White Paper 057
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Detailed chemical characterisation of pyrolysis oils from mixed waste plastic using GC×GC–TOF MS with thermal modulation

GC×GC–TOF MS with thermal modulation was used to provide detailed and sensitive characterisation of pyrolysis oil composition, to identify possible contaminants and help to refine process design.

Introduction

With the global push to move towards a circular economy, there is an increased focus on sustainable fuels, such as those from pyrolysis of solid plastic waste. Globally, we produce about 400 million tonnes of plastic waste on an annual basis, but it is estimated that less than 10% of this plastic waste is recycled[1]. There are two main routes for recycling – mechanical and chemical. Mechanical recycling involves the physical sorting, cleaning and reprocessing of waste materials, and is primarily suitable for easily sorted plastics, while chemical recycling employs chemical processes to break down plastics into their molecular components, allowing for a wider range of recyclable products.

Chemical recycling, specifically pyrolysis, offers a promising avenue for sustainable waste management and energy production[2]. The conversion of plastic waste into valuable resources can reduce the burden on landfills, minimise environmental pollution and promote the transition towards a circular economy.

Pyrolysis itself is a thermal decomposition process that, in the absence of oxygen and often in the presence of a catalyst, converts plastic waste into liquid and gaseous products. The resulting pyrolysis oils are considered a form of renewable energy and have the potential to serve as an alternative to fossil fuels in various industrial processes. These include power generation, heating, and transportation, or as a feedstock for the petrochemical industry.

However, the composition of pyrolysis oils can vary depending on the type of plastic feedstock used and the pyrolysis process parameters. Typically, pyrolysis oils contain a complex mixture of n-paraffins, iso-paraffins, olefins, diolefins, iso-olefins, naphthenes, and aromatics [3], but the presence of trace impurities, such as sulfur-, chlorine- and nitrogen-containing compounds, can affect the quality of the oil and its applicability. Unfortunately, the unknown chemical composition and extreme complexity of pyrolysis oils mean that analysing using conventional 1D GC–MS is challenging.

Comprehensive two-dimensional GC (GC×GC) is an advanced separation technique that has previously been applied for improved peak capacity in the analysis of pyrolysis oils [2–5]. In this study, we use the new INSIGHT-Thermal modulator coupled with the BenchTOF2™ time-of-flight mass spectrometer to provide sensitive, detailed characterisation of pyrolysis oil composition. Coupled with powerful software tools in the ChromSpace® platform, we showcase workflows to identify possible contaminants and ultimately help refine process design.

Experimental

Samples: Pyrolysis oils prepared from three different feedstocks (see Table 1 for details) were analysed. All samples were from a distillation cut covering 250-360°C (the 'diesel' fraction).

Sample introduction: 0.2 µL of each sample was injected with a split ratio of 100:1 and a ramped inlet temperature of 60°C to 350°C (at 600°C/min after 0.2 minutes).

GC×GC: INSIGHT®-Thermal modulator (SepSolve Analytical); Modulation period (PM) = 6.0s.

TOF MS: BenchTOF2™ mass spectrometer (SepSolve Analytical); Mass range: m/z = 35-600; Acquisition rate: 100 Hz.

FID: Temperature: 350°C; Air flow: 300 mL/min; H_2 fuel flow: 50 mL/min; Makeup flow (N_2): 47 mL/min; Acquisition rate: 100 Hz.

Software: ChromSpace® software (SepSolve Analytical) for full instrument control and data processing.

Please contact SepSolve for full analytical parameters.

Sample label	Feedstock	Polymer(s)
A	Waste packing foils	Polyethylene
B	Mix of waste packing foils and waste food packaging (e.g. yoghurt cups)	Polyethylene and polypropylene
C	Scrap tyres	Rubber

Table 1
Details of the pyrolysis oils analysed in this study

Results and discussion

The GC×GC–TOF MS colour plots obtained from the analysis of the three pyrolysis oils are provided in Figure 1, showing the excellent peak capacity achieved using the INSIGHT-Thermal modulator. The diversity of sample composition is also evident in the chromatograms, due to the different waste sources (Table 1) used in the production of the three pyrolysis oils. Note that the ability to apply ramps to the jet parameters means that the cold jet flow rate can be decreased as the run progresses, while the hot jet temperature is increased. This ensures efficient release of compounds of lower volatility, making the INSIGHT-Thermal ideally suited to the analysis of complex fuels, such as pyrolysis oils.

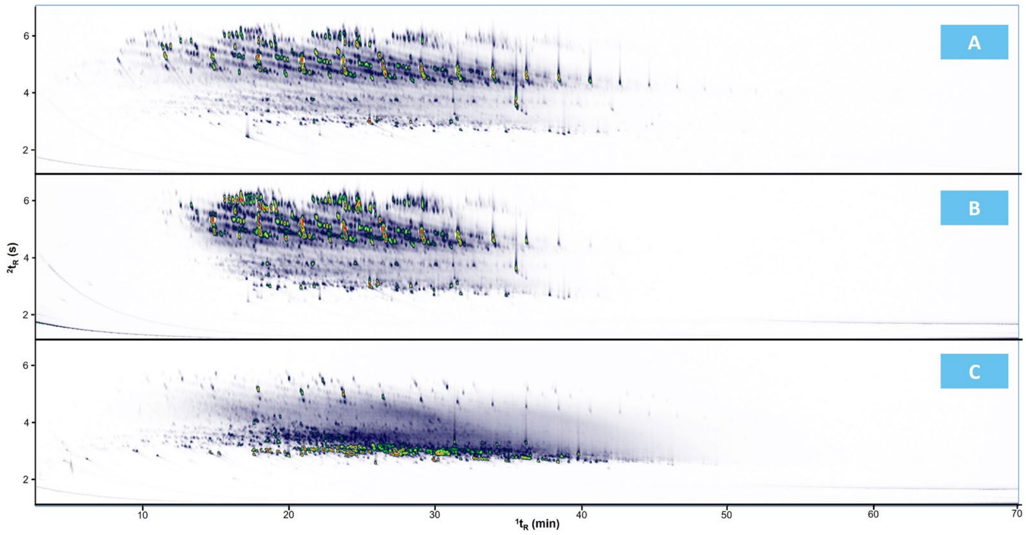

Figure 1
GC×GC–TOF MS colour plots for the three pyrolysis oils analysed in this study.

Pyrolysis oils can be used as a feedstock for the production of monomers that can go on to produce 'virgin' plastics for high-end applications. However, contaminants, such as nitrogen, oxygen and chlorine-containing compounds, can reduce the quality of the oil.

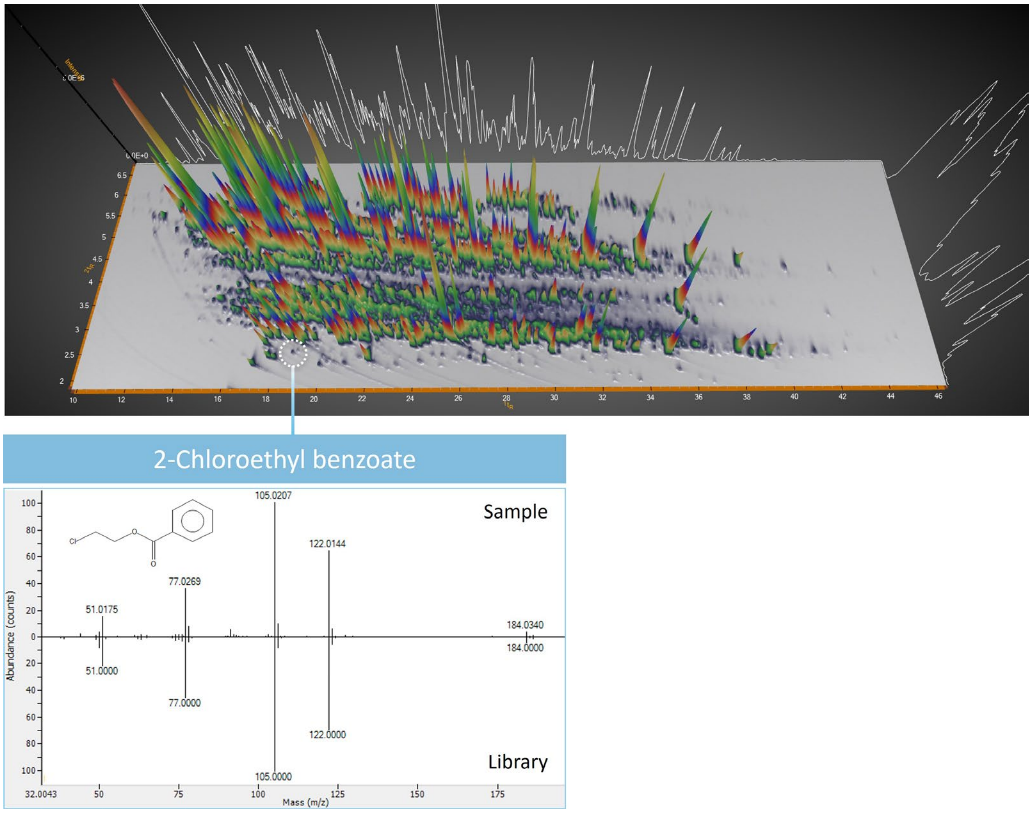

Figure 2

Separation and detection of a trace chlorinated compound in the pyrolysis oil from mixed waste plastic, confidently identified because of spectral quality and mass accuracy (<50 ppm) of the BenchTOF2 mass spectrometer.

Thermal modulators, such as INSIGHT-Thermal, have a major advantage in the detection of such trace contaminants, due to the focusing effect from the reconcentration of the analyte bands during the trapping process. In Figure 2, a trace chlorinated compound was confidently identified in the pyrolysis oil from mixed waste plastic. It is clear from the surface chart that this peak would have been masked by many other species in a 1D GC–MS separation and would likely have been overlooked.

Coupling GC×GC with mass spectrometry has an additional benefit in that mass spectral information can be used to search for compounds or classes of interest. In this study, scripting expressions were created in the Compound Explorer toolkit in ChromSpace software to automatically search the entire chromatogram for the nitrogen-containing quinolines and any sulfur-containing compounds (Figure 3). The expressions can be set up to be specific to an individual compound or class, or they can be broad to search for a distinctive isotope pattern (for example, chlorine) or neutral loss (as shown here for sulfur species). A new filtered chromatogram is generated showing only the peaks that pass the expression – making it easy to find compounds of interest, even if they are at trace levels.

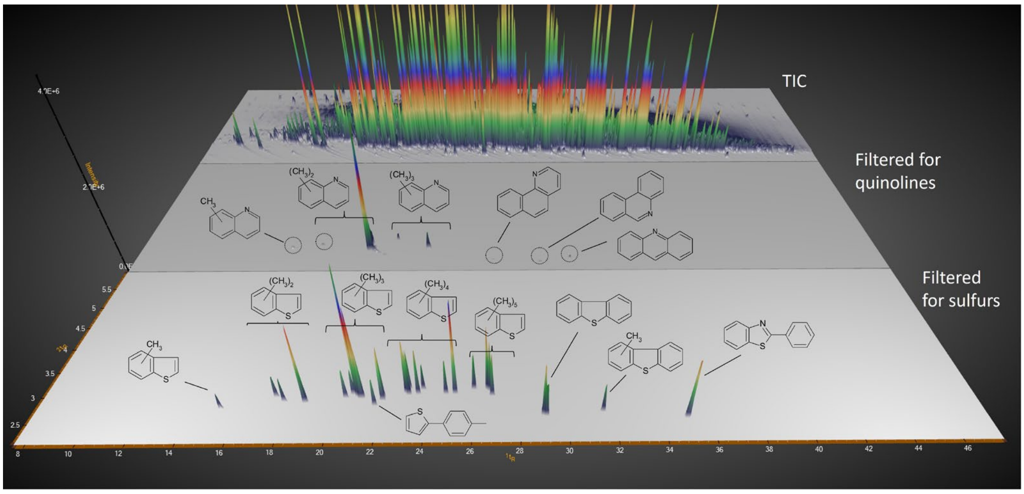

Figure 3

GC×GC–TOF MS colour plots showing the TIC of the pyrolysis oil from tyres (back plot), and two filtered chromatograms created using scripting expressions to search for the N-containing quinolines (middle plot) and all sulfur-containing compounds (front plot).

Despite the enhanced separation capacity of GC×GC using thermal modulation, the extreme complexity of such samples may still result in chemical classes overlapping in the two-dimensional space, as demonstrated by the 'Stencils' applied using ChromSpace software in Figure 4.

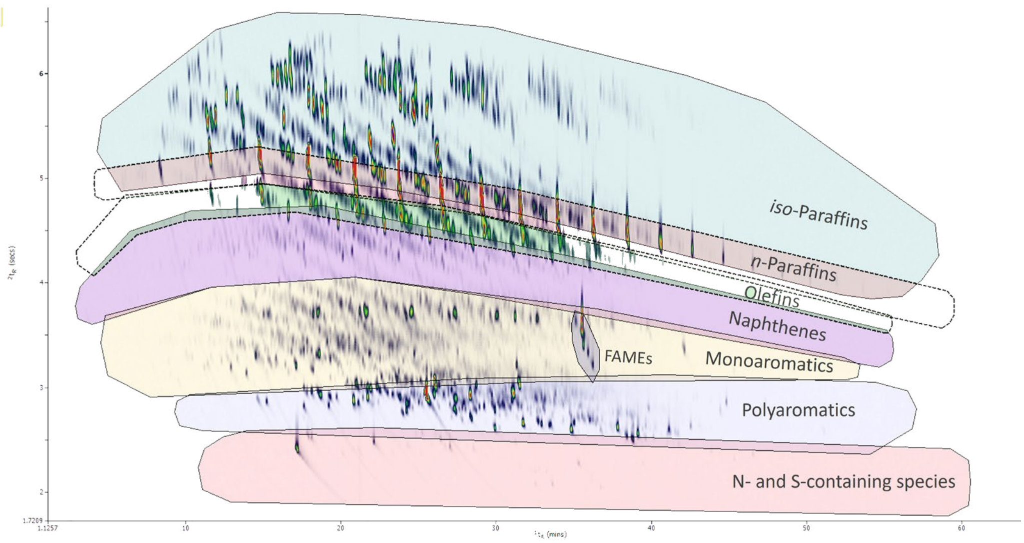

Figure 4

Group-type 'stencils' applied in ChromSpace for the main chemical classes identified in pyrolysis oil B.

To prevent contributions from other chemical classes that happen to elute in the same regions, the scripting expressions can also be applied within stencil regions to add selectivity. The expressions exploit diagnostic ions from each chemical class to correctly classify the peaks and exclude interferences, in an automated manner (Figure 5).

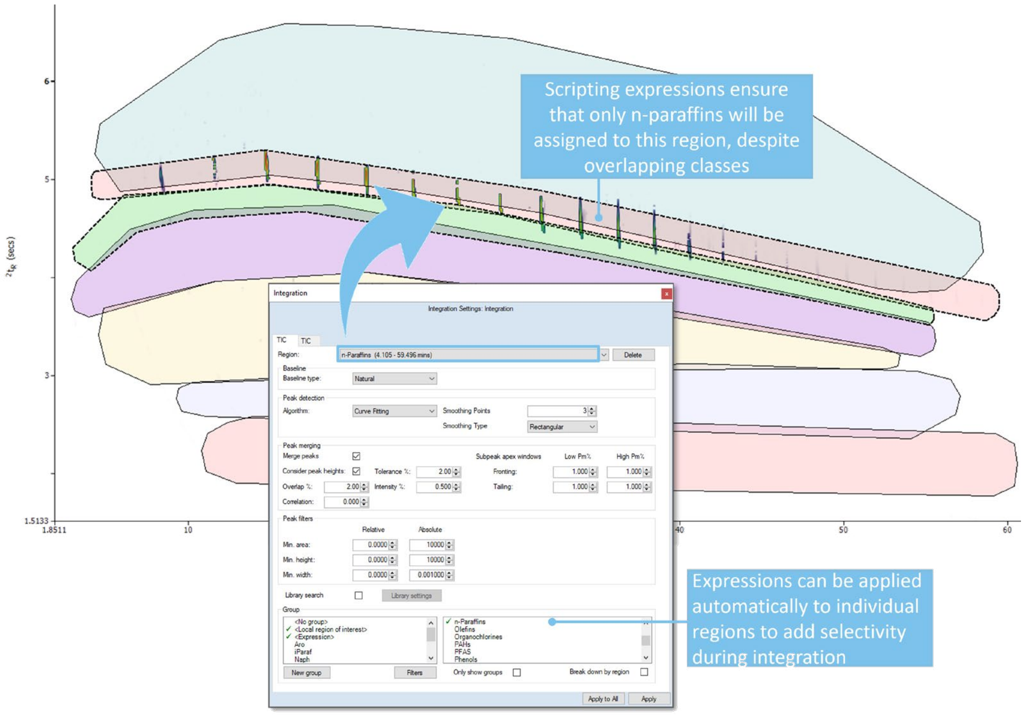

Figure 5

Using scripting expressions in ChromSpace software to ensure peaks are correctly classified within overlapping stencil regions – as applied to the n-paraffins region in this case.

Figure 5 shows an example expression applied to the 'n-Paraffins' region, and how it can be incorporated into the integration settings for automated classification and reporting. It is clear that only the n-paraffins pass these criteria. Therefore, the use of such expressions within the classification process prevents overlapping chemical classes (such as the iso-paraffins, in this case) from being incorrectly assigned in the final group-type report.

Conclusions

In this white paper, we have demonstrated how GC×GC–TOF MS with thermal modulation can provide the detailed characterisation required by novel (or sustainable) fuels and feedstocks, such as pyrolysis oils, to identify possible contaminants and help refine process design, specifically:

- Thermal modulation, using INSIGHT-Thermal, provides the peak capacity and sensitivity required to gain maximum detail on sample composition.
- Confident identification of trace contaminants is achieved thanks to the spectral quality and mass accuracy of the BenchTOF2 time-of-flight mass spectrometers.
- Full instrument control and data processing for streamlined workflows and simplified training requirements are provided through ChromSpace GC×GC software.

- Fast identifications of trace contaminants – including sulfur, nitrogen and chlorine-containing species – are possible using filtering expressions.
- Stencils, in combination with scripting expressions, offer a fast, yet accurate, group-type overview of sample composition.

For more information on this application or any of the techniques or products used, please contact SepSolve.

Acknowledgements

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References

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