TDTS 102

Investigation of the performance of sorptive extraction cartridges for air monitoring

Summary

It is demonstrated that despite the considerable advantages of sorptive extraction cartridges for sampling of semi-volatile analytes from liquids, they perform poorly for the higher-volatility analytes that are typically of interest in air monitoring and material emissions applications. For such cases, it is shown that pumped sampling into sorbent tubes offers much better performance for a wider range of analytes.

Introduction

Sorptive extraction onto cartridges (also known as stir bar sorptive extraction, SBSE) is a popular technology for extraction from liquids of volatile organic compounds (VOCs) with sufficiently large octanol–water partition coefficients. Such cartridges, of which Markes' SPE-tD™ cartridges are an example, are typically coated with poly(dimethylsiloxane) (PDMS) as a stationary phase. These reusable cartridges are introduced to the liquid sample and agitated, encouraging the compounds present to equilibrate between the aqueous matrix and the PDMS. The cartridges fit conveniently into empty industry-standard sorbent tubes (3½″ long × ¼″ o.d.), and are thus easily analysed by TD–GC/MS[1].

Due to the nature of the PDMS coating on sorptive extraction cartridges (SECs), retention of higher-boiling non-polar analytes is favoured (although thicker-film coatings can extend the range of polar analytes retained). This makes them suitable for the extraction of flavour/fragrance components from liquids[1], which are as a rule relatively non-volatile.

However, there has recently been some publicity given to the extension of SECs to air monitoring[2]. As they were not originally designed for this application, we were interested to compare their performance relative to sampling onto sorbent tubes.

In this Application Note we show that sorptive extraction, although giving good results for a sample of high-boiling poly-α-olefins, gives poor recovery of both the lighter components of a C_6–C_{16} material emissions standard and for volatiles in factory air, as expected. We demonstrate that sampling onto sorbent tubes (in this case by grab-sampling) is a far better option for such situations, providing a reliable means of obtaining the complete vapour profile.

Figure 1: Markes' SPE-tD sorptive extraction cartridges (bottom), and inserted into a glass tube ready for thermal desorption (top).

Experimental

(a) Poly-α-olefin oil

Sample loading:
A Markes Calibration Standard Loading Rig (CSLR™)[3] was used to load 0.1 µL of a poly-α-olefin mixture onto a conditioned two-bed sorbent tube packed with Carbograph™ 2TD and Carbograph 1TD. The tube was then analysed by TD–GC/MS (see below), with re-collection onto an SPE-tD tube (an empty glass sorbent tube loaded with an SPE-tD cartridge, retained with quartz wool and a spring). The SPE-tD tube was then run using TD–GC/MS, using identical conditions.

TD (UNITY 2™):

Focusing trap:	U-T11GPC-2S (general-purpose carbon)
Prepurge:	1 min to split (50 mL/min)
Tube desorption:	250 °C for 8 min, trap flow 40 mL/min, no split
Trap low:	10 °C
Trap high:	300 °C for 5 min, split on (50 mL/min)

GC/MS:

Column:	DB-5ms, 30 m × 0.25 mm × 0.25 µm
Oven program:	60 °C (2 min) then 25 °C/min to 300 °C (5 min), 1.3 mL/min constant flow
Mass range:	35–350 amu
MS source temp:	230 °C
MS quadrupole temp:	150 °C

(b) Material emissions standard

Sample loading:
A Markes Calibration Solution Loading Rig was used to load (in the gas phase) 1 µL of a 25 ng/µL 11-component material emissions standard onto a conditioned sorbent tube packed with Carbograph 2TD and Carbograph 1TD, and onto an SPE-tD tube (an empty glass sorbent tube loaded with an SPE-tD cartridge, retained with quartz wool and a spring).

The standard contained components in the range C_6–C_{16} (n-hexane, methyl isobutyl ketone, toluene, hexanal, butyl acetate, cyclohexanone, phenol, 1,2,3-trimethylbenzene, 4-phenylcyclohex-1-ene, butylated hydroxy toluene and n-hexadecane).

Both tubes were then analysed by TD–GC/MS (conditions as for (a)).

(c) Factory air

Grab-sampling (Easy-VOC™):
The Easy-VOC grab-sampler[4] was used to consecutively sample 5 × 100 mL of factory air onto a conditioned sorbent tube packed with Carbograph 2TD and Carbograph 1TD, and onto an SPE-tD tube (an empty glass sorbent tube loaded with an SPE-tD cartridge, retained with quartz wool and a spring). Both tubes were then analysed by TD–GC/MS (conditions as for (a)).

Results and discussion

(a) Poly-α-olefin oil

In the first part of the analysis, we compared the performance of SECs with sorbent tubes for a group of analytes that ought to give good results on both – a mixture of C_{20} poly-α-olefins, branched long-chain alkanes that are used as coolants or lubricants (for example in the aviation industry). The chromatograms for this mixture, sampled using both methods, are presented in Figure 2.

The performance of the sorbent tube and the SECs was found to be nearly identical, confirming the reliability of both types of device for sampling these relatively high-boiling analytes, and also demonstrating efficient re-collection from the sorbent tube to the SECs. The only significant difference is the two peaks at ~3.0 min and ~4.5 min, which are due to siloxane artefacts released from the SEC (note the comparatively low background levels from the carbon black sorbents).

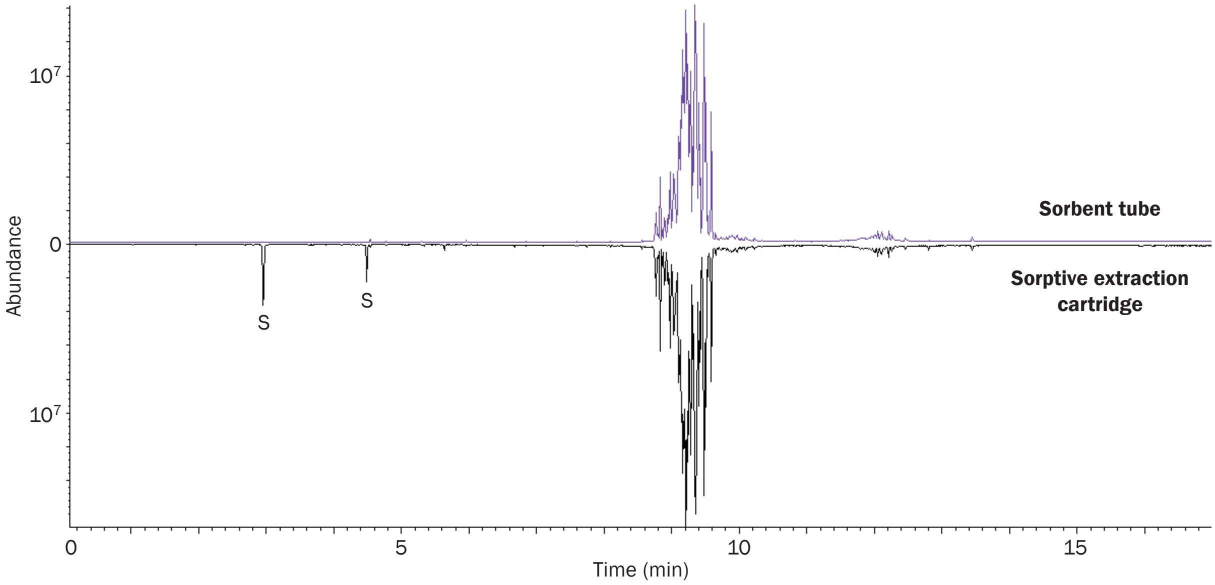

Figure 2: Poly-α-olefin oil loaded into a sorbent tube (top trace) and subsequently re-collected onto a sorptive extraction cartridge (bottom trace). Both were analysed by TD–GC/MS under identical conditions. S = Siloxane artefacts from the PDMS.

(b) Material emissions standard

To test how well the performance of the SECs extended to more volatile components, a clean sorbent tube and an SEC were each loaded with 25 ng of an 11-component 'material emissions' standard, containing C_6–C_{16} compounds, and analysed, under identical conditions, by TD–GC/MS.

The results of this (Figure 3) clearly show that the responses of the more volatile compounds (up to and including trimethylbenzene) are substantially reduced for the SEC sampler, indicating poor retention of these analytes on the PDMS substrate of the SEC. In particular, analysis of peak areas indicate unacceptably low relative retentions (≤25%) for hexane, methyl isobutyl ketone, toluene, hexanal and butyl acetate (Table 1).

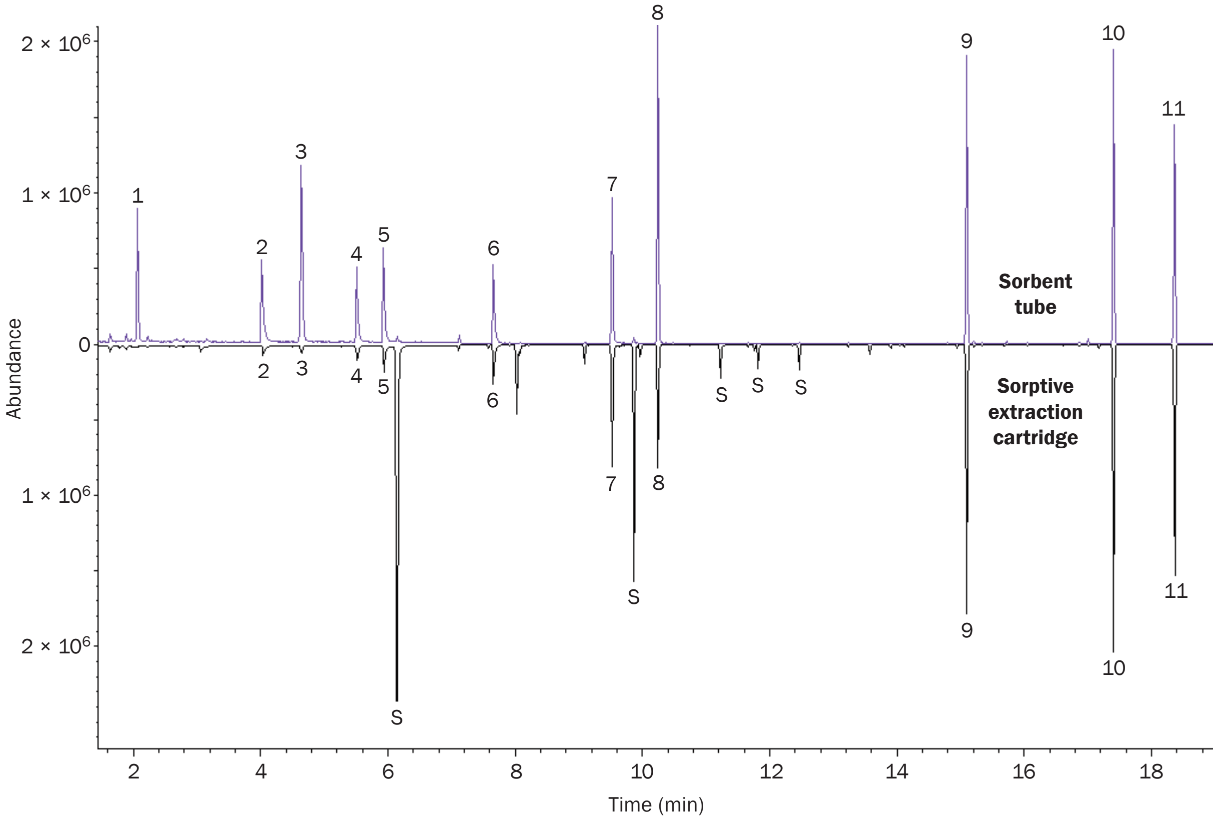

Figure 3: An 11-component 'material emissions' standard loaded into a sorbent tube (top trace) and onto a sorptive extraction cartridge (bottom trace). Both were analysed by TD–GC/MS under identical conditions. For peak labels see Table 1; S = Siloxane artefacts from the PDMS.

Peak no.	Compound	Recovery compared to sorbent tube (%)	b.p (°C)
1	Hexane	1	69
2	Methyl isobutyl ketone	11	118
3	Toluene	4	111
4	Hexanal	20	123
5	Butyl acetate	25	127
6	Cyclohexanone	48	156
7	Phenol	81	182
8	1,2,3-Trimethylbenzene	37	176
9	4-Phenylcyclohex-1-ene	85	235
10	Butylated hydroxy toluene	102	265
11	n-Hexadecane	98	281

Table 1: Recoveries of components of the 11-component 'material emissions' standard when sampled using a sorptive extraction cartridge, compared to loading direct onto a sorbent tube. Note how the components with a lower boiling point have lower recoveries.

(c) Factory air

To examine this effect further, and evaluate the performance of SECs for air monitoring in a real-world situation, 500 mL of factory air was sampled onto a sorbent tube and onto an SEC using an Easy-VOC grab-sampler. The results of this analysis are shown in Figure 4. Again, the data clearly demonstrates a greatly reduced response for lower-boiling analytes using SEC sampling. Clearly, if SECs were to be used in such a scenario, prospects for accurate measurement of airborne VOCs would be greatly diminished.

Conclusions

From these analyses, it is clear that sorptive extraction cartridges (SECs) provide poor retention of volatile analytes, and the vast majority of a range of vapour-phase organic pollutants found in factory air.

In contrast, TD tubes are routinely used to sample vapour-phase analytes spanning volatilities from C_3 to n-C_{32}, and they easily handle the C_6 to C_{20} compounds investigated here. Markes' TD systems have the added advantage of being able to split and re-collect samples, allowing important samples to be retained, or – as shown in the poly-α-olefin study – made available for re-analysis by a different method.

In conclusion, SECs are excellent for their intended application of sampling semi-volatile organics from liquids, but are not suitable for air monitoring situations.

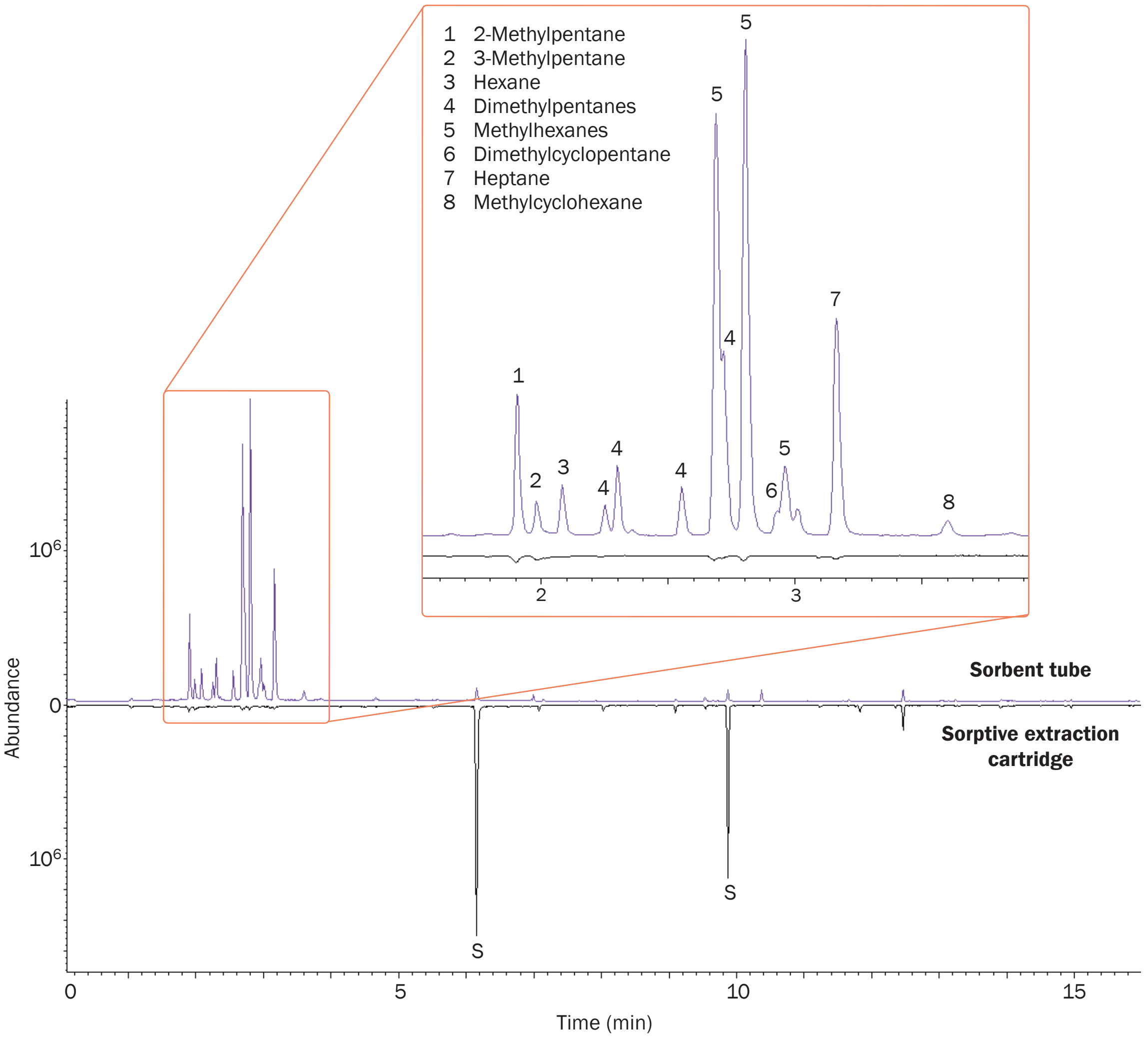

Figure 4: 500 mL of factory air grab-sampled into a sorbent tube (top trace) and onto a sorptive extraction cartridge (bottom trace). Both were analysed by TD–GC/MS under identical conditions. Note how the low-boiling hydrocarbons are scarcely retained on the sorptive extraction cartridge (inset).
S = Siloxane artefacts from the PDMS.

References and notes

1. Examples of the use of Markes' sorptive extraction cartridges (SPE-tD) can be found in:
   (a) Application Note TDTS 88 (fruit juice and wine);
   (b) Application Note TDTS 94 (beer);
   (c) Application Note ANBT10 from ALMSCO International (see http://www.almsco.com/downloads/application-notes.aspx).
2. The following application note describes the use of sorptive extraction cartridges to analyse ambient aircraft cabin air: http://www.leco.com/resources/application_notes/pdf/PEG4D_AIRCRAFT_CABIN_AIR_ANALYSIS_203-821-383.pdf.
3. See Application Note TDTS 7 for details of how to prepare and introduce thermal desorption standards onto sorbent tubes using the Calibration Solution Loading Rig.
4. For more information about the Easy-VOC, please visit http://www.markes.com/Instrumentation/Easy-VOC.aspx.

Trademarks

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