



UHPLC-HRAM-MS SCREENING SUPPORTS CHARACTERISATION OF PLASTIC WASTE PYROLYSIS OIL

A non-targeted UHPLC-HRAM-MS workflow can help laboratories compare complex plastic waste pyrolysis oil samples and identify heteroatom-containing molecular formulas that may affect steam cracker operation.

Introduction

Plastic waste pyrolysis oil is becoming more important as chemical recycling routes are developed for plastics that are difficult to recycle mechanically. Pyrolysis breaks polymeric material into smaller hydrocarbon-rich molecules, which can then be used as feedstocks for further conversion.

In a steam cracker, these materials can support the production of monomers such as ethylene and propylene. Those monomers can then be used to produce virgin polymers.

The analytical challenge is that pyrolysis oil is not a simple feedstock. It is a highly complex matrix that can contain hundreds or thousands of components. While hydrocarbons dominate, heteroatom-containing compounds can also be present. Oxygen-, nitrogen- and sulphur-containing species are particularly relevant because they can contribute to fouling, corrosion, emissions issues and contamination of product streams.

Why detailed pyrolysis oil analysis matters

The United Nations Environment Programme (UNEP) estimates that around 400 million tonnes of plastic waste were generated in 2024. Earlier UNEP reporting also notes that only around 9% of plastics produced have been recycled, with the remainder incinerated, landfilled or released to the environment.

Mechanical recycling remains important, but it cannot handle every polymer stream or contamination profile. Chemical recycling routes such as pyrolysis are therefore being investigated as a way to recover value from more difficult plastic waste fractions.

For refinery, petrochemical and analytical laboratories, the important question is whether a pyrolysis oil can be characterised well enough to understand its behaviour as a steam cracker feedstock. Fouling can cause loss of production, higher maintenance costs and operational disruption. Analytical methods that can distinguish feedstock types and flag problematic molecular classes are therefore valuable for quality assurance and quality control (QA/QC).

The role of UHPLC-HRAM-MS

Comprehensive two-dimensional gas chromatography-mass spectrometry (GC×GC(MS)) is often the first-choice technique for pyrolysis oil characterisation. It provides high separation power for volatile and semi-volatile compounds.

However, not every component in pyrolysis oil is suited to gas chromatography. Higher molecular weight compounds and thermally labile compounds can be difficult to analyse by GC-based methods. Ultra-high performance liquid chromatography coupled to high-resolution accurate-mass mass spectrometry (UHPLC-HRAM-MS) can provide complementary information for these fractions.

High-resolution accurate-mass data are important for non-targeted analysis. In the work described here, Orbitrap detection was used to support elemental formula prediction for unknown compounds in complex pyrolysis oil samples.

Plastic waste pyrolysis oil is becoming more important

Experimental approach

Pyrolysis oil samples were diluted 20-fold in tetrahydrofuran (HPLC grade) and passed through a 0.2 µm PTFE filter before injection.

The UHPLC-HRAM-MS system consisted of an Ultimate 3000 UHPLC coupled to a Q Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific). Chromatographic separation was performed on an Acquity BEH C18 column, 150 x 2.1 mm with 1.7 µm particle size, held at 35°C.

Milli-Q water with 0.1% formic acid and acetonitrile (LC-MS grade) were used as mobile phases. A linear gradient from 1% to 100% acetonitrile was applied at a flow rate of 0.25 mL/min. The injection volume was 2 µL.

Ionisation was performed using heated electrospray ionisation (HESI) in positive and negative modes. Samples and blanks were measured in duplicate in profile MS mode using a resolution of 70,000 @ m/z 200. This mode was selected for peak detection, alignment and statistical analysis.

A single profile MS / data-dependent MS/MS (ddMS2) measurement was also performed for each pyrolysis oil sample to support retrospective compound identification. Each sample measurement series was preceded by duplicate blank injections of tetrahydrofuran.

Data analysis workflow

The data were processed using Compound Discoverer™ 2.1 software (Thermo Fisher Scientific). The first step was to develop a general workflow for non-targeted analysis of complex pyrolysis oil samples.

The workflow consisted of connected processing nodes. These nodes covered data alignment, compound and peak detection, missing data filling, background signal marking and compound prediction.

Data alignment corrects retention time shifts between measurements. This is essential for sample-to-sample comparison, including duplicate injections and measurements collected on different days.

Compound and peak detection integrates mass spectral peaks from the base peak chromatogram and provides the input for elemental formula prediction. The background marking step identifies signals also present in blank measurements, such as solvent-related signals. Missing data filling identifies signals found in one duplicate measurement that may be absent from another.

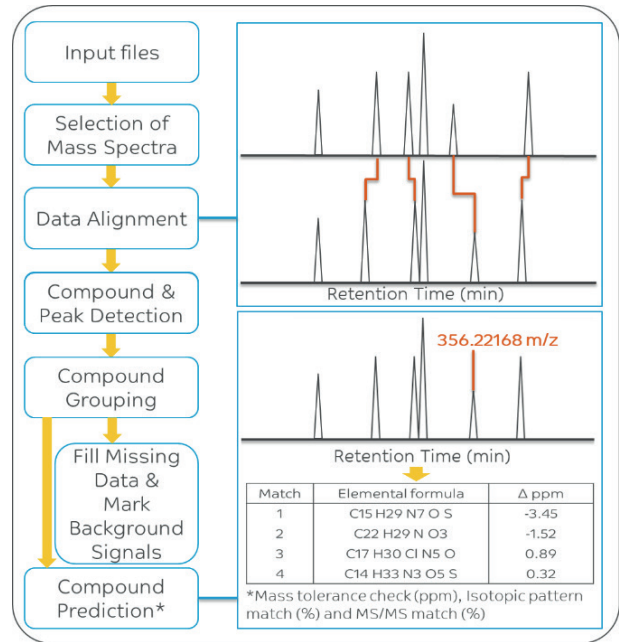


Figure 1: General workflow for non-targeted analysis of plastic waste pyrolysis oil samples, including data alignment and compound prediction

Elemental formula prediction

The compound prediction node assigns elemental formulas

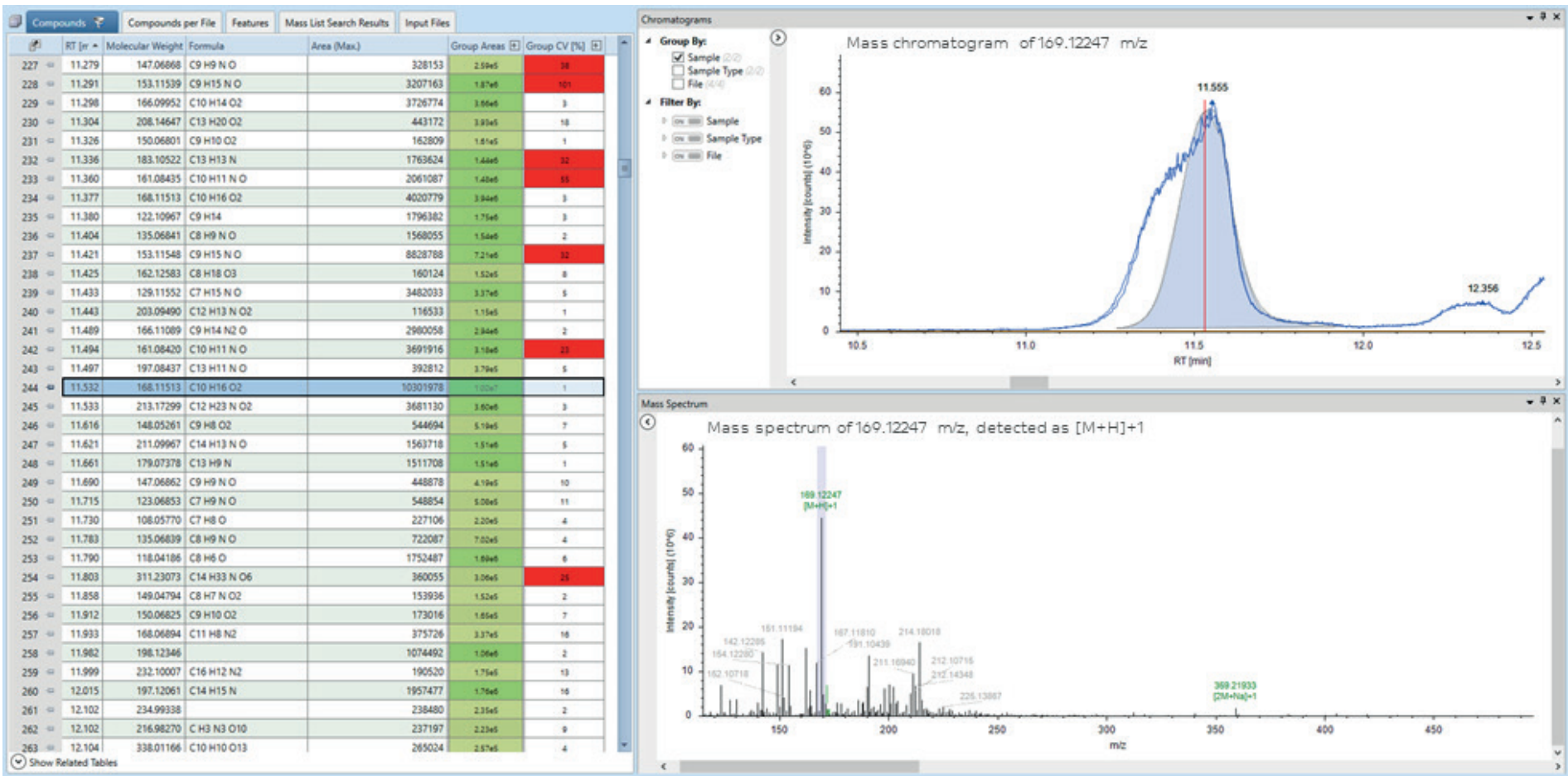


Figure 2: Compound Discoverer™ 2.1 output showing the mass spectrum and mass chromatogram of a highlighted component

to detected compounds. The settings include isotope pattern comparison, maximum element counts and the maximum number of possible formula predictions per compound.

For the tested pyrolysis oil datasets, the optimised workflow produced ≥90% correct elemental formula predictions for molecular weights up to 300 Da. This was confirmed by manual checking of around 150 of the highest-intensity components for each dataset. Above 300 Da, prediction reliability decreased as mass error increased.

The highest level of identification achievable in this type of non-targeted screening is molecular formula assignment. True compound identification would require MS/MS libraries, retention time data or reference standards that are not available for every component in these matrices.

Optimum example values used in the workflow included a maximum peak width of 0.2 min, an intensity tolerance of 30% and a spectral fit of 30%. The maximum peak width setting helped exclude broad or poorly defined signals from the peak list. The intensity tolerance and spectral fit settings supported isotope pattern matching during formula assignment.

Using contour plots for sample comparison

Compound Discoverer™ peak lists contain elemental formula, molecular weight, retention time and peak area for each detected compound. These lists can contain hundreds of entries, which makes direct manual comparison inefficient.

To make the data easier to compare, an external Matlab macro was developed to extract element counts from each formula and combine them with peak area. The converted output could then be imported into visualisation software for contour plotting.

Relevant plots for pyrolysis oil include number of carbon atoms versus number of oxygen atoms, number of carbon atoms versus number of nitrogen atoms, number of carbon atoms versus number of sulphur atoms and number of carbon atoms versus double bond equivalent (DBE). DBE indicates the level of unsaturation or aromaticity.

Formula	Molecular Weight	RT [min]	Area (Max.)	Group Areas
C10 H16 O2	168.11534	12.535	6926336	6.87e6
C8 H11 N O	137.08429	12.545	151259	1.43e5

Elemental Formula	Area	C	H	O	N	S	P	Cl	Si	F	Br
C10 H16 O2	6.87E+06	10	16	2	0	0	0	0	0	0	0
C8 H11 N O	1.43E+05	8	11	1	1	0	0	0	0	0	0

Figure 3: Partial peak list from Compound Discoverer™ and the converted dataset generated using the Matlab macro

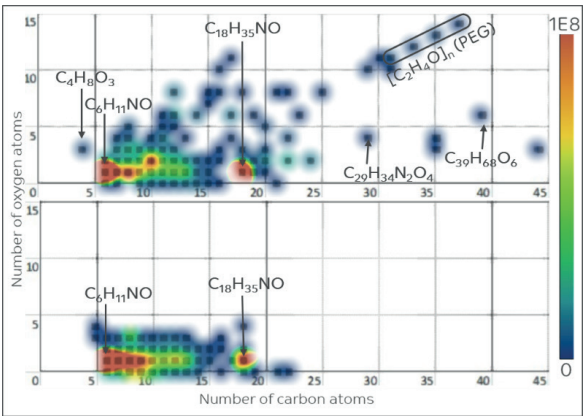


Figure 4: Contour plots of two plastic waste pyrolysis oil samples showing carbon number versus oxygen content

Findings from the pyrolysis oil samples

The contour plots allowed visual distinction between different pyrolysis oil samples. In the example shown in Figure 4, the upper sample contained more highly oxygenated species, including compounds with more than six oxygen atoms, than the lower sample.

The main compounds detected in the tested pyrolysis oils included CxHxN and CxHxNO species. Nitrogen-containing compounds are relevant because they can contribute to NOx formation under cracking conditions.

Oxygen-containing compounds were observed across a range of 0–6 oxygen atoms and 0–30 carbon atoms. Nitrogen-containing compounds were observed across a range of 0–6 nitrogen atoms and 0–20 carbon atoms.

Depending on the plastic waste material used for pyrolysis oil production, sulphur-containing compounds may also be expected. Some sulphur compounds can form H2S in the cracker and be removed downstream, while others may be more stable and contaminate aromatic products.

Practical significance for laboratories and operators

For petrochemical laboratories, the value of the workflow lies in rapid comparison of complex feedstocks. The method can help identify molecular classes that differentiate pyrolysis oil samples and may indicate increased risk of fouling, corrosion or downstream contamination.

The workflow does not replace targeted quantification, reference-standard confirmation or process-specific acceptance testing. It is best viewed as a non-targeted screening approach that can complement GCxGC(MS), targeted LC-MS methods and routine feedstock QA/QC.

For operators considering pyrolysis oil as a partial or full replacement for conventional feedstock, this type of screening can support feedstock qualification, supplier comparison and investigation of process incidents. Its usefulness depends on the quality of the sample set, blank control, data processing parameters and internal validation against operational outcomes.

Conclusion

A UHPLC-HRAM-MS method for non-targeted screening of complex plastic waste pyrolysis oil samples was developed using Orbitrap detection and Compound Discoverer™ data processing.

The combination of high-resolution accurate-mass detection, peak detection, alignment, isotope pattern matching and formula prediction produced ≥90% correct elemental formula predictions for tested compounds up to 300 Da. Reliability decreased above this mass range as mass error increased.

By converting peak lists into contour plots, large datasets could be compared at a glance. This gives laboratories a practical way to visualise differences between pyrolysis oil samples and assess heteroatom-containing compound classes that may affect steam cracker operation.

References

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