Application

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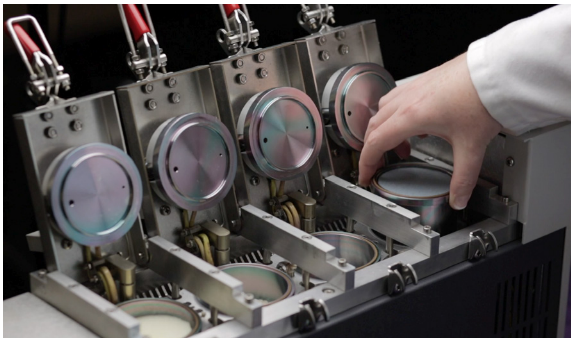
Application Note 067

An introduction to microchamber sampling for rapid screening of chemical emissions from construction materials and consumer products

Summary

This Application Note describes how volatile and semi-volatile organic compounds (VOCs and SVOCs) from products and materials can be rapidly sampled onto sorbent tubes using Markes' Micro-Chamber/Thermal Extractor (µ-CTE). Its modes of operation are described, evidence is presented for its performance, and the benefits for routine laboratory screening are explained.



Introduction

High-profile international regulatory developments and increased consumer awareness of hazardous chemicals in everyday products are driving global demand for improved assessment and labelling of products with respect to their intentional or unintentional release of chemicals – see Application Note 068.

These new regulations impact a large proportion of the manufacturing industry, with producers of flooring, furniture, wood-based products, insulation materials, spray polyurethane foam, coatings, adhesives, sealants, vehicle trim, domestic goods, cleaning products and medical devices being affected, together with all their suppliers.

Product certification typically requires both third-party testing by accredited laboratories, and implementation of simpler emissions screening methods as part of routine in-house product quality control. Thermal desorption (TD), used in conjunction with gas chromatography–mass spectrometry (GC–MS) is widely acknowledged as a valuable approach to such analysis (see Application Note 089), and is commonly used in conjunction with three sampling protocols, described below.

Reference tests using small chambers

The most widely recognised material emissions test methods for construction products ('reference tests') are carried out using relatively compact test chambers (typically 0.1–1 m^3), known as small chambers. A sample of the test material is placed into the chamber so that only the emitting surface is exposed. Volatiles are then swept onto a sorbent-packed tube in a flow of clean, humidified air at ambient (or slightly elevated) temperature. The sorbent tubes are then analysed using TD–GC–MS.

This procedure is typically carried out by accredited third-party laboratories as part of initial product certification or labelling, with the analysis conducted in accordance with one or more standard methods. Key methods include ISO 16000-6,[1] ISO 16000-9,[2] EN 13999 (for adhesives),[3] EN 16516,[4] ASTM D5116,[5] ASTM D6196,[6] and California Specification 01350.[7]

Reference tests like these provide the best available approach for simulating real-world use of products. However, they take a considerable time (typically 3–28 days per sample). This makes them expensive and impractical for routine quality control, or for research & development.

Direct desorption

Direct desorption is sometimes used to estimate emissions from a material or to measure its total content of VOCs and SVOCs. It is simple and readily automated, and avoids the labour-intensive sample preparation associated with conventional liquid extraction methods.

However, it is only applicable to small, relatively homogeneous samples, and results may not correlate well with data from 'surface-only' emission tests. The use of elevated temperatures (*e.g.* 90°C or 120°C) and the extraction of compounds from the whole sample, not just the surface, are also issues.

Microchambers

Microchambers such as Markes' Micro-Chamber/Thermal Extractor™ (µ-CTE™) are based on the same fundamental principles as small chambers, but in scaled-down form, meaning that equilibration and sampling can be carried out much more quickly. At the same time, the samples can be substantially larger than for direct desorption, which also results in improved reproducibility for composite samples. The operation and performance of the µ-CTE is the subject of this Application Note.

Figure 1: Markes' μ-CTE. Left: Six-chamber model. Right: Four-chamber model.

Overview of the μ-CTE

Markes' μ-CTE™ (Figure 1) overcomes the drawbacks of small chambers and direct desorption, so providing industry analysts with a versatile, easy-to-use tool for rapid emissions screening.

The chambers are held at room (or elevated) temperature under a flow of (optionally humidified) pure air or nitrogen. This releases the vapours dynamically from the sample, and these are then trapped on sorbent tubes connected to the outlet of each chamber. A constant flow of gas is maintained through each microchamber whether or not a sorbent tube is attached, and no pumps or additional mass flow control equipment is required. Once sampled, the sorbent tubes are analysed off-line using TD–GC–MS.

The μ-CTE is available in two models, both of which allow multiple samples to be tested simultaneously:

- The **four-chamber model** has a maximum temperature of 250°C and a chamber volume of 114 cm^3.
- The **six-chamber model** has a maximum temperature of 120°C and a chamber volume of 44 cm^3.

Both models of the μ-CTE offer three modes of operation:

- **Bulk emissions testing** is valuable for emissions profiling, and for testing of raw materials (Figure 2A).
- **Surface emissions testing** is suitable for determining area-specific emission rates from planar samples (Figure 2B). See Application Note 103 (flooring) and Application Note 130 (spray polyurethane foam).
- **Permeation testing** uses a dedicated accessory to allow volatiles permeating through a thin layer of material to be measured (Figure 2C). Full details of this mode of operation are provided in Application Note 121.

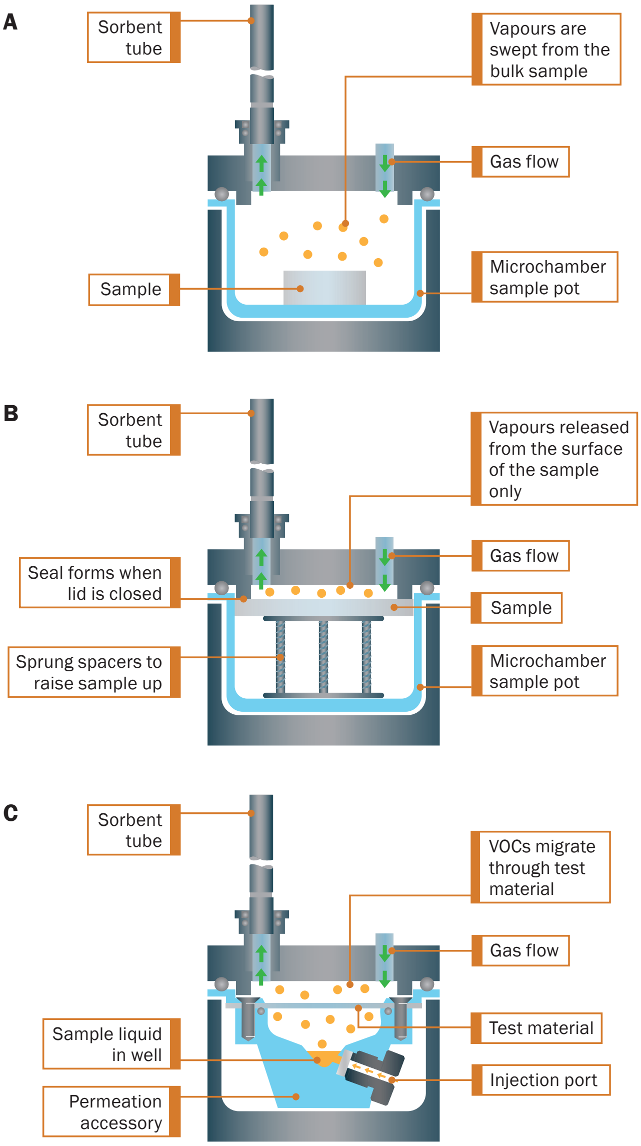


Figure 2: Operation of the μ-CTE for sampling emissions of volatile chemicals (**A**) from bulk samples, (**B**) from the surfaces of flat samples, and (**C**) permeating through a thin layer of material.

The μ-CTE is required for compliance with a number of standard methods, including ISO 12219-3 (automotive materials),[8] ISO 16000-25 (building products),[9] ASTM D7706 (products),[10] ASTM WK40293 (spray polyurethane foam),[11] the GUT Emission Test (carpets),[12] and VDI 2083-17 (cleanrooms).[13] It is also cited as a secondary screening method in EN 16402 (paints and varnishes)[14] and EN 16516 (construction products).[4]

Operation of the µ-CTE

Vapour sampling

When the µ-CTE has reached the set temperature, the microchambers containing the correctly-positioned samples are placed within it, and the lids sealed. A controlled flow of air/gas is passed through all chambers simultaneously. After equilibration (typically for 20–30 minutes), conditioned sorbent tubes are attached to each microchamber, and the air/gas flow sweeps vapours from the material and onto the sorbent tube.

Microchamber tests can be carried out at ambient or elevated temperature. For testing emissions from construction materials or products, moderate temperatures (30–60°C) are used to boost sensitivity and compensate for the relatively small sample size without affecting correlation with ambient-temperature data from small chambers. Typical equilibration times for sampling VOCs range from 20–30 min, with subsequent vapour sampling for 15–20 min at 50 mL/min. These conditions allow four or six samples to be processed every hour. Optional toggle valves allow the gas flow to unused chambers to be turned off, reducing gas consumption, and a Humidifier Accessory can supply the µ-CTE with 50% humidified air. This allows closer simulation of conditions used in reference tests, and can enhance the recovery of some less-volatile polar compounds.

The µ-CTE can also be operated at higher temperatures and flow rates for extended periods, for example when testing the emission of semi-volatile ‘fogging’ compounds from car trim materials or electronic components.

Off-line analysis of trapped vapours

After vapour sampling, the sorbent tubes are analysed by TD–GC–MS (for technical advice on optimising TD methods for material emission applications, see Application Note 056). The analytical process is carried out off-line, allowing a fresh set of samples to be introduced to the µ-CTE while analysis of the previous set continues.

Formaldehyde monitoring

Formaldehyde is too volatile and reactive to monitor using TD–GC methods, and so is usually sampled onto DNPH cartridges, followed by HPLC analysis in accordance with ISO 16000-3[15] or ASTM D5197.[16] The µ-CTE is compatible with these cartridges, but it should be noted that much larger volumes of vapour are typically sampled (*e.g.* 250 mL/min for 2–4 hours), limiting throughput to four or six samples every 2–4 hours.

Performance of the µ-CTE

This section briefly summarises performance characteristics of the µ-CTE. A full peer-reviewed paper on the subject has been published in *Analytical and Bioanalytical Chemistry*,[17] and is reproduced in Application Note 073.

Blank profile and sink effects

Blank profiles from the µ-CTE show low/sub-nanogram quantities of individual VOCs, and low levels of total VOC (TVOC) background, even at elevated temperatures (Figure 3). This satisfies the most stringent requirements of relevant standard methods.

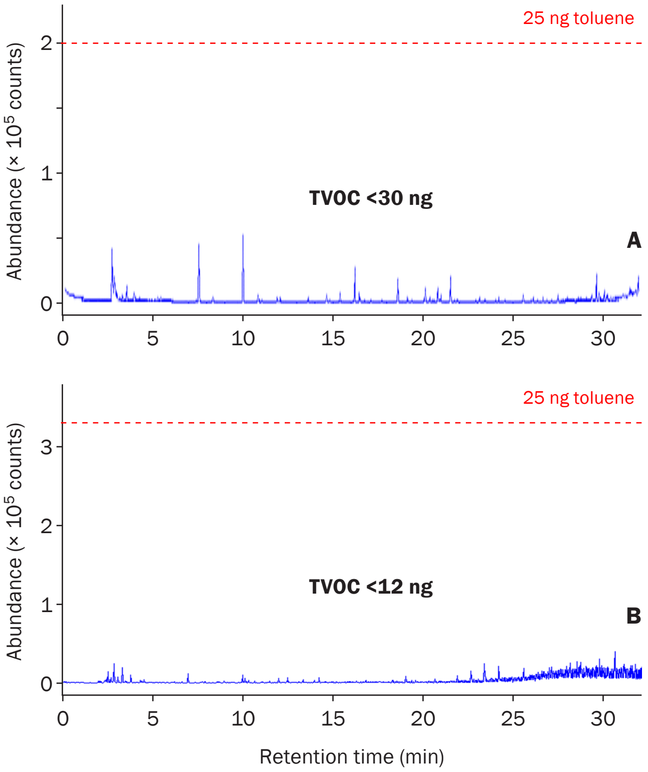


Figure 3: Blank profiles from (**A**) the six-chamber µ-CTE at 120°C and (**B**) the four-chamber µ-CTE at 250°C.

The independent heating of all µ-CTE components prevents surface adsorption/condensation and sample-to-sample carryover. Microchamber surfaces are constructed from inert-coated stainless steel to minimise sink effects (Figure 4), and microchamber/lid assemblies are easily removed from the µ-CTE for cleaning. PTFE inserts can be used to introduce liquid standards to empty microchambers for recovery tests.

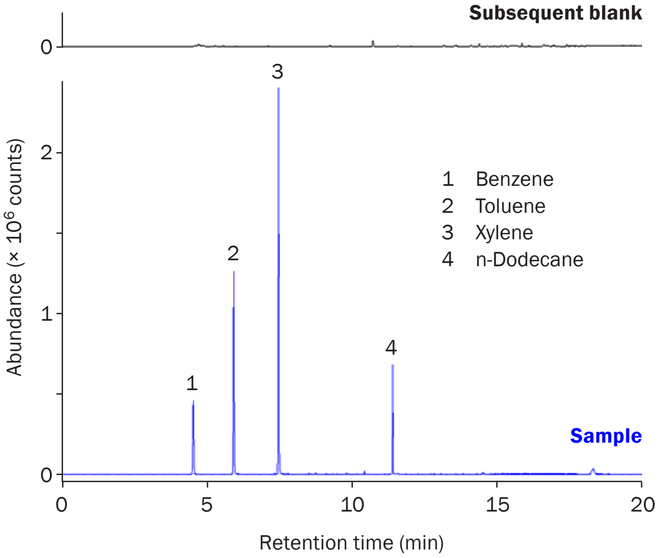


Figure 4: Running a standard followed by a blank shows the minimal carryover/sink effects of the µ-CTE. Conditions were 40°C at 50 mL/min for 20 min.

Air/gas flow within the microchambers

Patented technology[18] maintains a constant flow of air or gas through each microchamber, regardless of sorbent tube impedance (or whether a sorbent tube is attached at all). This is demonstrated in Figure 5 and Table 1. The absence of a pump or mass flow controller makes the system fundamentally easy to use, and ideal for routine operation by the manufacturing industry.

The orientation of the air/gas inlet at 90° to the emitting sample surface maximises turbulence and eliminates regions of zero or low flow. During surface emissions testing, air velocities are roughly uniform across the sample surface, and range from ~0.5 cm/s at 50 mL/min inlet gas flow, to ~5 cm/s at 500 mL/min.

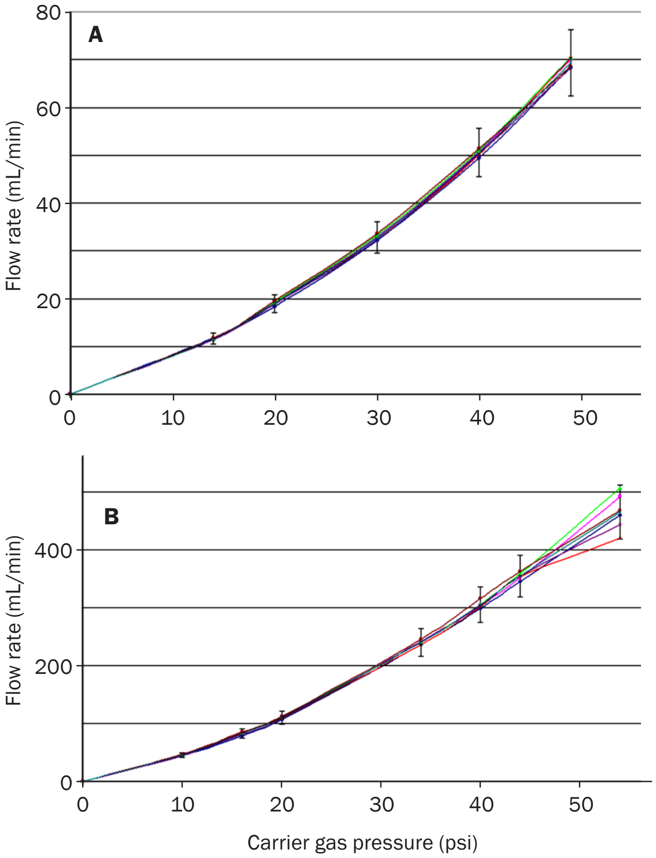


Figure 5: Stability of flow through six microchambers over (**A**) a low-flow range and (**B**) a high-flow range. Traces show the responses from each of the six microchambers, with error bars set at 10% of the mean value.

Tube	Low flow rate (mL/min)	High flow rate (mL/min)
None	42.4	346
Single-bed (Tenax® TA)	42.3	344
Three-bed (Tenax® TA–Carbograph™ 1TD–Carboxen™ 1003)	42.1	337

Table 1: The stability of flow through the microchambers is independent of sample tube impedance.

Bulk materials can simply be weighed directly into an empty microchamber, or into a custom-made 'sample boat' placed in the chamber. In this case, air velocity will be determined by the free volume within the microchamber and the air flow.

Degree of precision

In order to demonstrate the level of agreement between results obtained using the individual chambers in a μ-CTE, standards of toluene in methanol were introduced to each microchamber (Figure 6A). Results were found to vary within just ±5% across all six microchambers.

A similar experiment was carried out by introducing six identical samples of ABS terpolymer to the μ-CTE and monitoring emissions of butadiene and styrene. This time, the μ-CTE was operated at 65°C with vapour sampling at 50 mL/min for 15 min. The deviation of response across all six microchambers was 7.6% for butadiene and 5.4% for styrene (Figure 6B). This level of precision is remarkably good for any material emissions testing procedure.

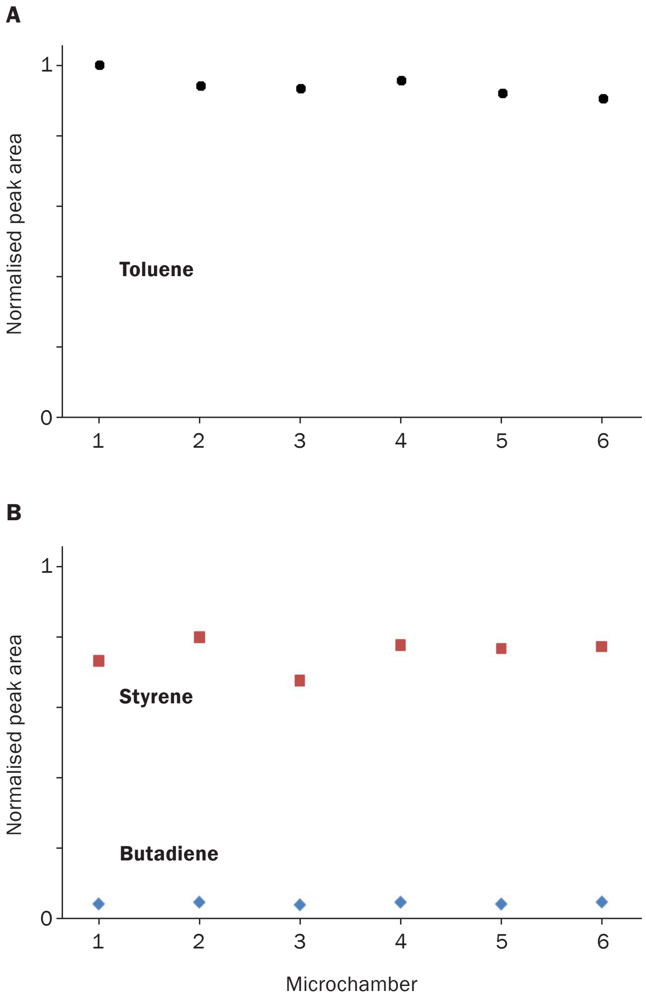


Figure 6: Precision of response for (**A**) a toluene standard and (**B**) two components of an ABS terpolymer sample. Conditions were 40°C with vapour sampling at 50 mL/min for 20 min.

Correlation with reference test methods for product emissions

Emissions data obtained using the µ-CTE has been shown to correlate in absolute terms with results from reference methods that specify small chambers (see Application Note 073). In addition, the fast emissions screening data obtained using the µ-CTE has been found to allow reliable estimation of longer-term results from small-chamber tests, enabling demonstration of continued compliance with certification requirements. More detail on this can be found in Application Note 069.

Applications of the µ-CTE

The µ-CTE is a versatile tool, compatible with a wide range of products and materials – examples are presented in two of Markes' Application Guides (Consumer Environmental Health and Automotive studies), and in the following Application Notes:

- Adhesives: 103
- Car trim: 093
- Flooring tiles: 103
- Glazing spacers: 103
- Lacquers: 103
- Polymer films and laminates (permeation): 121
- Pre-formed polyurethane foam (PUF): 113
- Plasterboard: 090
- Sealants (for museum display cases): 110
- Spray polyurethane foam (SPF): 130
- Wood (mahogany): 090

Conclusions

This Application Note has demonstrated that Markes' µ-CTE is valuable for assessing VOC and SVOC emissions from a wide range of construction materials and consumer products. Key benefits are reproducibility and speed of sampling – up to six samples can be processed in parallel in less than 60 minutes, enabling reliable comparison between samples and offering significant benefits for sample throughput.

Another major advantage of the µ-CTE is that the results obtained can be used to predict emissions from the expensive long-term certification tests required by national and global regulations, reducing costs and saving time in the process of optimising formulations.

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