

Fast, high sensitivity analysis of chlorophenols and common odorants to assess water quality by HiSorb™ TD-GC-MS

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Introduction

Chlorophenols are an important class of volatile organic compounds (VOCs) to monitor in water. At low levels they can negatively affect human health, harm aquatic wildlife and impart antiseptic-like tastes or odours that consumers find unpleasant.

They are used as disinfectants, pesticides and in industry as intermediates. Pentachlorophenol (5CP) and, to a lesser extent, 2,3,4,5-tetrachlorophenol (4CP) are widely used as wood preservatives for outdoor fixtures such as telegraph poles, fence posts and garden furniture¹ that can wash off and enter water streams. 5CP can break down in the environment, especially in the presence of microorganisms, losing chlorine atoms to give tetra- and trichlorophenols².

As a result, chlorophenols are regulated globally by the US Environmental Protection Agency (EPA), the Korean Ministry of Environment and the European Commission, with the EPA stipulating a limit of 1 µg/L for 5CP in drinking water³. Standard methods for detecting chlorophenols including ISO 8615-2:1999 and US EPA method 604 specify liquid-liquid extraction with derivatization. These methods are manual, generate a lot of solvent waste and use harmful derivatising agents.

In addition to chlorophenols, many other odorants commonly affect drinking and environmental waters, including methoxy-pyrazines, halogenated anisoles and some terpenes, e.g., geosmin and 2-methylisoborneol, naturally produced by microorganisms in the water. These compounds have extremely low human odour threshold limits - in the region of 1 to 10 ng/L⁴.

In this poster we demonstrate a faster and simpler solvent-free sample extraction method using HiSorb™ with thermal desorption (TD) analysis. Target chlorophenols and common odorants were analysed in a single GC run while achieving excellent sensitivity, detecting down to trace concentration levels as low as 2 ng/L. The method was also applied to five real-world samples to determine levels of odorants in different water sources.

Experimental

HiSorb, high-capacity sorptive extraction

Like solid-phase microextraction (SPME) but with up to 100x more phase, HiSorb extracts analytes by absorptive and/or adsorptive phases supported on a robust metal-core probe (Fig. 2). This larger phase capacity means more of each analyte can be extracted from a sample, either by headspace or immersive extraction. Compared with current techniques that are used for this application, Key advantages of using HiSorb for this application are compared with existing technique in Table 1.

As well as pure poly(dimethylsiloxane), PDMS, multi-phase HiSorb probes were also evaluated to understand how more adsorptive phases may further increase the detection limits achieved. These additional phases are carbon wide range (CWR) and divinylbenzene (DVB).

Capability	Technique		
	HiSorb	Liquid-liquid extraction	SPME
High capacity	✓	✗	✗
Solvent-free	✓	✗	✓
Headspace and immersive sampling	✓	✗	✓
Automatable	✓	✗	✓
Re-usable	✓	✗	✓
Prep-ahead	✓	✗	✗
Field sampling <i>in situ</i>	✓	✗	✓

Table 1: Comparison of extraction technique capabilities.

Standards and samples

A primary stock solution was prepared in methanol to a concentration of 10 mg/L (chlorophenols) or 1 mg/L (common odorants) and was stored at 4 °C. Ahead of each analytical batch, a secondary stock solution was freshly prepared from the primary stock by 1,000-fold dilution in HPLC-grade water. This secondary stock was used to generate calibration standards. Real-world samples were prepared in the same way, except that no standard mix was added. All samples were incubated at 45 °C with agitation speed 600 rpm for 1 hour.

Thermal desorption (TD) analysis

We used the Centri® 360 platform (Fig. 3) to fully automate all aspects of the sample extraction and concentration process, including injection to the GC-MS (Fig. 4). Manual, offline sampling using a benchtop agitator is possible, followed by TD-GC-MS analysis of HiSorb probes placed into empty TD tubes, for example, with the TD100-xr™ (Fig. 3).

Additional experimental conditions include:

TD:

- Probe desorption: 260 °C (15 min)
- Trap low: 30 °C
- Trap high: 320 °C (3 min)
- Split flow: 6 mL/min (4:1)

GC:

- Column: MEGA 5-MS 30 m x 0.25 mm x 0.25 µm
- Column flow: Helium, 2 mL/min
- Oven programme: 50 °C (5 mins), 10 °C/min to 280 °C (5 mins)



Figure 3: Markes' TD100-xr (top) and Centri 360 platform (bottom).

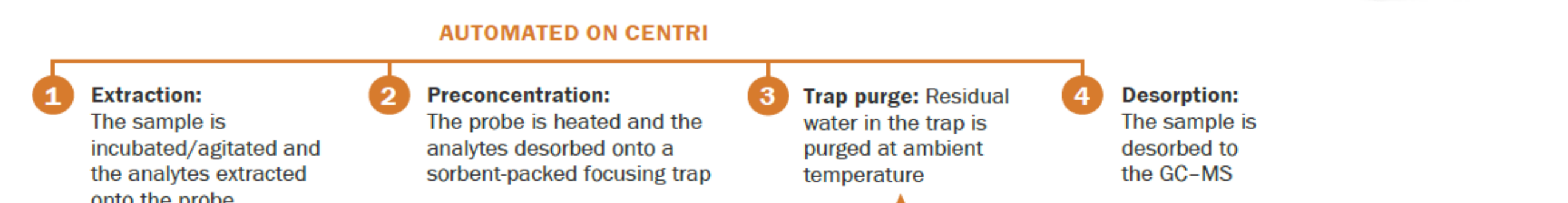


Figure 4: Schematic of the fully automated workflow available on Centri 360, from extraction to detection. Desorbed analytes are transferred to a backflush, cryogen-free, sorbent-packed focusing trap, where rapid trap heating (up to 100 °C/s) transfers analytes to the capillary column in a concentrated band of vapour.

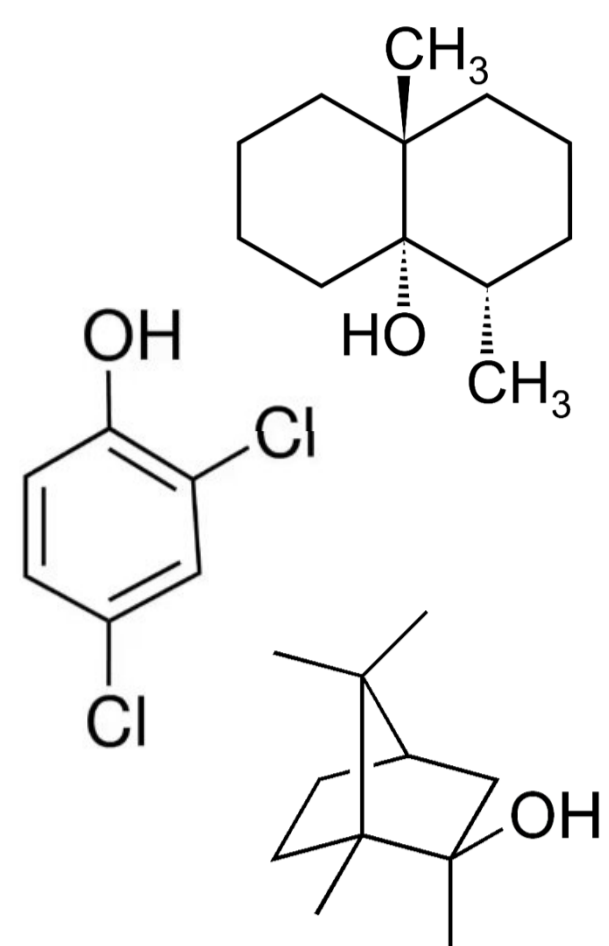


Figure 1: Three common odorants found in water sources, 2,4 dichlorophenol, geosmin and 2-methylisoborneol.

Results and discussion

Pure PDMS-only HiSorb

All compounds were successfully extracted with excellent linearity (>0.995) and reproducibility as relative standard deviation (RSD's) less than 10% (n=7, 200 ng/L (chlorophenols) or 20 ng/L (other odorants)).

#	Compound	R ²	Cal range (ng/L)	RSD (%)	LOD (ng/L)	LOQ (ng/L)
1	2-Chlorophenol	0.9995	20 – 1,500	3.15	5.12	17.07
2	2-Isopropyl-3-methoxypyrazine	0.9993	2 – 150	5.15	0.24	0.79
3	3-Chloroanisole	0.9998	2 – 150	4.33	0.21	0.7
4	4-Chloroanisole	0.9998	2 – 150	2.43	0.29	0.96
5	2-Chloroanisole	0.9999	2 – 150	1.57	0.18	0.59
6	2,4-Dichlorophenol	0.9999	20 – 1,500	2.1	2.73	9.1
7	2-Isobutyl-3-methoxypyrazine	0.9998	2 – 150	4.06	0.32	1.1
8	2-Methylisoborneol	0.9997	2 – 150	4.55	0.3	0.99
9	2,4,6-Trichloroanisole	0.9997	2 – 150	8.86	0.12	0.39
10	2,4,6-Trichlorophenol	0.9962	200 – 15,000	8.24	170	566
11	Geosmin	0.9996	2 – 150	6.55	0.51	1.7
12	2,3,4-Trichloroanisole	0.9998	2 – 150	3.42	0.24	0.8
13	2,3,4,6-Tetrachlorophenol	0.9986	200 – 15,000	8.35	352	1,173
14	2,4,6-Tribromoanisole	0.9996	2 – 150	6.11	0.38	1.28
15	Pentachlorophenol	0.9988	200 – 15,000	7.73	900	2,966

Table 2: Full compound list highlighting calibration ranges, linearity, reproducibility, LOD's and LOQ's for each compound using PDMS.

Assessing multi-phase HiSorb probes

DVB/CWR/PDMS was superior probe for most compounds, with a dramatic difference for chlorophenols. Peak areas were up to 73-fold higher for pentachlorophenol when using this probe vs. pure PDMS. With an additional adsorptive phase, compounds were more effectively extracted. The large surface area on the probe provides more available active sites to which more of each analyte can bind, leading to this increase in analyte response.

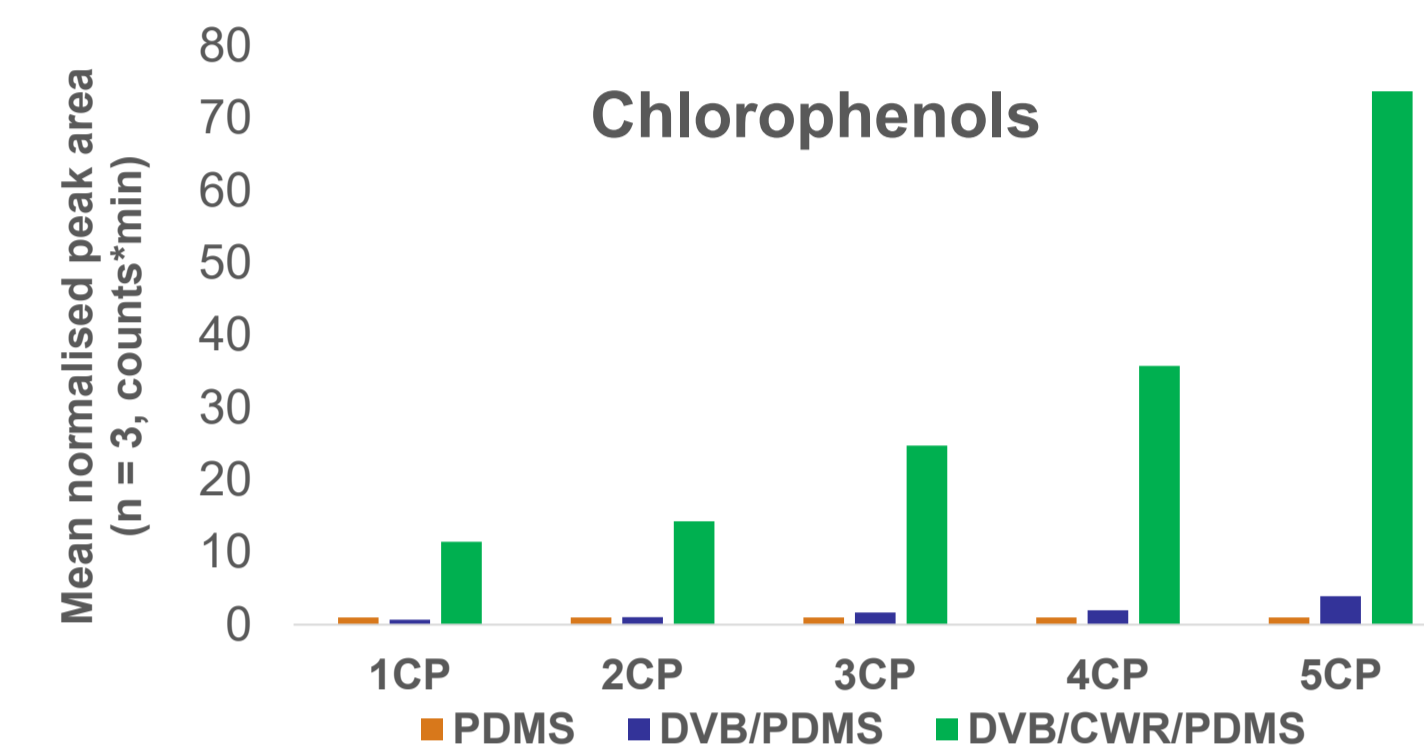


Figure 5: Bar charts of chlorophenols and other odorants analysed in HPLC grade water, with peak areas normalised to the peak area for PDMS.

Improved LOD and LOQ results

With the addition of multi-phases, because the peak response substantially improving for all compounds (Fig. 5) the LODs and LOQs for the chlorophenols were also drastically improved. The most significant change was noticed with 5CP and 4CP, where the LOD was reduced from 900 ng/L to 5.38 ng/L (167 times lower) and 352 ng/L to 8.76 ng/L (40 times lower) respectively. Therefore, due to this increase in sensitivity, the DVB/CWR/PDMS phase was further utilised for extraction of real-world samples.

Real-world samples

Five real-world samples (Table 3) were analysed in triplicate (n=3) with a 4th replicate spiked with analytes at 50 ng/L (chlorophenols) or 5 ng/L (others). These samples originated from different areas of the UK.

Geosmin was a pervasive odorant found in all samples except the branded bottled spring water (sample E). However, its levels were generally below the threshold for human detection (~ 10 ng/L).

2-Methylisoborneol was also detected at trace levels. Common odorants were mostly only detected in pond water (sample F), which was also the only sample type with a perceptible odour. It is likely that this odour was due to the chloroanisoles and methoxypyrazines, some of which have odour thresholds in the range of 0.1 – 4 ng/L.

Where chlorophenols were present, 5CP was the most abundant, with 4CP and 3CP present at decreased levels. 5CP is a common wood preservative and can degrade to 4CP and 3CP, especially in the presence of microbes. The likely source of chlorophenols is run-off of 5CP followed by degradation. 2-Chlorophenol, 2,4-dichlorophenol, 2,3,4-trichloroanisole and 2,4,6-tribromoanisole weren't detected in any sample.

Sample	Description
A	Soft tap water from site A
B	Hard Tap water from site B
C	Soft Tap water from site C
D	Raw spring water from site C's source
E	Branded bottled spring water
F	Water from a garden pond
G	Water from lake G
H	Water from lake H
I	Freshly collected rainwater

Table 3: Descriptions of all samples analysed, categorised A-I.

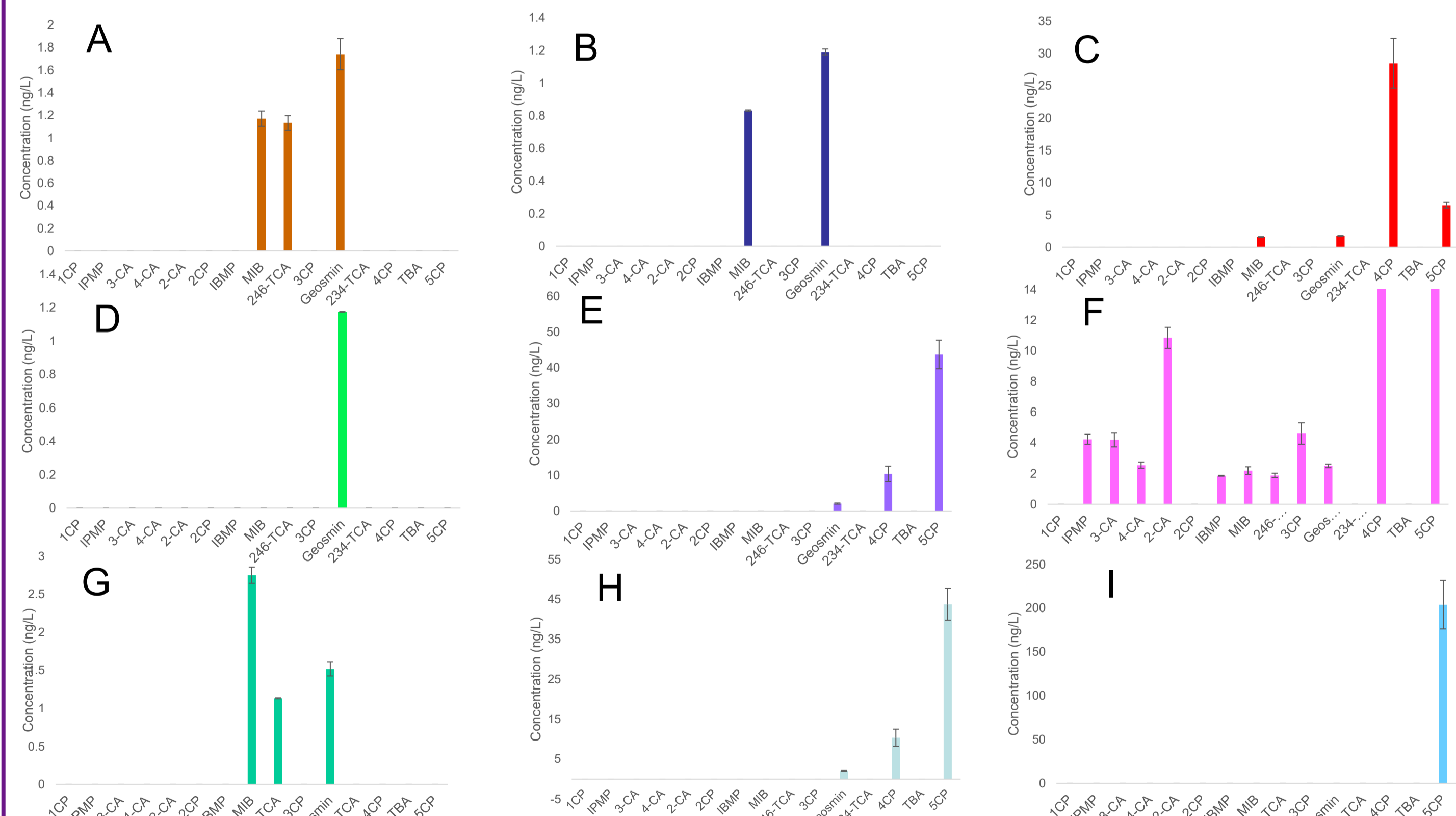


Figure 6: Bar charts comparing concentrations of target analytes detected in real-world samples labelled A-I (Table 3).

Conclusions

A simple, fast, highly-sensitive and solvent-free method for the analysis of chlorophenols and common odorants in water was developed, thanks to:

- Increased phase capacity and surface area with HiSorb compared to SPME.
- Multi-phase combinations improving extraction and sensitivity by adding another extraction pathway for target analytes.
- Robust HiSorb design allowing immersive extraction. The phase is in direct contact with analytes in the sample matrix, simplifying and expediting the extraction process.
- Secondary refocusing and analyte preconcentration on a cryogen-free trap with rapid backflush desorption, delivering sharp chromatographic peaks.
- Backflush trap operation further enabling analysis of a wide analyte range using multi-bed sorbents, and purging of interferences such as water away from the analytical system, improving the quality of results and extending column and detector lifetime.

References: 1. <https://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants/toxicants/chlorophenols-2000> 2. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5129356/>