# Characterization of Pyroplastic Samples Gathered Following the Largest Recorded Maritime Spill of Microplastics: The Sinking of the M/V X-Press Pearl

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## INTRODUCTION

In 2021 a major fire on board the container ship M/V X-Press Pearl, followed by its sinking resulted in the largest recorded release of microplastics (MPs) into the marine environment. Samples collected from the beaches of Sri Lanka following the disaster included relatively pristine polyethylene pieces, burnt nurdles and combustion remnants. The pyroplastic component of the spill presents additional challenges for MP analysis over and above those posed by MPs unaffected by fire. Pyroplastics, for instance, have a greater ability to camouflage among natural organic matter. This increases the probability that the concentration of MPs in environmental samples could be under-reported or missed altogether. In turn, this leads to the need for more comprehensive, specific chemical characterization of pyroplastic MPs[1].

Polycyclic aromatic hydrocarbons (PAHs) are one class of molecules of concern in pyroplastics. Analysis for PAHs is commonly performed using GC-MS and is limited to a list of 16 compounds. Previous high temp GC analysis of these samples using GC-APCI MS/MS indicated the presence of more compounds and compound classes than the targeted PAHs[2]. That work also indicated the presence of major sample components that are not compatible with GC/MS due to properties such as boiling points >500°C. This led to direct analysis with an atmospheric solids analysis probe capable of reaching 650°C which resulted in detection of analytes >600 Da. It is expected that because these high boiling compounds are less volatile and less likely to be water-soluble, they have the potential to serve as higher specificity, longer-lived markers of pyroplastics collected from marine environments.

*Figure 1. SELECT SERIES™ Cyclic™ IMS mass spectrometer (left) and the atmospheric solids analysis probe (ASAP)*

*Figure 2. X-Press Pearl Fire* *Image: Sri Lanka Ports Authority*

## METHODS

Extracts of the MP samples were prepared using a DCM-based microextraction method as described in James, 2023. Samples included white relatively pristine nurdles, burnt plastic pieces and aggregated combustion remnants (Figure 3). Direct probe analysis using atmospheric pressure protonation and charge exchange ionization was performed on a SELECT SERIES Cyclic ion mobility mass spectrometer (cIMS) in positive ion mode. Probe temperature was ramped 50°C to 650°C in 12 steps of 50°C across 20 min. The Pattern Analysis Application (PAA) was used to screen the data for PAH-like chemical components in the MP extracts, by employing compound class-specific filters. Processed outcomes including derived parameters were exported to Spotfire® (Cloud Software Group, Inc) for further visualisation.


*Figure 3. Field samples of nurdles in white, burnt and combustion remnant form*

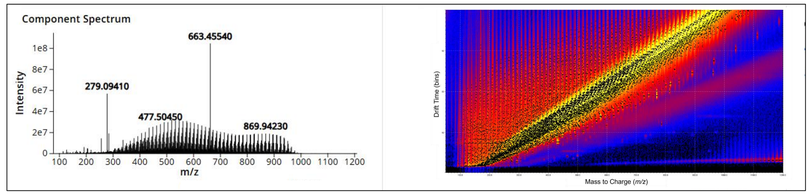


*Figure 4. Complexity of burnt sample extract. Left: A composite component MS spectrum. Right: Plot of the drift time versus m/z for the detected ions in the burnt sample. The black dots are indicative of peaks detected in the sample.*

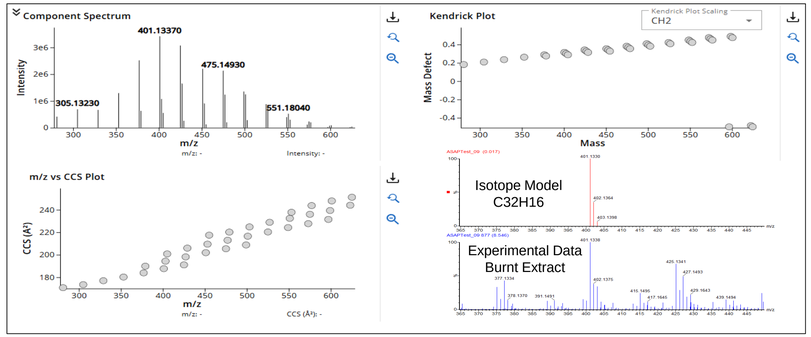


*Figure 5. High molecular weight PAHs discriminated by the waters_connect Pattern Analysis Application in burnt sample extract. Inset (bottom right) shows tentative identification for the most abundant HMW PAH*

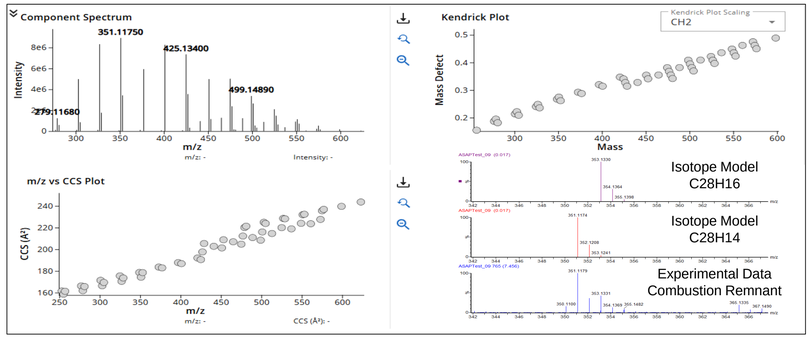


*Figure 6. High molecular weight PAHs discriminated by the waters_connect Pattern Analysis Application in combustion remnant sample extract. Inset (bottom right) shows possible identifications for most abundant HMW PAHs*

## DISCUSSION

The simple microextraction sample preparation employed, combined with the elimination of chromatographic separation provides access to high molecular weight PAHs, but, results in highly complex spectral data. Ion mobility combined with high resolution MS does provide some resolving power back into the analysis, but, at the cost of even higher data density. This increases the importance of having software that can automate the processing of data to extract significant patterns that might otherwise be lost in the noise of a wide variety of high abundance, interfering matrix components.

Figures 4 demonstrates the data complexity in the burnt sample extract. Figures 5 and 6 are results from the Pattern Analysis filtering the detected ions to likely PAHs of interest in the 300 – 600 Da range based on mass defect, CCS, and observed sequences. The inset spectra show a tentative identification of the most abundant component found in each pyroplastic sample extract as its protonated form, $[M+H]^+$.

Next, the use of charge exchange ionization, which produces molecular ions of the form $M^{+\cdot}$, was investigated on a second system. This stage of the work aimed at exploring additional capabilities in the application to further facilitate PAH analysis. One element of this was the creation of a library of 660 PAHs created using National Institute of Standards and Technology (NIST) Special Publication 922 Polycyclic Aromatic Hydrocarbon Structure Index[3]. After application of similar workflow steps as previous data, results were compared with the library and are summarized in Figure 7 for the burnt (upper) and combustion remnant extracts (lower).

An additional library of oxygenated PAHs was also compared with the data resulting in the list below of additional possible components[4].

| | |
|---|---|
| Anthraquinone | C14H8O2 |
| Pyrene-1,8-dione | C16H8O2 |
| Dimethylanthraquinone | C16H12O2 |
| 5,12-Naphthacenequinone | C18H10O2 |
| Benzo[a]pyrene-6,12-dione | C20H10O2 |
| Benzo[a]pyrene-1,3(2H,12aH)-dione | C20H12O2 |
| (Benzoylphenyl)phenylmethanone | C20H14O2 |
| Pentacene-6,13-dione | C22H12O2 |

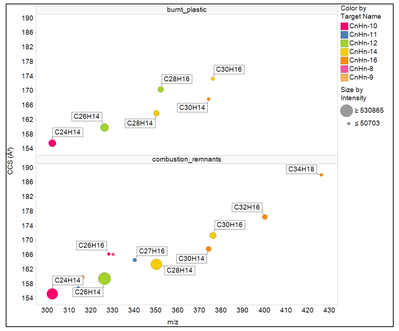


*Figure 7. Unique & common components in pyroplastic samples. Upper – burnt. Lower – combustion remnant.*

## CONCLUSION

- **Pyroplastic samples gathered from the environment following the sinking of the X-Press Pearl were found to contain significant levels of PAHs up to 600 Da**
- **The Pattern Analysis Application applied filters based on mass defect, mass accuracy and CCS to effectively identify series of PAHs in complex sample extracts**
- **cIMS with direct probe sample introduction provides separation of HMW PAHs with high boiling points and low vapor pressures that are incompatible with high temperature GC/MS**

### References

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**Conflict of Interest Disclosure:**

The authors declare no competing financial interest.

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