for the analysis of bio-oils
- Separation of standards by family (carbohydrates, polyphenols, linear compounds)
- Determination of different isomers in bio-oil using standards
- Different isomeric profiles in different bio-oils for the same molecular formula

Acknowledgments

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References

[1] Mase, C. et Al. Journal of Analytical and Applied Pyrolysis 2024, 177.

[2] Wootton, C. et Al. Anal. Chem. 2024, 96 (28), 11343–11352