



Application Note 291

A straightforward method for the analysis of PAHs in water by high-capacity sorptive extraction and TD-GC-MS

Regulatory limits on the levels of polycyclic aromatic hydrocarbons (PAHs) in water demand highly sensitive and rapid analytical methods. In this application note, we describe the use of HiSorb high-capacity sorptive extraction probes, in combination with Centri 90 preconcentration trapping technology, to detect PAHs at low-ppt concentrations in various water samples, with excellent reproducibility and quantitative analysis up to 300 ppt. The method is fully automated, with parallel processing of samples to ensure high throughput, and with hydrogen carrier gas chosen in this case to keep GC run times as short as possible.

Introduction

PAHs are semi-volatile organic compounds (SVOCs) with toxic, genotoxic and carcinogenic properties¹ that are emitted into the atmosphere by human activities such as fossil fuel combustion and vehicle emissions, as well as by natural events such as forest fires or volcanic eruptions. Once in the air they enter waterways via deposition and rainfall runoff and then persist there. Waterborne PAHs therefore pose a long-term environmental hazard, as well as a risk to human health should they enter drinking water supplies.² As such, levels of PAHs in both environmental and drinking waters are monitored and regulated across the globe. For example, the EU directive 2020/2184 stipulates a maximum of 100 ng/L for the sum of several PAHs in drinking water, and 10 ng/L for the particularly carcinogenic PAH benzo[a]pyrene.³

There is therefore a need for analytical methods that are sensitive enough to detect PAHs in water at these low concentrations and also rapid enough to handle large numbers of samples efficiently. Small sample volumes are also beneficial, as this reduces the costs associated with sample transport and storage. Liquid/liquid extraction (LLE) coupled with gas chromatography-mass spectrometry (GC-MS) is commonly used to analyse PAHs, but this methodology involves a multi-step, manual sample preparation stage, reducing throughput and increasing the risk of operator error. It also generates large volumes of solvent waste that are costly to dispose of and that may cause environmental harm.⁴

Here, a straightforward, fully automated method for PAH analysis using HiSorb high-capacity sorptive extraction probes (Figure 1) is described. Due to their robust design, HiSorb probes are well-suited for direct immersion into the water

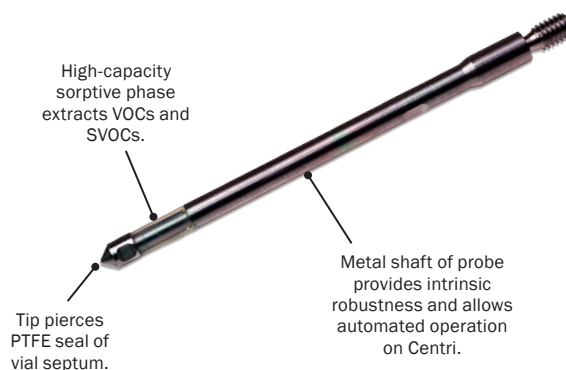


Figure 1: HiSorb probe.

matrix, allowing for efficient transfer even of large, high-boiling PAHs to the sorptive phase. Subsequent heating of the probes then releases analytes, and in this case the probes were thermally desorbed in a Centri 90 unit (Figure 2), with analytes swept onto an electrically-cooled focusing trap packed with a sorbent combination specially suited for SVOCs like PAHs. Subsequent rapid heating of the trap (up to 100°C/s) in a reverse flow of carrier gas ensures analytes are transferred to the GC column in a narrow band of vapour, producing sharp peaks that improve limits of detection (LODs) and quantitation (LOQs).

Coupling HiSorb with Centri allows the workflow to be fully automated, with no user intervention required from the moment samples are loaded onto the sample tray (Figure 3). Compatibility with hydrogen carrier gas ensures short GC

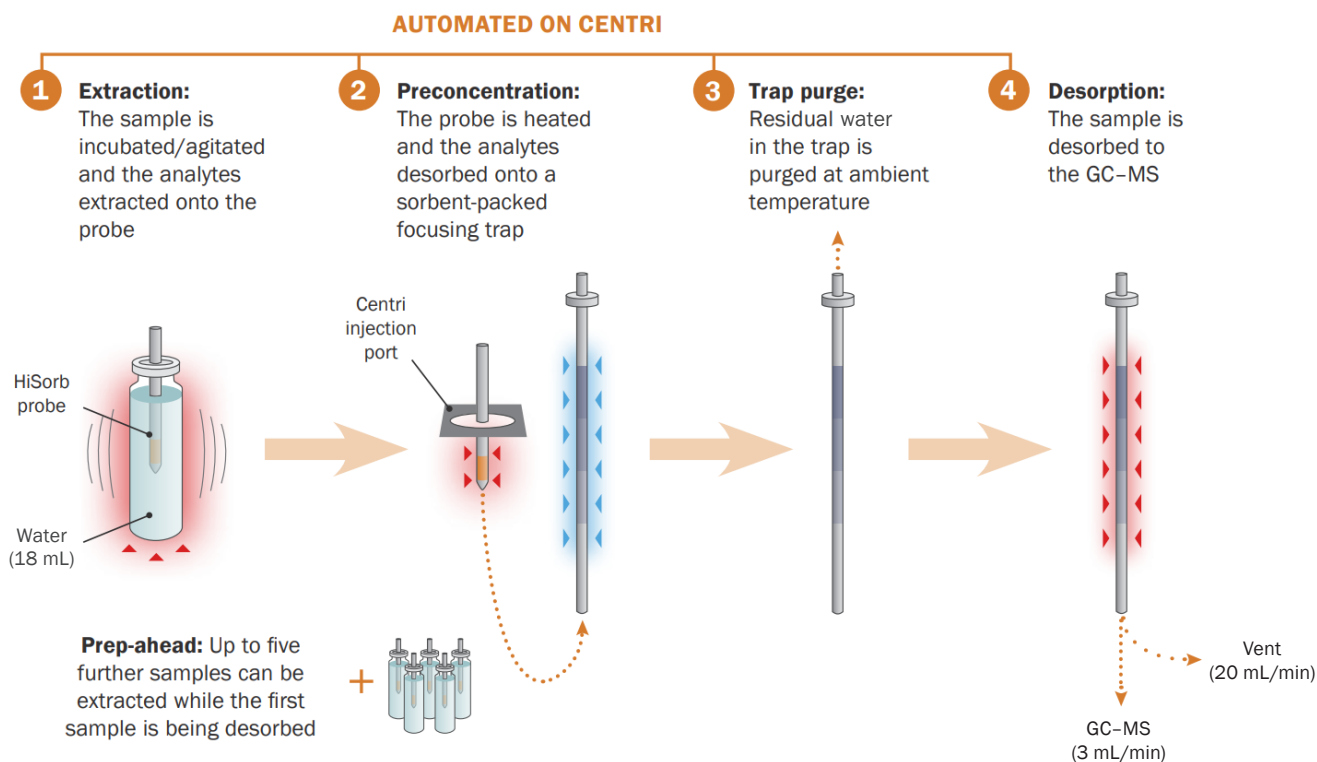


Figure 2: Workflow for PAH analysis on Centri.

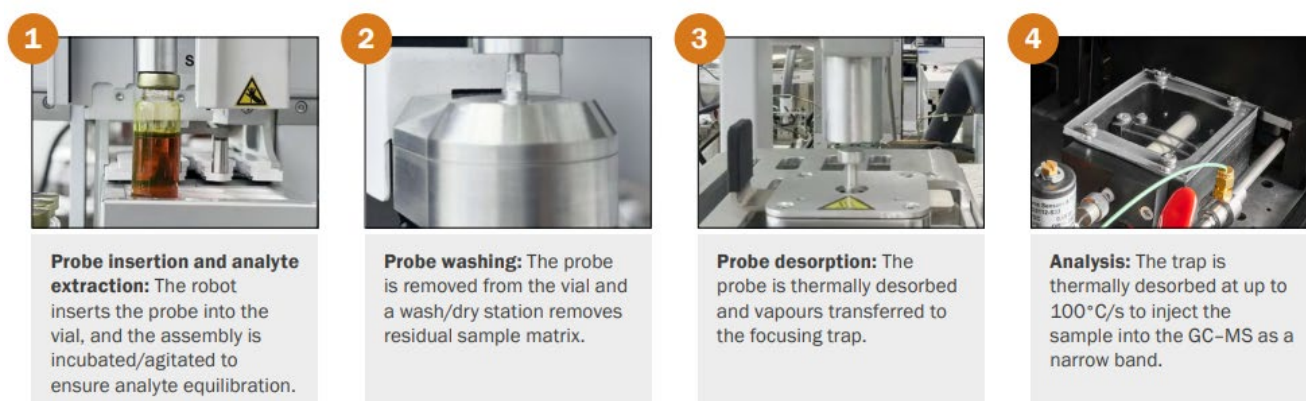


Figure 3: HiSorb automation on Centri 90. To see HiSorb automation in motion, please see ref. 5.

cycle times, while sample overlap, in which multiple samples are extracted simultaneously, minimises GC downtime. Therefore, the HiSorb–Centri method is straightforward, requiring very little sample preparation, generates no solvent waste, and is rapid enough to be readily applied to large sample batches.

In this report, the method is shown to be linear, reproducible and highly sensitive, with LODs well below regulatory requirements. Use of the method on both drinking water and environmental waters demonstrates applicability to a wide range of real-life water matrices.

Experimental

Preparation of laboratory standards

Laboratory standards for method development and validation were prepared by combining a mix of 18 PAHs (Table 1) with HPLC-grade water in industry-standard 20 mL headspace vials for a final concentration of 1–300 ng/L per PAH. An internal standard (IS) mix containing three deuterated PAHs (Table 1, *italic text*) was also added to achieve a final concentration of 100 ng/L each. Blanks comprised only HPLC-grade water and IS. In all cases, final volumes were 18 mL. After addition of all components, vials were crimp-capped and added to the Centri sample tray.

No.	Compound	Internal standard no.	B.p. (°C)	RT in helium (min)	RT in hydrogen (min)	Quant ion	Qualifier ion
1	Naphthalene	5	218	9.29	6.34	128	64
2	2-Methylnaphthalene	5	242	10.20	6.96	142	115
3	1-Methylnaphthalene	5	242	10.33	7.04	142	115
4	Acenaphthylene	5	280	11.32	7.70	152	76
IS1	Acenaphthene-D ₁₀	—	279	11.50	7.83	164	80
5	Acenaphthene	5	279	11.54	7.85	153	76
6	Fluorene	8	295	12.15	8.27	166	82
IS2	Phenanthrene-D ₁₀	—	340	13.27	9.02	188	94
7	Phenanthrene	8	340	13.29	9.03	178	76
8	Anthracene	8	340	13.34	9.07	178	89
9	Fluoranthene	8	375	14.73	10.00	202	101
10	Pyrene	14	404	14.99	10.17	202	101
11	Benz[a]anthracene	14	438	16.44	11.15	228	114
IS3	Chrysene-D ₁₂	—	448	16.46	11.16	240	120
12	Chrysene	14	448	16.50	11.18	228	114
13	Benzo[b]fluoranthene	14	481	17.68	11.97	252	126
14	Benzo[k]fluoranthene	14	480	17.70	11.99	252	126
15	Benzo[a]pyrene	14	495	18.00	12.20	252	126
16	Indeno[1,2,3-cd]pyrene	14	536	19.30	13.09	276	138
17	Dibenzo[a,h]anthracene	14	524	19.33	13.12	278	139
18	Benzo[ghi]perylene	14	550	19.64	13.33	276	138

Table 1: Target compounds. IS = Internal standard. RT = Retention time.

Preparation of water samples

The four water samples (Table 2) were all collected from South Wales, UK. Sample water and the IS mix were combined in 20 mL headspace vials to a final volume of 18 mL.

Sample extraction

Platform: Centri 90
 HiSorb probe: PDMS, standard length (part number H1-DXAAC-06)
 Sample equilibration: 1 min at 65°C, 500 rpm
 Sample extraction: 2 h at 65°C, 500 rpm

Thermal desorption

Probe desorption: 20 min at 300°C, 100 mL/min
 Flow path: 250°C
 Focusing trap: 'PAH/SVOC' (part number U-T19PAH-2S)
 Trap low: -25°C
 Trap purge: 1 min at 25°C, 50 mL/min
 Trap desorption: Max heating rate to 380°C, 10 min (helium) or 7 min (hydrogen)
 Split flow: 20 mL/min (7.6:1 split ratio)

GC-MS

GC inlet: 300°C
 Column: 5-MS, 30 m × 0.25 mm, 0.25 µm
 Carrier gas: Helium or hydrogen
 Oven programme: Helium: 50°C (5 min), 20°C/min to 310°C (5 min)
 Hydrogen: 50°C (3.5 min), 30°C/min to 310°C (3.5 min)
 Column flow: 3 mL/min
 MS transfer line: 300°C
 Detection: Selected ion mass (SIM) mode using quant and qualifier ions (see Table 1).

Sample	Description	Appearance
A	Drinking water from an indoor tap	Colourless, no particulates
B	As for sample A, after passing through a kitchen water purifier	Colourless, no particulates
C	Lake water from an industrial area	Faintly yellow, a few small particulates
D	Lake water from a semi-rural area	Faintly yellow, a few small particulates

Table 2: Water samples studied.

Results and discussion

Method development

The high boiling point of some PAHs (Table 1) could lead to poor desorption efficiency from the trap or probe, as well as condensation within the analytical flow path, leading to carryover and poor recovery. Method parameters were therefore selected to minimise these issues, drawing on previous work analysing PAHs in air.^{6,7} The Centri flow path was heated to 250°C to prevent analyte condensation, and various probe desorption times and temperatures were tried, in order to identify parameters that did not cause significant carryover. Cooling the trap to sub-zero temperatures during probe desorption helped focus PAHs at the front of the trap, ensuring efficient transfer during subsequent trap desorption. Consequently, carryover on the trap, injector (to account for the full flow path) and probe were all found to be minimal (Table 3).

Compound	Carryover (%)		
	Trap	Injector	Probe
Naphthalene	3.24	1.54	1.79
2-Methylnaphthalene	0.79	0.50	0.90
1-Methylnaphthalene	0.45	0.25	0.82
Acenaphthylene	0.06	0.21	0.31
Acenaphthene	0.13	0.15	0.34
Fluorene	0.50	0.58	0.66
Phenanthrene	0.41	1.01	1.31
Anthracene	0.34	0.27	0.32
Fluoranthene	0.20	0.56	0.86
Pyrene	0.19	0.59	0.95
Benz[a]anthracene	0.18	0.49	0.65
Chrysene	0.27	0.56	0.85
Benzo[b]fluoranthene	0.19	1.34	1.41
Benzo[k]fluoranthene	0.23	1.28	1.56
Benzo[a]pyrene	0.34	0.74	1.25
Indeno[1,2,3-cd]pyrene	0.34	1.24	3.15
Dibenzo[a,h]anthracene	0.51	1.52	3.20
Benzo[ghi]perylene	0.45	1.26	4.13
Mean	0.49	0.78	1.36

Table 3: Carryover determined as peak area from a trap, injector or probe blank as a percentage of the peak area from a 300 ng/L laboratory standard.

Chromatography

Centri 90 is independently certified as safe for use with hydrogen as the GC carrier gas. Hydrogen is less costly to acquire than helium, can be produced via a generator (avoiding the inconvenience and potential downtime associated with changing cylinders), and allows for shorter GC run times without sacrificing analyte resolution, potentially enhancing sample throughput.⁸

Chromatographic performance with helium and hydrogen carrier gas was therefore compared, with adjustments made to the GC programme to ensure faster elution of compounds with the latter (see Experimental). Trap desorption time was also reduced to take advantage of more efficient desorption in hydrogen.⁸ The result was that elution of all target analytes was achieved within 13.5 min with hydrogen, compared with 21 min with helium (Figure 4) – a reduction of approximately 35%.

PAH chromatography is characterised by critical pairs – compounds that elute very close together and have the same quant ion (Table 1), making them potentially difficult to distinguish.⁹ Here, all compounds were chromatographically resolved, with both helium and hydrogen carrier gas providing clear separation of peak apices even for the closest-eluting critical pair, benzo[b]fluoranthene and benzo[k]fluoranthene (Figure 5), so that accurate integration could be achieved. Therefore, hydrogen carrier gas allowed GC run times to be reduced without sacrificing analyte separation.

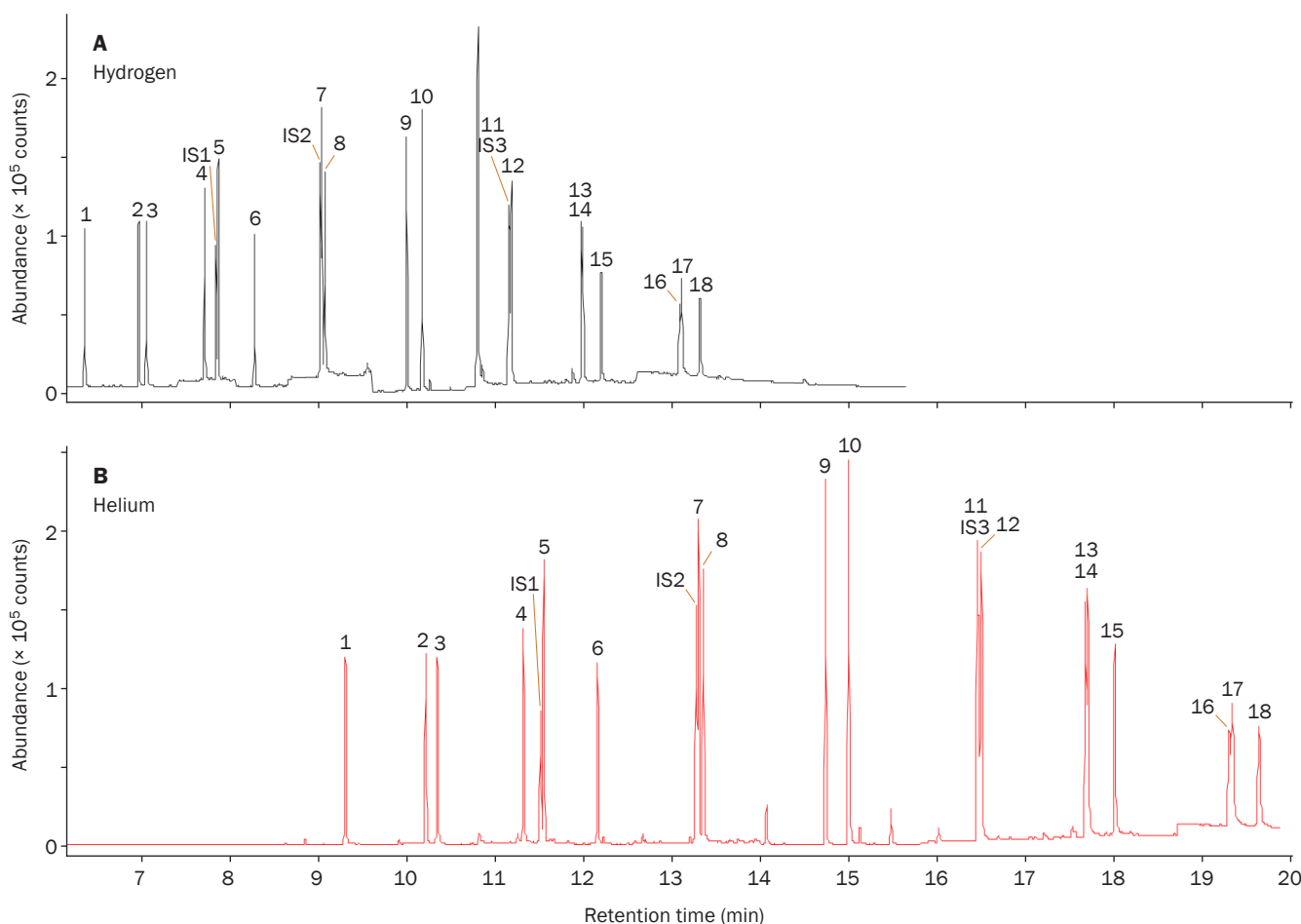


Figure 4: HiSorb analysis of PAHs (Table 1) at 100 ng/L using (A) hydrogen or (B) helium as the GC carrier gas. Peak identities are listed in Table 1.

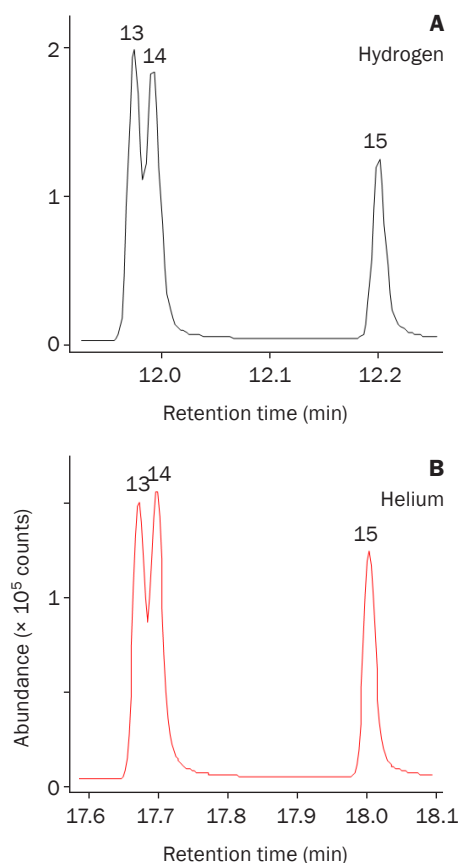


Figure 5: Benzo[b]fluoranthene (peak 13), benzo[k]fluoranthene (peak 14) and benzo[a]pyrene (peak 15), analysed with (A) hydrogen and (B) helium as the GC carrier gas, showing apex separation of peaks 13 and 14, the closest-eluting critical pair.

Method validation

Subsequent method validation work used hydrogen carrier gas. IS-corrected peak areas for the 18 target compounds (Table 1) were used for all metrics. Linearity was assessed from 1 to 300 ng/L over an 8-point calibration, with correlation coefficients (r^2) being above 0.998 for all compounds, with a mean of 0.9996 (Table 4). Reproducibility was taken as the relative standard deviation (RSD) of 10 replicates at 50 ng/L, with RSD below 10% for all compounds (Table 4). This compares favourably with other sorptive extraction methods from water, which often struggle to achieve RSDs below 10% for late-eluting PAHs.^{10,11}

Sensitivity was determined from 12 replicates at 5 ng/L. The standard deviation of these replicates was compared to a calibration curve to determine an equivalent concentration in ng/L, and this value was multiplied by 3 to give the LOD and by 10 to give the LOQ. LOQs for all compounds were below 6 ng/L, indicating excellent sensitivity (Table 4). Crucially, the LOQ for benzo[a]pyrene (2.66 ng/L) was well below the 10 ng/L maximum permitted in drinking water by EU directive 2020/2184,³ making the HiSorb method suitable for regulatory compliance testing.

Compound	r^2	RSD (%)	LOD (ng/L)	LOQ (ng/L)
Naphthalene	0.9999	3.92	1.38	4.60
2-Methylnaphthalene	0.9999	4.65	1.43	4.75
1-Methylnaphthalene	0.9999	3.32	1.04	3.46
Acenaphthylene	0.9995	3.77	0.77	2.56
Acenaphthene	0.9998	2.76	0.68	2.28
Fluorene	0.9999	4.14	0.97	3.23
Phenanthrene	1.0000	0.62	1.32	4.39
Anthracene	1.0000	1.74	0.76	2.54
Fluoranthene	0.9998	2.88	0.64	2.12
Pyrene	0.9998	2.80	0.61	2.04
Benz[a]anthracene	1.0000	1.73	0.49	1.64
Chrysene	1.0000	2.05	0.70	2.34
Benzo[b]fluoranthene	0.9994	5.28	0.61	2.02
Benzo[k]fluoranthene	0.9996	5.24	0.90	3.01
Benzo[a]pyrene	0.9997	4.93	0.80	2.66
Indeno[1,2,3-cd]pyrene	0.9985	7.90	1.66	5.52
Dibenzo[a,h]anthracene	0.9988	8.28	0.96	3.20
Benzo[ghi]perylene	0.9987	9.17	1.65	5.50
Mean	0.9996	4.18	0.97	3.21

Table 4: Performance metrics for HiSorb extraction of PAHs from water.

Water samples

The four water samples listed in Table 2 were analysed (Figures 6 and 7), with concentrations being determined by comparing IS-corrected peak areas to a calibration curve. Target PAHs were considered present at known concentration if their calculated concentrations exceeded the LOQ, and were considered present at trace levels if their calculated concentrations were lower than the LOQ but higher than the LOD.

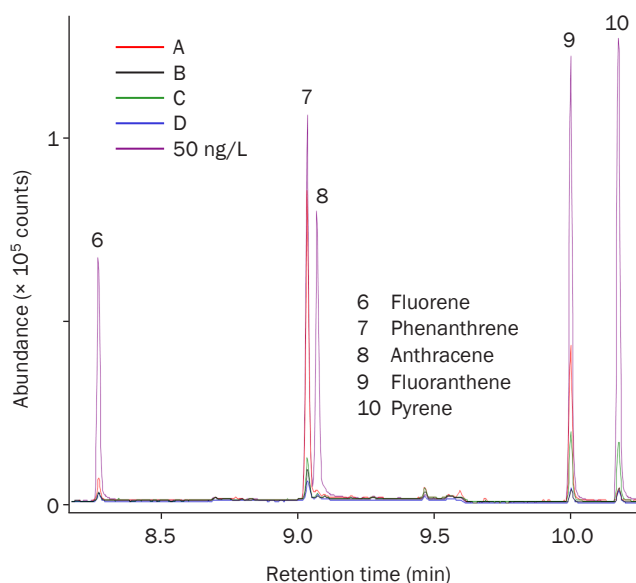


Figure 6: HiSorb extraction results for the four water samples (A to D) and HPLC-grade water with PAHs added to 50 ng/L.

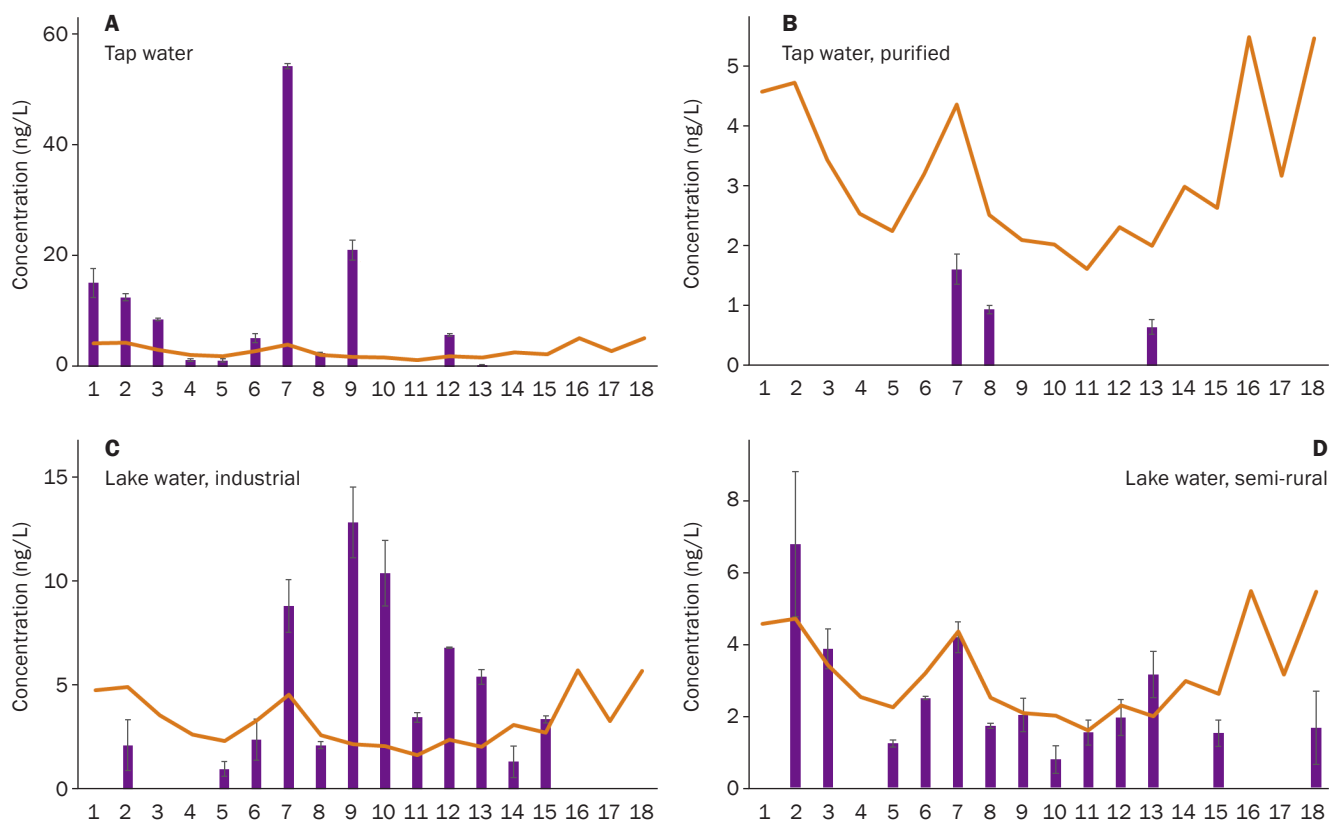


Figure 7: PAH levels in four water samples. Orange lines indicate the LOQ for each compound. Compounds detected below the LOQ cannot be formally quantified and are said to be present at trace levels. Error bars are standard deviations ($n = 3$). Compound identities are given in Table 1.

The tap water (sample A) showed surprisingly high levels of phenanthrene (54 ng/L) and fluoranthene (21 ng/L), with several other PAHs also surpassing the LOQ. However, none of the compounds regulated by the EU were present above trace levels, indicating this water remained safe to drink by the standards of the EU directive. High levels of phenanthrene could potentially interfere with quantitation of its critical pair partner, anthracene, but the chromatographic separation achieved between these two compounds allowed them to be easily distinguished into two clear peaks (Figure 6). Therefore, while phenanthrene levels were high in tap water, anthracene levels were confidently determined to be below quantifiable levels. When water from the same tap was passed through a kitchen water purifier, only trace amounts of PAHs remained (Figure 7). The manufacturer describes the purifier as containing a UV lamp and “multi-stage carbon filtration”, and it’s likely that this carbon filter is responsible for removing PAHs from the tap water.

Comparison of the two lake water samples (samples C and D) showed that, while both contained several PAHs at detectable levels, only two compounds exceeded the LOQ in sample D, while seven did in sample C (Figure 7). Sample C was collected from a lake abutting an industrial estate, and it’s possible that PAH run-off from local industrial activities may contribute to PAH contamination. In contrast, sample D was collected from a lake in a semi-rural area with minimal industrial activity in the immediate surroundings.

Though sample C contained more PAHs than sample D, neither sample approached the levels of phenanthrene or fluoranthene in the tap water (sample A). This suggests that the PAHs in the tap water did not come from local natural waterways but rather were introduced at some point during the water treatment process.

Conclusion

This application note describes 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 automation on the Centri platform contributed to high throughput, while hydrogen carrier gas enabled shorter GC runs without sacrificing chromatographic separation, even enabling good separation of critical pairs to be achieved.

Some PAHs can be challenging to analyse due to their low volatility, but our validation data shows excellent reproducibility and linearity metrics and no significant carryover, even for the least volatile compounds. Limits of quantitation were below 6 ng/L (6 ppt) for all of 18 target PAHs, with the LOQ for the particularly carcinogenic compound benzo[a]pyrene being well below regulatory requirements.

This work has explored the use of immersive HiSorb for the analysis of PAHs in various water samples; however, there is scope for the method to be applied to other aqueous

matrices, such as beverages. For example, alcoholic beverages aged in wood-fired barrels often acquire PAH contamination from the wood.¹² Immersive HiSorb, automated on Centri, could provide a sensitive, high-throughput method for the quantitation of PAHs in such drinks.

References

1. M. A. Mallah et al., Polycyclic aromatic hydrocarbon and its effects on human health: An overview, *Chemosphere*, 2022, 296: 133948, <https://doi.org/10.1016/j.chemosphere.2022.133948>.
2. A. Mojiri, J.L. Zhou, A. Ohashi, N. Ozaki and T. Kindaichi, Comprehensive review of polycyclic aromatic hydrocarbons in water sources, their effects and treatments, *Science of the Total Environment*, 2019, 696: 133971, <https://doi.org/10.1016/j.scitotenv.2019.133971>.
3. Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption, European Union, 2020, <http://data.europa.eu/eli/dir/2020/2184/oj>.
4. Z.A. Temerdashev, T.N. Musorina, T.A. Chervonnaya and Z.V. Arutyunyan, Possibilities and limitations of solid-phase and liquid extraction for the determination of polycyclic aromatic hydrocarbons in environmental samples, *Journal of Analytical Chemistry*, 2021, 76: 1357–1370, <https://doi.org/10.1134/S1061934821120133>.
5. HiSorb automation [video], Markes International, <https://youtu.be/8UeBsEepGEk>.
6. Markes Application Note 115: Simple and reliable quantitation of ppt-level PAHs in air by TD–GC–MS, <https://markes.com/content-hub/application-notes/application-note-115>.
7. Markes Application Note 139: High-performance analysis of polycyclic aromatic hydrocarbons (PAHs) by TD–GC–MS: Method validation and case-study, <https://markes.com/content-hub/application-notes/application-note-139>.
8. Markes Application Note 156: Using hydrogen carrier gas to enhance TD–GC–MS methods for semi-volatile organic compounds (SVOCs) in air: An illustration with polyaromatic hydrocarbons (PAHs), <https://markes.com/content-hub/application-notes/application-note-156>.
9. S.A. Wise, L.C. Sander and M.M. Schantz, Analytical methods for determination of polycyclic aromatic hydrocarbons (PAHs) – A historical perspective on the 16 U.S. EPA priority pollutant PAHs, *Polycyclic Aromatic Compounds*, 2015, 35: 187–247, <https://doi.org/10.1080/10406638.2014.970291>.
10. W.J. Havenga and E.R. Rohwer, The use of SPME and GC-MS for the chemical characterisation and assessment of PAH pollution in aqueous environmental samples, *International Journal of Environmental Analytical Chemistry*, 2000, 78: 205–221, <https://doi.org/10.1080/03067310008041342>.
11. A. Kremser, M.A. Jochmann and T.C. Schmidt, PAL SPME Arrow – Evaluation of a novel solid-phase microextraction device for freely dissolved PAHs in water, *Analytical and Bioanalytical Chemistry*, 2016, 408: 953–952, <https://doi.org/10.1007/s00216-015-9187-z>.
12. L. King, R. Aplin, C. Gill and T. Naimi, A state-of-the-science review of alcoholic beverages and polycyclic aromatic hydrocarbons, *Environmental Health Perspectives*, 2024, 132: 016001, <https://doi.org/10.1289/EHP13506>.

Centri® and HiSorb™ are trademarks of Markes International.

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.