Application

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Application Note 113

Extending the compatible analyte volatility range for indoor air quality and material emissions testing using multi-bed sorbent tubes

Summary

This Application Note summarises two important and independent studies aimed at extending the compatible analyte range of tests used to determine chemicals released from materials, and associated indoor air quality measurements. The papers compare the performance of single-bed Tenax TA tubes to those packed with multiple sorbents, and demonstrate how the latter guarantee improved recovery of very volatile compounds without compromising the recovery or stability of heavier target analytes.

Introduction

Selection of sorbents for thermal desorption (TD) sampling tubes and focusing traps involves consideration of a range of factors, including the strength of the sorbent–sorbate interaction, artefacts, hydrophobicity, inertness and mechanical strength. Packed with appropriate sorbent(s), a TD sampling tube can achieve quantitative retention and release of compounds ranging from C_2 hydrocarbons and freons to semi-volatiles such as PCBs, phthalates and PAHs, without exceeding optimised tube dimensions and without requiring liquid cryogen coolant.

Material emissions test methods have traditionally been targeted at relatively narrow analyte ranges – typically from n-hexane to n-C_{16} or, in some cases, from n-hexane to n-C_{22}. Such methods typically use tubes packed with Tenax® TA,[1,2] and although this sorbent has many desirable qualities (for example, hydrophobicity, low inherent artefacts, good recovery of semi-volatiles and inertness), it is not suitable for some very polar compounds, and is too weak for quantitative retention of species more volatile than n-hexane.

Therefore, with the growing demand to measure very volatile and semi-volatile toxic compounds, increasing attention has been given to the use of sampling tubes packed with additional sorbents.[3] In these so-called ‘multi-bed’ tubes, up to four sorbents are arranged in order of increasing strength from the sampling end, so that the less volatile, ‘sticky’ components only encounter the weakest sorbent, and are easily released when the gas flow is reversed during the subsequent thermal desorption process.

For this reason, multi-bed sorbent tubes are commonly used in ambient (outdoor) air monitoring,[4] and allow a wider volatility range of components to be quantitatively sampled and analysed. A recent revision of the key international standard method for material emissions testing and indoor air quality monitoring (ISO 16000-6)[1] includes the option to use multi-bed sorbent tubes. The type of multi-bed sorbent tube referred to in the new standard was used in the two studies reported here.[5,6]

Experimental

The protocols used are briefly summarised here – full details can be found in the cited references.

All experiments used **stainless steel 3½″ × ¼″ sorbent tubes** from Markes International, packed either with Tenax TA or with quartz wool–Tenax TA–Carbograph™ 5TD. All tubes were stringently conditioned before use using Markes’ **TC-20™** off-line tube conditioner. The conditioned tubes were capped prior to and after sampling with two-piece brass long-term storage caps fitted with PTFE ferrules.

Markes’ **Micro-Chamber/Thermal Extractor™** was used to sample volatiles emitted by polyurethane (PU) foam onto the sorbent tubes, followed by analysis using Markes’ **TD100-xr™** automated thermal desorber (Figure 1) with GC–MS.

Figure 1: Markes’ TD100-xr automated thermal desorber.

Emissions from polyurethane (PU) foam[5]

PU foam was freshly cut from a composite door known to release a mixture of very volatile, volatile and semi-volatile organic compounds (VVOCs, VOCs and SVOCs). Material samples were placed into individual micro-chambers equilibrated at 23°C and the emissions sampled onto the two types of sorbent tube. Two identical tubes, in series, were used in each case – a front 'sampling' tube, and a rear 'back-up' tube to collect any analytes that broke through. Sampling conditions were (a) 60 min with an air flow of ~80 mL/min, to generate the chromatograms shown in Figure 2, and (b) 15 min with an air flow of 50 mL/min, to generate the mean values shown in Figure 3.

Stability studies[6]

To generate the results shown in Figure 4, a mixture of chemical standards relevant to material emissions testing was loaded onto sorbent tubes in the gas phase (with or without methanol, as necessary) to give a nominal loading of 100 ng per component, with a bubbler used to generate humid atmospheres.

Results and discussion

Figure 2 compares emissions from the PU foam sample sampled using the two types of tube. It is immediately apparent that the multi-bed tubes show better recovery of the lightest analytes, n-pentane (b.p. 36°C) and methylcyclobutane (b.p. 36°C), with no detectable breakthrough of either analyte on the respective back-up tubes.

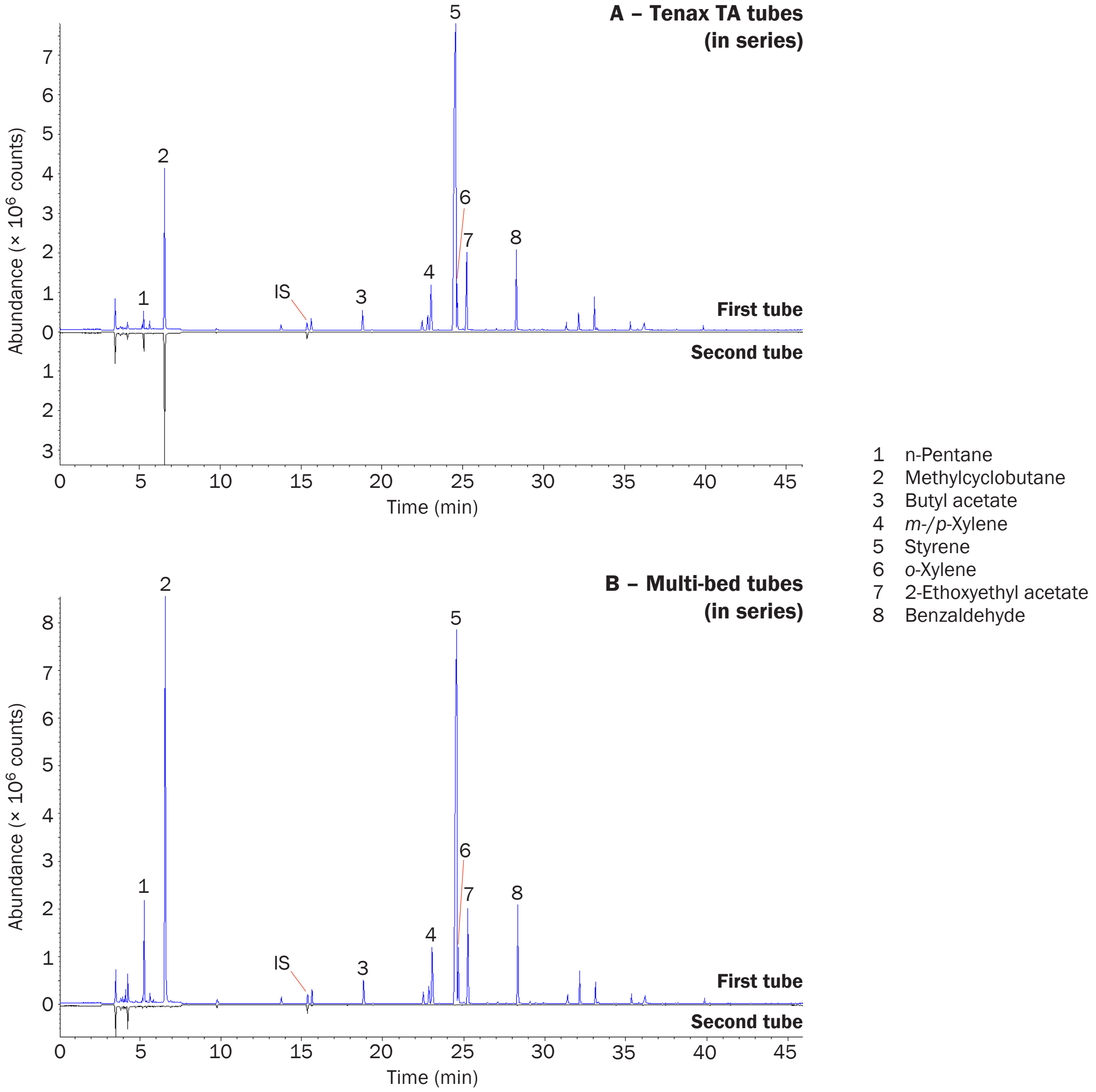

Figure 2: Analysis of emissions from PU foam (sampling volume ~4.6 L), sampled using the Micro-Chamber/Thermal Extractor onto (**A**) two Tenax TA tubes connected in series, and (**B**) two multi-bed tubes connected in series. Analysis used a TD100-xr automated thermal desorber and GC–MS. Internal standard (IS) = toluene-d_8.
Adapted from ref. 5 with permission from the Royal Society of Chemistry and the authors.

These results are confirmed by the analysis shown in Figure 2, which used the same setup except with a lower flow rate and shorter sampling time, more typical of a standard sampling protocol.

In the past, there have been concerns that, during storage, less volatile analytes might migrate from weaker sorbents to stronger sorbents within multi-bed tubes – a phenomenon that would result in compounds being irreversibly bound to the stronger sorbent. However, the 4-week stability data presented in Figure 3 shows that the performance of the multi-bed sorbent tubes was at least equal to that of the Tenax TA tubes. The authors note that while further tests on tubes loaded at higher humidities would be desirable, the results of this study indicated that the effect of humidity is relatively small.

Care must be taken with storage for extended periods on multi-bed sorbents (*i.e.* more than 2 months), because compounds can migrate to the strong sorbent and become irreversibly bound. The paper pointed out that, whatever the sorbent combination used, it is still advisable to analyse tubes as soon as possible after sampling, and ideally within 4 weeks.

Conclusions

These results demonstrate that multi-bed sorbent tubes packed with quartz wool, Tenax TA and Carbograph 5TD are compatible with an extended analyte range compared to single-bed Tenax TA tubes. As well as allowing simultaneous active/pumped sampling of volatiles from n-butane to n-C_{30}, the stability of a number of volatile analytes is found to be very similar on both tube types, confirming the suitability of these multi-bed tubes for a range of TD applications.

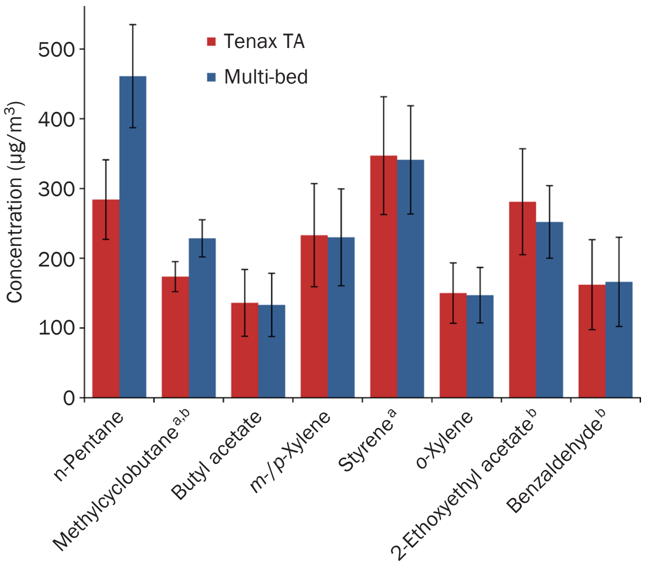

Figure 3: Mean concentrations (n = 7–9) with standard deviations for eight dominant compounds in the analysis of emissions from PU foam (sampling volume 0.75 L), sampled using the Micro-Chamber/Thermal Extractor onto two Tenax TA tubes connected in series (red), and two multi-bed tubes connected in series (blue). Analysis used a TD100-xr automated thermal desorber and GC–MS. [a] Values divided by 10 for ease of comparison. [b] No pure standard was available, and so quantitation used toluene equivalents.
Adapted from ref. 5 with permission from the Royal Society of Chemistry and the authors.

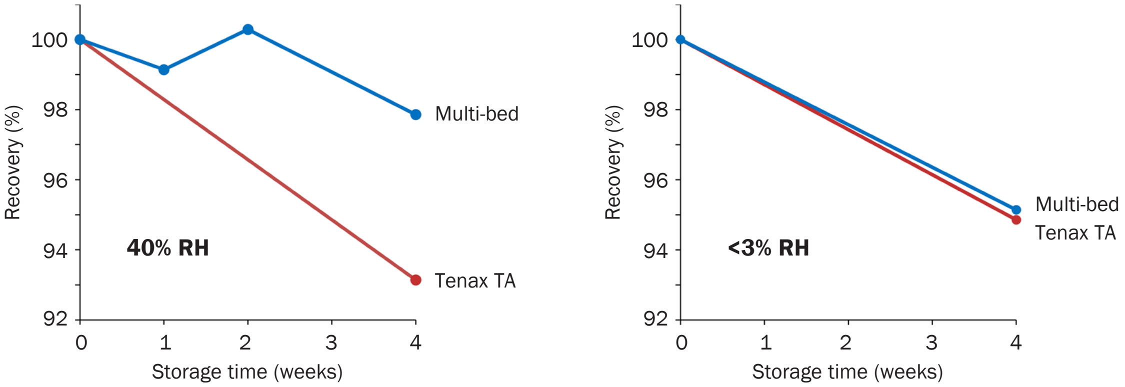

Figure 4: Mean percentage recoveries for n-hexane, methyl isobutyl ketone, toluene, butyl acetate, cyclohexanone, 1,2,3-trimethylbenzene and 4-phenylcyclohexene (nominally 100 ng each) from Tenax TA and multi-bed sorbent tubes (n = 5), stored for up to 4 weeks at room temperature, after loading using air of moderate and low relative humidity (40% RH and <3% RH). The individual 4-week recoveries across all seven compounds with a 40% RH loading were between 93% and 104%.
Image generated from data in ref. 6 with the permission of the authors.

Acknowledgement

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References

1. 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. Annex D specifies multi-bed sorbent tubes packed (as in this study) with quartz wool–Tenax TA–Carbograph 5TD, as an alternative to single-bed Tenax TA tubes.
2. EN TS 16516: Construction products: Assessment of emissions of regulated dangerous substances from construction products – Determination of emissions into indoor air.
3. A wide range of weak, medium and strong sorbents are commercially available for air monitoring – see Application Note 005 for a quick guide. For further information on sorbent selection, see: E. Woolfenden, Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods, *Journal of Chromatography A*, 2010, 1217: 2685–2694, http://dx.doi.org/10.1016/j.chroma.2010.01.015.
4. US EPA Method TO-17: Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes.
5. V.M. Brown and D.R. Crump, An investigation into the performance of a multi-sorbent sampling tube for the measurement of VVOC and VOC emissions from products used indoors, *Analytical Methods*, 2013, 5: 2746–2756, http://dx.doi.org/10.1039/c3ay40224j.
6. V.M. Brown, D.R. Crump, N.T. Plant and I. Pengelly, Evaluation of the stability of a mixture of volatile organic compounds on sorbents for the determination of emissions from indoor materials and products using thermal desorption/gas chromatography/mass spectrometry, *Journal of Chromatography A*, 2014, 1350: 1–9, http://dx.doi.org/10.1016/j.chroma.2014.05.011.

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