Development of online coupling between supercritical fluid chromatography and 18 T FTICR MS for the molecular characterization of wood bio-oil

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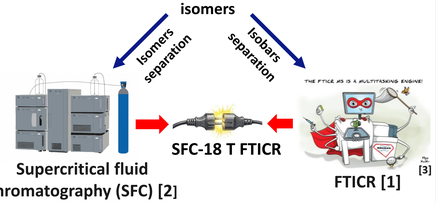
Introduction

New **environmentally friendly energy** → **Wood bio-oil**

Understanding the bio-oil composition

Complex mixture with a high number of isobars and isomers



Materials

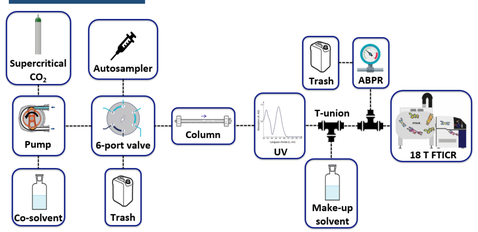
Waters Acquity UPC²

- Possibility to cover a **large range of polarity** (Unified chromatography) [4].
- **Isomer** separation (in reverse phase or normal phase)
- **Good efficiency** at **high flow rates** (1–3 ml/min)

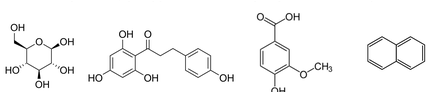
18-T FTICR MS tims-MRMS

- Very high accuracy **(< 0.1 ppm)**
- **Resolution** of several **millions** can be achieved
- Scan time is **several seconds** [1 to 10 s]

Methods



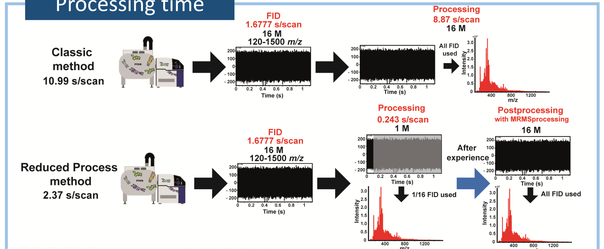
A list of **24 standards** has been created to cover **the variety of compound families** found in bio-oils, (**wide range of polarities such as** fatty acids, polyphenols and polysaccharides).

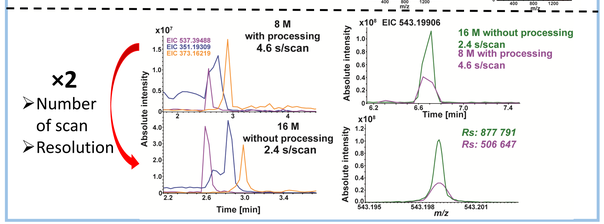


Numerous **chromatographic and spectrometric parameters** were **optimized** using **standards and bio-oil**, including the injection solvent, injection volume, choice of co-solvent, free induction decay (FID), accumulation time… (see below)

Chromatographic conditions		Spectrometric parameters	
Column	BEH (100 x 3.0 mm , 1.7 µm)	**Source**	ESI (−)
Co-solvent	MeOH/ACN	**Accumulation time (ms)**	450
Flow rate (ml/min)	0.7 mL/min, ABPR = 150 bar	**Frequency (MHz)**	6
Make-up Solvent	90/10 MeOH/Water + 0.2% NH_4OH, 0.3 mL/min	**FID**	1.677 s, m/z 120-1500, 16 M
Injection condition	10 µL in ACN	**Time of flight (Tof)**	0.8 ms

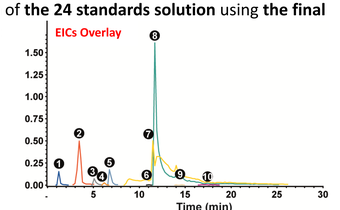
Processing time





Result with standards

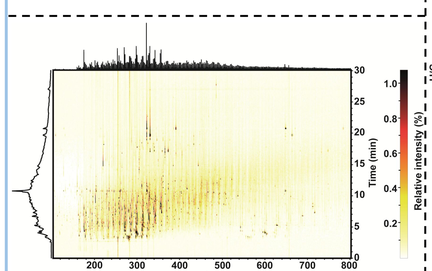
Injection of **the 24 standards solution** using **the final method**:

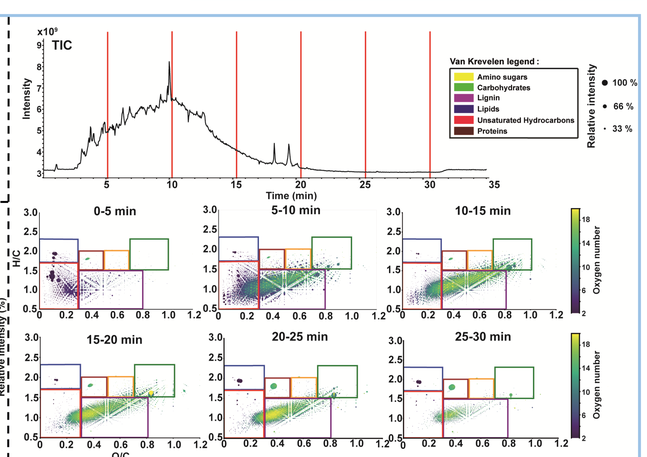


#	RT [min]	Compound name	Oxygen number
1	1.33	2,6-diterbuthyl-4-methylphenol	1
2	3.54	palmitic acid	2
3	5.18	acetosyringon	4
4	6.25	vanillic acid	4
5	6.85	ferulic acid	4
6	11.12	levoglucosan	5
7	11.56	taxifolin	7
8	11.78	phloretin	5
9	14.72	D-(+)-xylose/D-(−)-lyxose	5
10	17.17	Glucose/D-Mannose	6

Result with bio-oil

- Analysis of a **pine bio-oil at 40 g/L** in **16 M** and a **reduced processing method (2.4 s/scan)**
- Attribution of **12 434 molecular formulas**
- **Many isomers** have been successfully **separated**





Conclusion

- Many **chromatographic and spectrometric parameters** were successfully optimized
- **The scan speed and flow rate were adjusted** to ensure the best compromise between SFC and FTICR

- Using this method, a **resolution of 1 400 000 at m/z 400** was achieved, and more than **10 000 molecular formulas** were identified in ESI (−).

References

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[3] Krankr et Damour « Journey to the center of the magnet », **2025**

[4] Taguchi, K et al.*J. Chromatogr. A* **2014**, *1362*,270–277.

Acknowledgments

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