Application Note 259

Improving the performance of headspace sampling using trap-based preconcentration

This study shows how large-volume extraction and splitless injections can be used to improve the sensitivity of the conventional headspace technique without compromising chromatography, as well as simplifying method development.

Headspace sample injection for GC and GC–MS is a mature technique that is used in a wide variety of applications. However, some aspects of method development for conventional static headspace can be time-consuming.

Background to Centri®

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 extraction using HiSorb™, high-capacity sorptive extraction 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 – including profiling of foods, beverages and fragranced products, environmental monitoring, clinical investigations and forensic analysis.

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.

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

A particularly important consideration is the injection volume, which can be limited by either injector loop size, injection time or capacity of the injection liner (and exceeding the liner volume can cause chromatographic problems, especially for early-eluting compounds). One solution to this problem is to use a split flow, which may give better chromatography, but results in less sample reaching the detector. Balancing these factors can be difficult, and add significant time to method development.

Such difficulties can be overcome – and the applicability of headspace extended – by using a focusing trap prior to injection into the GC. In this study we show how the electrically-cooled, cryogen-free focusing trap in the Centri® sample extraction and enrichment platform allows efficient preconcentration of headspace samples, even for large volumes in splitless mode.

This focusing trap can contain a variety of sorbents, and using temperatures ranging from ambient to -30°C, can efficiently trap VOCs released from a sample. The trap is then ballistically heated (up to 100°C/s) in a reverse flow of carrier

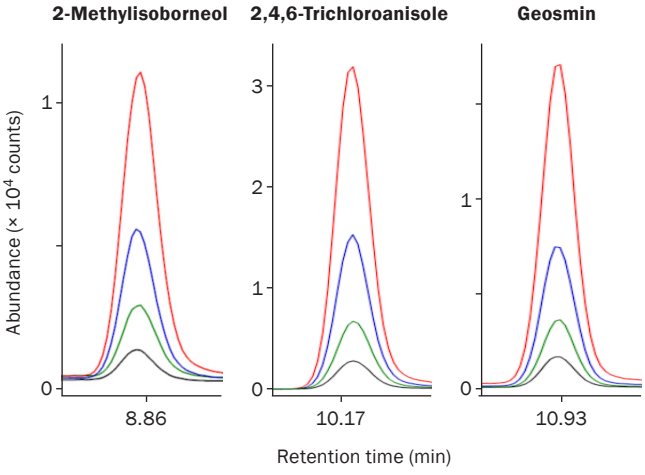

Figure 1: TIC headspace–trap profiles for three water odorants in a 0.5 ppb standard, run using splitless headspace injections of 0.5 mL (—), 1 mL (—), 2 mL (—) and 5 mL (—).

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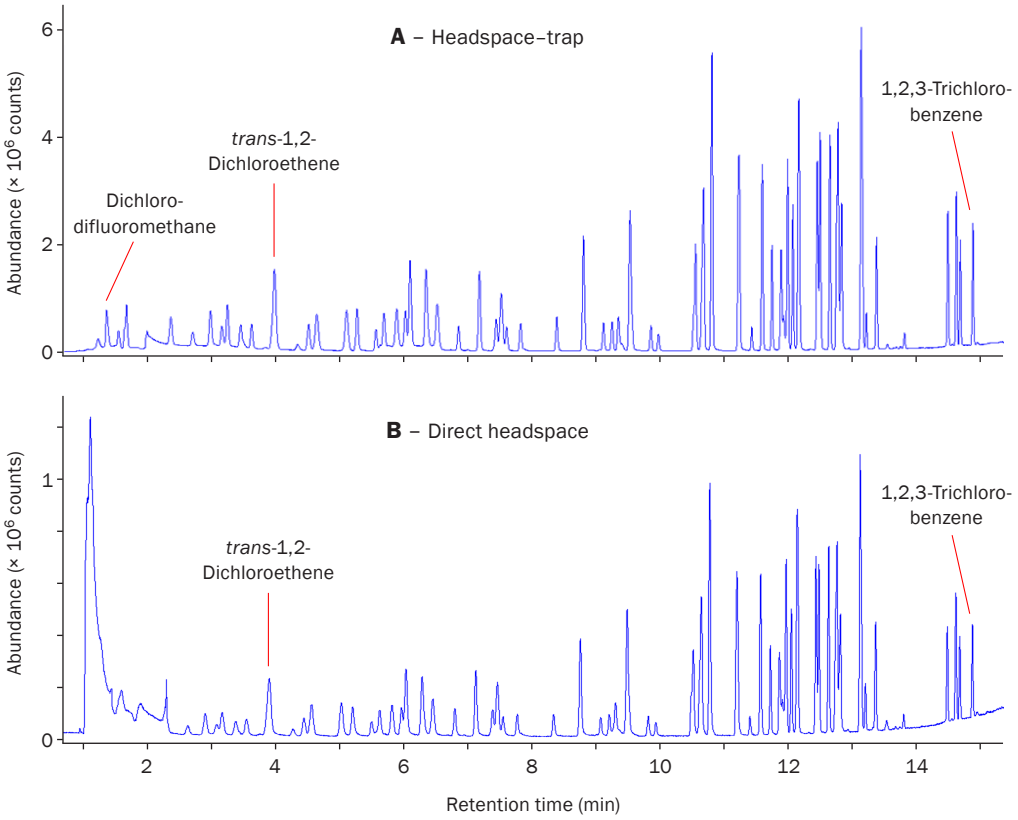

Figure 2: TIC profiles for VOCs and SVOCs in a 20 ppb standard, analysed using a 5:1 split ratio in (**A**) headspace–trap and (**B**) direct headspace modes.

gas ('backflush') to transfer the analytes to the GC in ~100 µL of gas, resulting in a tight band of analytes at the head of the column and sharp chromatographic peaks, even using low-split or splitless modes.

Figure 1 demonstrates how headspace preconcentration on Centri yields undiminished performance even for **large extraction volumes** run in splitless mode. It is clear that the peak shape does not degrade as the extraction volume increases from 0.5 mL to 5 mL, meaning better signal-to-noise ratios, higher sensitivity and more accurate quantitation than for conventional static headspace.

To compare the **effect of trapping** on chromatographic peak shape, a VOC/SVOC standard was analysed in headspace–trap and direct headspace modes, both with a 5:1 split ratio (Figure 2). The headspace–trap profile shows good peak shape across the chromatogram, unlike the direct headspace profile, which shows some poor-quality chromatography, especially at retention times <5 min.

To further demonstrate the excellent chromatography achievable for **early-eluting compounds** using headspace–trap, Figure 3 shows profiles of the very volatile dichloro-difluoromethane and chlorodifluoromethane. Both components show Gaussian peak shape.

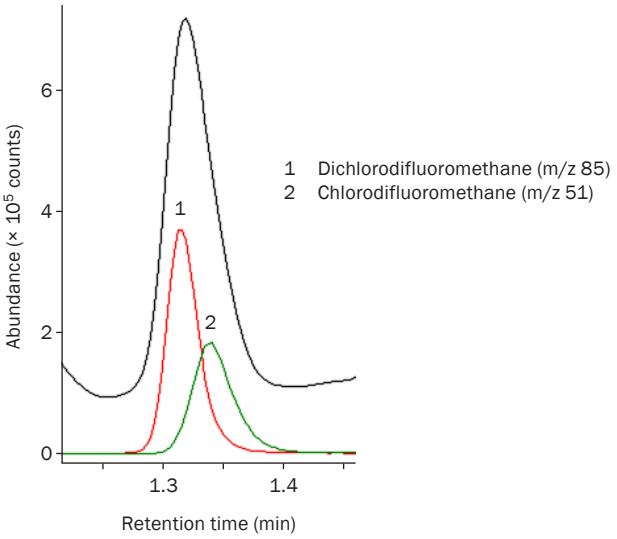

Figure 3: EIC profiles for two very volatile compounds, run in headspace–trap mode.

In conclusion, the data presented shows that large-volume and splitless injections can be carried out using headspace–trap mode on Centri, without the need for the careful optimisation required when using conventional headspace methods. In both cases, sharp chromatographic peaks are obtained, even for early-eluting compounds.

In addition, Centri allows direct headspace and headspace–trap analyses to be carried out without user intervention as part of the same automated sequence, facilitating method development. A further advantage associated with the focusing trap is the ability to re-collect split flows onto a thermal desorption tube, for repeat analysis or method validation. On Centri, all of these operations are automated, greatly improving efficiency for high-throughput laboratories.

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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