In-depth characterization of complex molecules using GC×GC-TOFMS

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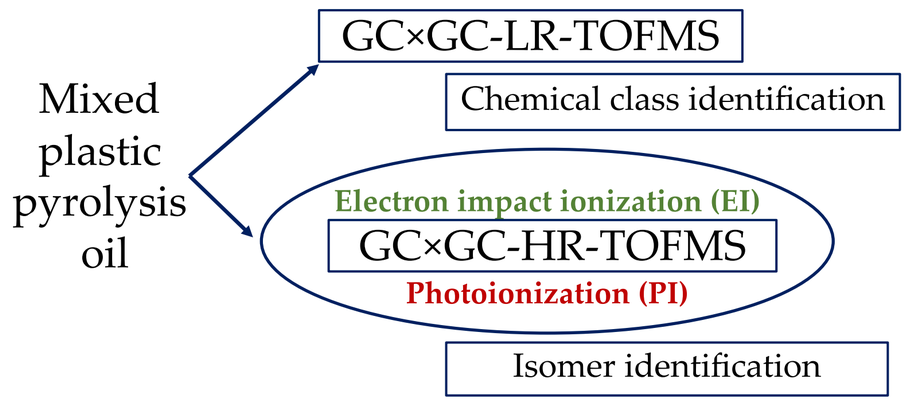
Background

- Plastic waste production is increasing at an alarming rate.
- Pyrolysis is a promising method for plastic waste management that involves breaking down the material's macromolecular structure into small molecules and producing various types of hydrocarbons.
- Plastic pyrolysis oil can provide monomers, fuel, and chemicals, but there are still bottlenecks limiting its industrial applications.
- **An advanced molecular description is necessary to enhance the conversion and valorization processes.**

Aim of work



Results

Class identification by FM-GC×GC-LR-TOFMS

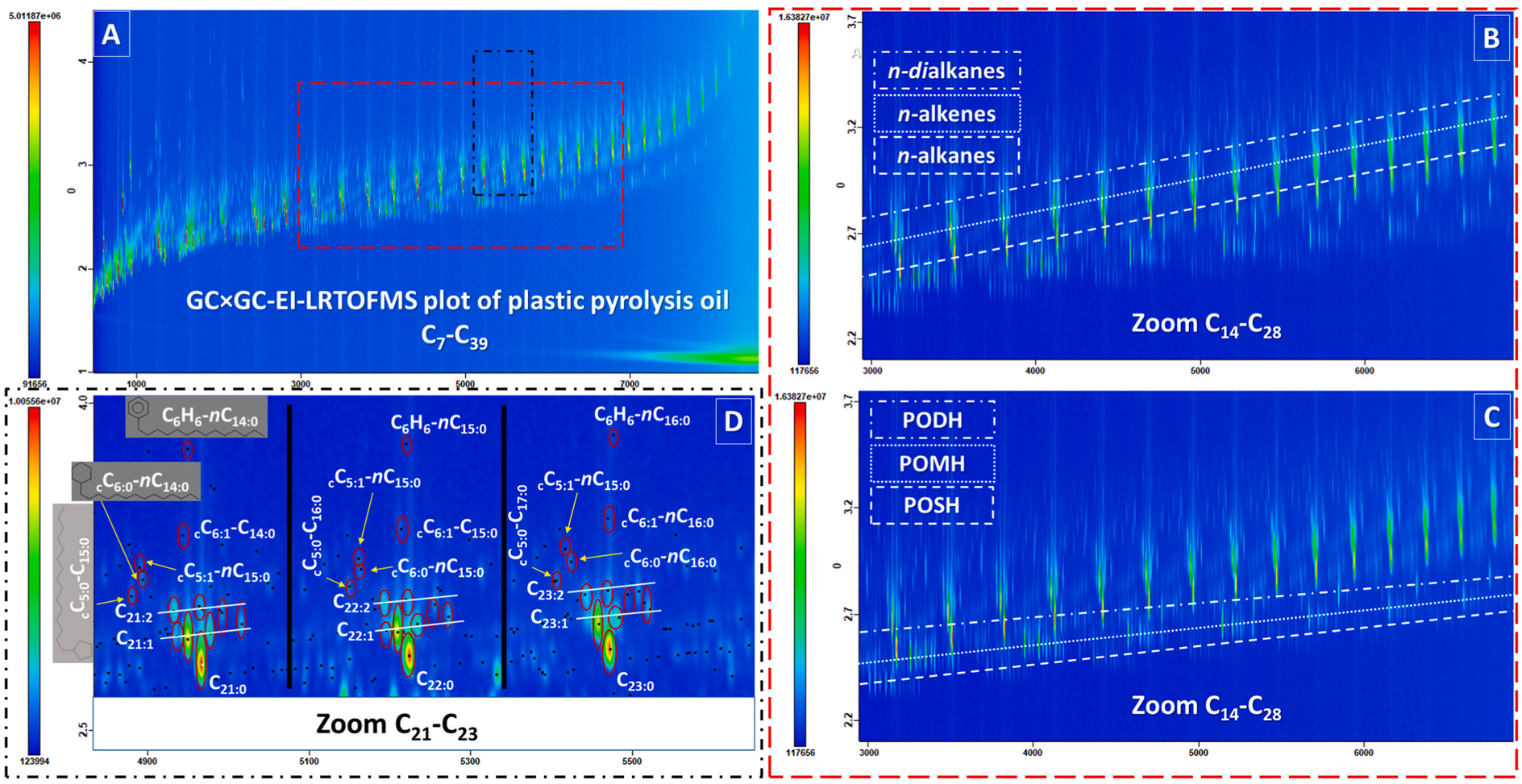


Figure 1:(A) FM-GC×GC-LR-EI-TOFMS chromatogram of plastic pyrolysis oil**; (B–C)** Expansion of the red-dotted line in Fig. 1A in the range of C_{14} -C_{28}; B: GC×GC distribution of linear hydrocarbons (saturated, mono-, and di-unsaturated); **(C)** GC×GC distribution of polyolefins hydrocarbons (POH): saturated (POSH), mono- (POMH) and di-unsaturated (PODH) **(D)** Expansion of the black-dotted line in Fig. 1A in the range of C_{21}-C_{23}; chemical class separation according to the carbon group.

Column Configuration:
[1]D: Rxi-5MS (30m,0.25mm ID,0.25 µm)
[2]D: Rxi-5sil MS (1.3m,0.25mm ID,0.25 µm)

- Identification of observed the chemical species is highly challenging.
- Hydrocarbons present have similar MS fragmentation patterns with EI, even if lower kinetic energies than 70 eV is applied, making their identification a difficult task.
- The use of LRI as an additional identification filter can help to rule in/out compound identities during the identification process, but not always this information is available, nor when a most common non-polar column is used as a [1]D column.
- With the increasing number of carbons, the number of isomers grows exponentially.

Chemical structure prediction by PTV-GC×GC-EI/PI-HRTOFMS

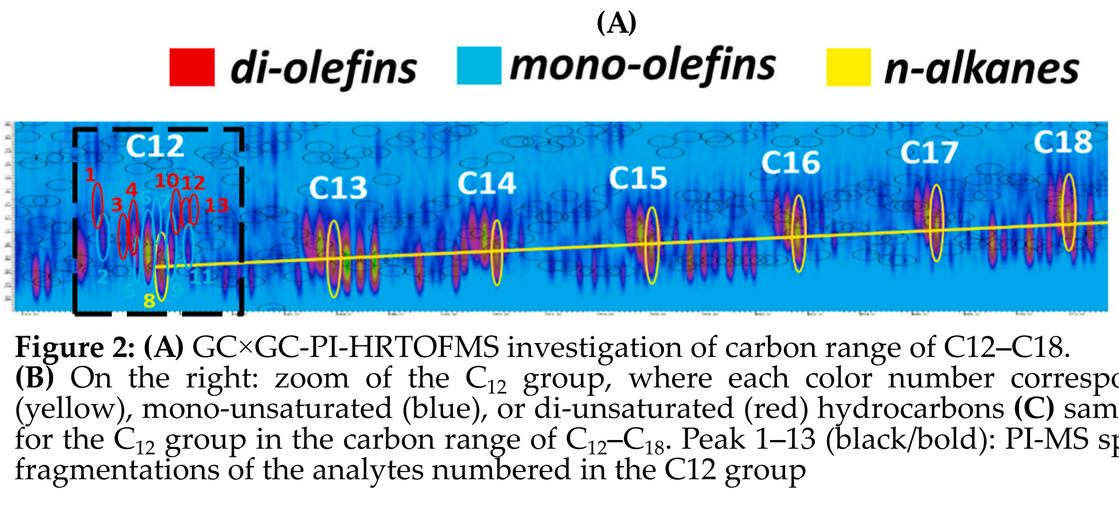


Figure 2: (A) GC×GC-PI-HRTOFMS investigation of carbon range of C12–C18. **(B)** On the right: zoom of the C_{12} group, where each color number corresponds to saturated (yellow), mono-unsaturated (blue), or di-unsaturated (red) hydrocarbons **(C)** same chemical classes for the C_{12} group in the carbon range of C_{12}–C_{18}. Peak 1–13 (black/bold): PI-MS spectra and pattern fragmentations of the analytes numbered in the C12 group

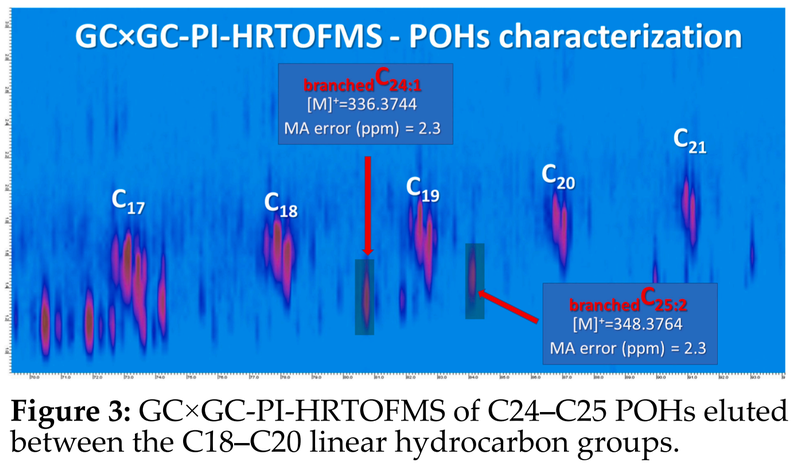


Figure 3: GC×GC-PI-HRTOFMS of C24–C25 POHs eluted between the C18–C20 linear hydrocarbon groups.

some olefin structures were predicted but not accurately identified, prediction was based on the relative intensity of fragment ions

Conclusion

- Identification of main chemical classes was performed by GC×GC-EI-TOFMS, but presence of several isomeric species and homologs series didn't allow reliable molecular identification, except for few compounds that showed both MS% > 800 & LRI ±20.
- The identification of several isomers was conducted by the interpretation of PI mass spectra from GC×GC-HRTOFMS, leading to a putative identification of molecules not previously identified using the most common EI-MS approach.
- The structured chromatographic separation provided a sort of chemical fingerprint composed of different chemical classes from which different levels of information can be extrapolated[1].

Reference: [1] Beccaria, Marco, et al. "Analysis of mixed plastic pyrolysis oil by comprehensive two-dimensional gas chromatography coupled with low-and high-resolution time-of-flight mass spectrometry with the support of soft ionization." Talanta 252 (2023): 123799.

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