

Application Note 130

Microchamber sampling and TD-GC-MS analysis of chemical emissions from spray polyurethane foam (SPF) in accordance with ASTM standard WK40293

Summary

This Application Note describes the use of Markes' high-temperature Micro-Chamber/Thermal Extractor (μ -CTE), followed by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS), to analyse potentially hazardous volatile and semi-volatile organic compounds (VOCs and SVOCs) emitted from spray polyurethane foam (SPF), in accordance with the forthcoming ASTM standard WK40293.



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 chemicals, and particularly for ongoing quality control, there is a need for manufacturers to develop a reliable standard method for assessing emissions of chemicals from applied SPF.

ASTM standards relating to SPF

To address the issues surrounding SPF quality control, industry, regulators and analytical chemists have collaborated on the development of standards relating to the analysis of chemical emissions from SPF. Accordingly, in 2013, a standard practice was released by ASTM.¹ This defines a procedure for the spraying, sampling, packaging of SPF, and for the preparation of test specimens.

At the time of writing (July 2017), several other ASTM standards relating to the assessment of emissions from SPF are in various stages of preparation.^{2,3} One of these, Work Item WK40293,³ describes the use of Markes' Micro-Chamber/Thermal Extractor to sample volatile and semi-volatile organic compounds (VOCs & SVOCs) from cured SPF, and is expected to be published in late 2017. Analysis of SPF in accordance with this method is the subject of this document.

The Micro-Chamber/Thermal Extractor™ (μ -CTE™)

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

With the sample material in place, the lids are closed, and a flow of pure air is applied, with the chambers being held at a set temperature. After an appropriate period of equilibration, a sorbent tube is attached to the outlet of each chamber to trap VOC/SVOCs released from the sample (Figure 1). Alternatively, in the case of formaldehyde monitoring, DNPH cartridges can be placed on the outlet, and subsequently analysed using HPLC.

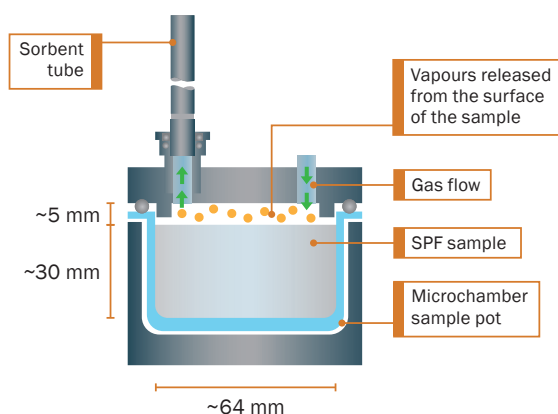


Figure 1: Cross-section of the μ -CTE showing its operation for sampling emissions from cylindrical sections of SPF. Spacers can be used to raise the sample up to the correct height if it is not deep enough.

Two models of the μ -CTE are available, which differ in the number and size of chambers and the maximum temperature to which they can be heated. Only the high-temperature model is specified within the ASTM SPF standard, and this has four chambers with a diameter of 64 mm, and a maximum temperature of 250°C. The availability of multiple 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.

Experimental

The procedure outlined below is a typical procedure for freshly prepared SPF insulation products, including two-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. Once the emitted chemicals have been collected on sorbent tubes, they are analysed by TD-GC-MS in accordance with US EPA Method TO-17 or ISO 16000-6.

It should be noted that the method does not cover the sampling and analysis of MDI (subject of a separate method, currently in development), other isocyanates, and many semi-volatile organic compounds (SVOCs). Formaldehyde, because of its volatility and reactivity, is not compatible with TD-GC analysis, and is instead collected on DNPH cartridges, with analysis by HPLC, in accordance with ASTM D5197 and ISO 16000-3. Within the framework of WK40293, the same method is also used for the analysis of two less volatile aldehydes, acetaldehyde and propanal.

Internal standards:

Blowing agent: Dibromofluoromethane (200 ng per tube)
Other compounds: Toluene- d_8 (200 ng per tube)

Sample preparation:

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



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

transport to the laboratory. From this piece of SPF, a cylindrical section is cut out using a dedicated coring tool, and this is transferred to one of the chambers of the μ -CTE, in which it fits snugly in order to minimise surface effects (Figure 2).

Sample diameter: 64 mm
Sample depth: ~30 mm
Sample area: 0.00322 m²
Typical sample mass: 0.7–4.0 g

For the purposes of establishing method performance, it is recommended to use a generic SPF formulation spiked with the above-mentioned internal standards and 19 compounds. These include some compounds known to be part of the formulation, but also those identified as potential future targets (Table 1). However, for analyses of real samples, the method requires that all compounds are reported.

Sampling:

Sampling and analysis must be conducted as soon as possible after opening the airtight bag, and within 48 hours of spraying. Two sorbent tubes are listed in the method: Tube A is

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	<i>trans</i> -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-(<i>N,N</i> -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 included in the generic SPF formulation.

suitable for the less 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 less volatile blowing agents. 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 range of analytes.

Instrument: Micro-Chamber/Thermal Extractor (Markes International)

Sorbent tubes:⁴ Tube A (for VOCs and semi-volatile flame retardants): Quartz wool–Tenax® TA–Graphitised carbon black; Tube B (for very volatile blowing agents): Tenax TA–Graphitised carbon black–Carbonised molecular sieve

Chamber temp.: 35°C⁵

Chamber flow: 50 mL/min dry air (<1% RH)

Loading factor: 200 m²/m³

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 SVOCs⁶)

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 onto the two types of sorbent tubes. Chromatograms are shown in Figure 3.

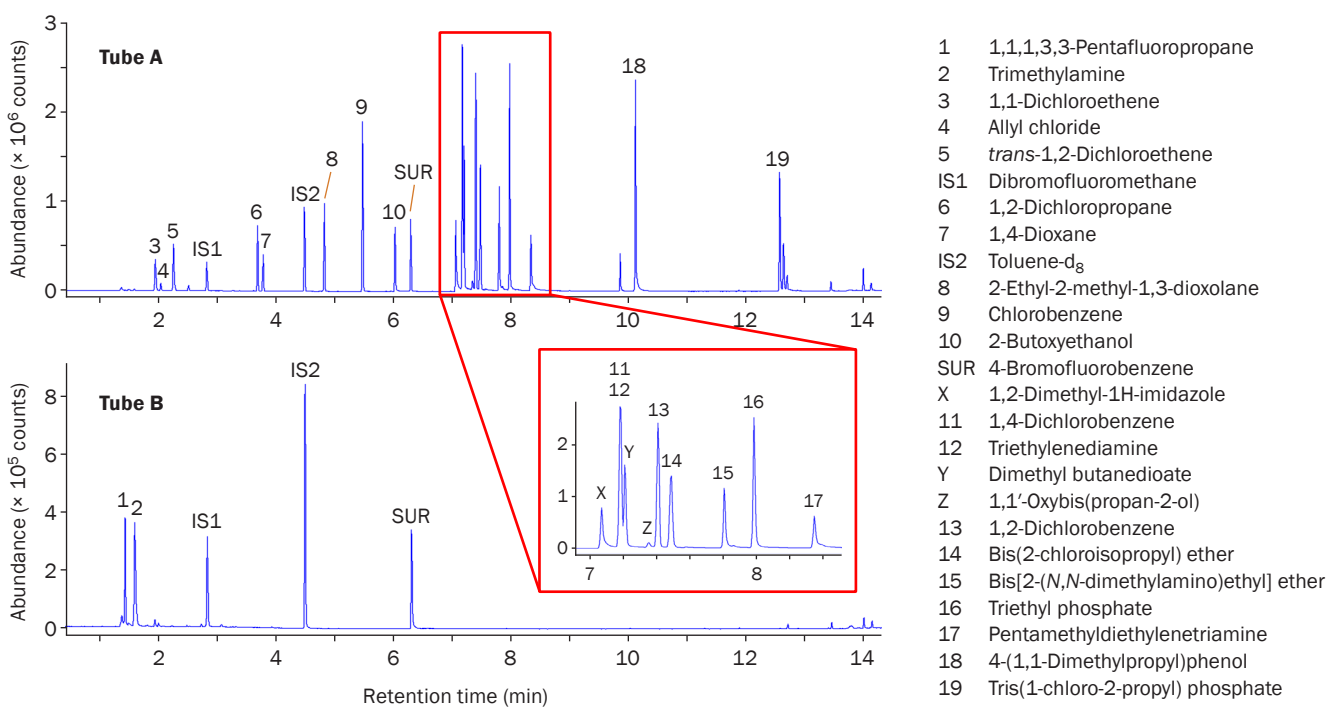


Figure 3: Parallel analysis of two sections of SPF using (top) Tube A for VOCs and semi-volatile flame retardants and (bottom) Tube B for very volatile blowing agents. Compounds spiked into the generic formulation are shown with numbers (1–19); compounds X, Y and Z are additional to that list. IS = Internal standard (spiked into sample). SUR = Surrogate (spiked onto tube).

The area-specific emission rate is given by:

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

$$= \frac{\text{Mass of compound (ng)}}{\text{Sampling rate (mL min}^{-1}) \times \text{Sampling time (min)}} \times \frac{\text{Air exchange rate, } N}{\text{Loading factor, } L} \quad (2)$$

N and L are defined as follows:

$$\text{Air exchange rate, } N = \frac{\text{Flow rate (mL min}^{-1})}{\text{Headspace volume (m}^3)} \quad (3)$$

$$\text{Loading factor, } L = \frac{\text{Surface area (m}^2)}{\text{Headspace volume (m}^3)} \quad (4)$$

Substituting expressions (3) and (4) into (2) gives:

$$\text{Area-specific emission rate (ng m}^{-2} \text{ min}^{-1}) = \frac{\text{Mass of compound (ng)}}{\text{Sampling rate (mL min}^{-1}) \times \text{Sampling time (min)}} \times \frac{\text{Flow rate (mL min}^{-1}) \times \text{Headspace volume (m}^3)}{\text{Headspace volume (m}^3) \times \text{Surface area (m}^2)} \quad (5)$$

Given that the sampling rate and flow rate are identical, then (5) can be simplified to:

$$\text{Area-specific emission rate (ng m}^{-2} \text{ min}^{-1}) = \frac{\text{Mass of compound (ng)}}{\text{Sampling time (min)} \times \text{Surface area (m}^2)} \quad (6)$$

Expressing the area-specific emission rate in conventional units of $\mu\text{g m}^{-2} \text{ h}^{-1}$ gives:

$$\text{Area-specific emission rate (}\mu\text{g m}^{-2} \text{ h}^{-1}) = 0.06 \times \frac{\text{Mass of compound (ng)}}{\text{Sampling time (min)} \times \text{Surface area (m}^2)} \quad (7)$$

Figure 4: Derivation of formula for determining area-specific emission rate.

All 19 compounds expected in the spiked generic SPF formulation are present, with three additional compounds (X, Y, Z) being identified using Tube A. For real-world samples, the longer sampling time and weaker sorbents for Tube A would be expected to result in breakthrough (and so reduced responses) for the most volatile species. In contrast, the shorter sampling time and modified sorbent packing for Tube B would result in strong responses for the blowing agents in the SPF formulation. In Figure 3, 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 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 4.

Using expression (7) with a sampling time of 30 min and a microchamber surface area of 0.03217 m², 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.

No.	Compound	Mass on-tube (ng)	Area-specific emission rate ($\mu\text{g m}^{-2} \text{ h}^{-1}$)
3	1,1-Dichloroethene	287.1	17.85
4	Allyl chloride	258.1	16.04
5	<i>trans</i> -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-(<i>N,N</i> -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 expression (6) in Figure 4.

Conclusions

In this study, we have shown how Markes' Micro-Chamber/Thermal Extractor (μ -CTE) can be used to sample VOCs and SVOCs from SPF in accordance with the forthcoming ASTM standard. The capability to simultaneously sample emissions from up to four samples enables time-efficient sampling onto the two tube types stipulated, and also speeds up routine screening of SPF samples.

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

Acknowledgements

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References

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. See www.astm.org/COMMIT/SUBCOMMIT/D2205.htm for a listing of current and forthcoming methods.
3. ASTM Work Item WK40293: New test method for determining chemical emissions from spray polyurethane foam (SPF) insulation using micro-scale environmental test chambers, www.astm.org/DATABASE.CART/WORKITEMS/WK40293.htm.
4. Breakthrough volumes on these tubes have been measured at ≥ 12 L, suggesting safe sampling volumes of 8 L.
5. The possible variation of emission profiles with temperature results in a need for the temperature of the microchambers to be tightly controlled ($\pm 1^\circ\text{C}$). This must be verified with a traceable device with an accuracy of at least $\pm 1^\circ\text{C}$ between 30°C and 40°C .
6. 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 only be used for informative purposes.

Trademarks

Micro-Chamber/Thermal ExtractorTM, μ -CTETM and TD100-xrTM are trademarks of Markes International.

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