



Application Note 255

Quantifying trace odorants in water by GC-MS with trap-based preconcentration: An assessment of high-capacity sorptive extraction

This study describes the use of the new Centri® sample extraction and enrichment platform to extract and quantify trace-level odorants in water, using headspace sorptive extraction with HiSorb probes – in conjunction with trap-based preconcentration and GC-MS. The detection of IPMP, IBMP, 2-MIB, 2,4,6-TCA and geosmin was well below the requirements of ISO 17943 and GB 5749, with linearities >0.996 and mean MDLs of the order of 1 ppt. We also describe the key attributes of HiSorb probes, and discuss the options offered by Centri, which include fully automated immersive sorptive extraction as well as headspace sorptive extraction.

Introduction

The presence of volatile organic compounds (VOCs) in drinking water can have a significant effect on consumer experience. The naturally occurring compounds geosmin, 2-methyl isoborneol (2-MIB) and 2,4,6-trichloroanisole (2,4,6-TCA) have particularly strong odours, and are often the source of complaints to water companies, while the emerging odorants 2-isopropyl-3-methoxypyrazine (IPMP) and 2-isobutyl-3-methoxypyrazine (IBMP) are also of concern. Reliable detection of these compounds is therefore important, but this is challenged by their low odour thresholds, which are typically at the low-ppt level.

In this study we demonstrate the fully automated sampling and detection of the five above-mentioned odorants at ppt levels in water using a headspace technique based on the principle of sorptive extraction – namely high-capacity sorptive extraction using HiSorb™ probes. Samples are extracted and preconcentrated on a focusing trap using the new cryogen-free Centri sample extraction and enrichment platform, and analysed by GC-MS operating in SIM mode. Excellent performance is achieved.

Experimental

Samples:

Calibration standards (Sections 1–8):

To assess the linearity of response for the calibration standards, a 100-ppm (100 µg/mL) stock solution of 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP), 2-methylisoborneol (2-MIB), 2,4,6-trichloroanisole (2,4,6-TCA) and geosmin was prepared in HPLC-grade methanol, then volumetrically diluted with water to provide seven solutions with concentrations ranging

from 1–100 ppt. 10 mL of each solution were then transferred to 20-mL headspace vials containing Na₂SO₄ (2.5 g, 25% w/v). The vials were then crimp-capped.

Extraction and enrichment:

Instrument: Centri (Markes International)

Headspace HiSorb high-capacity sorptive extraction:

Probe: Short-length (48 mm) stainless-steel HiSorb probe (Markes International part no. H1-XXABC)

Incubation: 65°C (30 min) at 600 rpm

Probe desorption: 250°C (12 min)

Preconcentration:

Flow path: 180°C

Focusing trap: 'Material emissions' (part no. U-T12ME-2S)

Purge flow: 50 mL/min (1 min)

Trap low: 20°C

Trap high: 260°C (5 min)

Split ratio: 4:1 for 1 ppb analysis; splitless for ppt analysis

GC-MS:

Column: MEGA®-5 MS, 30 m × 0.25 mm × 0.25 µm

Constant flow: Helium, 2.0 mL/min

Oven program: 60°C (2 min), then 10°C/min to 100°C, then 20°C/min to 190°C (0 min)

Transfer line: 280°C

Ion source: 300°C

Background to Centri and HiSorb

Markes International's Centri system for GC-MS is the first platform to offer high-sensitivity unattended extraction and enrichment of VOCs and SVOCs in solid, liquid and gaseous samples.

Centri allows full automation of immersive and headspace sampling using HiSorb high-capacity sorptive probes. It also offers full automation of headspace, SPME and tube-based thermal desorption with enrichment. Leading robotics and analyte-trapping technologies are used to improve sample throughput and maximise sensitivity for a range of applications.

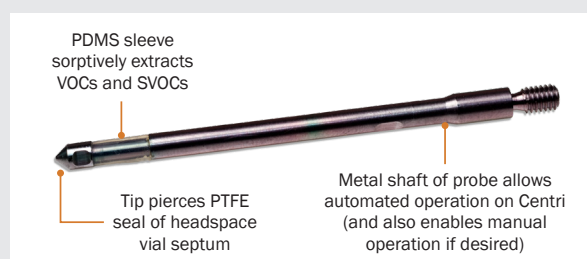
In addition, Centri allows samples from any injection mode to be split and re-collected onto clean sorbent tubes, avoiding the need to repeat lengthy sample extraction procedures and improving security for valuable samples, amongst many other benefits.



The HiSorb capability deployed in this study involves use of robust metal probes fitted with a section of high-capacity sorbent polymer, to extract and enrich compounds from liquids and solids.

Samples contained in standard 20 mL or 10 mL vials are loaded onto Centri, and the HiSorb probe inserted into the vial for either immersive or headspace extraction. The probe is then automatically washed, dried and desorbed, with the analyte vapours concentrated on the Centri focusing trap prior to GC-MS injection.

For more on Centri and HiSorb, visit www.markes.com.



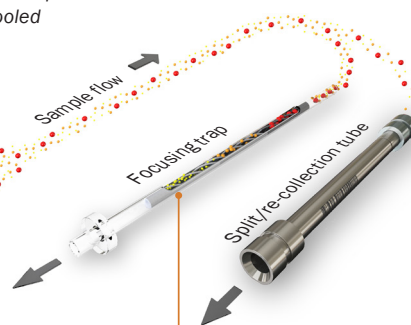
ANALYTE TRAPPING ON CENTRI *(optional for headspace and SPME)*

1 Sample focusing

Extracted analytes are swept into Centri's electrically-cooled focusing trap.

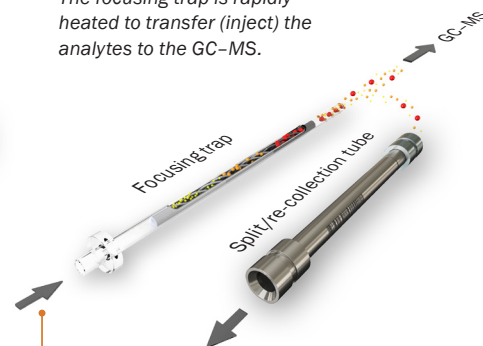
HiSorb high-capacity sorptive extraction
Headspace
SPME
Thermal desorption

Gas-phase internal standards can be introduced to the Centri trap in the carrier gas stream, as a check on the focusing and desorption processes.



2 Trap desorption

The focusing trap is rapidly heated to transfer (inject) the analytes to the GC-MS.



The carrier gas flow reverses during trap desorption to allow simultaneous analysis of compounds over a wide volatility range (VOCs and SVOCs).

Experimental (cont.)

Quad:	200°C
Mass range:	m/z 40–350
Solvent delay:	5 min
SIM mode:	m/z 137 (IPMP), 124 (IBMP), 95 (2-MIB), 195 (2,4,6-TCA), 112 (geosmin)
Tune mode:	E-tune

Results and discussion

1. Method development – Salt addition

A well-established protocol for headspace extraction of aqueous samples is the addition of salts, such as NaCl or Na₂SO₄, to reduce the solubility of organic solutes, and hence increase their headspace concentrations.

Figure 1 shows the effect of adding 25% w/v Na₂SO₄. The substantial differences in relative response between analytes may be explained by the non-linear effect of salting out and its dependence, to a large extent, on analyte polarity (amongst other factors).

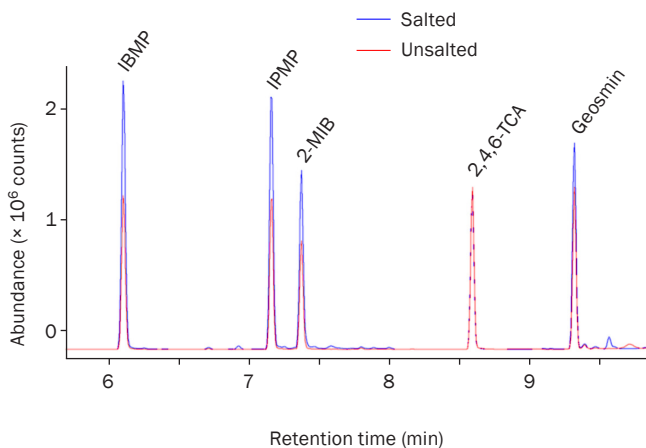


Figure 1: Overlaid splitless SIM profiles for the five target odorants in the headspace of the 1 ppb standard, using sorptive headspace sampling, with the addition of 25% w/v Na₂SO₄ (blue), and without Na₂SO₄ (red).

2. Method development – Sample incubation

To assess the optimum sample incubation time, peak areas for the odorants were evaluated at various times from 5 minutes to 2 hours. It was found that above 30 minutes, gains in peak areas are not significant, so this value was used in all subsequent work. Figure 2 shows extraction for the representative odorant IPMP.

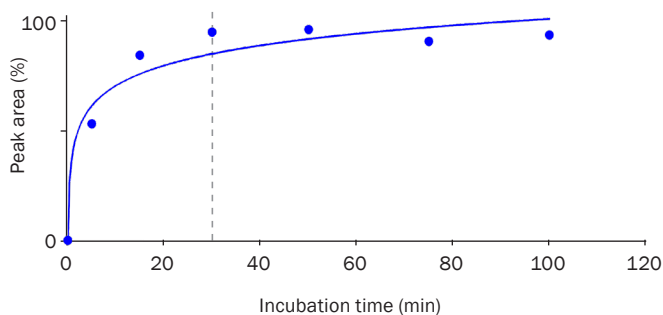


Figure 2: Plots of IPMP peak area vs. incubation time, in the headspace of the 1 ppb standard, using HiSorb sampling. An incubation time of 30 min was used in subsequent work.

3. Odorant recovery

Figure 3 shows good recovery at low ppt-levels for all odorants, which are much lower than those required in the ISO method.

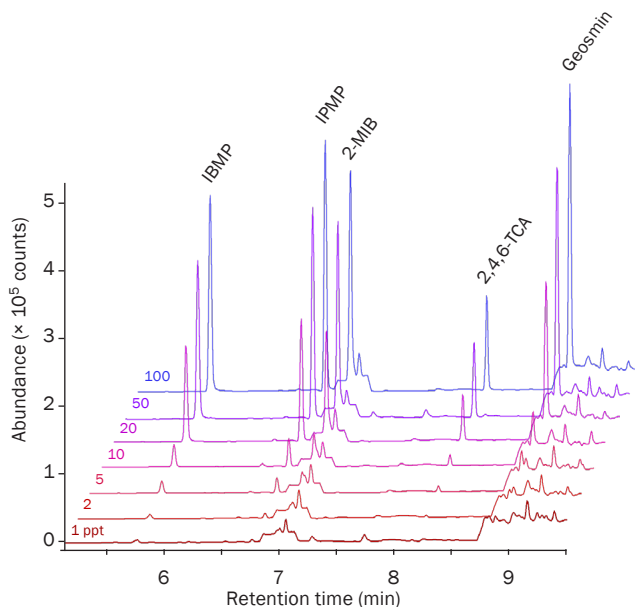


Figure 3: Stacked splitless SIM profiles for the five target odorants in the headspace of the 1–100 ppt standards, using HiSorb sampling. See Figure 7 for an expansion of the 1 ppt data.

4. Linearity

Figure 4 shows the excellent linearity of response obtained for all five analytes from 1–100 ppt, showing that accurate quantitation can be achieved using HiSorb.

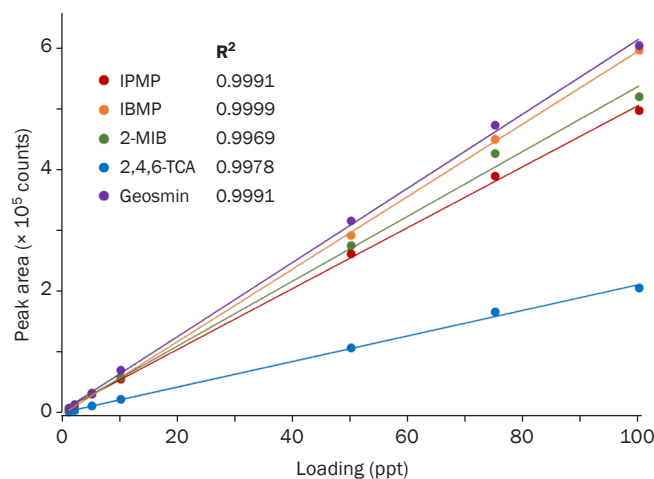


Figure 4: Calibration curves for the five target odorants in the headspace of the 1–100 ppt standards (n = 3), using HiSorb sampling.

5. Split and splitless analysis

To maximise sensitivity for GC–MS analyses of trace-level water odorants, it is necessary to use splitless injection. Unfortunately, most preconcentration systems cannot accommodate the very low trap flow rates needed to avoid chromatographic band-broadening effects. Such effects can be exacerbated by limitations in lower trap temperature, trap heating rate and trap design.

In contrast, the narrow-bore focusing trap used in Centri can accommodate the very low flows needed for splitless analysis, features electrical cooling down to -30°C , and can be heated at rates up to $100^{\circ}\text{C}/\text{s}$. This results in highly efficient analyte trapping and release, providing excellent peak shape and accurate results over a wide analyte range, as illustrated by the splitless analysis of the five target odorants in Figure 3.

The benefit of this is clear from Figure 5, which shows the increase in response obtained when using splitless analysis (compared to split).

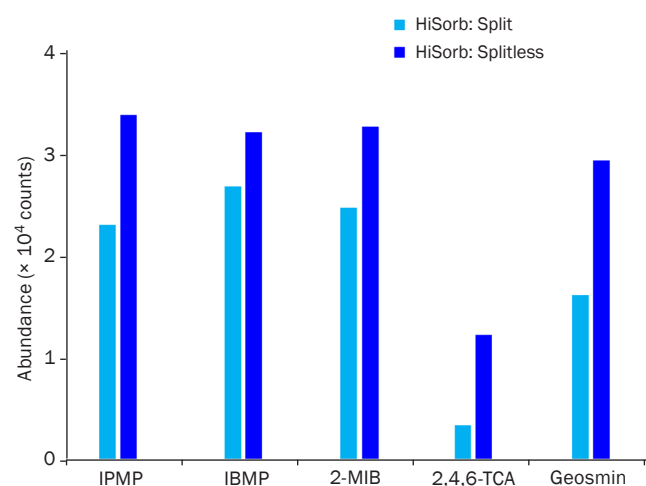


Figure 5: Peak areas for the five target odorants in the headspace of the 5 ppt standard, using HiSorb sampling.

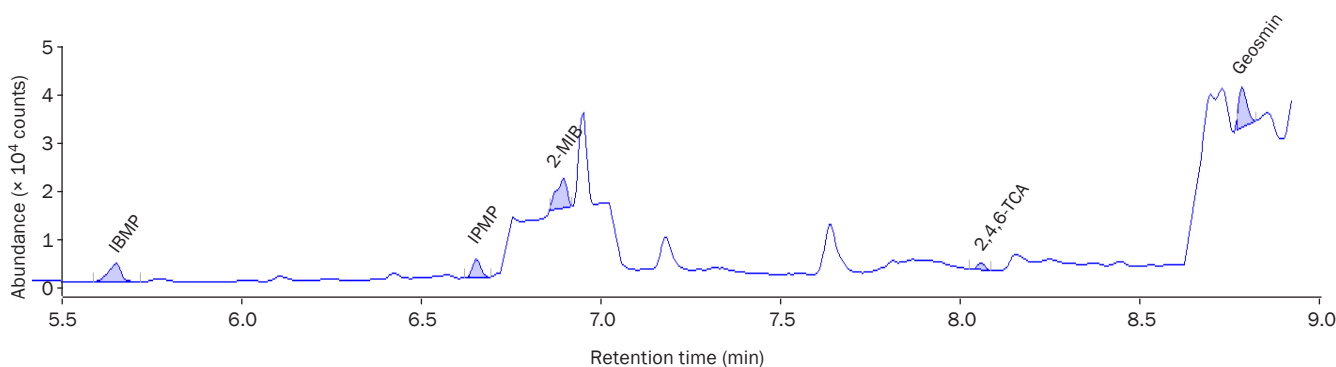


Figure 6: Splitless SIM profile for the five target odorants in the headspace of the 1 ppt standard, using HiSorb sampling.

6. Detection limits, reproducibility and recovery

Method detection limits (MDLs) were calculated based on the raw peak areas from nine replicate splitless injections of a 5 ppt standard, using the Student's t-value for 99% confidence of 3.36. MDLs, recoveries and RSDs are shown in Table 1.

MDLs are of the order of 1 ppt, which is within the 10 ppt requirement for geosmin and 2-MIB stipulated in ISO 17943¹ and the Chinese regulation GB 5749² (which uses test method GB/T 32470³). The mean peak area RSDs based on external standards are 4–8%, and adoption of an internal standard would improve these further. Figure 6 shows the response for the five odorants at 1 ppt for both sampling modes.

Compound	HiSorb		
	MDL (ppt)	Recovery (%)	RSD (%)
IPMP	1.68	103.1	9.74
IBMP	2.37	116.9	12.08
2-MIB	1.02	117.0	5.20
2,4,6-TCA	1.18	102.4	6.88
Geosmin	1.35	118.9	6.77
Mean	1.52	112.0	8.13

Table 1: MDLs, recoveries and RSD values (with no internal standard correction) for the five target odorants in the headspace of the 5 ppt standard (n = 9), using HiSorb sampling.

7. Parallel sample preparation and analysis

The ability to overlap the sampling and analysis of a sequence of samples (often referred to as 'prep-ahead') is very useful for improving sample throughput and the Centri robot offers this capability in all sample modes.

It is important to note that although analyte desorption from HiSorb probes takes longer than for SPME fibers because of the higher phase loading, the prep-ahead capabilities of Centri overcome this, to allow greater sample throughput.

Figure 7 compares the overall time required to sample and analyse a sequence of six typical samples in three modes of operation. A comparison is also made with the SPME technique which is the method used in ISO 17943.

On Centri, the HiSorb probes can be detached from the robotic tool, enabling the robot to perform other duties and so allowing simultaneous extraction from up to six vials. This results in an overall sequence of just 2 hours, which is substantially less than the 6 hours needed for SPME-trap, for which the fiber remains fixed to the tool during sampling. The result is therefore increased productivity of the GC-MS system.

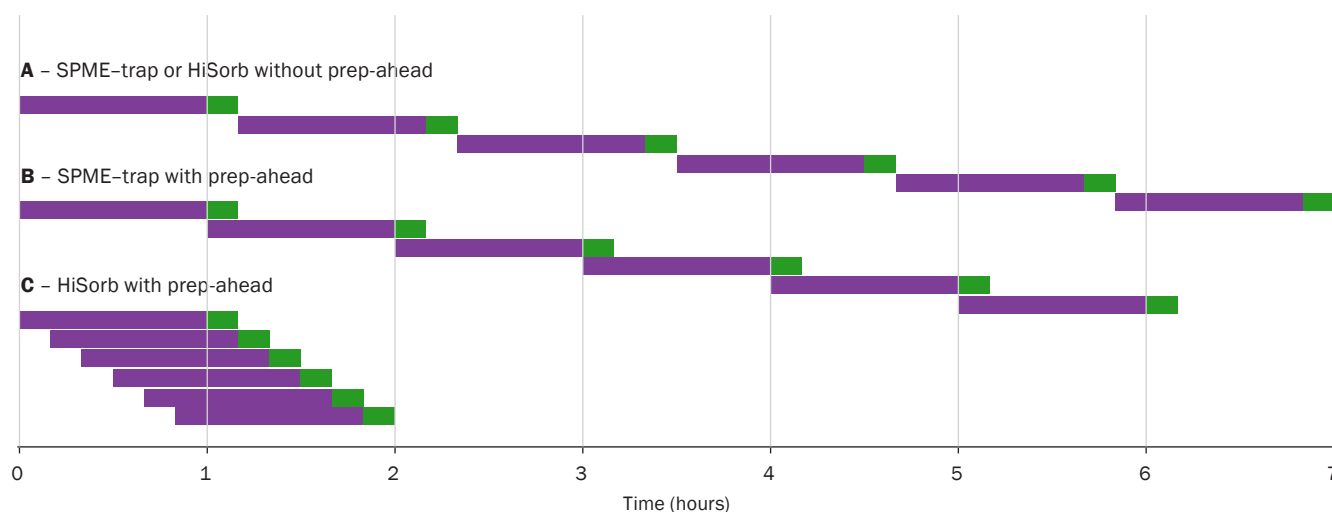


Figure 7: Comparison of overall sequence times for three operational modes on Centri, for a set of six samples with a typical 60-minute incubation time (■) and a 10-minute GC run-time (■).

Conclusions

This study has shown that the new Centri sample extraction and enrichment platform can be used to extract and quantify trace-level odorants in water, using HiSorb high-capacity sorptive extraction probes, in conjunction with trap-based preconcentration and GC-MS.

The major advantages of HiSorb are:

- **Sensitivity:** The high sorptive phase capacity of HiSorb probes allows for an improvement in the extraction of compounds for detection, particularly those at low-levels. The use of the focusing trap on Centri enables precise control of split ratios for low-split operation, and also full splitless analysis for maximum sensitivity without compromising peak shape. Samples can also be enriched by concentrating multiple extracts from the same sample onto the same focusing trap prior to desorption if required.
- **Robustness:** Metal-core HiSorb probes are inherently more robust than delicate SPME fibers, making them suitable for immersive sampling, easier to handle and much less prone to accidental breakage.

- **Sample throughput:** Both SPME-trap and HiSorb extraction are fully automated on the Centri platform, but the greater overlap possible in 'prep-ahead' mode with HiSorb means that sample sequences can be completed in a significantly shorter time-frame, with corresponding gains in laboratory productivity and data quality.
- **Cost per sample:** A final consideration is the cost of consumable items, with individual HiSorb probes being 30-50% of the cost of SPME fibers.

In summary, the multi-mode capability of Centri enables laboratories carrying out water analysis to select the best sampling/injection option for the sample in question, giving them the flexibility to adapt to individual requirements and changing analytical needs.

References and notes

1. ISO 17943: Water quality – Determination of volatile organic compounds in water – Method using headspace solid-phase micro-extraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC-MS), International Organization for Standardization, 2016, www.iso.org/standard/61076.html.
2. GB 5749: 生活饮用水卫生标准 [Standards for drinking water quality], Chinese Ministry of Health, 2006.
3. GB/T 32470: 生活饮用水臭味物质土臭素和2-甲基异茨醇检验方法 [Organic compounds in drinking water – Test methods of geosmin and 2-methylisoborneol], Chinese National Health Commission, 2016.

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

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