Non-Target Analysis of Waste Plastic Pyrolysis Oils (WPPO) by GCxGC-HRTOFMS

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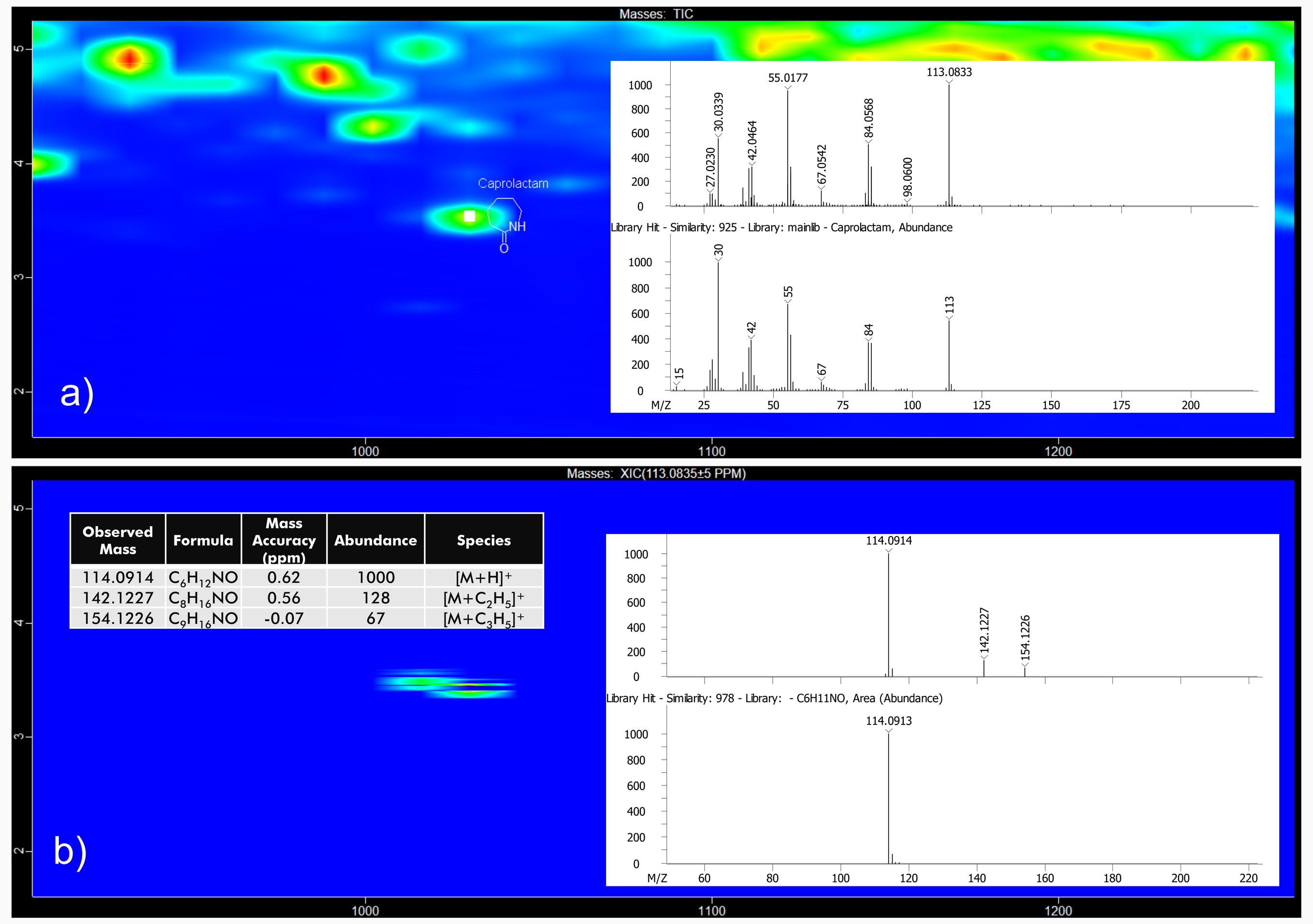
Abstract

Waste plastic pyrolysis oils (WPPO) are of growing interest as a more environmentally friendly alternative feedstock for producing chemicals and fuels. However, as WPPO are often produced from diverse sources with varying degrees of purity and cleanliness, more comprehensive analysis becomes necessary as compounds that are not typically found in traditional petrochemical sources can be present in these oils. Targeted screening is not enough to fully safeguard processes from potentially undesirable contaminants, which can reduce efficiency of reactions and foul production lines. To fully understand the chemical composition of such complex mixtures, non-targeted analysis is essential. This poster focuses on analysis of different WPPO samples using an unparalleled non-target discovery tool: the Pegasus® HRT⁺4D which offers comprehensive two-dimensional gas-chromatography coupled to high-resolution time-of-flight mass spectrometry (GCxGC-HRTOFMS) capable of multi-mode ionization with electron ionization (EI), positive chemical ionization (PCI), and electron capture negative chemical ionization (ECNI).

Fig 1. Pegasus HRT⁺4D TOFMS with Multi-Mode Source™ (MMS) used for non-target characterization of samples.

Confirmation of Individual Analyte Identification



Observed Mass	Formula	Mass Accuracy (ppm)	Abundance	Species
114.0914	$C_6H_{12}NO$	0.62	1000	$[M+H]^+$
142.1227	$C_8H_{16}NO$	0.56	128	$[M+C_2H_5]^+$
154.1226	$C_9H_{16}NO$	-0.07	67	$[M+C_3H_5]^+$

Fig 2. Zoomed-in contour plots of waste tire pyrolysis oil with a) TIC from EI analysis with Peak True spectra of caprolactam with corresponding NIST Library spectra showing excellent similarity match score of 925/1000 and b) m/z 113.0835 from CI analysis with Peak True spectra of corresponding peak with excellent isotopic fidelity match of 978/1000 for the $C_6H_{11}NO$ formula mass. Table of major CI adducts all confirm formula with mass accuracies less than 1 ppm. GCxGC was beneficial for isolating this feature from within the complex sample.

Various Sources of WPPO

Polypropylene/Polyethylene Plastic

Waste Tires (butadiene/styrene rubber)

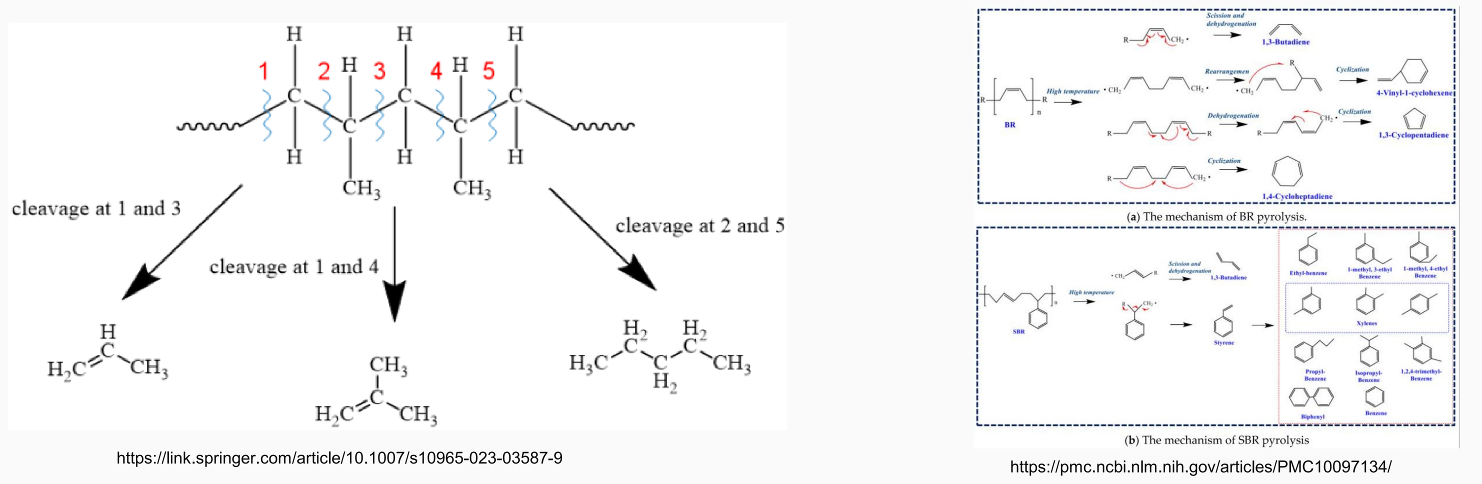


Fig 3. Pyrolysis product pathways for polypropylene/polyethylene and butadiene/styrene rubber.

GCxGC Sample Comparison with Multi-Mode Ionization

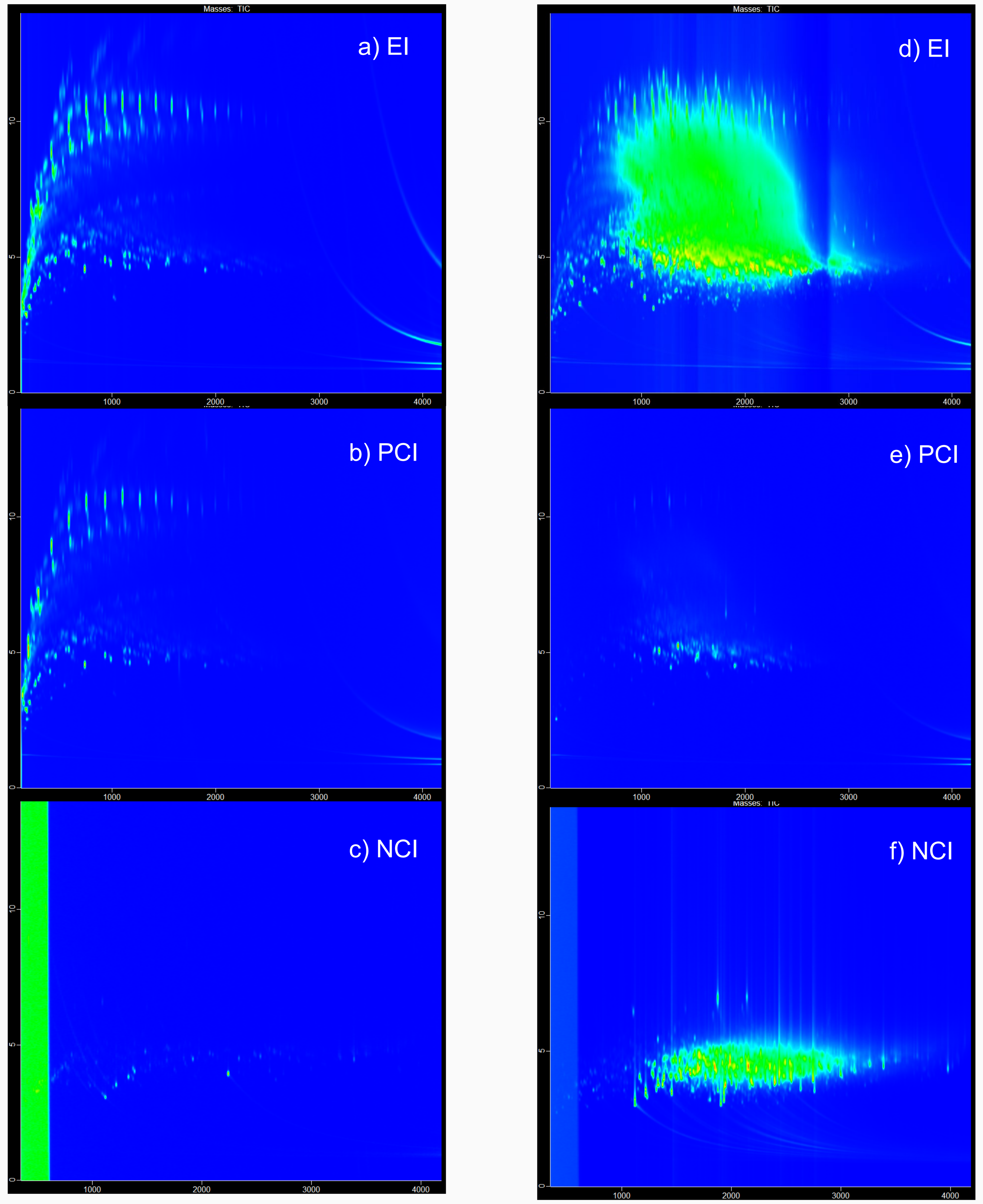


Fig 4. Different WPPO samples were analyzed. Full TIC contour plots compare the distribution of analytes and selectivities of the multi-mode ionization source with a)-c) showing a sample of polypropylene/polyethylene plastic pyrolysis oil and d)-f) showing a sample of waste tire pyrolysis oil. The difference is readily apparent and can be further explored with various software tools.

Advanced Peak Filtering Highlights Peaks of Interest

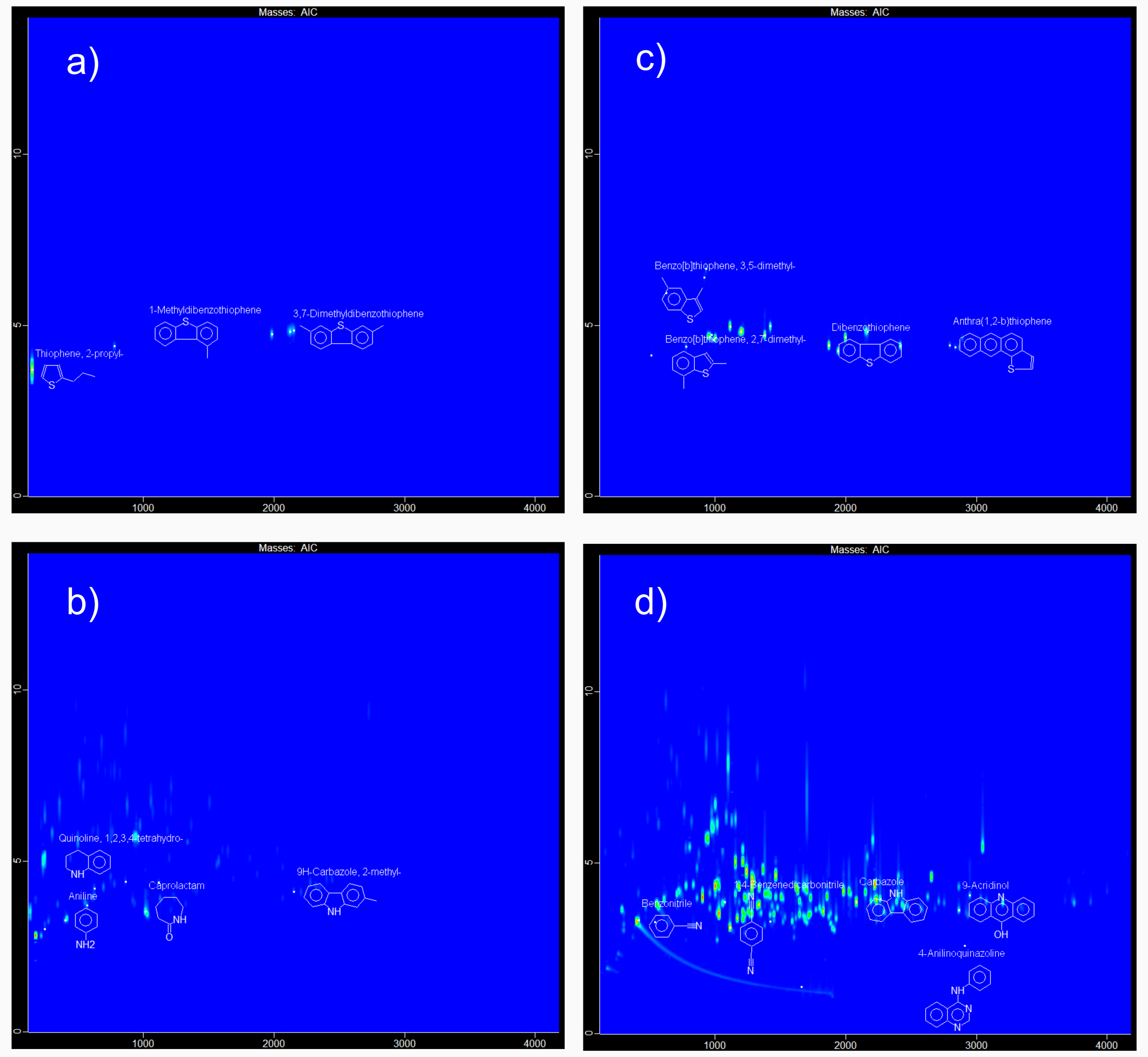
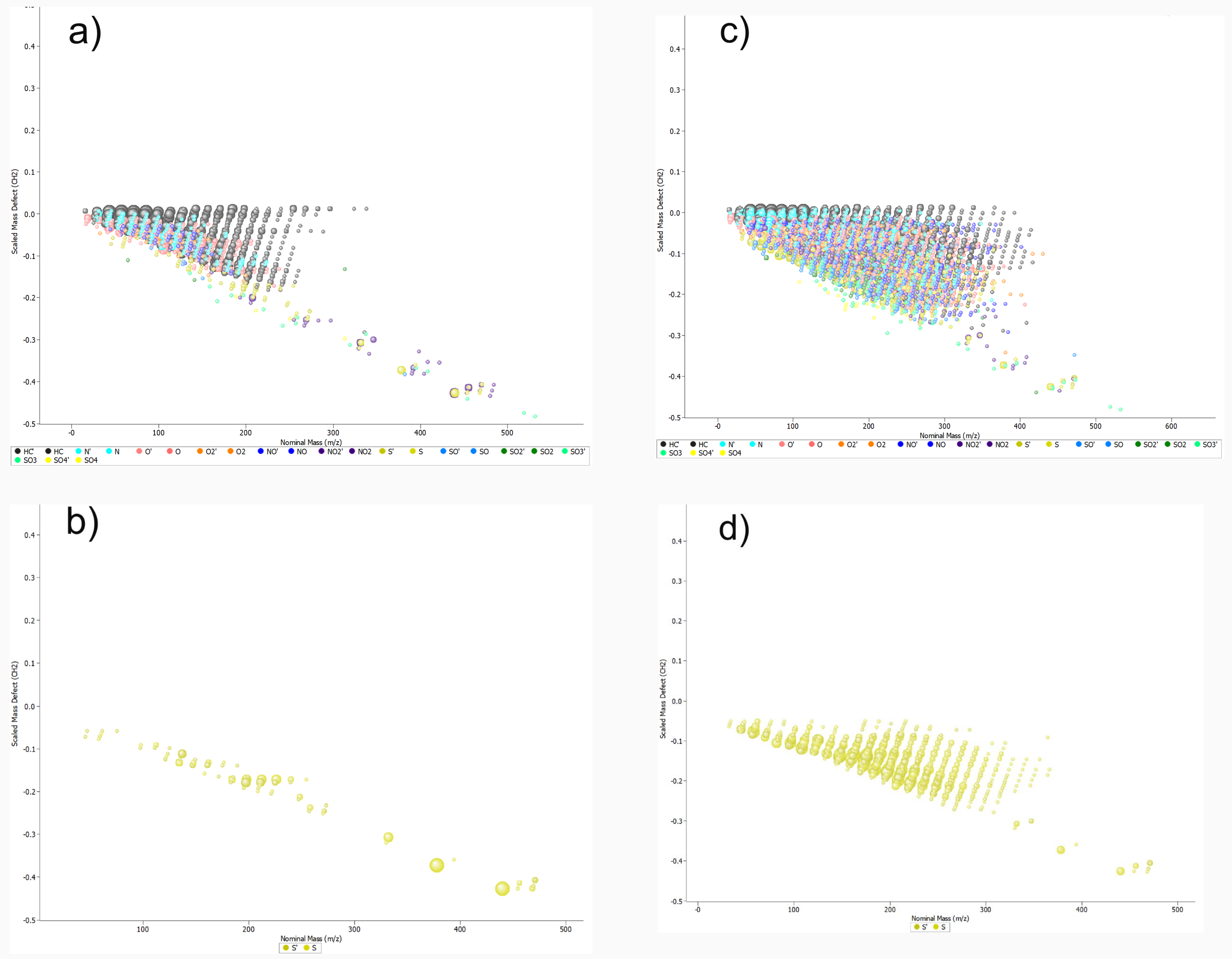


Fig 5. ChromaTOF peak finding and optional peak filters can be used to focus the data review on specific analytes of interest. Peak labels and structures can be automatically overlaid for easy determination of peak identities, allowing for quick determination of clusters in GCxGC elution space of similar compounds of potential interest. For example, full contour plots of EI analysis showing AIC traces, which only display signal from peaks that meet specific filtering criteria are shown for a) polypropylene/polyethylene plastic pyrolysis oil peaks with library similarity scores of >800/1000 and formula that include at least one sulfur atom; b) polypropylene/polyethylene plastic pyrolysis oil peaks with library similarity scores of >800/1000 and formula that include at least one nitrogen atom; c) waste tire pyrolysis oil peaks with library similarity scores of >800/1000 and formula that include at least one sulfur atom; and d) waste tire pyrolysis oil peaks with library similarity scores of >800/1000 and formula that include at least one nitrogen atom. While there are many more peaks than labels that appear in these plots, labels can selectively be applied only to chosen peaks of interest.

Spectral Analysis Tools for Revealing Heteroatomic Species

Fig 6. Colorized scaled mass defect plots generated using the Spectral Analysis Tools software package highlight masses from the entire chromatographic sample that correspond to defined formula series that selectively correspond to values expected for heteroatomic species. Data from PCI analyses, which provide higher incidence of molecular ions and fewer fragment masses, are displayed on a) scaled mass defect plot of polypropylene/polyethylene plastic pyrolysis oil sample filtered to show only masses belonging to a defined mass defect series; b) scaled mass defect plot of polypropylene/polyethylene plastic pyrolysis oil sample filtered to show only single sulfur atom-containing masses; c) scaled mass defect plot of waste tire pyrolysis oil sample filtered to show only masses belonging to a defined mass defect series; and d) scaled mass defect plot of waste tire pyrolysis oil sample filtered to show only single sulfur atom-containing masses. Each displayed mass can then be selected and displayed back on the GCxGC contour plot or chromatogram to more easily select for peaks of interest.



Conclusion

The *Pegasus* HRT⁺4D high-resolution TOFMS generates comprehensive non-targeted characterization data that allows for clear differentiation between two types of WPPO samples. This multidimensional analysis provides the enhanced chromatographic resolution of GCxGC, which separates individual oil components chromatographically in an easy-to-comprehend layout of fairways of similar chemical structures, and the powerful analyte identification abilities of complementary ionization modes that can provide both detailed structural information and the high mass-accuracy molecular formulae for individual species. Feature-rich chromatographic and spectral views combined with a full complement of customizable software tools facilitate detailed interrogation of data, providing flexible workflows for simplified interpretations of complex data.