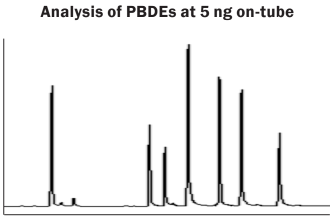
Application Note 140

Quantitative analysis of airborne semi-volatile flame retardants using sorbent tube sampling with TD–GC–MS

Summary

This study introduces the results of research into the performance of sorbent-tube sampling and Markes' thermal desorption (TD) systems for the analysis of two classes of flame retardants of current concern – polybrominated diphenyl ethers (PBDEs) and organophosphates (OPs). Key indicators of method performance for these challenging semi-volatile compounds are reproducibilities <10.3%, carryovers <3.2%, linearities >0.998 and LODs <0.171 ng/m^3, with a field study demonstrating the detection of OPs in indoor air at low ng/m^3 levels.


Analysis of PBDEs at 5 ng on-tube

Introduction

Flame retardants (FRs) are a diverse group of chemicals that are widely applied to furnishings and electronic equipment in order to comply with regulations on flammability. Three of the most important classes of flame retardants are:

- Polybrominated diphenyl ethers (PBDEs) – This is a group of 209 compounds with a strong tendency to persist in the environment, although they are now less commonly found in consumer products due to tight restrictions on their use in the EU and USA.
- Organophosphates (OPs or OPFRs) – These are symmetrically-substituted triesters of phosphoric acid, usually categorised as chlorinated or non-chlorinated. They are now commonly used in place of the phased-out PBDEs, and some of them are also used as plasticisers and lubricants.
- 'Novel' brominated flame retardants (NBFRs) are a diverse group of compounds that have also emerged in recent years as alternatives to PBDEs – but like that group they may also have a tendency to bioaccumulate. Examples include multiply-brominated derivatives of simple aromatics, diphenylethanes and medium-chain alkyl benzoates.

None of the FRs listed above are chemically bound to the substrate, meaning that they readily migrate into indoor air and dust, resulting in long-term exposure. This is of concern because many FRs are suspected of being harmful to humans, although (with the exception of PBDEs) knowledge of health impacts is limited. This uncertainty is compounded by the lack of information on the FRs used in consumer items, and the constant emergence of novel compounds and formulations. Reliable analysis of these challenging semi-volatile compounds in various substrates at low concentrations is therefore a priority.

A key aspect that needs to be taken into consideration during sampling of airborne FRs – which also applies to many other SVOCs of current concern – is the tendency of the lower-volatility compounds to bind to airborne particulate matter. This partitioning is reflected in standard practice for the analysis of airborne flame retardants, which typically involves pumped sampling onto a quartz filter to trap the particulates, backed-up with a polyurethane foam cartridge to collect the vapour-phase fraction. Analytes are then solvent-extracted from the two phases and concentrated using rotary evaporation and other traditional techniques, with subsequent analysis of the concentrated extracts by GC or GC–MS. This is the approach taken in ISO 16000-31,[1] which relates to monitoring of airborne OPs.

However, these approaches suffer from several disadvantages, including:

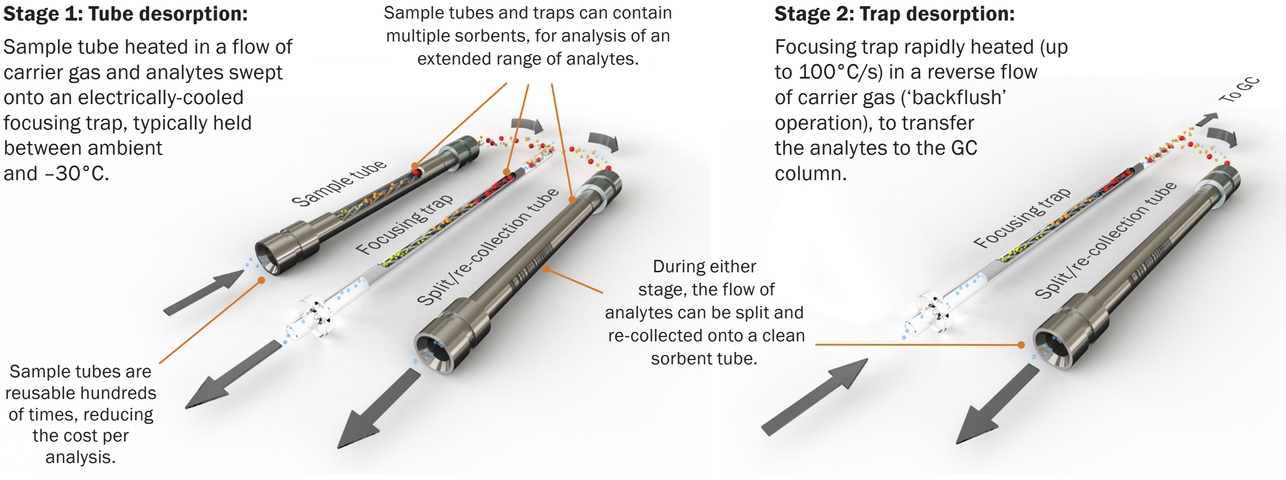
- The need for labour-intensive solvent-based sample preparation steps.
- Incomplete and/or variable extraction efficiency, which compromises repeatability.
- Susceptibility to errors such as artefact introduction and losses of the more volatile target compounds during concentration steps.
- The need 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),[2] and is now increasingly being applied to measurement of SVOCs, including compounds boiling up to n-C_{44} (b.p. 550°C). 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 next page), which allows smaller air volumes to be collected using portable battery-operated low-flow pumps.

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.

Sample tubes are reusable hundreds of times, reducing the cost per analysis.

With regard to FRs, TD has been applied to the analysis of:

(a) PBDEs, OPs and NBFRs in the vapour-phase, sampled by pumping air onto a sorbent-packed TD tube.[3]

(b) PBDEs bound to airborne particulates, sampled by pumping air onto a section of quartz filter, subsequently placed in an empty TD tube.[4]

(c) OP emissions from insulation boards and accumulated indoor dust, using dynamic headspace devices to sample air onto sorbent-packed TD tubes.[5]

In all cases thermal desorption of the tube is followed by analyte focusing and GC analysis. This study is based on work on PBDEs and OPs from the first of these reports,[3] and shows previously unpublished chromatographic data regarding the performance of pumped-tube sampling in conjunction with TD using Markes' TD100-xr thermal desorber (Figure 1) and GC–MS analysis.

Figure 1: Markes' TD100-xr thermal desorber.

Experimental

The conditions described below are recommended as suitable for the majority of FR analyses; full details of sampling procedures have been reported by Lazarov *et al.*[3]

Sample:
High-purity chemicals were used for this study. Standard solutions in methanol of the compounds listed in Table 1 were prepared, at concentrations ranging from 1 to ~13 ng/µL (for PBDEs) and 1.5 to ~55 ng/µL (for OPs). Each solution (1 µL) was loaded onto a pre-conditioned sorbent tube packed with beds of Tenax® TA and PDMS. However, inert-coated stainless steel 'SVOC' sorbent tubes (Markes International part no. C2-AAXX-5342) have equivalent performance, and we would recommend these for FRs.

A dynamic efficiency study with three gas volumes (432, 864 and 1296 L) indicated no breakthrough, and therefore the largest of these was selected both as the volume of clean air used to simulate typical air sampling volumes (in the method validation study), and as the actual sampling volume (in the real-air study). In both cases the flow rate was 300 mL/min for 72 h.

TD:

Instrument:	TD100-xr™ (Markes International)
Focusing trap:	'High-boilers' (Markes International part no. U-T1HBL-2S)
Tube desorption:	300°C (10 min) with a flow rate of 20 mL/min
Trap desorption:	10°C to 400°C (10 min), at maximum heating rate
Flow path:	250°C

No.	Full name	Abbreviation	CAS No.	SIM m/z
Polybrominated diphenyl ethers (PBDEs)				
1	2,2,4′-Tribromodiphenyl ether	PBDE-28	41318-75-6	406
2	2,2′,4,4′-Tetrabromodiphenyl ether	PBDE-47	5436-43-1	486
3	2,3′,4,4′-Tetrabromodiphenyl ether	PBDE-66	189084-61-5	486
4	3,3′,4,4′-Tetrabromodiphenyl ether	PDBE-77	93703-48-1	486
5	2,2′,3,4′,4-Pentabromodiphenyl ether	PBDE-85	182346-21-0	406
6	2,2′,4,4′,5-Pentabromodiphenyl ether	PBDE-99	60348-60-9	406
7	2,2′,4,4′,6-Pentabromodiphenyl ether	PBDE-100	189084-64-8	406
Organophosphate flame retardants (OPs)				
8	Tripropyl phosphate	TPP	513-08-6	141
9	Tri-n-butyl phosphate	TNBP	126-73-8	155
10	Tris(2-ethylhexyl) phosphate	TEHP	78-42-2	211
11	Triphenyl phosphate	TPhP	115-86-6	326
12	Tricresyl phosphate (o-, *m*-, *p*-)	TMPP	1330-78-5	367
13	Tris(2-chloroethyl) phosphate	TCEP	115-96-8	249
14	Tris(2-chloro-1-methylethyl) phosphate (mixture of stereoisomers)	TCIPP	13674-87-8	277
15	Tris(1,3-dichloro-2-propyl) phosphate	TDCIPP	13674-84-5	191

Table 1: The PBDEs and OPs examined in the current study.

GC:

Column:	ZB-SemiVolatiles™, 30 m × 0.25 mm × 0.25 µm
Column flow:	3 mL/min
Oven ramp:	100°C (7 min), then 10°C/min to 300°C (13 min)
Inlet:	320°C

MS:

Aux heater:	320°C
Ion source:	250°C
Mass range:	Selected ion mode (SIM) was used for the most intense fragment of each compound (see Table 1).

Results and discussion

1. Reproducibility

To test the reproducibility of the system for this type of analysis, replicates of nanogram-level standards were loaded onto tubes and analysed. Figure 2 shows the mean responses from the target analytes, indicating RSD values below 10.3% in all cases, and hence within the limit of 15–20% set out in ISO 16000-31.

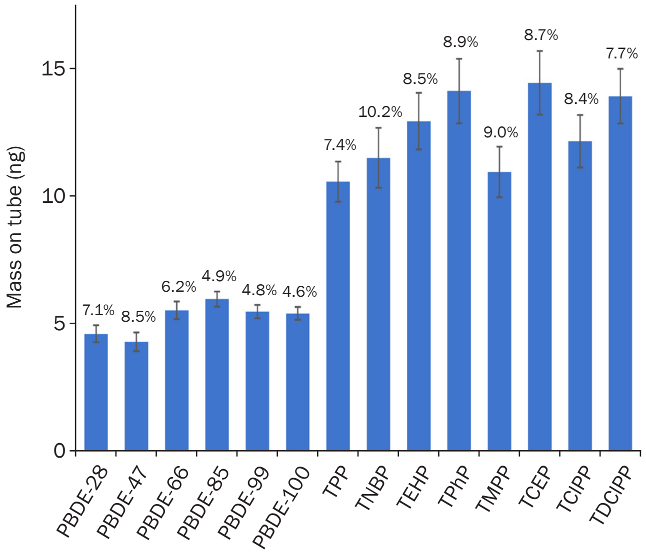


Figure 2: Mean response reproducibilities and RSDs for nanogram-level standard mixes (n = 6). Error bars: ± standard deviation.

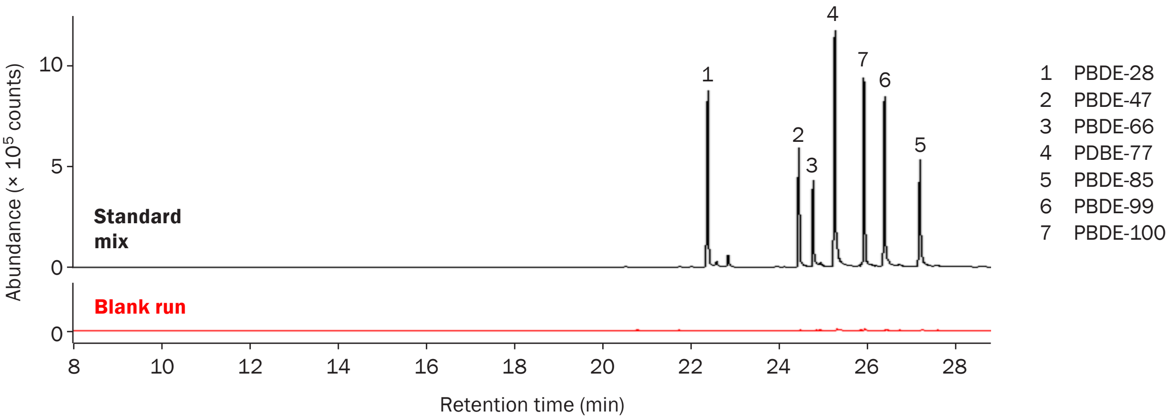


Figure 3: Top: Detection of PBDEs in a standard mix at 5 ng on-tube (m/z 406 + 486). Bottom: Subsequent analysis of a blank tube.

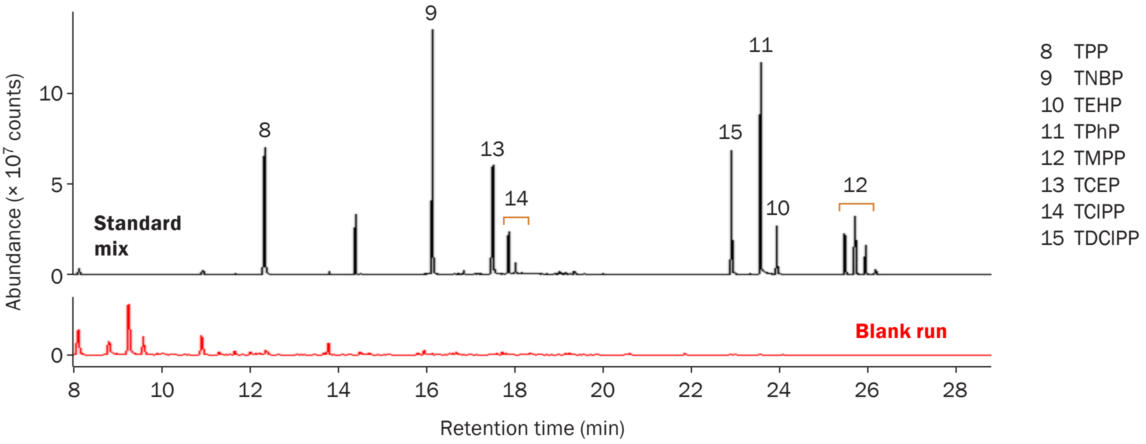


Figure 4: Top: Detection of OPs in a standard mix at 50 ng on-tube (m/z 141 + 155 + 191 + 211 + 249 + 277 + 326 + 367. Bottom: Subsequent analysis of a blank tube.

2. Carryover

Figure 3 shows the chromatographic response for 5 ng of the standard mix of PBDEs (equivalent to 25 ng/m^3 in a typical 200 L air sample) and for a subsequent blank run, showing carryover values of <2.5% for all compounds. Figure 4 shows analogous data for a 50 ng of the OP mix (equivalent to 250 ng/m^3 in a typical 200 L air sample), and indicates values <1.5% for all compounds except TEHP, which was 3.2%. These very low carryover values are attributable to the high temperatures of the flow path (250°C) and GC inlet (320°C).

3. Linearity

Tubes loaded with standards at the low to mid-nanogram level were used to calculate linearities, which were found to be excellent, with all R^2 values above 0.998 (Table 2 and Figure 5).

Name	R^2
PBDE-28	1.0000
PBDE-47	0.9999
PBDE-66	0.9999
PBDE-85	0.9996
PBDE-99	0.9997
PBDE-100	0.9997
TPP	0.9988
TNBP	0.9995
TEHP	0.9995
TPhP	0.9999
TMPP	0.9996
TCEP	0.9997
TDClPP	0.9993
TClPP	0.9993

Table 2: Linearity values (n = 3), at 1 to ~13 ng on-tube for PBDEs, and 1.5 to ~55 ng on-tube for OPs.

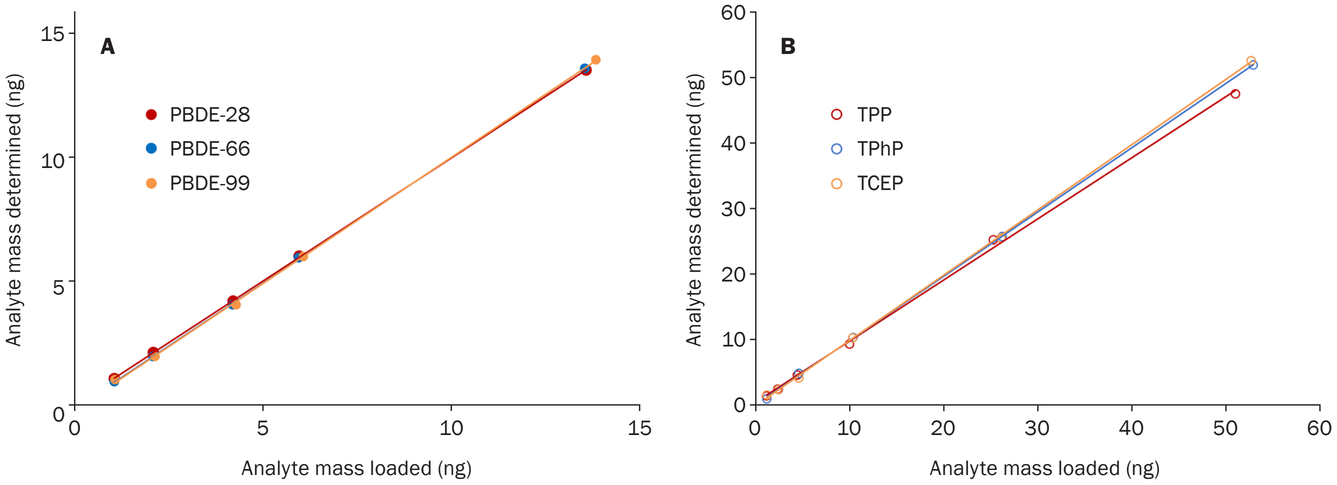


Figure 5: Example linearity plots for (**A**) diphenyl ethers substituted with three, four and five bromines, and (**B**) phosphate esters substituted with alkyl, aryl and chloroalkyl groups.

4. Limits of detection

Determination of LODs was based on the analysis of ten tubes spiked with the standard mix, determining the signal-to-noise ratio at this level and extrapolating the calibration curve to the concentration at which the signal-to-noise ratio was equal to 3. Values varied from 0.006 ng/m^3 for PBDE-28 to 0.171 ng/m^3 for TCEP – far below the 10 ng/m^3 value stipulated in ISO 16000-31. A full listing of values can be found in Lazarov *et al.*[3]

5. Real air sample

To assess the performance of the sorbent tube approach for monitoring OPs in a field study, 1296 L of air in an electrical workshop was pumped onto a sorbent tube and assessed for the presence of the target compounds by TD–GC–MS (Figure 6). TCEP and TCIPP were found at low ng/m^3 levels, which is typical for this type of indoor environment. A full set of results, including quantitation data, is available in Lazarov *et al.*[3]

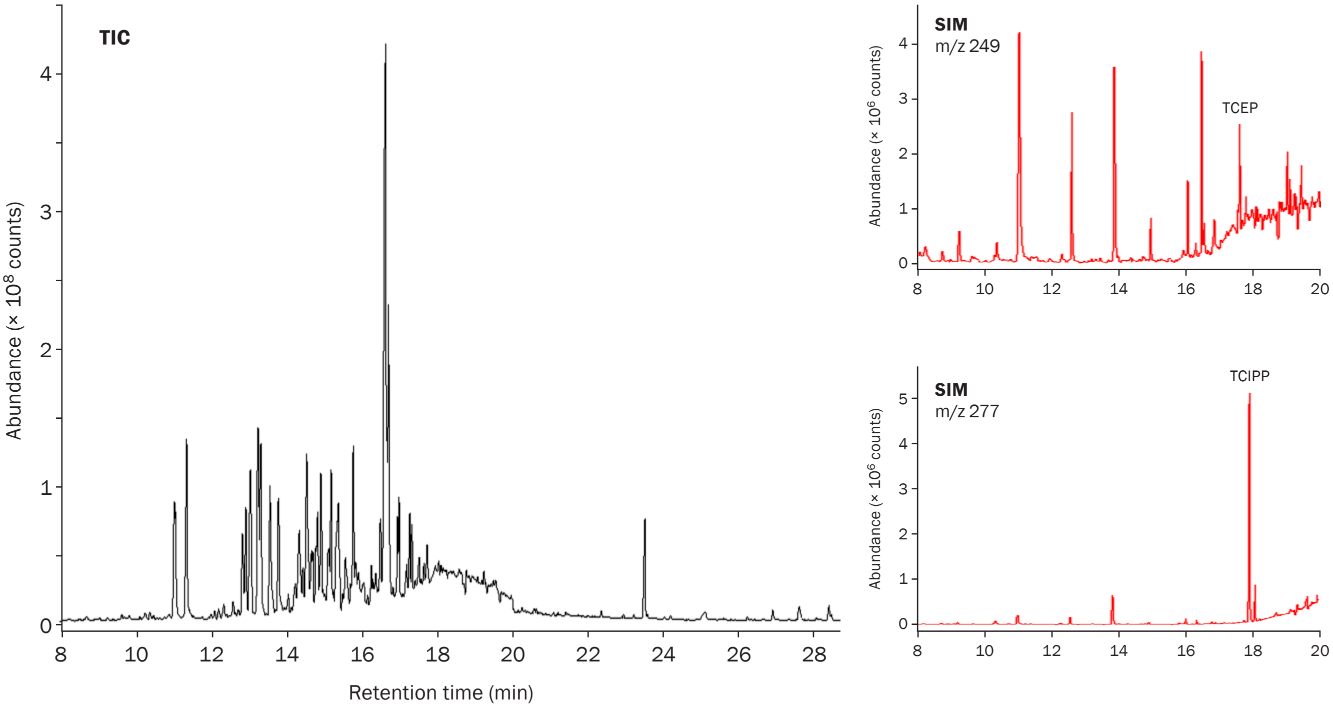


Figure 6: Analysis of 1296 L of air from an electrical workshop using sampling onto sorbent tubes followed by TD–GC–MS analysis. The insets show SIM chromatograms highlighting the detection of two target OPs.

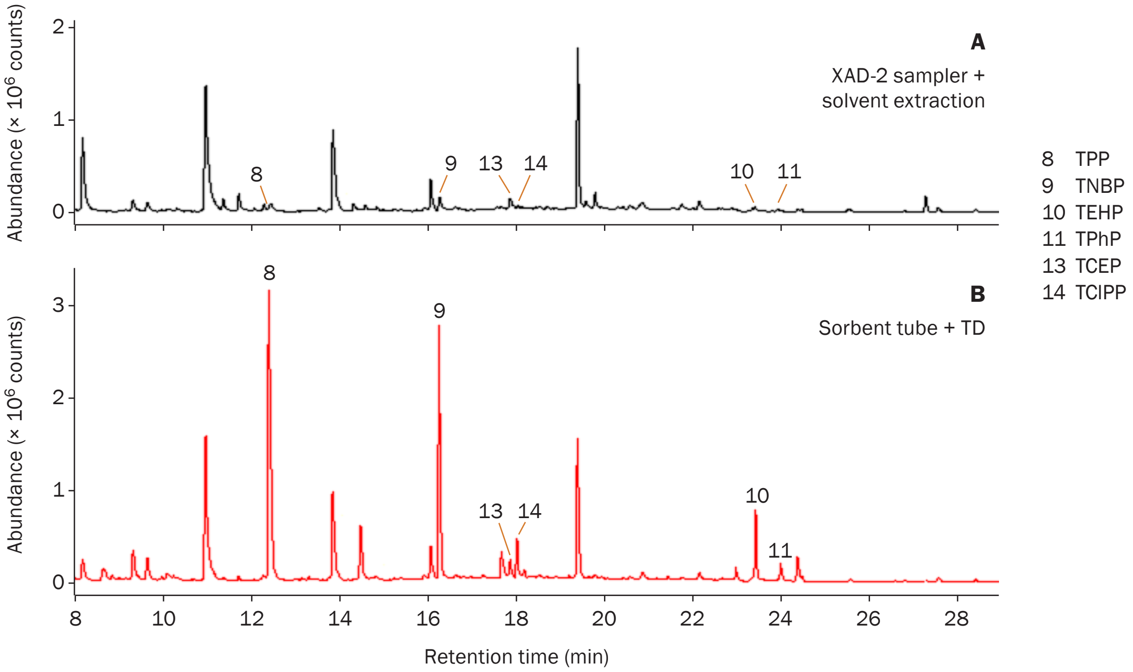


Figure 7: Comparison of the performance of two sampling approaches for the monitoring of OPs in a standard atmosphere, by pumped sampling onto: (**A**) an XAD-2 sampler followed by solvent extraction and GC–MS analysis; (**B**) a sorbent-packed TD tube followed by TD–GC–MS analysis.

6. Comparison of sampling approaches

In addition to the productivity advantages of TD compared to conventional sampling procedures, further work has shown that TD also offers better sensitivity and lower artefact levels for OPs in air (Figure 7), while still correlating well with XAD-2 sampling followed by solvent extraction.

Conclusions

This study demonstrates that sorbent-tube sampling with analysis on Markes' TD systems provides excellent performance for a range of PBDE and OP flame retardants. Key results include reproducibilities comfortably below those stipulated in ISO 16000-31, low carryover, excellent linearity and LODs below 0.2 ng/m^3.

TD system performance for other SVOCs has also been studied, and is described in Application Notes 136 (long-chain hydrocarbons), 137 (PCBs), 138 (phthalates) and 139 (PAHs).

Acknowledgements

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References

1. ISO 16000: Indoor air – Part 31: Measurement of flame retardants and plasticizers based on organophosphorus compounds – Phosphoric acid ester, International Organization for Standardization, 2014. The description of the sampling system references ISO 16000: Indoor air – Part 13: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDDs/PCDFs) – Collection on sorbent-backed filters, International Organization for Standardization, 2008.
2. 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.

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.
4. F. Mercier, P. Glorennec, O. Blanchard and B. Le Bot, Analysis of semi-volatile organic compounds in indoor suspended particulate matter by thermal desorption coupled with gas chromatography/mass spectrometry, *Journal of Chromatography A*, 2012, 1254: 107–114, http://dx.doi.org/10.1016/j.chroma.2012.07.025.
5. (a) B. Lazarov *et al.*, Influence of suspended particles on the emission of organophosphate flame retardant from insulation boards, *Environmental Science and Pollution Research*, 2016, 23: 17183–17190, http://dx.doi.org/10.1007/s11356-016-6886-8; (b) I. Liagkouridis, B. Lazarov, G. Giovanoulis and I.T. Cousins, Mass transfer of an organophosphate flame retardant between product source and dust in direct contact, *Emerging Contaminants*, 2017, 3: 115–120, http://dx.doi.org/10.1007/s11356-016-6886-8.

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