

Application Note 136

The performance of thermal desorption for the quantitative analysis of long-chain hydrocarbons

Summary

This study investigates the ability of Markes' thermal desorption (TD) systems to monitor semi-volatile organic compounds (SVOCs), using a wide range of n-alkanes (n-C₁₆ to n-C₄₄) as a model. We demonstrate how modern TD technology delivers robust and repeatable results for compounds across this wide boiling range and can therefore be used to enhance GC-MS analysis of trace SVOCs in air and other matrices. We also show how highly repeatable re-collection of TD samples is a convenient approach to validating analyte recovery in accordance with standard methods.

Introduction

Many SVOCs – including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), flame retardants, and some phthalate esters – are considered to be hazardous to human health, and may also be persistent environmental pollutants. As a result, they are the focus of growing environmental and product-safety concerns, which in turn is driving demand for improved monitoring and analytical methods.

Monitoring SVOCs in ambient air has traditionally involved pumped sampling of large volumes of air through a quartz or glass fibre filter to collect the particulate fraction, backed-up with a polyurethane foam cartridge or other sorbent to trap the vapour-phase fraction. Analytes are then solvent-extracted from the two phases and concentrated using rotary evaporation or other traditional techniques, with subsequent analysis of the concentrated extracts by GC or GC-MS.

However, these approaches suffer from several disadvantages, including:

- The need for labour-intensive solvent-based sample preparation steps.
- Incomplete and/or variable extraction efficiency, which compromises repeatability.
- Susceptibility to errors such as artefact introduction and losses of the more volatile target compounds during concentration steps.
- The need for cumbersome, mains-powered high-flow sampling pumps.

The technique of thermal desorption (TD), in conjunction with GC or GC-MS, has been used for several decades to

overcome these issues for the monitoring of lower-boiling airborne volatile organic compounds (VOCs),¹ and is now increasingly being applied to SVOC measurement.^{2,3} As well as completely avoiding the need for manual solvent extraction/dilution and its associated disadvantages, TD offers a huge improvement in sensitivity because of the use of two-stage sample focusing (see boxed text on the text page), which allows smaller air volumes to be collected using portable battery-operated low-flow pumps.

Assessing the compatibility of GC-based systems with semi-volatiles typically uses high-boiling compounds prone to condensation within the flow path, such as the unbranched long-chain hydrocarbons from n-C₁₆ (b.p. 287°C) to n-C₄₄ (b.p. 550°C). In this study a standard mix of n-alkanes was used to confirm the excellent performance of Markes' thermal desorbers for SVOC analysis.

Experimental

Sample:

A liquid standard solution of hydrocarbons from n-C₁₆ to n-C₄₄ in cyclohexane (1 µL, 100 ng per compound) was loaded onto a pre-conditioned inert-coated stainless steel 'SVOC' sorbent tube (Markes International part no. C2-AAXX-5342). The tube was purged with pure carrier gas for 3 minutes at a flow of 100 mL/min to ensure all analytes were swept onto the sorbents in the tube and to selectively eliminate solvent.

TD:

Instrument: TD100-xr™ (Markes International)
Focusing trap: 'General-purpose carbon' (part no. U-T11GPC-2S)
Tube desorption: 320°C (15 min), at a flow of 50 mL/min
Trap desorption: 25°C to 350°C (10 min), at maximum heating rate
Outlet split flow: 50 mL/min
Flow path: 250°C

GC:

Column: BPX5™, 15 m × 0.25 mm × 0.25 µm
Column flow: 3 mL/min
Oven ramp: 100°C (2 min), then 20°C/min to 320°C (10 min)
Inlet: 320°C

FID:

Detector: 350°C
Acquisition rate: 20 Hz

Background to thermal desorption

Thermal desorption is a versatile, solvent-free pre-concentration technique for gas chromatography that is used to analyse volatile and semi-volatile organic compounds (VOCs and SVOCs) in air/gas, liquids and solids.

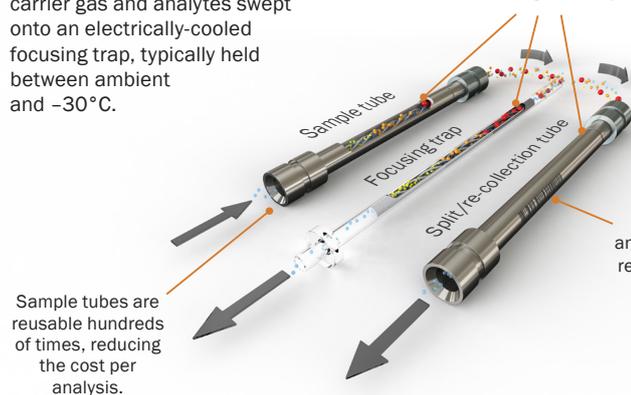
By concentrating organic analytes present in air (or released from a sample) into a very small volume of carrier

gas in a two-stage process (see below), TD maximises sensitivity for trace-level target compounds, helps to minimise interferences, and routinely allows analyte detection at the ppb level or below. It also greatly improves sample throughput, by combining sample preparation, desorption/extraction, pre-concentration and GC injection into a single automated process.

Stage 1: Tube desorption:

Sample tube heated in a flow of carrier gas and analytes swept onto an electrically-cooled focusing trap, typically held between ambient and -30°C .

Sample tubes and traps can contain multiple sorbents, for analysis of an extended range of analytes.



Stage 2: Trap desorption:

Focusing trap rapidly heated (up to 100°C/s) in a reverse flow of carrier gas ('backflush' operation), to transfer the analytes to the GC column.

During either stage, the flow of analytes can be split and re-collected onto a clean sorbent tube.



Results and discussion

1. Desorption efficiency and analyte recovery

Markes' TD systems (manual and automated) are unique in allowing samples to be split and quantitatively re-collected onto a clean sorbent tube at the tube desorption and/or trap desorption stages (see boxed text). Re-collected samples can then be re-analysed for validation of analyte recovery as described in key international standards.^{1c,d} Quantitative re-collection of samples also overcomes the 'one-shot' limitation of traditional TD systems, and allows samples to be re-analysed under the same or different conditions – for

example, with a selective detector or at a different split ratio to extend the dynamic range.

To assess hydrocarbon recovery during the TD process, the desorbed standards were subjected to six consecutive cycles of re-collection and re-analysis (Figure 1), and the results show excellent correlation between the predicted mass on-tube and measured response across the entire volatility range, including n-C₄₀ and n-C₄₄.

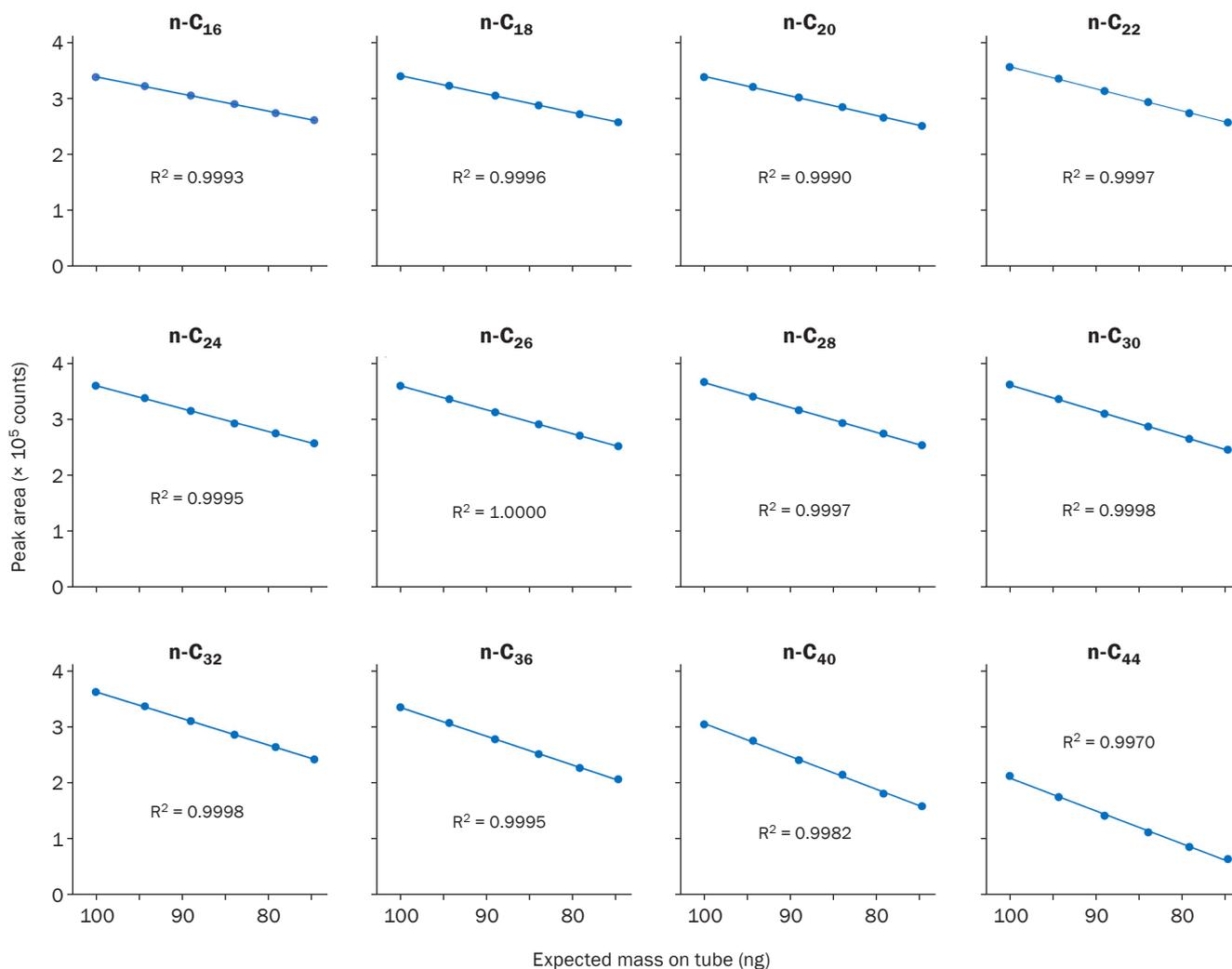


Figure 1: Plots showing mean obtained responses ($n = 4$) vs. the expected mass on-tube, for the original run of the standard mix at 100 ng on-tube (left-most data point in each plot) and five successive analyses of the same sample, following re-collection of the split portions onto clean sorbent tubes using an outlet split ratio of 17.7 : 1.

2. Analyte recovery

Optimum recovery of any SVOC is critically dependent on the construction and temperature-uniformity of the sample flow path within the thermal desorber. For example, if the flow path heating is inadequate, or it contains cold spots (parts of the flow path that don't reach set point), then the recovery of higher-boiling compounds may be compromised, leading to lower responses, poor chromatography and higher background levels (Figure 2).

3. Carryover

Figure 3 shows the chromatographic responses obtained from a tube spiked with the standard mix, and subsequent desorptions of an empty tube and the original sample tube. Very low carryover is demonstrated in all cases.

It is worth noting that the analyte masses introduced to the sample tubes (in this case 100 ng per compound) represent a 'worst-case scenario', and that masses collected during environmental air monitoring for SVOCs would normally be significantly lower, reducing carryover even further.

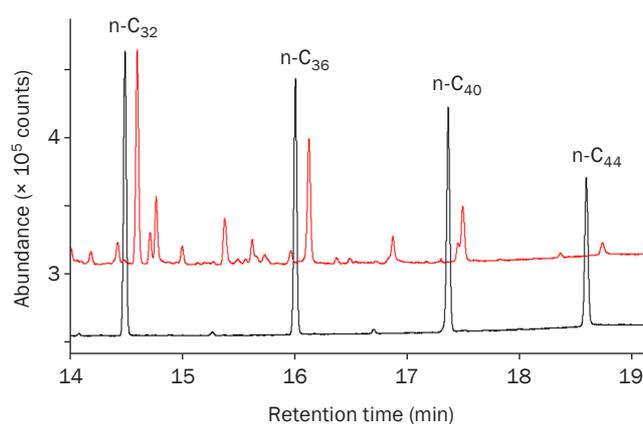
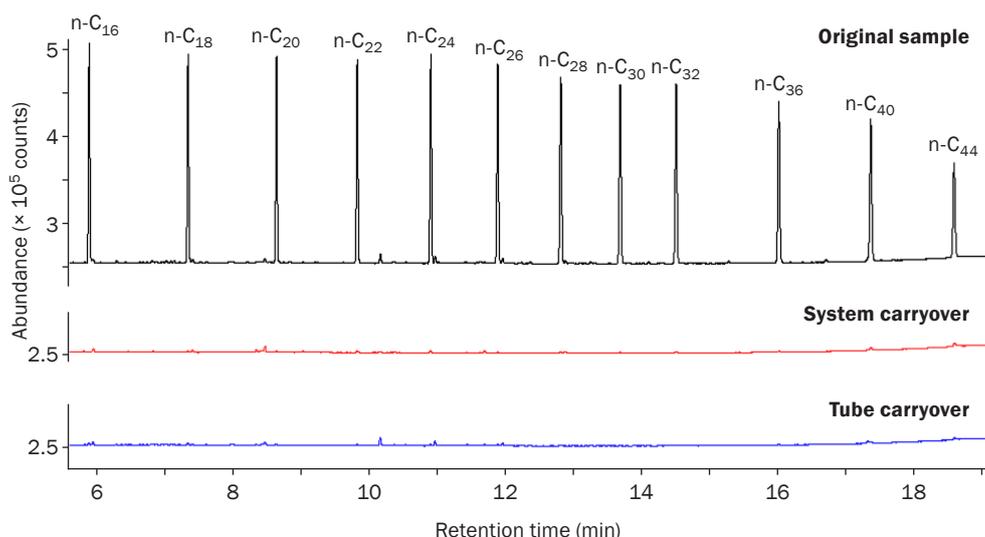


Figure 2: Analyses of the standard mix at 100 ng on-tube, showing a typical response for the heaviest hydrocarbons (black trace), and the effect of a 'cold spot' in the flow path (red trace).



Alkane	System carryover (%)	Tube carryover (%)
n-C ₁₆	0.197	0.329
n-C ₁₈	0.501	0.385
n-C ₂₀	0.560	0.225
n-C ₂₂	0.751	0.374
n-C ₂₄	0.883	0.491
n-C ₂₆	0.627	0.559
n-C ₂₈	0.463	0.479
n-C ₃₀	0.390	0.461
n-C ₃₂	0.363	0.347
n-C ₃₆	0.829	0.453
n-C ₄₀	1.721	0.278
n-C ₄₄	2.999	0.097

Figure 3: Analysis of the standard mix at 100 ng on-tube (black), a subsequent desorption of an empty tube (red, indicating system carryover), and a subsequent desorption of the original sample tube (blue, indicating tube carryover). Carryover values are means of 24 runs.

Conclusions

This study shows that Markes' TD systems – and specifically the TD100-xr automated thermal desorber (Figure 4) used here – provide highly predictable recovery and very low carryover for the analysis of long-chain alkanes ranging from n-C₁₆ to n-C₄₄.

TD system performance for other SVOCs has also been studied, and is described in Application Notes [137](#) (PCBs), [138](#) (phthalates), [139](#) (PAHs) and [140](#) (flame retardants).



Figure 4: Markes' TD100-xr thermal desorber.

References and notes

1. Key standard methods are: (a) US EPA Method TO-17: Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes, US Environmental Protection Agency, 1999; (b) ISO 16017: Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography – Part 1: Pumped sampling, International Organization for Standardization, 2000; (c) ISO 16000: Indoor air – Part 6:

Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FID, International Organization for Standardization, 2011; (d) ASTM D6196: Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for VOCs in air (and material emissions chambers), American Society for Testing and Measurement, 2015; (e) Chinese EPA Method HJ 644: Ambient air – Determination of volatile organic compounds – Sorbent adsorption and thermal desorption/gas chromatography mass spectrometry method, 2013; (f) Chinese EPA Method HJ 732: Stationary source emission. Determination of volatile organic compounds. Sorbent adsorption and thermal desorption gas chromatography mass spectrometry method, 2014.

2. B. Lazarov *et al.*, Optimisation steps of an innovative air sampling method for semi volatile organic compounds, *Atmospheric Environment*, 2013, 79: 780–786, <http://dx.doi.org/10.1016/j.atmosenv.2013.07.059>.
3. B. Lazarov *et al.*, Air sampling of flame retardants based on the use of mixed-bed sorption tubes – A validation study, *Environmental Science and Pollution Research*, 2015, 22: 18221–18229, <http://dx.doi.org/10.1007/s11356-015-5028-z>.

Trademarks

TD100-xr™ is a trademark of Markes International.

BPX5™ is a trademark of SGE Analytical Science (Trajan Scientific).

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