

Novel methodology for analysis of PAHs in water by high capacity sorptive extraction and TD-GC-MS

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Introduction

Polycyclic aromatic hydrocarbons (PAHs, Figure 1) are semi-volatile organic compounds with toxic, genotoxic and carcinogenic properties [1]. Levels of PAHs in both environmental and drinking water are regulated across the globe. For example, the EU stipulates a max of 100 ng/L (parts per trillion) for the sum of several PAHs in drinking water and a max of 10 ng/L for the particularly carcinogenic benzo[a]pyrene [2]. Sensitive analytical methods are therefore required to ensure regulatory compliance. Here, a straightforward method was developed using HiSorb™ high-capacity sorptive extraction probes and gas chromatography-mass spectrometry (GC-MS).

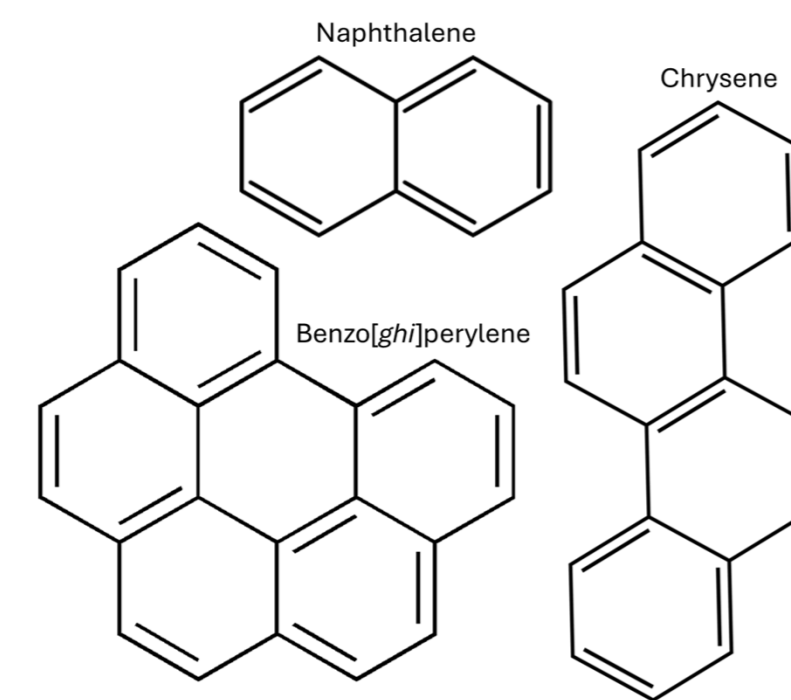


Figure 1: Example PAHs.

Experimental

Sample preparation

Unlike common liquid/liquid extraction (LLE) methods, which often involve extensive manual handling steps [3], sample preparation for HiSorb was very straightforward. 18 mL of sample matrix (water) was pipetted into a 20 mL industry standard headspace vial, 90 µL of internal standard (IS) containing deuterated PAHs was added, and the vial was capped. Laboratory standards were prepared by combining an 18-PAH mix with HPLC-grade water and IS.

HiSorb: High-capacity sorptive extraction

HiSorb probes comprise a sorptive phase supported by a robust metal core (Figure 2). The core is resistant to breakage, while the 60 µL sorptive phase (polydimethylsiloxane [PDMS] in this case) has a higher volume and therefore greater capacity than most other sorptive devices. Analytes are released from the probe *via* thermal desorption.

Figure 2: Standard length HiSorb probe bearing PDMS phase.

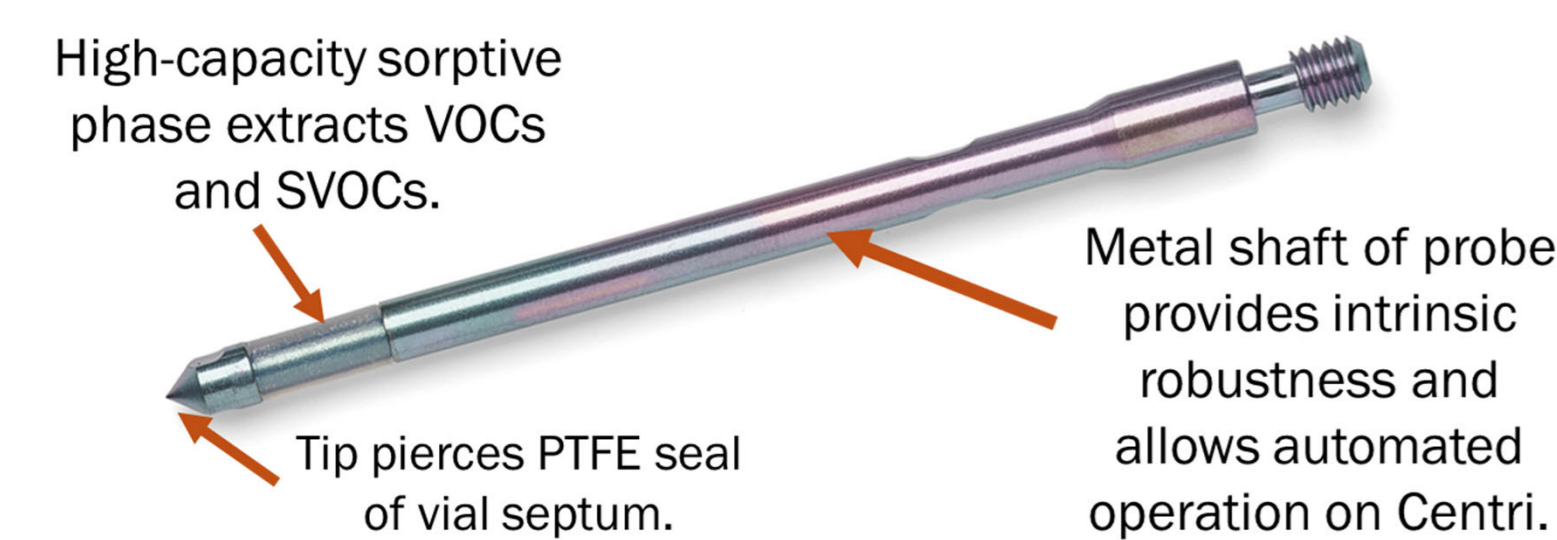
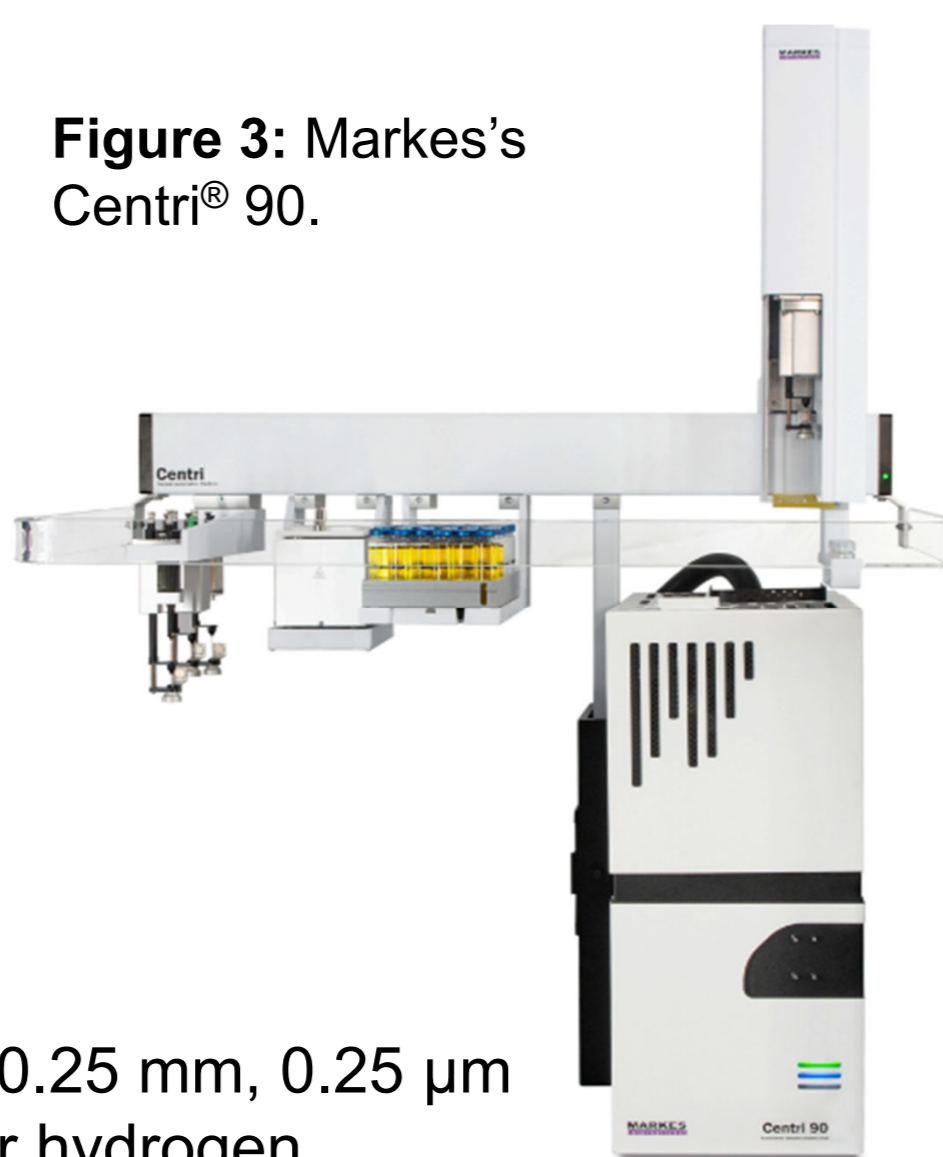


Figure 3: Markes's Centri® 90.



Sample extraction: 60°C (120 mins), agitation at 500 rpm.

TD:

- Probe desorption: 300 °C (20 min)
- Trap low: -25 °C
- Trap purge: 25 °C (1 min)
- Trap high: 380 °C (7 min)
- Split flow: 20 mL/min (7.6:1)

GC-MS:

- Column: 5-MS 30 m, 0.25 mm, 0.25 µm
- Carrier gas: Helium or hydrogen
- Column flow: 3 mL/min
- Oven programme: Carrier gas dependent
- Detection: Single quadrupole MS in selected ion monitoring (SIM) mode.

Method automation

The HiSorb method was performed on a Centri 90 platform (Figure 3). Centri 90 uses the HiSorb 90 tool and dedicated rail-mounted modules (Figure 4) to automate HiSorb analysis and deliver analytes to a focusing trap. To see HiSorb automation in action, scan the QR code (Figure 5).

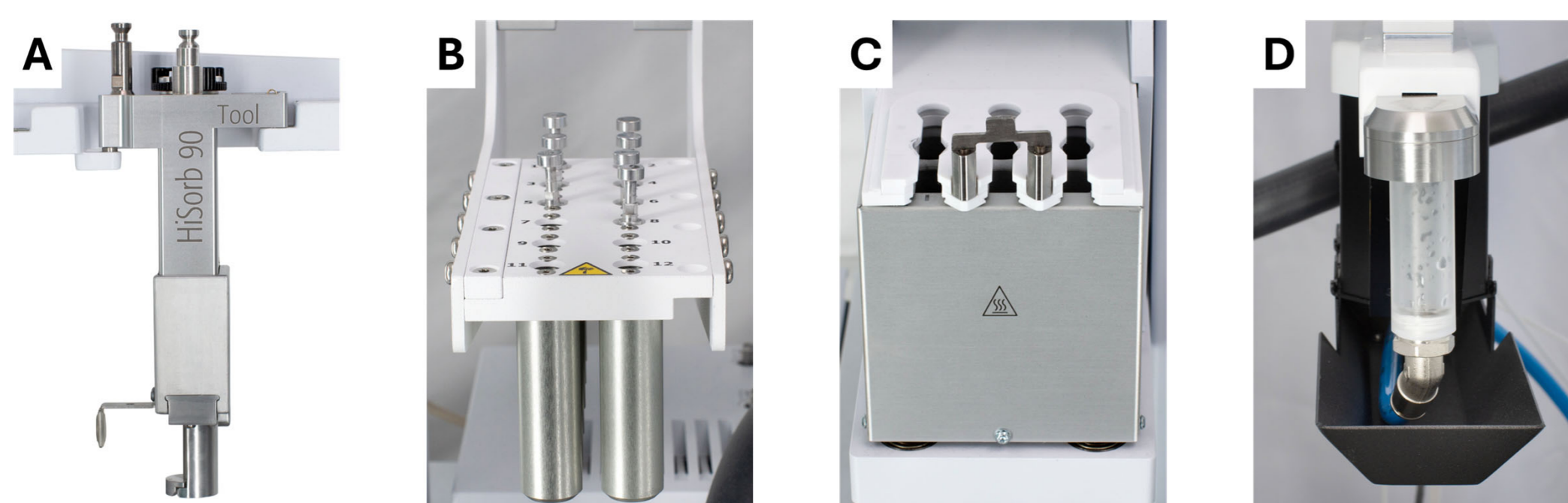


Figure 4: HiSorb 90 tool (A), rail-mounted HiSorb storage tray (B), standard agitator with HiSorb lid (C) and rail-mounted HiSorb wash/dry station (D) used for HiSorb automation on Centri 90.

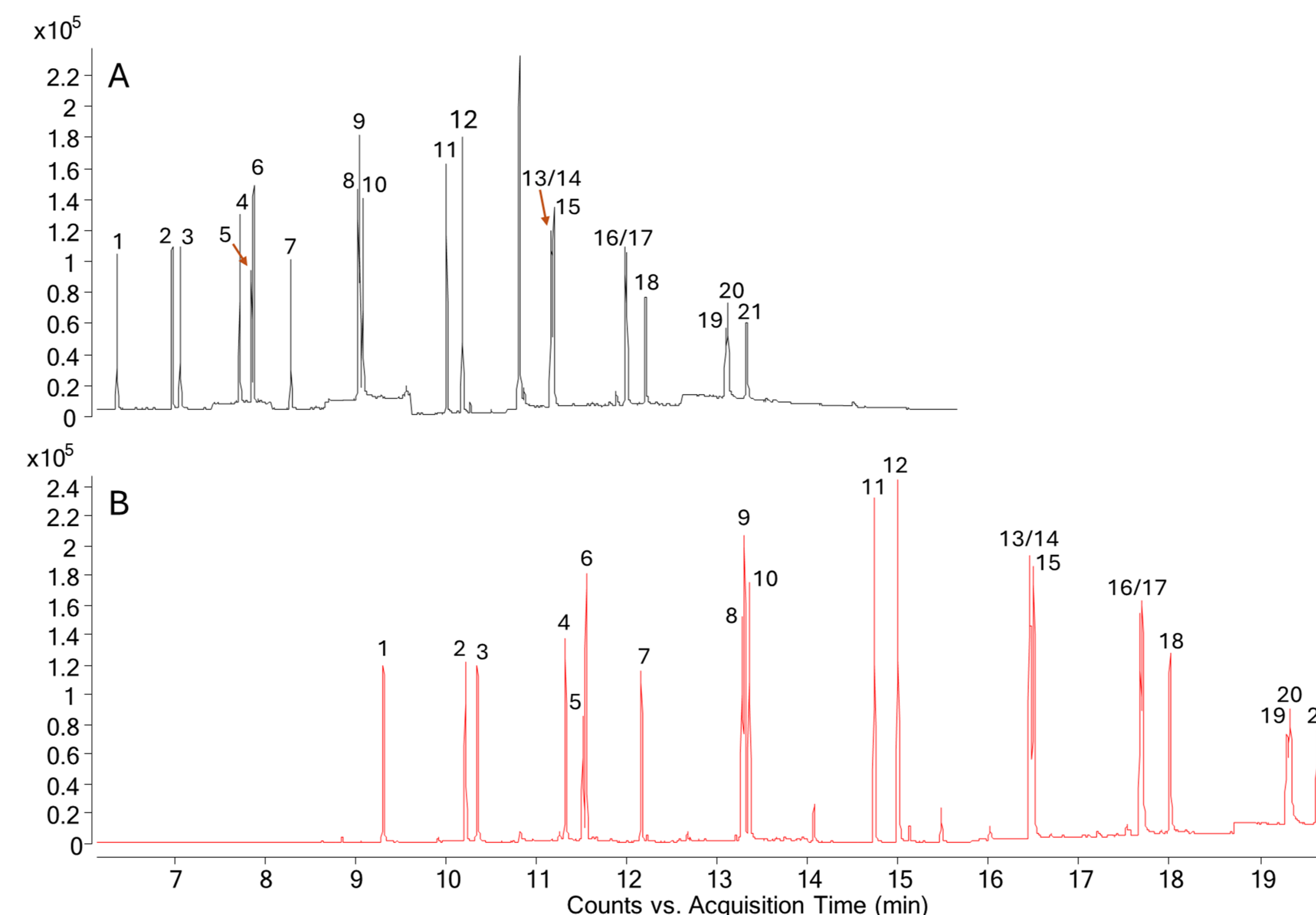


Figure 5: QR code for HiSorb automation video.

Results and discussions

Carrier gas comparison

Centri 90 is compatible with both helium and hydrogen carrier gas. Hydrogen carrier provides better resolution than helium, allowing for shorter run times without sacrificing chromatographic separation. We compared performance with both carrier gas options, finding a 33% reduction in GC run time with hydrogen (Figure 6).



#	Compound	#	Compound	#	Compound	#	Compound
1	Naphthalene	7	Fluorene	13	Benz[a]anthracene	19	Indeno[1,2,3-cd]pyrene
2	2-Methylnaphthalene	8	Phenanthrene-D10	14	Chrysene-D12	20	Dibenzo[a,h]anthracene
3	1-Methylnaphthalene	9	Phenanthrene	15	Chrysene	21	Benzo[ghi]perylene
4	Acenaphthylene	10	Anthracene	16	Benzo[b]fluoranthene		
5	Acenaphthene-D10	11	Fluoranthene	17	Benzo[k]fluoranthene		
6	Acenaphthene	12	Pyrene	18	Benzo[a]pyrene		

Figure 6: Total ion chromatograms (TICs) produced for a HiSorb extraction of PAHs at 100 ng/L in HPLC-grade water using hydrogen (A) or helium (B) carrier gas. Compounds in italics are internal standards.

Analyte separation

PAH standards are characterised by so-called "critical pairs", that are challenging to resolve. We achieved good resolution of all target compounds, with clear separation of peak apices even for the closest-eluting critical pair (Figure 7), allowing accurate integration.

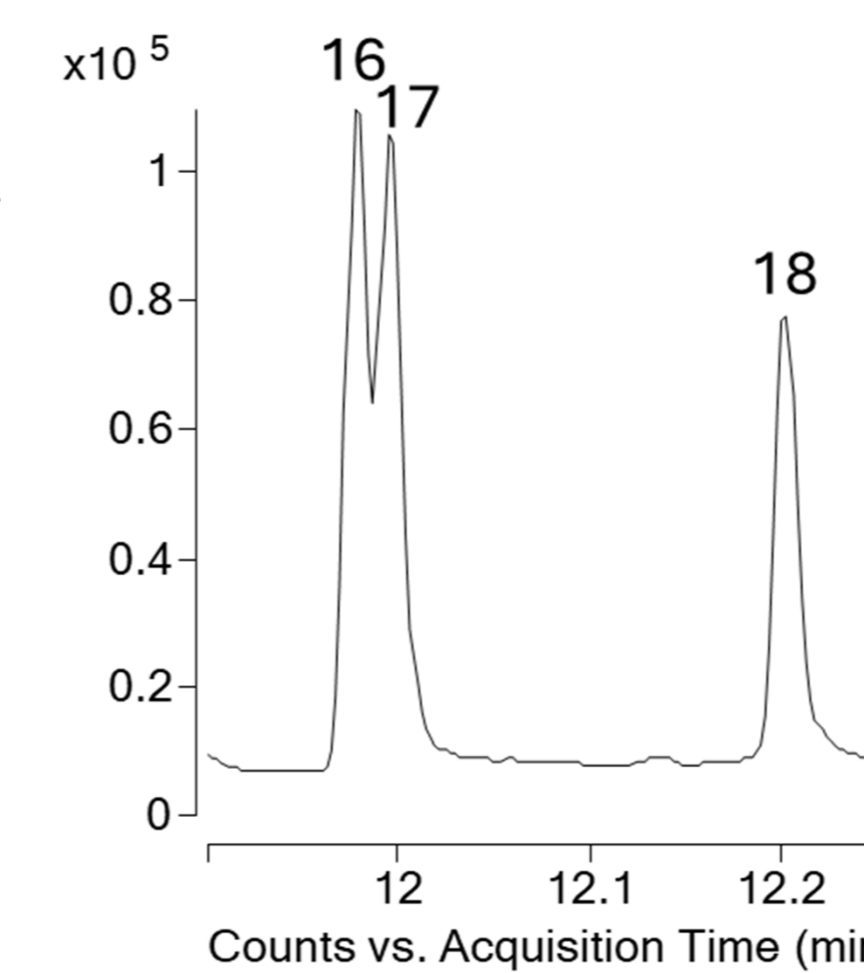


Figure 7: Zoom of Figure 6A highlighting separation of benzo[b]fluoranthene (16) and benzo[k]fluoranthene (17).

Method validation

Table 1: Method validation results for HiSorb extraction of PAHs in water.

Characteristic	Metric / unit	Mean	Min	Max	Benzo[a]pyrene
Linearity (8-point)	r2	0.9960	0.9985	1.000	0.9997
Reproducibility (n = 10)	RSD, %	4.18	1.73	9.17	4.93
Desorption efficiency	Carryover, %	1.36	0.34	4.13	1.25
Sensitivity	LOD, ng/L	0.97	0.49	1.66	0.80
	LOQ, ng/L	3.21	1.64	5.52	2.66

Method validation results (Table 1) showed excellent linearity and reproducibility, with minimal carryover even of the least volatile PAHs. Limits of detection (LOD) and quantitation (LOQ) indicated excellent sensitivity. Benzo[a]pyrene is particularly carcinogenic. We confirmed excellent performance for benzo[a]pyrene, including an LOQ well below the 10 ng/L EU drinking water limit (Table 1), hence the method is suitable for regulatory compliance screening.

Water samples

The HiSorb method was applied to four water samples (Table 2), all collected from Wales, UK.

Table 2: Water samples used in this study.

Sample	Description	Appearance
A	Tap water, labelled suitable for drinking	Colourless, no particulates
B	Water from same source as sample A after passing through a kitchen water purifier	Colourless, no particulates
C	Lake in industrial estate	Faintly yellow, few small particulates
D	Lake in semi-rural area	Faintly yellow, few small particulates

Water sample results are given in Figure 8 and summarised here.

- Tap water (A) contained high levels of phenanthrene (54 ng/L) and fluoranthene (21 ng/L).
- These were effectively filtered out by the water purifier such that the filtered water (B) contained no PAHs at quantifiable levels (orange line).
- That PAH levels were higher in the industrial lake water (C) than the semi-rural lake water (D) suggests a degree of industrial contamination affecting the former.
- PAH levels in neither lake water sample approached the high levels of seen in the tap water, suggesting tap water contamination does not come from local natural waterways.
- No sample had significant levels of the particularly carcinogenic benzo[a]pyrene.

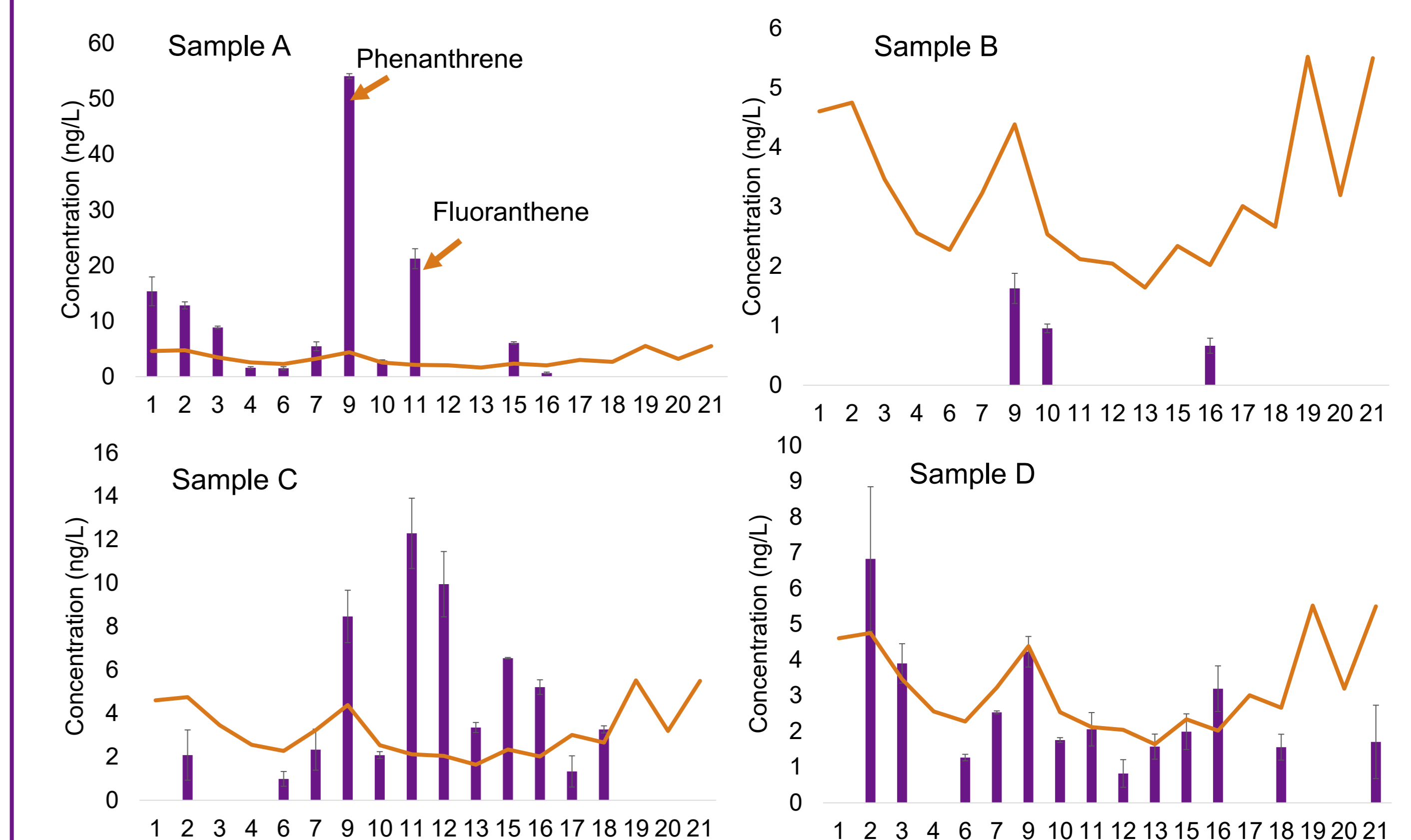


Figure 8: PAH levels in 4 water samples. Orange lines indicate LOQ for each compound. Error bars are standard deviations (n = 3). Compound identifications are given in Figure 6.

Conclusions

- We have developed a, highly-sensitive and solvent free method for the analysis of PAHs in water using HiSorb high-capacity sorptive extraction probes with GC-MS.
- Simple sample preparation and full Centri automation contributed to high throughput.
- Hydrogen carrier gas enabled shorter GC runs without sacrificing chromatographic separation.
- Limits of quantitation were below 6 parts per trillion for all compounds, with validation data showing excellent reproducibility and linearity metrics with no significant carryover.
- Analysis of real water samples demonstrated the applicability of the method to a range of water matrices.

References

- [1] M. A. Mallah et al., Chemosphere 2022, 133948. [2] Directive (EU) 2020/2184. 2020. [3] A. Mojiri et al., Sci. Total Environ. 2019, 133971.