Application Note 267

Enhancing sensitivity for headspace and headspace-SPME analysis: The benefits of a trap-based approach

This short review discusses how sorbent-packed focusing traps can be used to enhance sensitivity for headspace and headspace-SPME sampling of trace-level VOCs and SVOCs, thus allowing more (and better-quality) information to be obtained from every sample. Options covered include the use of larger headspace extraction volumes, repeat extractions from a single vial, and low-split or splitless analysis. Each option is illustrated with data acquired on the automated Centri® sample extraction and enrichment platform for GC–MS. Also discussed are the advantages that trapping offers for water management.

Introduction

It is well-known that analyte recovery and sensitivity for static (or equilibrium) headspace analysis of liquid or solid samples by GC–MS is affected by a number of sample preparation parameters. These include agitation speed, sampling time, incubation temperature and (for aqueous samples) ionic strength. In addition, sampling of headspace onto solid-phase microextraction (SPME) fibers is affected by the type of fiber (single-phase or multi-phase) and issues of analyte polarity.

Once these factors are optimised and the type of detector has been decided, any further gains in sensitivity need to come from the sample delivery system itself. This can be done by changing the method parameters to increase the on-column loading of the sample – for example, through adjustment of the headspace extraction volume and concentration, and use of low-split or splitless injection. However, most headspace instruments provide very limited ability to change these parameters, without degrading peak shape/symmetry, response and resolution.

In this study, we demonstrate how sample trapping for the headspace and headspace-SPME modes on the Centri® platform can overcome these problems, enabling larger headspace extraction volumes and multiple injections (enrichment) to be used without a loss in chromatographic performance.

Background to Centri

The Centri system from Markes International (Figure 1) enhances both research and routine work. It is the first GC–MS sample preparation platform to offer high-sensitivity unattended extraction and enrichment of volatile and semi-volatile organic compounds (VOCs and SVOCs) in solid, liquid and gaseous samples. Centri allows full automation of immersive (and headspace) sampling using HiSorb™ high-capacity sorptive extraction, headspace, SPME, and tube-based thermal desorption (TD), all operating in combination with advanced cryogen-free focusing for optimum sensitivity. Centri is integrated with leading robotics to maximise uptime and improve sample throughput.

Figure 1: The Centri sample extraction and enrichment platform.

A key feature of Centri is the sorbent-packed focusing trap (Figure 2), which enables analytes to be selectively focused and released, without the requirement for liquid cryogen. The trap can contain up to four sorbents of increasing strength, enabling a broad range of compounds to be retained and released in a single run. All extraction, enrichment and trapping operations on Centri are easily configured through the control software.

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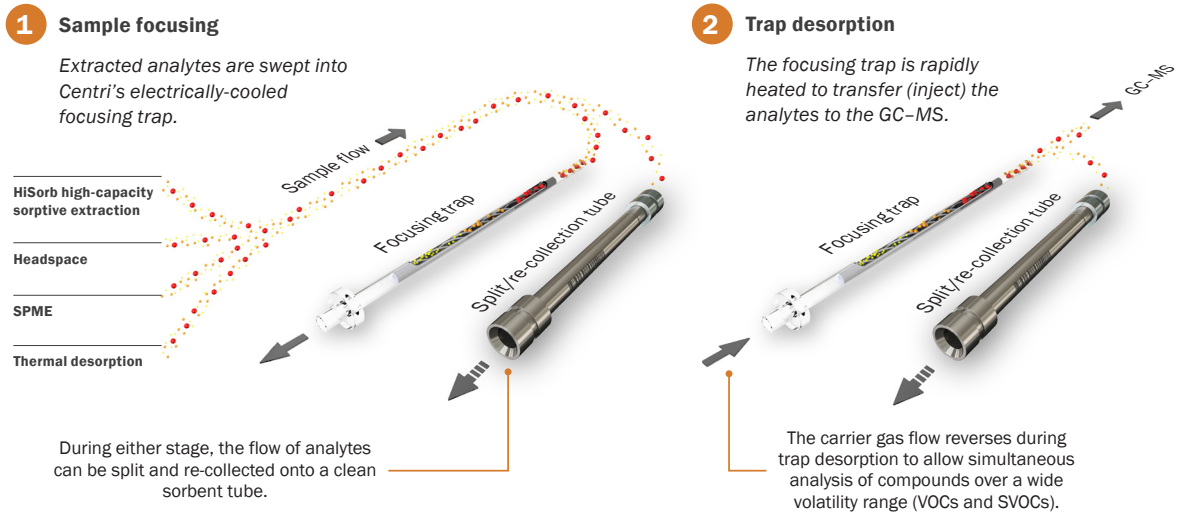

Figure 2: The operation of trap-based focusing on Centri.

The focusing trap is integral to the high-capacity sorptive extraction and TD modes, and significantly enhances the sensitivity of headspace and headspace-SPME compared with direct transfer to the GC. (Indeed, Centri is the only system offering headspace-SPME with trap-based preconcentration). The benefits of this trapping capability for headspace analyses are discussed in the section "Enrichment options".

Water management

An important consideration with any type of sample enrichment technique is preventing excessive amounts of water entering the analytical system. High concentrations of water can negatively impact analyte response and repeatability, and can also reduce the lifetime of the column and detector.

Headspace analysis of aqueous samples introduces a mass of water vapour to the instrument that is in direct proportion to the extraction volume. In contrast, for headspace-SPME the mass of water retained is a function of the relative hydrophobicity of the sampling phase, which is itself dependent upon the number and types of sorbent materials used.

In either situation, the use of a focusing trap on Centri opens up three approaches to water management:

- **Selection of focusing-trap sorbents:** The type and number of sorbents used to pack the focusing trap can be optimised to minimise the amount of water on-column, as well as to provide the best performance for the analytes in question.
- **Optimisation of the trap-low temperature:** Combining optimum sorbent selection with precise control of trapping temperatures to 20–25°C minimises water retention, while still ensuring quantitative focusing of the widest range of organic vapours, including very volatile compounds.
- **Use of a trap purge:** Prior to trap desorption, a flow of ambient-temperature carrier gas can also be passed through the focusing trap in the sampling direction to remove excess water. Parameters are defined in the Centri method, with the default flow being 50 mL/min for 1 min.

Use of these approaches is discussed alongside the other benefits of trapping in the sections below.

Enrichment options

Option 1: Increasing the headspace extraction volume

Most headspace systems limit the amount of sample that can be injected into the GC to about 1 mL. This is necesssary to avoid exceeding the capacity of the GC inlet liner and/or the GC column, which can cause asymmetric or split peaks, with obvious consequences for accurate integration and quantitation. The problem is exacerbated for highly volatile compounds, which may not always be well-focused on the column.

Centri overcomes these issues by allowing the headspace extraction volume of a single sample to be increased up to 5 mL (automated using standard syringes). Overload of the injection-port liner is avoided by continuously sweeping the sample into the focusing trap at a specified flow rate.

Following this stage, the focusing trap is rapidly heated (up to 100°C/s) to inject the sample into the GC for separation. The flow rate and time period for this desorption are controlled so that the sample is concentrated into about 100 µL of carrier gas. This provides an enrichment factor of about 50, and introduces a sharp, concentrated band of analytes into the capillary column, which optimises the signal-to-noise ratio, leading to more confident identification and discovery of compounds in a sample matrix.

These parameters allow large extraction volumes to be efficiently introduced into the injection inlet and transferred (*via* the focusing trap) into the GC.

Examples A and B (on the next page) demonstrate the benefit of increasing the extraction volume.

Option 2: Using repeat extractions from a single vial

Sample enrichment is a process in which repeat extractions from a single vial are used to deliver sampled analytes into the same focusing trap. On heating the trap, the enriched sample is transferred to the GC column, with a consequent increase in detector response for each compound. This allows limits of detection (LODs) for existing analytical setups to be lowered, signal responses at existing LODs to be raised, and

the results of statistical calculations for reproducibility and recovery to be improved.

For headspace analysis, sample enrichment can be used with the full range of extraction volumes available on Centri (0.1 to 5 mL). The ability to prefill the vial with an equivalent volume of carrier gas prior to extracting the headspace volume balances the vial headspace pressure for the next extraction.

Example C demonstrates the benefit of using sample enrichment.

Option 3: Using splitless injection

The split ratio at the point of injection is an important consideration for both headspace and headspace-SPME techniques, because it directly affects column loading and therefore sensitivity. The lower the required LOD, the greater the on-column loading of sample must be, which requires a reduction in the split ratio.

However, lower split ratios (and hence lower split flows) can cause band broadening, either within the GC inlet or in the headspace-to-GC transfer line – an effect that is most noticeable with the more volatile compounds. Such broadening can be compounded by the effect of residual water on the chromatography.

However, on Centri, use of the focusing trap means split ratios can be controlled over a wide range, and single-digit values (or even splitless operation) can be used routinely for both headspace and headspace-SPME without compromising chromatographic performance. This is the case even when using GC–MS, which can be challenging because it requires the carrier flow to be the same as the column flow (typically 1–3 mL/min).

Examples A and B demonstrate the benefit of using splitless injection.

Examples of trap-based focusing

Example A: Headspace of water odorants

To demonstrate the beneficial effect of trapping upon large-volume headspace extractions, Figure 3 shows the peak shape for three common water odorants at volumes from 0.5–5 mL. Splitless injection was used for this analysis because it represents the most demanding scenario. The results show a direct increase in signal response as the volume increases, with no deterioration in peak symmetry or shape. For real samples, this could enable detection at low- or even sub-ppt levels, which is important for these compounds because of their very low odour threshold values.

Example B: Headspace of EPA 524.2 pollutants in water

To demonstrate how the use of a focusing trap packed with multiple sorbents can provide high performance across a wide analyte range, Figures 4 and 5 show selected results from the analysis of 5 mL of an EPA 524.2 mix, containing very volatile organic compounds (VVOCs) ranging in volatility from dichlorodifluoromethane (b.p. –29.8°C) to naphthalene (b.p. 218°C). As for example A, both use splitless injection.

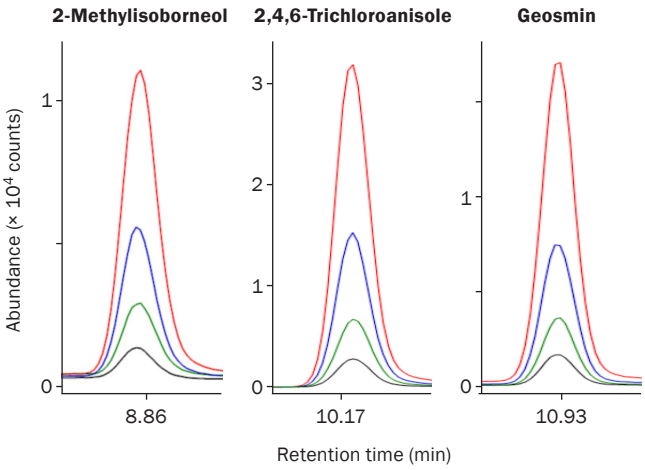

Figure 3: TIC profiles for 2-methylisoborneol (2-MIB), 2,4,6-trichloroanisole (TCA) and geosmin in a 0.5 ppb standard, using splitless injections of 0.5 mL (——), 1 mL (——), 2 mL (——) and 5 mL (——), with trap-based focusing.

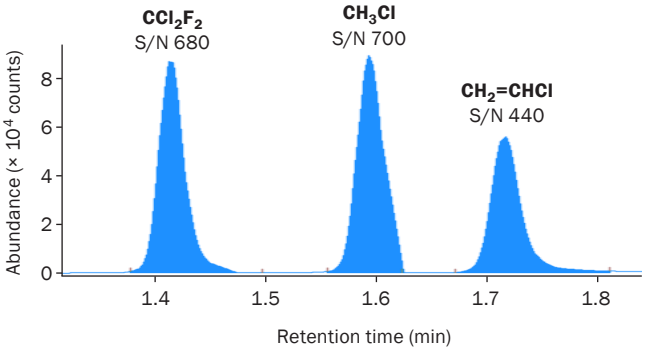

Figure 4: SIM profiles for dichlorodifluoromethane (b.p. –29.8°C), chloromethane (b.p. –23.8°C) and vinyl chloride (b.p. –13.4°C) in a 1 ppb standard using a splitless injection of 5 mL headspace, with trap-based focusing.

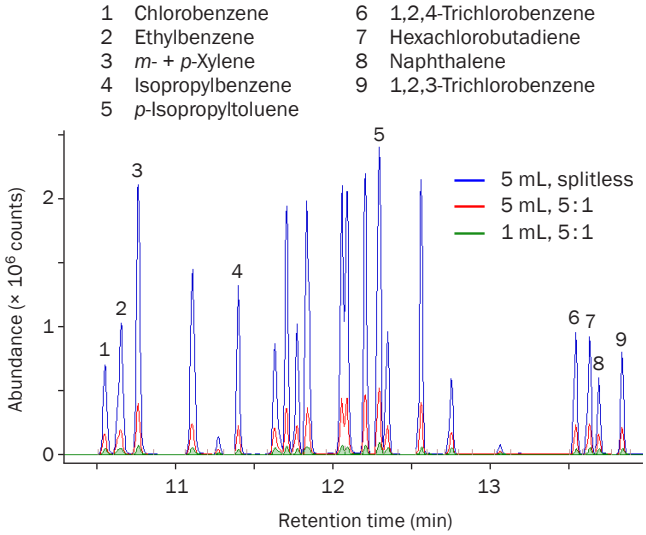

Figure 5: SIM profiles for SVOCs ranging from chlorobenzene (b.p. 132°C) to naphthalene (b.p. 218°C) in a 1 ppb standard using split or splitless injections of of 1 mL and 5 mL headspace, with trap-based focusing.

For the VVOCs, very little column focusing takes place, and so any peak broadening or splitting will be very evident at larger extraction volumes. This is therefore a real test of the trapping and desorption efficiency of the focusing trap, and Figure 4 shows excellent results for three of these compounds. In particular, the peaks are sharp, well-resolved, and have very good symmetry, which results in excellent signal-to-noise ratios. In this case, the focusing trap was held at 20°C during trapping, which still allows selective purging of water.

The same parameters also provide excellent results for the semi-volatile compounds in the mix, and Figure 5 shows the expected increase in response on increasing the extraction volume from 1 mL (green trace) to 5 mL (red trace), using a 5:1 split.[1] A corresponding splitless analysis of 5 mL (blue trace) then shows the additional increase in running the sample splitless.

Example C: Use of sample enrichment for headspace and headspace-SPME of shampoo

To demonstrate how trap-enabled enrichment can be used to enhance responses for trace-level analytes in regular headspace mode, Figure 6 shows the headspace profiles for a non-fragranced shampoo product, using a single extraction or two extractions (from the same vial), both in split mode. Both the more abundant components and trace-level analytes display an enrichment effect, enabling more confident identification of the latter. In addition, it is clear that the peak shape has not been affected across the volatility range, despite the doubling of on-trap extraction volume to 10 mL.

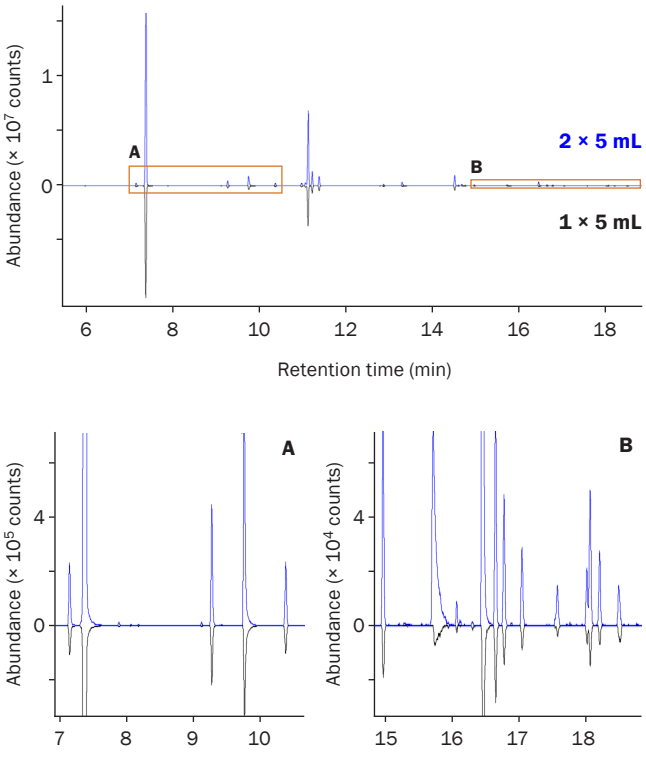

Figure 6: TIC profiles of a non-fragranced 'sensitive skin' shampoo, using headspace extraction volumes of 2 × 5 mL (blue trace) and 1 × 5 mL (black trace) with trap-based focusing and split injection. Panels A and B show expansions of the baseline.

Enrichment can also be implemented for the headspace-SPME mode, and Figure 7 compares the profiles for the same shampoo sample using a single extraction or two consecutive extractions (from the same vial). The response using two extractions doubles for most compounds, and the number of analytes detected (especially >18 min) is clearly greater than for the regular headspace mode, due to the preconcentrating effect of the multi-phase SPME fiber. Although in this case water management is still required, it is less of an issue than for regular headspace, due to the preconcentration of the sample on the SPME fiber, which has a small amount of somewhat hydrophobic sorbent.

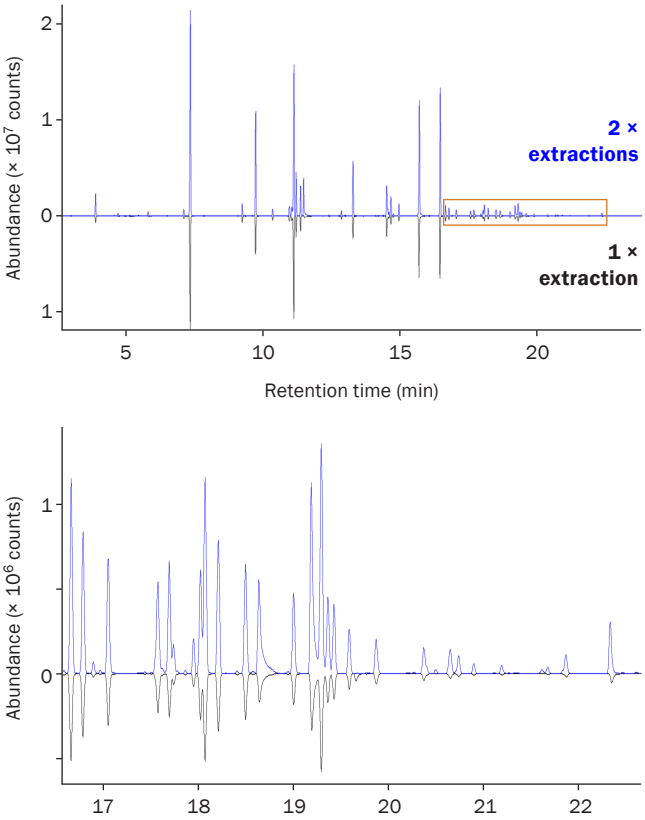

Figure 7: TIC profiles of a non-fragranced 'sensitive skin' shampoo product, using a split injection of 2 × headspace-SPME extractions (blue trace) and 1 × headspace-SPME extraction (black trace), using a three-phase SPME fiber and trap-based focusing for enrichment. The bottom panel shows an expansion of the baseline.

Conclusions

This application note has demonstrated the value of automated trap-based preconcentration on Centri for headspace and headspace-SPME sampling of trace-level organic compounds across a wide volatility range. In particular, trapping allows sample loading, and therefore sensitivity, to be increased by the following means, all without compromising chromatographic performance:

- Larger headspace extraction volumes – up to 5 mL in a single injection.
- Multiple headspace extractions injected onto the same trap.
- Low-split or splitless analysis.

In addition, the focusing trap:

- Opens up additional options for water management, including selection of focusing-trap sorbents, optimisation of the trap-low temperature, and use of a trap purge.
- Allows samples from any extraction 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.

Trap-based enrichment of headspace using the methods described here is of great benefit to environmental laboratories needing to attain ultra-low LODs, and for flavour/aroma analysts dealing with compounds that have very low odour thresholds. In the latter case, the enhanced on-column loading of compounds offered by trapping offers clear advantages for other detection techniques, such as olfactometry (and subsequent correlation to sensory analysis).

Notes

1. For further detail on the work using a 1 mL headspace extraction volume with a 5:1 split, shown in Example B, please refer to Application Note 256.

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