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Application Note 130

Microchamber sampling and TD–GC–MS analysis of chemical emissions from spray polyurethane foam (SPF) in accordance with ASTM D8142

Summary

This study describes the use of Markes' Micro-Chamber/Thermal Extractor (µ-CTE), followed by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS), to analyse volatile and semi-volatile organic compounds emitted from spray polyurethane foam, in accordance with ASTM D8142.

Introduction

Spray polyurethane foam (SPF) is a spray-applied polymer that is used to form a continuous layer on the internal surfaces of buildings. Its effectiveness as an insulator, speed of application, and compatibility with a range of surfaces means that it is widely used for building insulation and damp-proofing in the USA, and is rapidly gaining popularity elsewhere, especially in Asia and some European countries.

SPF is created on-site by mixing two liquids, known as the 'A side' and 'B side', which react and expand on contact to create a highly insulating foam that also seals gaps and forms a barrier to air and moisture. The 'A side' is commonly a mixture of methylene diphenyl diisocyanate (MDI) and polymeric methylene diphenyl diisocyanate (pMDI), while the 'B side' contains polyols (which react with the MDI to produce polyurethane), catalysts, blowing agents and flame retardants.

The presence of hazardous chemicals in these mixtures requires that strict safety procedures are followed during installation of SPF, including use of personal protective equipment. Even though this standard is not focused on misapplied foams, it is important to note that this is the cause of much of the concern regarding SPF. For example, if correct mixing procedures are not followed, then there is a risk of the SPF not being optimally formed, which can cause the gradual release of its component chemicals (at a rate that depends on environmental factors). This can lead to serious health effects for building occupants, including irritation of skin, airways and eyes, as well as respiratory sensitisation.

In order to understand the factors affecting release of these chemicals, and particularly for ongoing quality control, a need has emerged for reliable standard methods that enable assessment of emissions of these volatile and semi-volatile organic compounds (VOCs and SVOCs) from applied SPF.

Accordingly, industry, regulators and analytical chemists have collaborated on the development of two ASTM standards:

- ASTM D7859,[1] which defines a procedure for the spraying, sampling, packaging of SPF, and for the preparation of test specimens.
- ASTM D8142,[2] which describes the use of Markes' Micro-Chamber/Thermal Extractor™ (µ-CTE™) to sample VOCs and SVOCs from cured open-cell and closed-cell SPF.

This document describes the analysis of SPF in accordance with these standards, and presents results that show the performance of sampling using the µ-CTE, in conjuction with TD–GC–MS analysis.

Typical procedures

General points

The procedures described below are typical of those used for freshly prepared SPF insulation products. These methods can be used for individual-component, high-pressure or low-pressure formulations of open-cell and closed-cell SPF. However, the same setup (and similar conditions) are also applicable to existing installed SPF (for example, when odour issues are reported) or pre-formed blocks of polyurethane foam (PUF) used in furnishings.

It should be noted that the method does not cover the sampling and analysis of methylene diphenyl diisocyanate (MDI), other isocyanates, and many semi-volatile organic compounds. In the case of formaldehyde, the sampling procedure described below is applicable but the analysis method is different.[3]

Sample preparation

The standard method for the preparation of samples of SPF is described in ASTM D7859. In brief, the SPF is sprayed onto a 12″ × 12″ section of high-density polyethylene, and allowed to cure for 1 h before being packaged in an airtight bag for transport to the laboratory.

From the piece of SPF, a cylindrical section with 64 mm diameter is cut out using a dedicated µ-CTE SPF Sample Cutter (Figure 1), and this is transferred to one of the chambers of the µ-CTE (Figure 2). Sampling and analysis must be conducted as soon as possible after opening the airtight bag, and within 48 hours of spraying.

Figure 1: Markes' µ-CTE SPF Sample Cutter, with ejection disk and cutting mat.

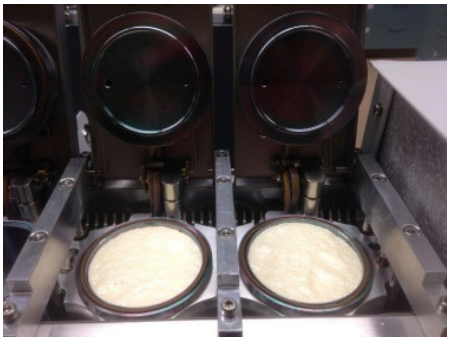


Figure 2: Generic closed-cell SPF samples in place within the µ-CTE.

Sampling and analysis

Two models of Markes' µ-CTE are available, and ASTM D8142 specifies the µ-CTE-250™ model for sampling volatiles released from SPF.

The µ-CTE-250 is a compact unit with four small cylindrical chambers, suitable for sampling chemical emissions from a wide variety of products and materials. In conjunction with analysis using thermal desorption (TD) and GC–MS, it has become very popular for the fast, inexpensive screening of emitted chemicals as part of compliance with industry regulations.

The operation of the µ-CTE-250 is as follows. With the sample material in place, the lids are closed, and a flow of purified air is applied, with the chambers being held at a set temperature (typically 35°C for this method, but the instrument can be set to a maximum of 250°C). After an appropriate period of equilibration, a sorbent tube is attached to the outlet of each chamber to trap volatile chemicals released from the sample (Figure 3).

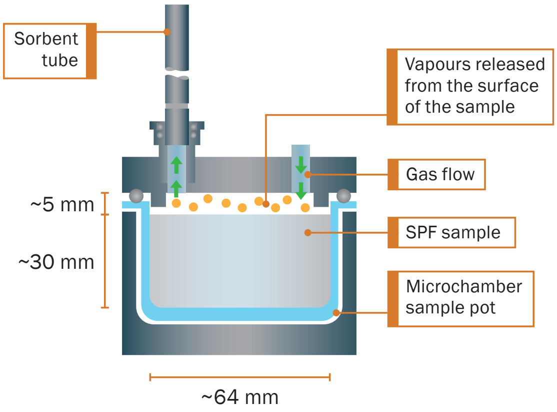


Figure 3: Cross-section of one of the four sample chambers of the µ-CTE-250, showing its operation for sampling emissions from cylindrical sections of SPF. Spacers can be used to raise the sample up to the correct height if it is not deep enough.

Two sorbent tubes are listed in the method:

- Tube A is suitable for volatile and semi-volatile compounds, because it allows sampling for longer durations without overloading the tubes with blowing agent.
- Tube B is suitable for smaller-volume sampling of the very volatile compounds.

Typically, sampling from a single section of SPF is conducted first onto Tube B, and then onto Tube A, in order to achieve optimum results for the full analyte range. The availability of four chambers, as well as allowing rapid screening of multiple samples, means that duplicate materials can be sampled in parallel under the same conditions, for assessing reproducibility.

Once the emitted chemicals have been collected on sorbent tubes using the µ-CTE-250, they are analysed by TD–GC–MS in accordance with ISO 16000-6[4] or US EPA Method TO-17.[5]

Temperature validation

ASTM D8142 requires measurement of the temperature of individual chambers of the µ-CTE-250 before they are used for the first time, and within 90 days of any subsequent use. Routine monitoring is easily performed by inserting a thermocouple into the sampling port of the µ-CTE-250, whereas more rigorous assessment of temperature performance is carried out by filling the chamber with deionised water to 50–75% of the chamber volume. The chamber is then set to heat at 35°C for at least 90 min, and the temperature is measured using a sensor inserted through the sampling port.

Chamber calibration

In addition to temperature validation, it is also advisable to check that the overall process of sampling is consistent between the individual chambers of the µ-CTE-250.

Figure 4: Markes' µ-CTE Chamber Calibration Tool, comprising PTFE sample block, blanking screw (which ensures a uniform sample surface for optimum airflow during sampling) and handle (for easy removal of the sample block).

Markes' µ-CTE Chamber Calibration Tool (Figure 4) makes it easy to achieve this. The PTFE sample block, which is the same height as a typical sample of SPF, is first placed into each chamber. A known volume of standard is then introduced into each of the three wells, and the sampling/GC method run as usual. The result is that the response is similar to that obtained from an SPF sample, but in a way that eliminates sample-to-sample variation, so allowing the responses from each chamber to be checked for consistency.

To demonstrate this process, the same amount of a mix comprising equal masses of benzene, toluene, ethylbenzene, *p*-xylene, n-decane, n-dodecane and n-hexadecane was loaded onto each of four calibration tools within the µ-CTE-250. Figure 5 shows the results, with RSDs being ≤12% for all seven compounds.

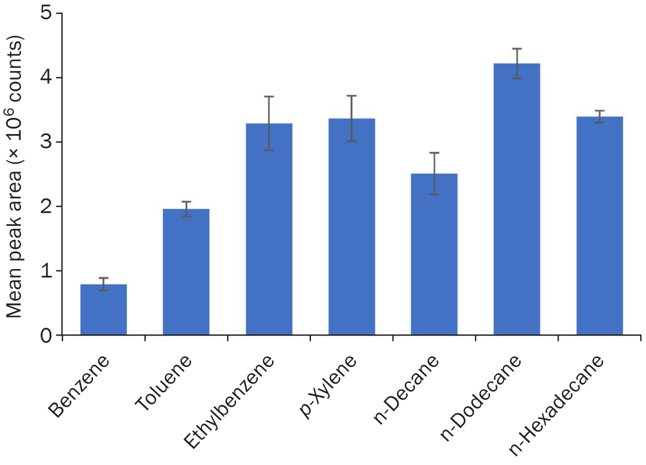


Figure 5: Mean responses (n = 4) for each component in 1 µL of the standard mix, acquired on the four chambers within a single µ-CTE-250 instrument.

The same process was then run again, but with different volumes of sample, to determine linearity of response (Figure 6). The results show that the following processes are all operating consistently at different analyte loadings: (a) injection into the well of the calibration tool, (b) extraction of VOCs by dynamic headspace, (c) sampling onto the sorbent tube, (d) TD–GC–MS analysis.

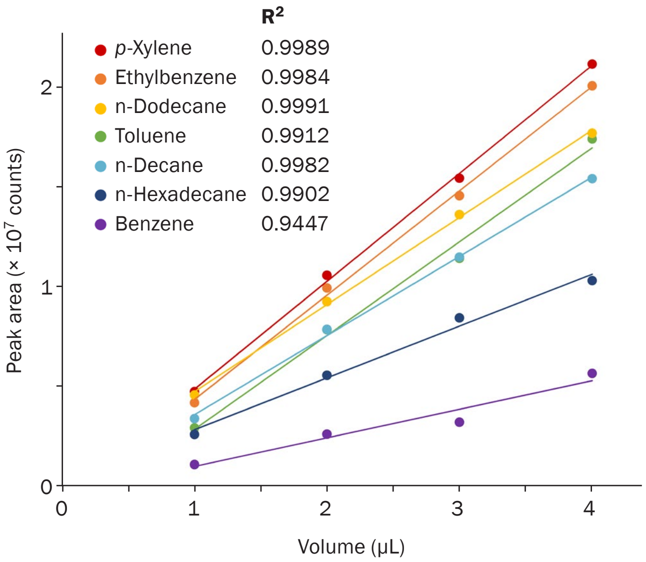


Figure 6: Linearity of response for each component in the standard mix from 1–4 µL, acquired on the four chambers within a single µ-CTE-250 instrument.

Experimental

Standards:
For the purposes of establishing method parameters, a generic SPF formulation was spiked with a mix of 19 compounds characteristic of SPF emissions (Table 1) and two internal standards (toluene-d_8 and the blowing agent dibromofluoromethane), in conjunction with a sorbent tube loaded with a surrogate (4-bromofluorobenzene). However, although the compounds listed in Table 1 are important, analyses of real SPF samples must report all compounds.

No.	Compound	CAS No.
1	1,1,1,3,3-Pentafluoropropane	460-73-1
2	Trimethylamine	75-50-3
3	1,1-Dichloroethene	75-35-4
4	Allyl chloride	107-05-1
5	*trans*-1,2-Dichloroethene	156-60-5
6	1,2-Dichloropropane	78-87-5
7	1,4-Dioxane	123-91-1
8	2-Ethyl-4-methyl-1,3-dioxolane	4359-46-0
9	Chlorobenzene	108-90-7
10	2-Butoxyethanol	111-76-2
11	1,4-Dichlorobenzene	106-46-7
12	Triethylenediamine	280-57-9
13	1,2-Dichlorobenzene	95-50-1
14	Bis(2-chloroisopropyl) ether	108-60-1
15	Bis[2-(*N*,*N*-dimethylamino)ethyl] ether	3033-62-3
16	Triethyl phosphate	78-40-0
17	Pentamethyldiethylenetriamine	3030-47-5
18	4-(1,1-Dimethylpropyl)phenol	80-46-6
19	Tris(1-chloro-2-propyl) phosphate	13674-84-5

Table 1: List of compounds spiked into the generic SPF formulation.

Sample (see also notes under ‘Typical procedures’):

Sample diameter:	64 mm
Sample depth:	~30 mm
Sample area:	0.00322 m^2
Typical sample mass:	0.7–4.0 g

Sampling (see also notes under ‘Typical procedures’):

Instrument:	µ-CTE-250 (Markes International)
Sorbent tubes:[6]	Tube A: ‘Material emissions’ (C3-AAXX-5304) Tube B: ‘Universal’ (C3-AAXX-5266)
Chamber temp.:	35°C[7]
Chamber flow:	50 mL/min dry air (<1% RH)
Loading factor:	200 m^2/m^3
Air change rate:	188 h^{-1}
Area-specific flow rate:	0.9–1 m/h
Equilibration time:	2 h
Sampling points:	2 and 24 h (for VOCs only); 2, 24, 48, 72 and 168 hours (for VOCs and SVOCs[8])
Sampling time:	Up to 2 h

TD (typical parameters):

Instrument:	TD100-xr™ (Markes International)
Flow path:	160°C
Split in standby:	10 mL/min
Cold trap:	‘Material Emissions’ trap containing quartz wool, Tenax TA and a graphitised carbon black (part no. U-T12ME-2S)
Dry-purge:	1 min, 20 mL/min flow to split
Prepurge:	0.1 min, default
Primary desorb:	270°C (8 min)
Trap flow:	35 mL/min, splitless
Pre-trap-fire purge:	1 min, 35 mL/min trap flow, 50 mL/min split flow
Trap low:	25°C
Trap high:	300°C (3 min)
Outlet split:	50 mL/min
Overall TD split	34.3 : 1

GC (typical parameters):

Transfer line:	Base-deactivated
Column:	Low-polarity, amine-optimised 5% diphenyl–95% dimethylpolysiloxane, 30 m × 0.25 mm × 0.5 µm
Column flow:	1.5 mL/min, constant flow
Oven program:	40°C (2 min) then 20°C/min to 300°C (2 min)
Total run time:	17.0 min
Carrier gas:	Helium

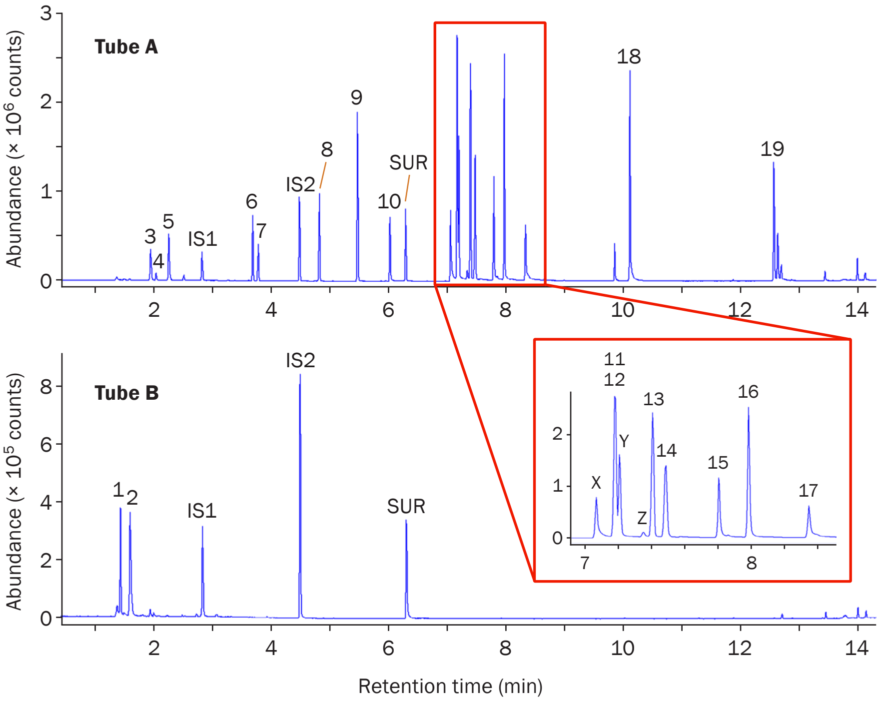
MS (typical parameters):

MS source:	230°C
MS quad:	150°C
MS transfer line:	250°C
Mass scan range:	m/z 40–550

Results and discussion

Chromatography

Two sections of SPF were prepared as described above, and sampled in parallel using the µ-CTE-250 onto Tubes A and B. Chromatograms are shown in Figure 7. All 19 compounds expected in the spiked generic SPF formulation are present, with three additional compounds (X, Y, Z) being identified using Tube A.



1	1,1,1,3,3-Pentafluoropropane
2	Trimethylamine
3	1,1-Dichloroethene
4	Allyl chloride
5	*trans*-1,2-Dichloroethene
IS1	Dibromofluoromethane
6	1,2-Dichloropropane
7	1,4-Dioxane
IS2	Toluene-d$_8$
8	2-Ethyl-2-methyl-1,3-dioxolane
9	Chlorobenzene
10	2-Butoxyethanol
SUR	4-Bromofluorobenzene
X	1,2-Dimethyl-1H-imidazole
11	1,4-Dichlorobenzene
12	Triethylenediamine
Y	Dimethyl butanedioate
Z	1,1′-Oxybis(propan-2-ol)
13	1,2-Dichlorobenzene
14	Bis(2-chloroisopropyl) ether
15	Bis[2-(*N*,*N*-dimethylamino)ethyl] ether
16	Triethyl phosphate
17	Pentamethyldiethylenetriamine
18	4-(1,1-Dimethylpropyl)phenol
19	Tris(1-chloro-2-propyl) phosphate

Figure 7: Parallel analysis of two sections of SPF using (top) Tube A for VOCs and semi-volatile flame retardants and (bottom) Tube B for very volatile blowing agents. Compounds spiked into the generic formulation are indicated with numbers (1–19); compounds X, Y and Z are additional to that list. IS = Internal standard (spiked into sample). SUR = Surrogate (spiked onto tube).

It is worth noting that for real-world samples, the longer sampling time and weaker sorbents in Tube A would result in breakthrough for very volatile species. In contrast, the shorter sampling time and different sorbents in Tube B enable sampling of very volatile species in the SPF formulation. In Figure 7, note the excellent peak shape for even the most volatile species, reflecting the highly efficient trapping and desorption achievable using Markes' thermal desorbers.

Emission calculations

In order to be able to relate the quantities of VOCs released from the SPF in the µ-CTE-250 to those obtained in larger environmental chambers or standard rooms, it is necessary to convert the masses of compounds collected on the sorbent tube to an area-specific emission rate. The relevant calculations are outlined in Figure 8.

Using the formula derived in Figure 8, with a sampling time of 30 min and a microchamber surface area of 0.03217 m^2, values for the area-specific emission rates were determined from the masses retained on Tube A in the current study. These are shown in Table 2.

The area-specific emission rate, A, is given by:

$$A\ (\text{ng m}^{-2}\ \text{min}^{-1}) = \text{VOC concentration}\ (\text{ng mL}^{-1}) \times \text{Area-specific flow rate}\ (\text{mL m}^{-2}\ \text{min}^{-1})$$

The individual parts of this expression can be expanded as follows:

$$\frac{\text{Mass of compound (ng)}}{\text{Sampling rate (mL min}^{-1}) \times \text{Sampling time (min)}} \times \frac{\text{Air exchange rate}, N}{\text{Loading factor}, L}$$

$$\frac{\text{Flow rate (mL min}^{-1})}{\text{Headspace volume (m}^{3})}$$

$$\frac{\text{Surface area (m}^{2})}{\text{Headspace volume (m}^{3})}$$

Substituting these back into the original equation gives:

$$A\ (\text{ng m}^{-2}\ \text{min}^{-1}) = \frac{\text{Mass of compound (ng)}}{\text{Sampling rate (mL min}^{-1}) \times \text{Sampling time (min)}} \times \frac{\text{Flow rate (mL min}^{-1})}{\text{Headspace volume (m}^{3})} \times \frac{\text{Headspace volume (m}^{3})}{\text{Surface area (m}^{2})}$$

In the µ-CTE the sampling rate and flow rate are identical and cancel out, and the headspace volume expressions also cancel out:

$$A\ (\text{ng m}^{-2}\ \text{min}^{-1}) = \frac{\text{Mass of compound (ng)}}{\cancel{\text{Sampling rate (mL min}^{-1})} \times \text{Sampling time (min)}} \times \frac{\cancel{\text{Flow rate (mL min}^{-1})}}{\cancel{\text{Headspace volume (m}^{3})}} \times \frac{\cancel{\text{Headspace volume (m}^{3})}}{\text{Surface area (m}^{2})}$$

This leaves:

$$A\ (\text{ng m}^{-2}\ \text{min}^{-1}) = \frac{\text{Mass of compound (ng)}}{\text{Sampling time (min)} \times \text{Surface area (m}^{2})}$$

Using conventional units of µg m^{-2} h^{-1} gives:

$$\boxed{A\ (\mu\text{g m}^{-2}\ \text{h}^{-1}) = \frac{\text{Mass of compound (ng)}}{\text{Sampling time (min)} \times \text{Surface area (m}^{2})} \times 0.06}$$

Figure 8: Derivation of formula for determining area-specific emission rate.

No.	Compound	Mass on-tube (ng)	Area-specific emission rate (μg m^{-2} h^{-1})
3	1,1-Dichloroethene	287.1	17.85
4	Allyl chloride	258.1	16.04
5	*trans*-1,2-Dichloroethene	405.0	25.18
6	1,2-Dichloropropane	410.1	25.50
7	1,4-Dioxane	408.6	25.40
8	2-Ethyl-4-methyl-1,3-dioxolane	394.7	24.54
9	Chlorobenzene	404.5	25.15
10	2-Butoxyethanol	447.3	27.81
X	1,2-Dimethyl-1H-imidazole	702.6	43.68
11	1,4-Dichlorobenzene	398.3	24.76
12	Triethylenediamine	436.9	27.16
Y	Dimethyl butanedioate	472.8	29.39
Z	1,1′-Oxybis(propan-2-ol)	281.5	17.50
13	1,2-Dichlorobenzene	394.7	24.54
14	Bis(2-chloroisopropyl) ether	395.4	24.58
15	Bis[2-(*N*,*N*-dimethylamino)ethyl] ether	482.6	30.00
16	Triethyl phosphate	544.9	33.87
17	Pentamethyldiethylenetriamine	460.6	28.63
18	4-(1,1-Dimethylpropyl)phenol	448.6	27.89
19	Tris(1-chloro-2-propyl) phosphate	461.7	28.71

Table 2: Masses of analytes retained on Tube A and conversion to area-specific emission rates using the formula derived in Figure 8.

Conclusions

This study shows how Markes' Micro-Chamber/Thermal Extractor (μ-CTE-250) can be used to sample VVOCs, VOCs and SVOCs from SPF in accordance with ASTM D8142. The capability to simultaneously sample emissions from up to four samples enables time-efficient sampling onto the two tube types specified, and also speeds up routine screening of SPF samples.

Used in conjunction with TD–GC–MS, the μ-CTE-250 is able to provide data on the area-specific emission rates of chemicals from SPF. Accordingly, the new ASTM standard recognises the μ-CTE-250 as a valuable tool for SPF manufacturers needing to demonstrate quality control and understand the factors affecting emissions from their products.

Acknowledgements

Markes International gratefully acknowledges John Sebroski at Covestro LLC (Pittsburgh, PA, USA) for reviewing a draft of this document, and for his work as the task group chair for ASTM D8142.

References and notes

1. ASTM D7859: Standard practice for spraying, sampling, packaging, and test specimen preparation of spray polyurethane foam (SPF) insulation for testing of emissions using environmental chambers, ASTM International, 2013, www.astm.org/Standards/D7859.htm.
2. ASTM D8142: Standard test method for determining chemical emissions from spray polyurethane foam (SPF) insulation using micro-scale environmental test chambers, ASTM International, 2017, www.astm.org/Standards/D8142.htm.
3. Sampling and analysis of formaldehyde is not compatible with TD–GC analysis, because of its volatility and reactivity. However, DNPH cartridges can be placed on the outlets of the μ-CTE, and subsequently analysed using HPLC (in accordance with ASTM D5197 and ISO 16000-3).
4. ISO 16000-6: Indoor air. 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, www.iso.org/standard/52213.html.
5. US EPA Method TO-17: Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes, US EPA, 1999, www3.epa.gov/ttn/amtic/airtox.html.
6. Breakthrough volumes on these sorbent tubes have been measured at ≥12 L, suggesting safe sampling volumes of 8 L.
7. The possible variation of emission profiles with temperature results in a need for the temperature of the microchambers to be tightly controlled (±1°C). This must be verified with a traceable device with an accuracy of at least ±1°C between 30°C and 40°C.
8. Note that some SVOCs may take longer than 2 h to equilibrate using these conditions, so for such compounds the reading at 2 h should be used for information only.

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