Application Note 259

Improving the performance of headspace sampling using trap-based preconcentration

This study shows how large-volume and splitless injections can be used to improve the sensitivity of headspace sampling 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.

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 focusing trap in the Centri® automated multi-mode 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 ambient or sub-ambient temperatures, can efficiently trap VOCs released from a sample. The trap is then ballistically heated (up to 100°C/s) in a reverse direction to transfer the analytes to the GC in a small volume of carrier gas (~100 µL), 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 injection volumes** run in splitless mode. It is clear that the peak shape does not degrade as the injection volume

Background to Centri®

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

Centri allows full automation of sampling using HiSorb™ high-capacity sorptive extraction, headspace, SPME, and tube-based thermal desorption. 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.

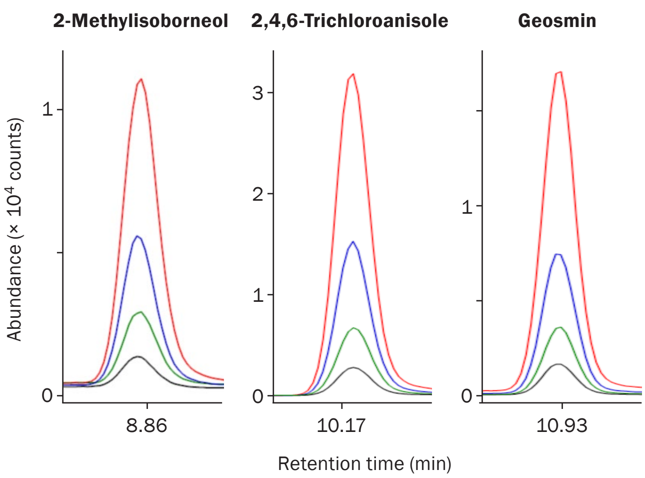

Figure 1: TIC headspace–trap profiles for three water odorants in a 0.5 ppb standard, run using splitless headspace injections of 0.5 mL (—), 1 mL (—), 2 mL (—) and 5 mL (—).

Markes International Ltd
T: +44 (0)1443 230935 F: +44 (0)1443 231531 E: enquiries@markes.com

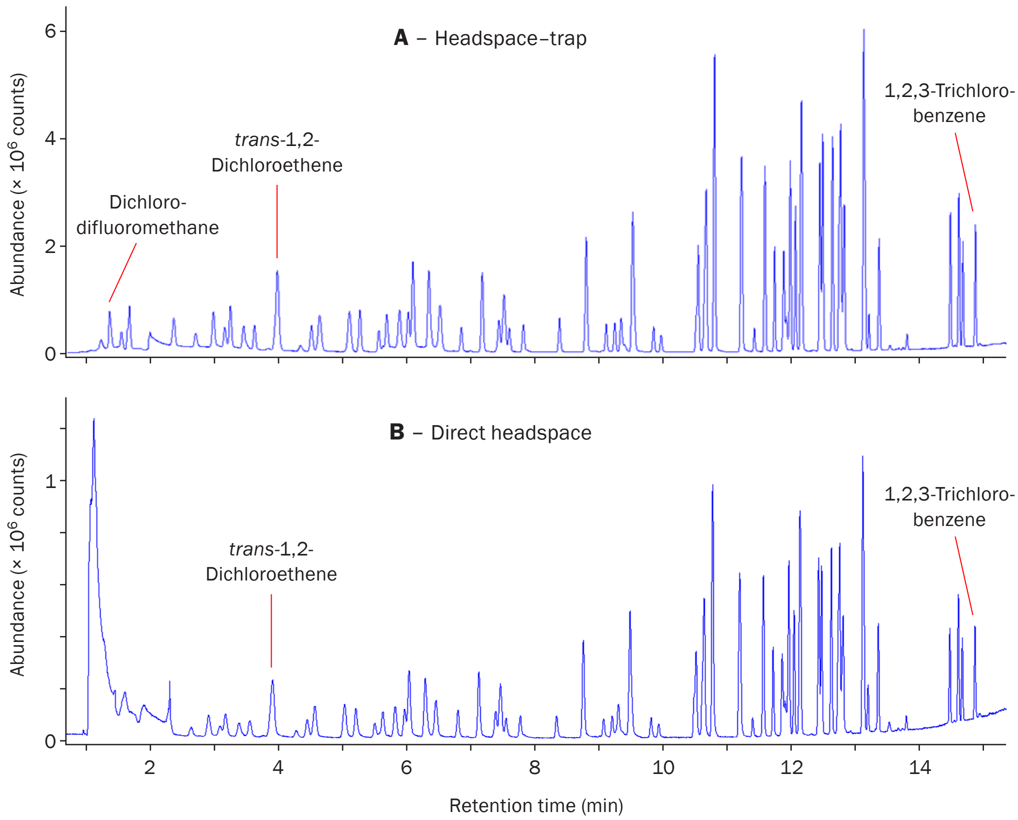

Figure 2: TIC profiles for VOCs and SVOCs in a 20 ppb standard, run using a 5:1 split in (**A**) headspace–trap and (**B**) direct headspace modes.

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 run in headspace–trap and direct headspace modes, both with a 5:1 split (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 dichlorodifluoromethane and chlorodifluoromethane. Both components show Gaussian peak shape.

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 careful optimisation. 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 trapping 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.

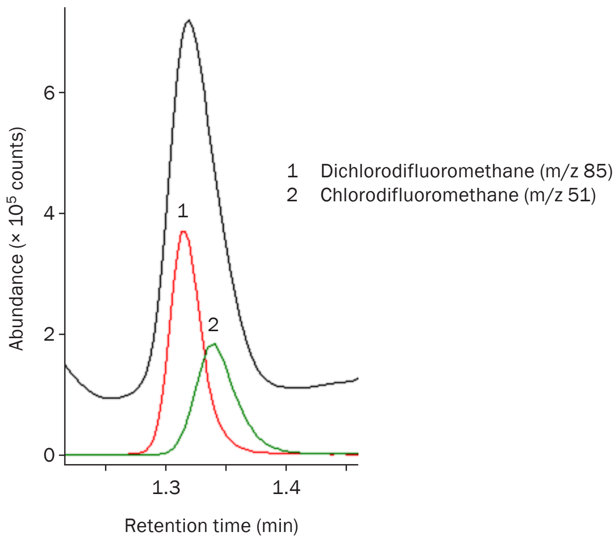

Figure 3: EIC profiles for two very volatile compounds, run in headspace–trap mode.

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