

# ANALYSIS OF HIGH MASS POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) EXTRACTED FROM MICROPLASTICS SPILLED IN THE MARINE ENVIRONMENT

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## INTRODUCTION

In 2021 the container ship M/V X-Press Pearl caught fire and later sank off the coast of Sri Lanka. Over 1600 tons of polyethylene pellets, aka nurdles, were aboard the ship along with 25 tons of nitric acid which began to leak and is suspected to be the cause of the fire that lead to the sinking. To add to the witches brew of ingredients in this fire were fertilizers and explosives being transported and flame retardants deployed to douse the fire. When combined with abundant, naturally-occurring compounds found in the marine environment, the need arises to characterize the composition of intact, burned, and broken pieces of the spilled plastic later collected from kilometers of Sri Lankan beaches<sup>1</sup>.



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

## METHODS

### Samples:

Three different categories of MP samples were characterized as white, burnt and combustion remnants (CRs). White nurdles are those with little or no visible color or physical transformation. Burnt describes the pieces that experienced discoloration due to the fire. Combustion remnants are agglomerations composed primarily of melted plastic that was deformed and discolored in the fire (Figure 3).

Standard reference materials (SRMs) from the National Institute of Standards and Technology (NIST) 1991 Mixed Coal Tar/Petroleum Extract and 1649a Urban Dust were included in this work. 1991 was diluted 10:1 in methylene chloride. 1649a is solid and was extracted using the same simple, generic microextraction technique based on sonication and centrifugation which was also used for MP samples and is detailed in James 2023.



Figure 3. Nurdle samples

Determining the distribution and abundance of PAHs in the samples is important for characterizing the source of the microplastics (MPs) and in selecting appropriate handling, disposal and/or recycling methods. Both traditional and advanced GC/MS methods such as 2D GC are suitable for the determination of PAHs up to 302 Da which is useful for such purposes as the differentiation of pyrogenic versus petrogenic inputs<sup>2</sup>. However, the toxicity characteristics of samples has demonstrated poor correlation with low mass (<302 Da) PAHs in past studies<sup>3</sup>. For that reason this work was aimed at investigating the routine analysis of higher mass PAHs in the range of 314 to 424 Da to provide access to additional analytes that may better correlate with toxicity as well as to provide the possibility of additional source markers.

## METHODS

### GC/MS Conditions:

Column: Rxi-5HT 15m x 0.25mm x 0.10 μm (Restek)  
Temp Program: 30.8 min runtime (see below)  
Carrier Gas: Nitrogen (N<sub>2</sub>) - flow program below  
GC: 8890 (Agilent)  
Injection: Split 10:1, SSL at 380°C, 100% graphite o-ring, 4 mm straight liner with wool, graphite ferrules on head and tail of column, high temp BTO septum  
Mass Spectrometer: Xevo™ TQ Absolute tandem quadrupole system  
Ionization: GC-APCI+ , dry source, charge exchange  
Corona current: 2.0 μA  
Cone gas: 270 L/hr (N<sub>2</sub>)  
Make up gas: 350 L/hr (N<sub>2</sub>)  
Aux Gas: 200 L/hr (N<sub>2</sub>)  
CID Gas: 0.40 mL/min (N<sub>2</sub>)  
Acquisition: MRM

Ramp (°C/min)	Temp °C	Hold (min)
Initial	40	0.5
14	160	0
22	395	11

Ramp (mL/min per min)	Flow (mL/min)	Hold (min)
Initial	0.60	0
0.015	0.90	0
0.150	3.0	0

## RESULTS

Due to the lack of availability of standards for PAHs in the range of 314 to 424 Da, a class-specific MRM based acquisition scheme was developed. When using charge transfer ionization the precursor mass for an MRM transition is the same as the nominal mass of the analyte. Furthermore, among the well characterized lower mass PAHs, the neutral losses of both 2 and 4 Da are common and differentiating from other compound classes due to the high collision energy (CE) required to generate them. Therefore, given a list of target analyte masses or elemental compositions it is possible to create MRM transitions even in the absence of individual standards. An additional observation among the low mass PAHs is that the optimum CE increases with increasing molecular weight. After using these observations to create preliminary MRM transitions, additional optimization of CE was performed using multiple injections of NIST SRMs that exhibited peaks in each of the 16 MRM functions. For this stage, preference was given to the most intense peak with a width that indicated the likelihood of it being a single analyte. In Figure 4, for example, the peak at 19.55 min is for an analyte eluting at 395°C with a precursor mass of 374 Da and peak width of 3.8s. For reference the 326 Da peak at 17.49 min has an intensity >4e6 counts. The list of 16 specific HWW PAH precursor masses to target in this work was established using reported detected species from multiple sources<sup>4,5,6,7</sup>. Among these prior studies, on-line or off-line sample pre-fractionation was used prior to analysis in all cases and analytical strategies included combined use of both LC/UV and GC/MS.

## RESULTS

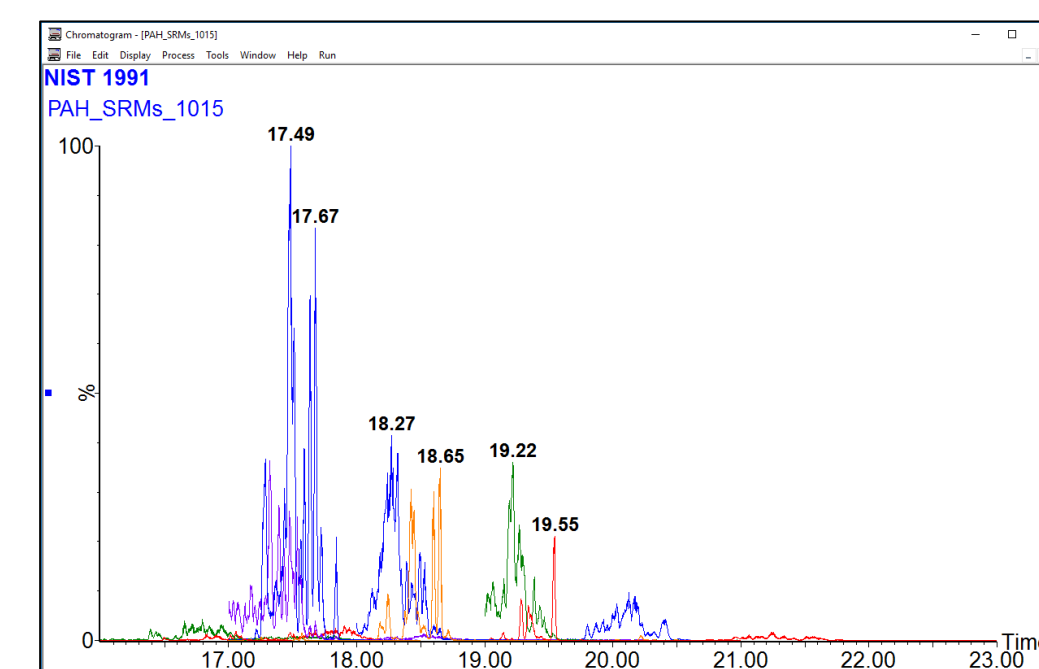


Figure 4. PAH distributions in NIST 1991 mixed coal tar/petroleum extract, overlaid TICs 314 - 424 Da

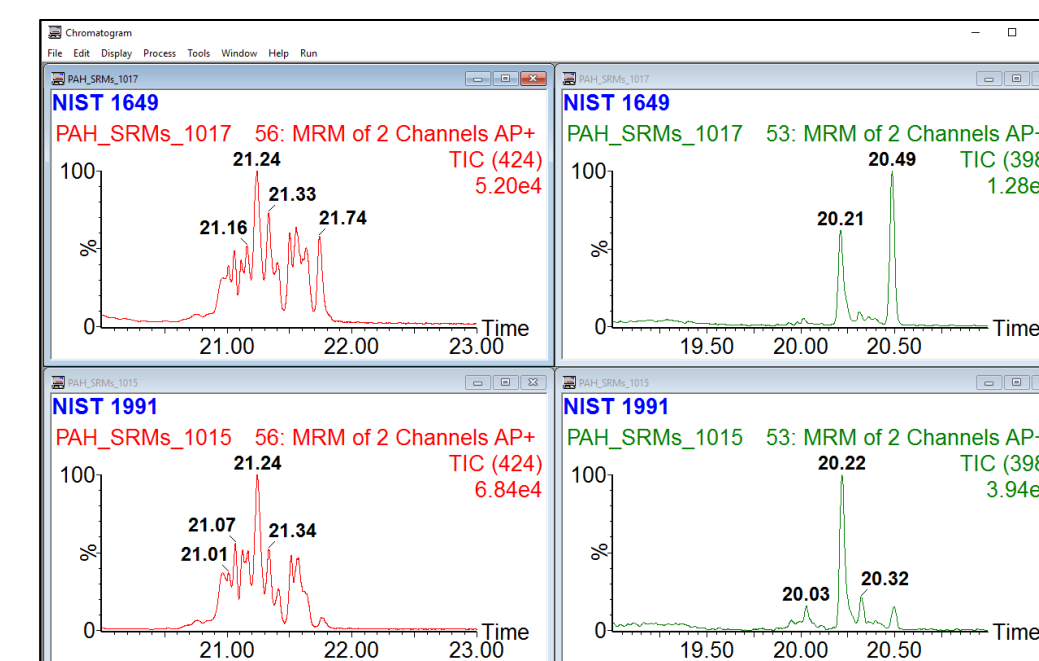


Figure 5. Comparing NIST 1649a urban dust and NIST 1991 coal tar SRMs, EICPs

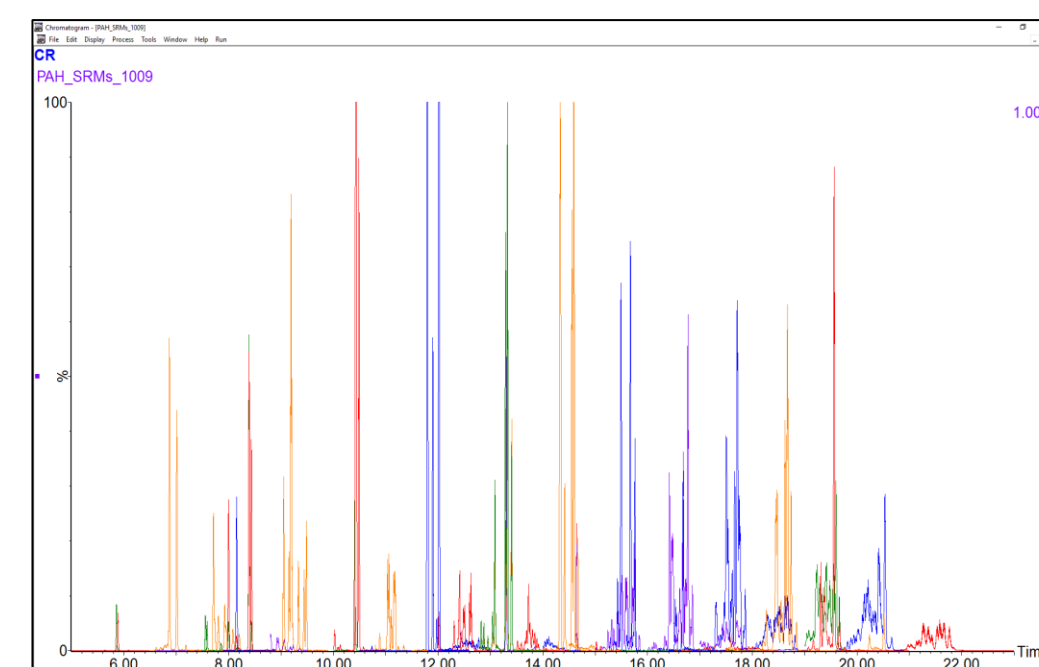


Figure 6. Combustion remnant extract, 128 - 424 Da overlaid TICs

## DISCUSSION

Figure 5 compares HMW PAHs found in urban dust and coal tar SRMs. Note that analytes as high as 398 Da exhibit EICPs with potential to add specificity to sample characterization. The 424 Da trace shows the chromatographic limitations of the 15 m column despite its tolerance for high temperature (to 400°C) use.

Figure 6 shows all analytes from 128 to 424 Da that were monitored for in the CR extract. Several analytes eluting < 15 min saturate the detector and would require a higher split ratio or dilution for quantitative analysis. Benzo [ghi] perylene is seen in the blue trace at 15.65 min along with anthanthrene at 15.74 min.

Figure 7 shows the comparison of the three different MP types for analytes of 302 (red), 326 (green), 350 (orange) and 374 Da (blue). Note that both the abundance and distribution of PAHs is different across different sample types.

Figure 8 compares analyte profiles between the CR and NIST 1649a using analytes of 350, 374, and 398 Da. Peak at 20.51 min <6 s wide.

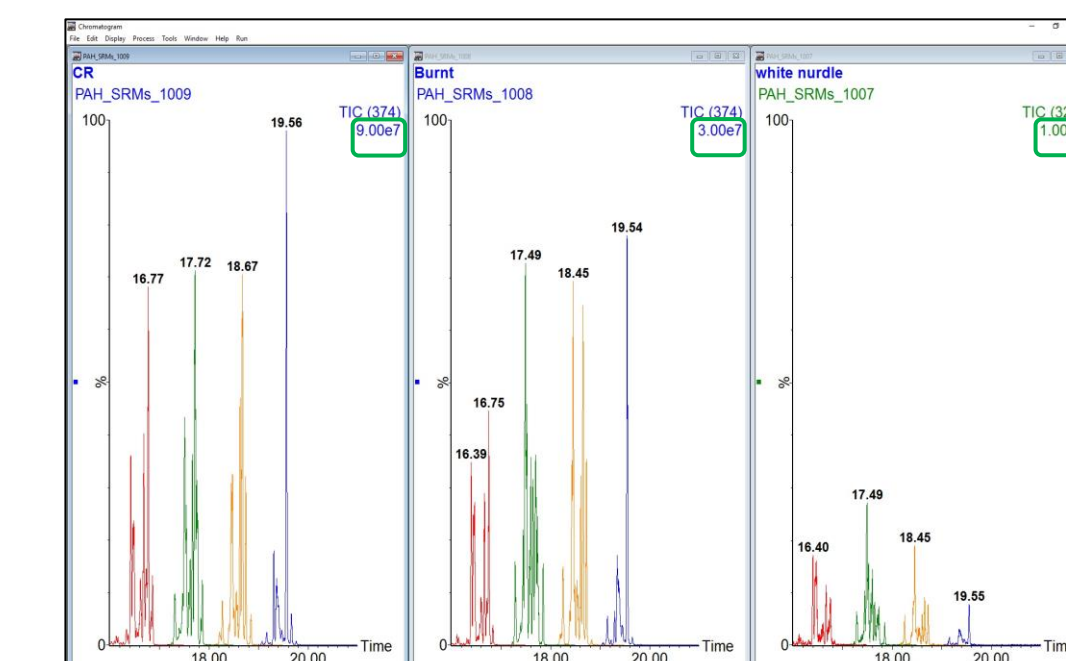


Figure 7. Comparison of select HWM PAHs in MP sample extracts

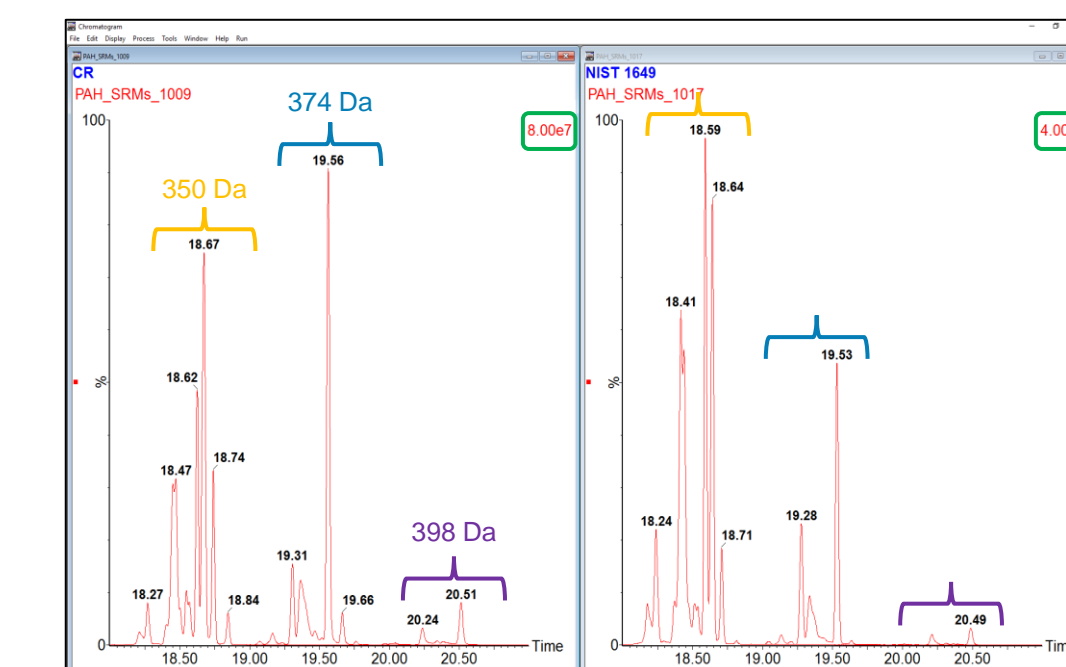


Figure 8. Comparing the distribution and abundance of select HWM PAHs in the CR sample and NIST 1649a

## DISCUSSION

- The combustion remnant and burnt samples contained >500x and >250x, respectively, of the levels of high mass PAHs found in white nurdles.
- Quantification of high mass PAHs show that white samples have <1%, burnt have 18.2% and CR has 40.7% by mass when comparing the cumulative response for all analytes detected in NIST 1597.

## CONCLUSIONS

- Analysis of an expanded range of high molecular weight PAHs in unfractionated extracts of MPs was achieved using a standard GC-APCI QqQ configuration combined with a simple, generic microextraction
- Charge transfer, atmospheric pressure chemical ionization facilitated the implementation of a class-specific MRM acquisition scheme
- Only minor modification to the GC method used for lower mass PAHs is required
- Nitrogen carrier gas achieved elution of HWM PAHs with symmetric, narrow peaks through the use of flow programming
- Further investigation of HMW PAHs for potential source markers and toxic compounds is enabled with this approach

### References

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### Conflict of Interest Disclosure:

The authors declare no competing financial interest.  
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