Improved characterisation of materials using pyrolysis with GC×GC and BenchTOF2 MS

Pyrolysis coupled with two-dimensional gas chromatography and time-of-flight mass spectrometry (Py–GC×GC–TOF MS) can be used for quality control of consumer products, including tyres, plastics and paper.

Introduction

Pyrolysis involves the thermal degradation of a sample in the absence of oxygen to produce smaller molecules (or pyrolysates) that are more amenable to analysis by gas chromatography with mass spectrometry (GC–MS). It is a useful technique for the characterisation of solid samples, such as paper and polymers, as well as insoluble samples, which are difficult to introduce into a GC–MS system by any other approach. The direct sample introduction also means that very small sample quantities are required, in the range of micrograms to milligrams.

For these reasons, pyrolysis coupled with GC–MS (Py–GC–MS) has been widely adopted for materials characterisation to provide important compositional and structural information without sample pre-treatment. It has already been applied across a range of application areas, such as the investigation of polymer blends in biodegradable bags[1] and forensic investigation of tyre rubber at road traffic accidents.[2]

Here, we use the OPTIC-4 Pyro multi-mode inlet for pyrolysis of liquids or solids at temperatures up to 700°C with fast heating speeds up to 60°C /s. The samples are pyrolysed directly inside the inlet, meaning that no expensive external instruments are required. Additionally, when coupled with SepSolve's sample preparation robot (SPR), the process can be fully automated using the liner exchanger (LINEX) option.

However, the resulting chromatograms (or pyrograms) are often extremely complex, meaning multiple co-elutions are observed when using conventional 1D GC. In recent years, the complexity of such samples has been revealed using comprehensive two-dimensional GC (GC×GC).

In this study, we demonstrate how the increased separation capacity of GC×GC using INSIGHT® flow modulation, coupled with highly-sensitive confident identification by BenchTOF2™ time-of-flight mass spectrometers (TOF MS), provides improved characterisation of materials such as tyres, paper and plastics.

Experimental

Samples: Various materials (~10–20 mg of each) were analysed in this study including (1) a range of plastics (see Table 1 for full details), (2) standard printer paper and glossy photo paper and (3) sections of used tyres from four different manufacturers.

Pyrolysis: OPTIC-4 Pyro multi-mode inlet (GL Sciences) using difficult matrix introduction (DMI) micro-vials and liners; Temperature: 600°C for 1 min; Split ratio: 500:1.

GC×GC: INSIGHT flow modulator (SepSolve Analytical); Modulation period (P_M) = 3.0 s.

TOF MS: BenchTOF2 time-of-flight mass spectrometer (SepSolve Analytical); Mass range: m/z 30–600.

Software: ChromSpace® software (SepSolve Analytical) for full instrument control and data processing with chemometric comparisons by ChromCompare+ (SepSolve Analytical).
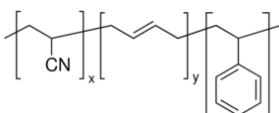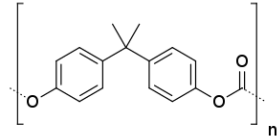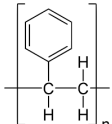
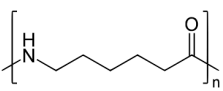Please contact SepSolve for full analytical parameters.
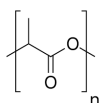
Plastic	Repeating unit
Acrylonitrile butadiene styrene (ABS)	
Polycarbonate	
Polystyrene	
Nylon	
Polylactic acid (PLA)	

Table 1

Plastics analysed in this study and their chemical structure repeating units.

Results and discussion

1. Comparing the composition of plastics

Figure 1 provides the Py–GC×GC–TOF MS chromatograms for the analysis of five different plastics. It is clear from the chromatograms that the plastic polymers have different compositions – in fact, the repeating units (Table 1) for each polymer are typically seen as the most intense peaks within the chromatograms (as annotated).
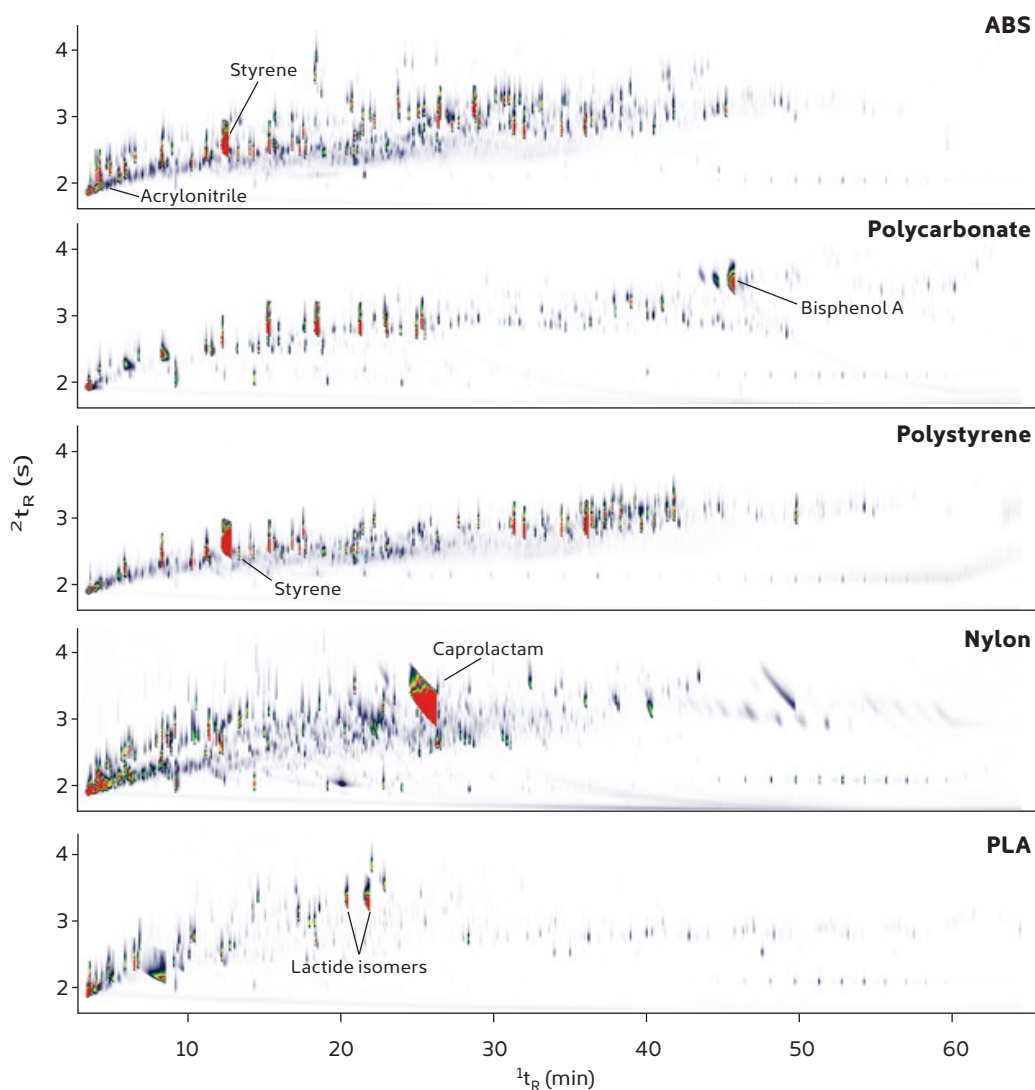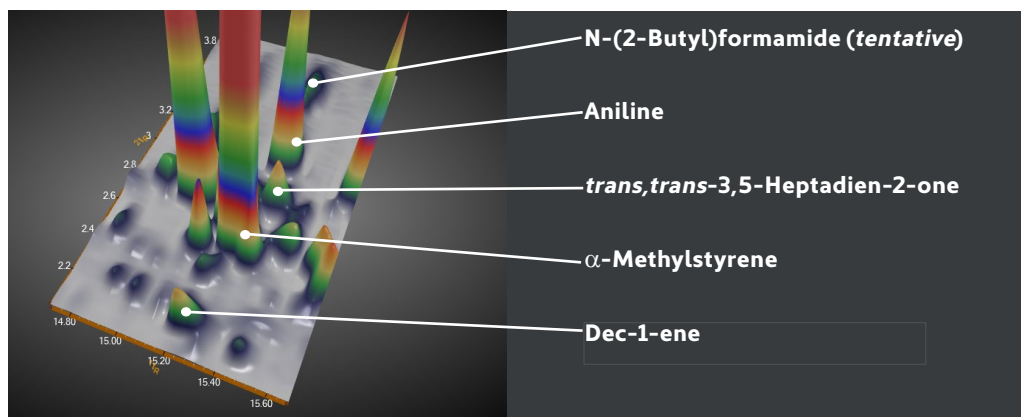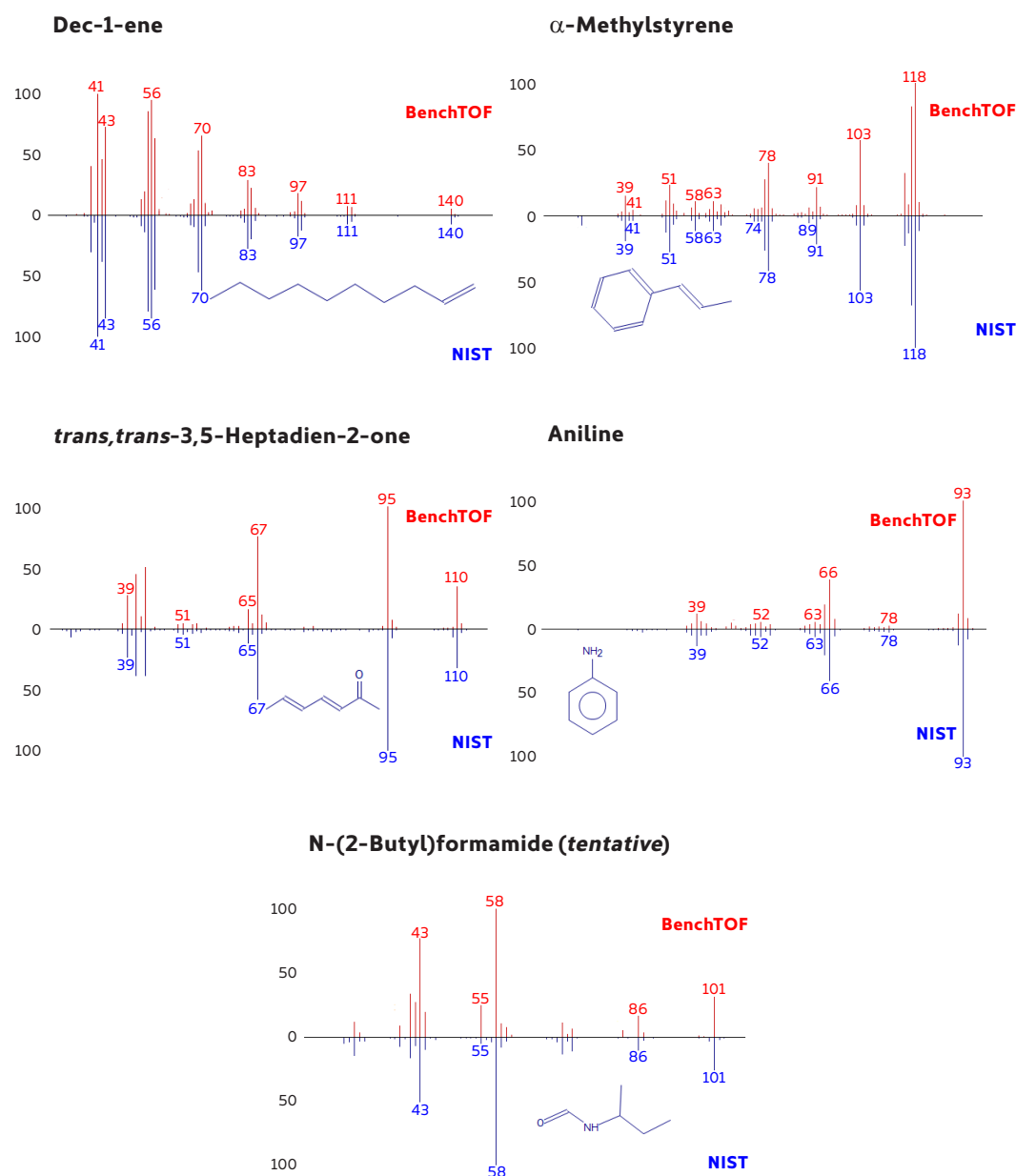

Figure 1

Py–GC×GC–TOF MS chromatograms for different types of plastic.

The chromatograms also demonstrate why GC×GC–TOF MS was chosen for this study. The enhanced region of the chromatogram for nylon in Figure 2 illustrates this further with the separation of five components that would have co-eluted in a 1D GC analysis. With GC×GC–TOF MS, the components are separated in the second dimension, for confident identification and greater insight into the sample composition. This level of detail is imperative for quality control and in the investigation of new materials, for example in the development of 'green' polymers such as polylactic acid (PLA).

N-(2-Butyl)formamide (*tentative*)

Aniline

trans,trans-3,5-Heptadien-2-one

α-Methylstyrene

Dec-1-ene

Figure 2

Enhanced region of the Py–GC×GC–TOF MS chromatogram for nylon with identifications by BenchTOF2 spectra (top, red) against the NIST and Wiley libraries (bottom, blue).

Dec-1-ene

α-Methylstyrene

***trans,trans*-3,5-Heptadien-2-one**

Aniline

N-(2-Butyl)formamide (*tentative*)

It is important to note that the rapid secondary separations in GC×GC frequently result in peak widths less than 100 ms, so detector speeds of 100 Hz are essential to maintain at least 10 datapoints across a peak. BenchTOF2 is inherently well-suited to handling such narrow GC peaks, since TOF mass spectrometers are dispersive (not scanning) instruments, and so effectively monitor all masses at once with fast acquisition rates. The ability to record full-range mass spectral information to extremely high densities enables TOF MS to handle the narrowest peaks encountered in well-optimised GC×GC couplings.

Furthermore, the INSIGHT flow modulator not only provides consumable-free GC×GC, but also the simple configuration of parallel detection, meaning that TOF MS data can be acquired for identification as well as FID for 'gold standard' quantitation.

2. Comparison of paper quality

To compare the profiles of different types of paper, a basic printer paper (uncoated) and a photo paper (gloss coated) were analysed. Figure 3 shows the chromatograms obtained by Py–GC×GC–TOF MS analysis of the two paper samples.
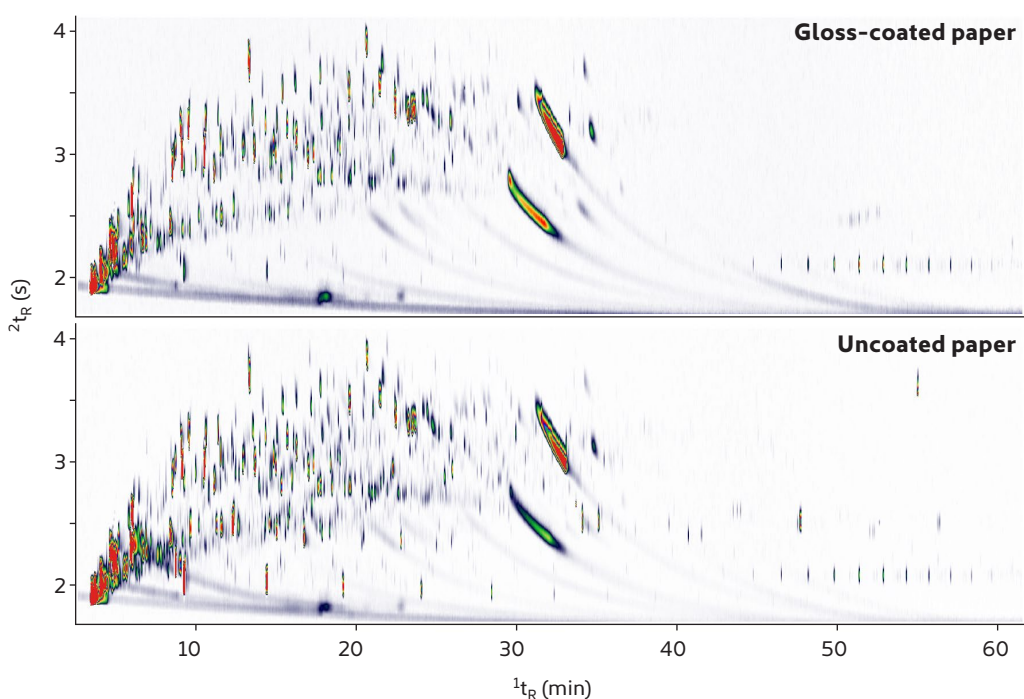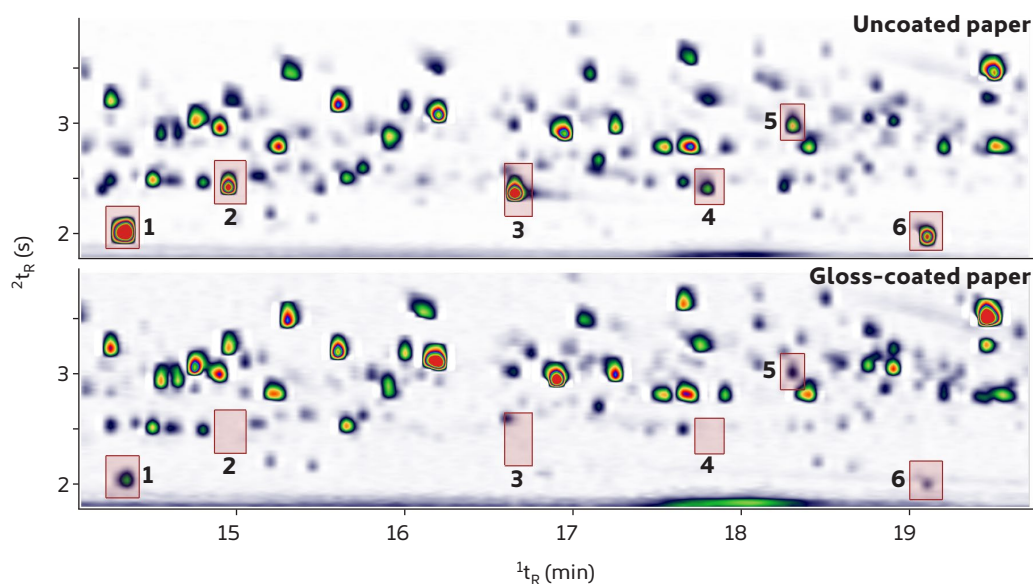

Figure 3

Py–GC×GC–TOF MS chromatograms for glossy and standard paper.

Figure 4 shows an enhanced region of the chromatograms with a selection of compositional differences highlighted between the coated (gloss) and uncoated paper. These components were all present in significantly higher amounts in the coated paper, indicating that they may have originated from the coating substance. Indeed, compounds such as 2-ethylhexanol and n-butyl methacrylate are known to enhance gloss coatings.
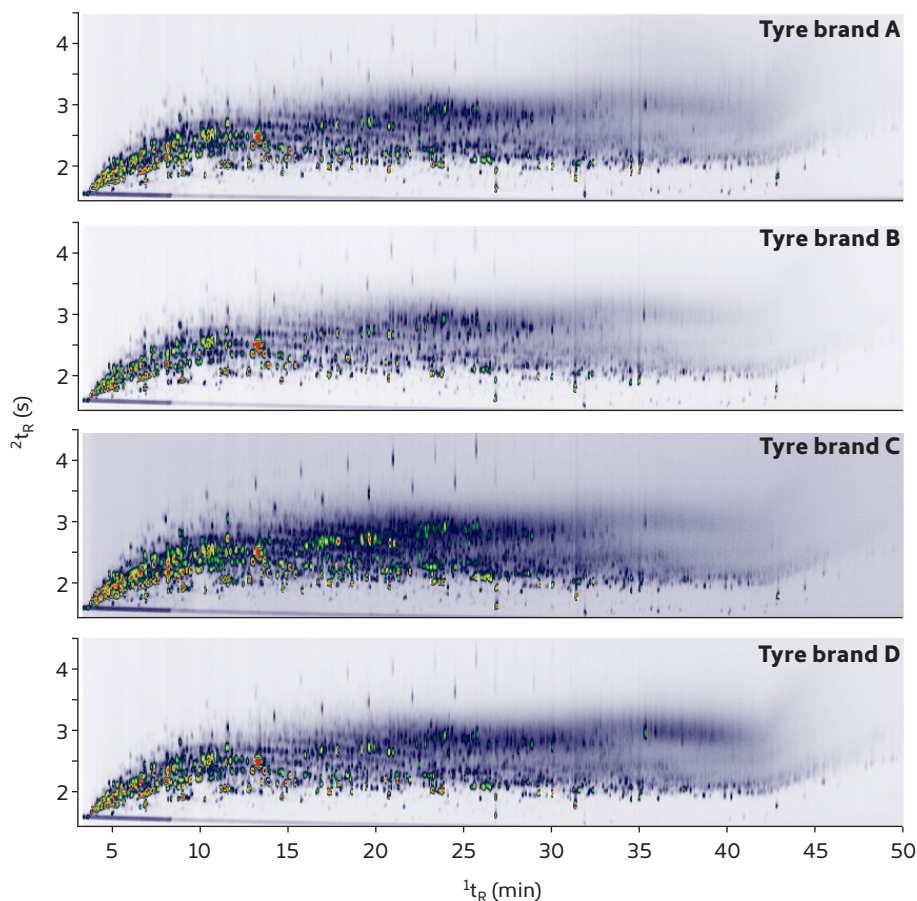

Figure 4

Enhanced region of Py–GC×GC–TOF MS chromatograms for standard and glossy paper with key compositional differences highlighted.

1 = **Octamethylcyclotetrasiloxane**   4 = **Isobutyl tiglate**
2 = **n-Butyl methacrylate**   5 = **Acetophenone**
3 = **2-Ethylhexanol**   6 = **Decamethylcyclopentasiloxane**
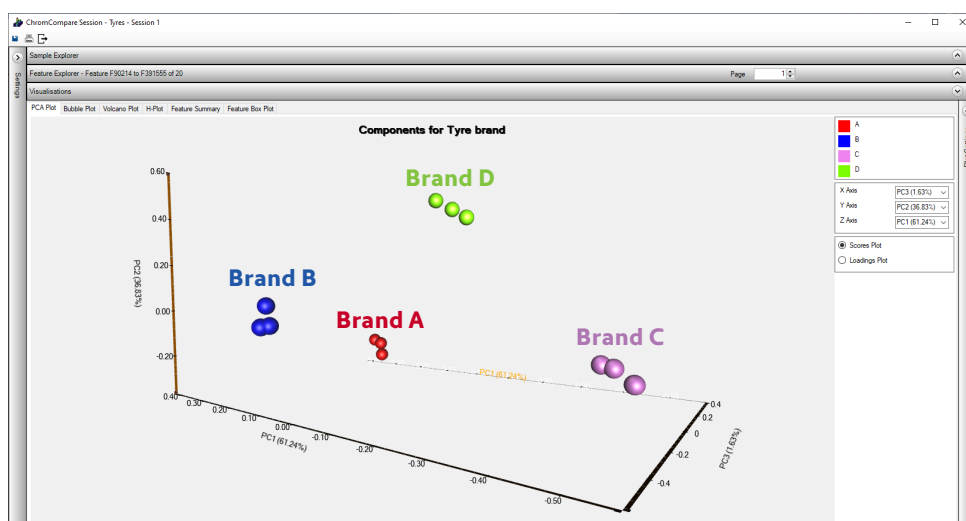
3. Comparison of tyre rubber

Finally, sections of four used tyres from different manufacturers were subjected to Py–GC×GC–TOF MS (Figure 5). Each chromatogram contained over one thousand individual peaks, making GC×GC–TOF MS a necessity for their separation and identification.

However, the greater level of detail means it would be extremely time-consuming to compare each chromatogram peak-by-peak. Instead, we used ChromCompare+ software to automatically compare the raw chromatograms using an untargeted tile-based approach. This approach splits the chromatogram into small tiles and sums the signal for each m/z channel in each tile – then automatically collates this information for every sample.

Figure 6 shows the resulting principal components analysis (PCA) score plot for triplicate analysis of each tyre brand by Py–GC×GC–TOF MS. Here, untargeted data analysis found over 400,000 individual features for each chromatogram, which were then filtered down using Feature Discovery to show the top 20 most significant differences between the brands. The PCA score plot clearly shows distinct clustering of the tyres from each manufacturer, indicating that differences were uncovered in their compositions.

The ChromCompare+ software then allows these differences to be reviewed easily as feature summary charts and identified using comparison of BenchTOF2 spectra against commercial libraries. Figure 7 shows one such example where an aniline compound was uncovered in tyre brand C only. This difference was discovered automatically by ChromCompare+ software but would have taken days' worth of laborious review to find through manual approaches.
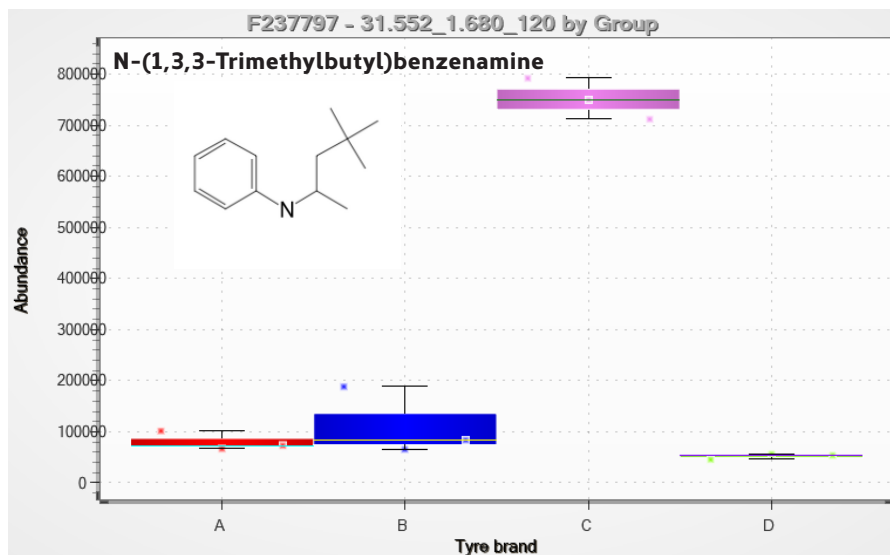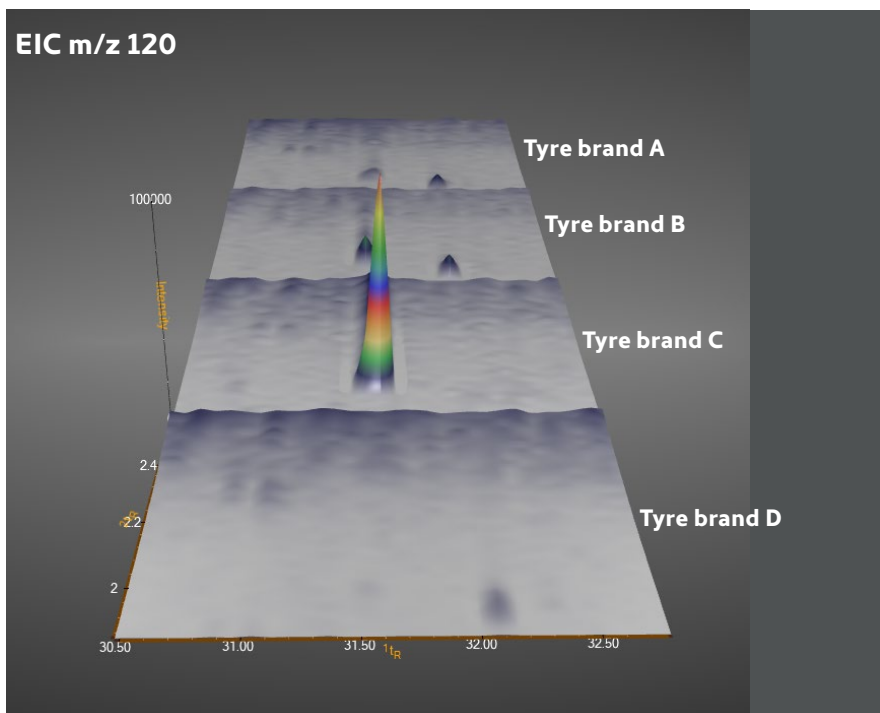

Figure 7

Box and whisker plots in ChromCompare+ (top) showing key differences for tyre brands A–D with the relevant section of the chromatograms displayed (bottom).

Conclusions

The described Py–GC×GC–TOF MS system has been shown to provide improved characterisation of materials, specifically:

▶ OPTIC-4 Pyro multi-mode inlet (in connection with SepSolve's sample preparation robot) provides simple, automated pyrolysis of liquids or solids at temperatures up to 700°C directly inside the inlet, meaning that no expensive external instruments are required.

▶ GC×GC using the INSIGHT flow modulator provides enhanced separation for improved discovery of sample composition and robust quality control of sample batches.

▶ Reference-quality spectra generated by BenchTOF2 mass spectrometers enable key additives and contaminants to be confidently identified.

▶ Streamlined workflows are possible using ChromSpace® software for full instrument control and powerful data processing with the option to add powerful chemometrics with ChromCompare+ to automatically find the differences between complex pyrograms.

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

References

[1] P. Rizzarelli et al., *Journal of Analytical and Applied Pyrolysis*, 2016, 117: 72–81, https://doi.org/10.1016/j.jaap.2015.12.014.

[2] L. Gueissaz and G. Massonnet, *Forensic Science International*, 2013, 230: 46–57, https://doi.org/10.1016/j.forsciint.2012.10.013.

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