Thermal Desorption Technical Support

Note 67: Introducing the Micro-Chamber/Thermal Extractor™ (µ-CTE™) for rapid screening of chemicals released (emitted) by products and materials

Keywords:

REACH, IgCC, CPD/CPR, DNPH cartridge, wood, semi-conductor, car trim

Introduction

Recent regulatory activity is driving demand for material emissions testing. Such activities include:

- the adoption of the Registration Evaluation and Authorisation of CHemicals (REACH) directives (Europe and China)
- the inclusion of tighter controls on chemical emissions from construction products in new US building codes (the International Green Construction Code [IgCC] initiative)
- mandating emissions testing under the European Construction Products Directive/Regulation (CPD/CPR).

These new regulations involve taking environmental and consumer health into consideration as an 'Essential Requirement' for product certification. Evaluating the potential environmental and health impact of a product or material means assessing the nature and level of chemicals being released under normal use (see TDTS Note 68 for more details). Product certification may require both third-party testing by accredited labs (using reference methods) and implementation of simpler emissions screening methods as part of routine product quality control (QC) in-house.

The most widely recognised material emissions test methods for construction products were the product of many years of development. These 'reference tests' are carried out using small emissions test chambers (typically 0.1–1 m^3) or cells. A sample of the test material/product is placed into the chamber or cell, such that only the emitting surface is exposed. Volatile and semi-volatile emissions are swept onto a sorbent tube in a flow of clean, humidified air at ambient (or slightly elevated) temperature. The sorbent tubes (typically Tenax® TA or carbon sorbents) are then analysed using thermal desorption (TD) with GC/MS (see TDTS Notes 55 and 56). Relevant standard methods include ISO/EN 16000-6/-9/-10/-11, CEN TC351 WG2 protocols and ASTM standards D5116, D6196 and D7143. These are typically carried out by accredited third-party laboratories as part of initial product certification or labelling.

Reference tests like these provide the best available approach for simulating real-world use of products; however, they take a considerable length of time, typically 3–28 days per sample. This makes them expensive and impractical for use in manufacturing, *e.g.* for routine QC of emissions or for research & development.

Direct TD/extraction of volatile and semi-volatile organic compounds (VOCs & SVOCs) from a material is sometimes used to estimate emissions or to measure its total (S)VOC content (see TDTS Notes 9, 40, 59 and 65). Direct TD overcomes the labour-intensive sample preparation processes associated with conventional liquid extraction methods. It involves weighing a small sample (typically 10–100 mg) of the material into an empty TD tube and applying heat and a flow of inert gas. (S)VOCs are swept from the sample, refocused (concentrated) and then injected into the GC or GC/MS.

Direct TD is a simple, readily-automated procedure; however, results may not correlate well with data from 'surface-only' emission tests. Key issues include the limited sample size, the use of significantly elevated temperatures (*e.g.* 90°C or 120°C) and the extraction of (S)VOCs from the whole sample, not just the surface. Correlation is particularly poor for complex composite samples.

Introducing the Micro-Chamber/Thermal Extractor (μ-CTE)

Figure 1: Markes' Micro-Chamber/Thermal Extractor units

To address the limitations of direct TD for surface emissions sampling, Markes International has developed the multi-sample Micro-Chamber/Thermal Extractor (μ-CTE). This provides industry and researchers with a versatile and straightforward tool for rapid emissions screening. Based on the same fundamental principles as small emissions test chambers and cells, the μ-CTE can be used either for testing surface emissions (*i.e.* to produce data that correlates with reference emissions tests), or extraction of bulk (content) emissions (*e.g.* polymer pellets or small, plastic, moulded components).

Markes' two μ-CTE units comprise either four or six micro-chambers (36 mm depth x ~64 mm i.d. [114 mL max. volume] or 28 mm depth x ~45 mm i.d. [44.5 mL max. volume], respectively), which allow multiple samples to be tested simultaneously (Figure 1). When testing surface emissions, the sample is raised within the chamber until the collar projecting down from the lid comes into contact with the sampling surface (Figure 2). The area of exposed sample surface in the four- and six-chamber μ-CTE units is 246 mm^2 and 128 mm^2, respectively. Samples of different thickness can be accommodated using appropriately sized spacers. Alternatively, a small amount (grams) of the test sample can be weighed into the bottom of each micro-chamber for bulk emissions (or content) testing (Figure 2).

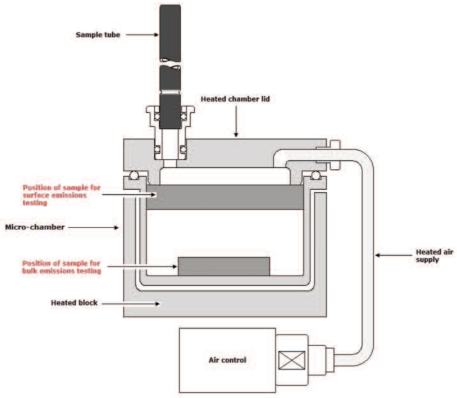

Figure 2: Schematic of a single micro-chamber, depicting use for surface or bulk emissions testing

Micro-Chamber/Thermal Extractor: Description of operation

When the μ-CTE unit has reached its prescribed temperature, the individual micro-chambers containing correctly-positioned samples are placed in the unit and the lids are sealed. A controlled flow of air or inert gas is passed through all chambers simultaneously. After an equilibration period (typically 20–30 minutes), conditioned sorbent tubes are attached to each micro-chamber to begin the vapour sampling process. As the pure air or gas passes over the surface or around the bulk sample, vapours are swept from the material, out of the micro-chamber and onto the attached sorbent tube.

The micro-chambers are also compatible with measuring formaldehyde emissions using DNPH cartridges.

Patented technology[1] maintains a constant flow of air or gas through each micro-chamber regardless of sorbent tube impedance or whether a sorbent tube is attached (Figures 3 and 4, Table 1); no pump or mass flow controller is required. This makes the system fundamentally easy to use, and ideal for routine operation by the manufacturing industry.

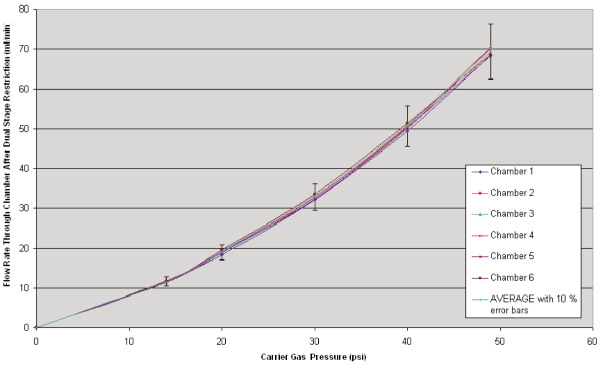

Figure 3: Stability of flow through six micro-chambers over a low flow range (5–50 mL/min)

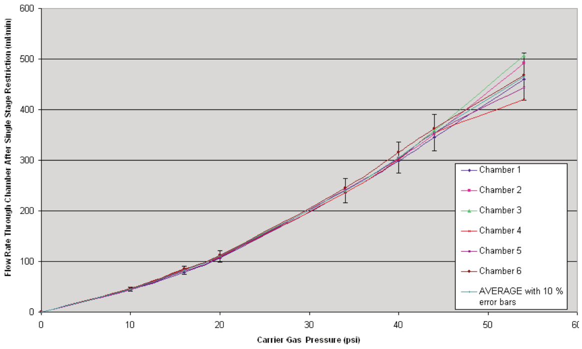

Figure 4: Stability of flow through six micro-chambers over the high flow range (50–500 mL/min)

Tube	Low flow rate (mL/min)	High flow rate (mL/min)
No tube	42.4	346
Single sorbent (Tenax® TA)	42.3	344
Three-bed sorbent (Tenax TA®/Carbograph™ 1TD/Carboxen 1003)	42.1	337

Table 1: Illustrating the stability of micro-chamber flow, independent of sample tube impedance

Micro-chamber tests can be carried out at ambient or elevated temperatures. In the case of testing emissions from building materials/products, moderate temperatures (*i.e.* 30–60°C) are used to boost sensitivity and compensate for the relatively small sample size without affecting the correlation with data from conventional chambers/cells at ambient temperature. Typical equilibration times range from 20–30 minutes for VOCs, with subsequent vapour sampling (15–20 minutes) at 50 mL/min. These conditions allow four or six samples to be processed every hour.

Formaldehyde monitoring, *e.g.* according to ISO 16000-3 or ASTM D5197, typically requires much larger volumes of vapour to be sampled (*e.g.* 250 mL/min for 2–4 hours) and may require humidification of the inlet gas supply. Throughput in this case is therefore limited to four or six samples every 2–4 hours.

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.

Offline analysis of trapped vapours

After vapour sampling, trapped organic vapours undergo analysis by TD–GC(MS), as per standard methods ISO 16000-6, ISO/EN 16017-1, ASTM D6196, *etc*. Alternative analysers, for example systems combining TD with process MS or e-nose detectors, may also be applicable in some cases.

The analytical process is carried out offline, allowing a fresh set of samples to be introduced to the µ-CTE while analysis of the previous set is ongoing. Offline operation also allows chemical analysis by third-party laboratories if preferred.

Key performance criteria

Blank profile and sink effects

Blank profiles from Markes' µ-CTE units show low/sub-nanogram quantities of individual VOCs, and low levels of total VOC (TVOC) background, even at elevated temperatures (Figure 5). This satisfies the most stringent requirements of relevant standard methods.

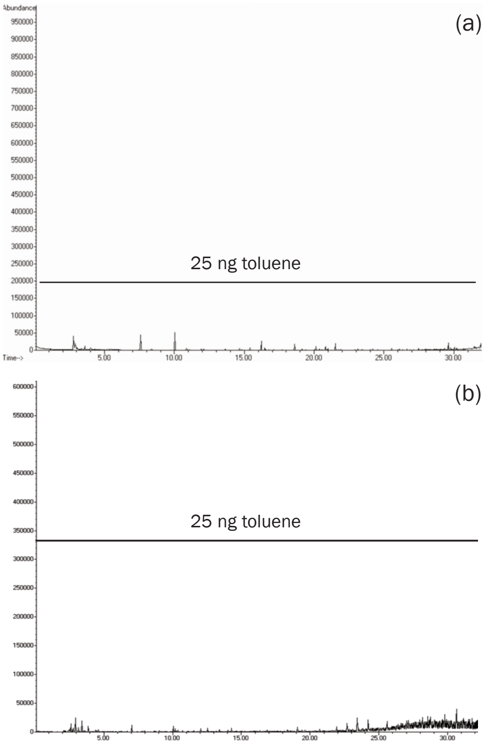

Figure 5: (a) Blank profile from six-chamber unit at 120°C (TVOC <30 ng); (b): Blank profile from four-chamber unit at 200°C (TVOC <12 ng)

The independent heating of all μ-CTE components (sample pans, chamber lids, air/gas supply tubing, *etc.*) prevents surface adsorption/condensation and sample-to-sample carryover. Internal surfaces which come into contact with sample vapours are constructed from inert-coated stainless steel to minimise sink effects (Figure 6). Micro-chamber and lid assemblies are readily removed from the μ-CTE for easy cleaning.

Special PTFE inserts are also available for the introduction of liquid standards to empty micro-chambers for recovery tests.

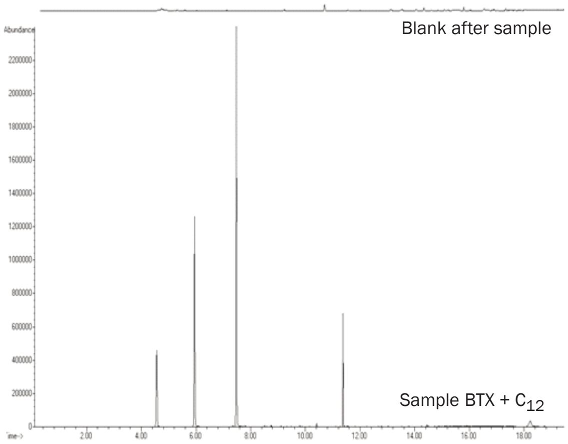

Figure 6: Carryover/sink effects (μ-CTE conditions: 40ºC, 50 mL/min air flow, sampled for 20 min)

Air/gas flow within the micro-chamber

Surface emissions testing using the μ-CTE requires 45 or 64 mm diameter circular samples to be cut or punched from the material, such that they fit snugly into the appropriate micro-chambers. Each μ-CTE system arrives with a set of sample spacers, some of which have compression springs. These are placed underneath the sample inside the micro-chamber, so that the emitting surface is presented to the air flow at the correct height, regardless of material thickness. A collar projecting down from the chamber lid helps to define the exact surface area and the depth of airspace above the sample. It also helps prevent emissions from the sides and rear of the sample from diffusing into the air space and contributing to the results.

The orientation of the air/gas inlet at 90º to the emitting sample surface maximises air turbulence and eliminates areas of still or low-flow air/gas. 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.

Materials for bulk emissions testing or odour/fragrance profiling may simply be weighed directly into an empty micro-chamber, or into a custom-made ‘sample boat’ which is subsequently placed into the chamber itself. In this case, air velocity will be determined by the free volume within the micro-chamber (*i.e.* the proportion of the total 44.5 mL or 114 mL volume which is not occupied by sample) and the air flow.

Degree of precision

In order to demonstrate the degree of precision between the individual chambers in a single μ-CTE unit, toluene standards, prepared in methanol, were introduced to each micro-chamber (Figure 7a). Conditions were set at 40ºC with 50 mL/min air flow and sampled for 20 minutes. Variation of results for each micro-chamber was found to be within ±5%, demonstrating minimal data variation across all six μ-CTE chambers.

A similar experiment was carried out by introducing six replicates of an ABS terpolymer and monitoring 1,3-butadiene and styrene emissions. This time, the μ-CTE was operated at 65ºC with vapour sampling at 50 mL/min for 15 minutes. Data showed 7.6% deviation for 1,3-butadiene and 5.4% for styrene across all six micro-chambers (Figure 7b). This level of precision is remarkably good for any material emissions testing procedure.

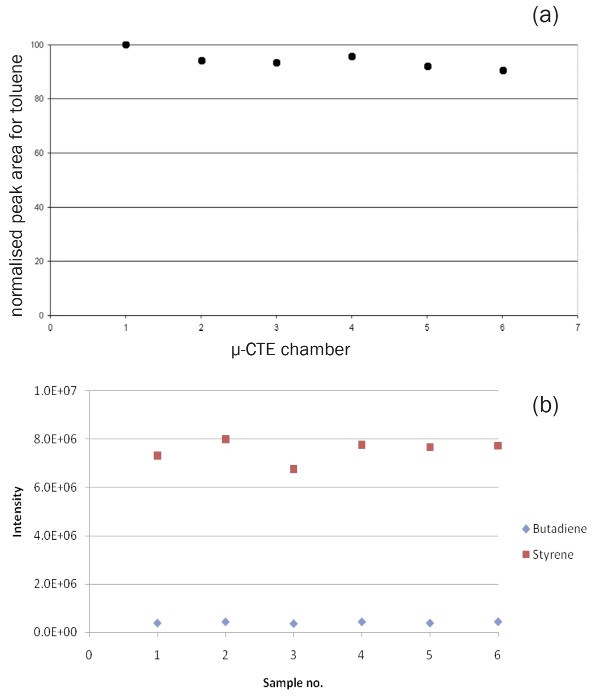

Figure 7: (a) Precision of μ-CTE chambers for the toluene standard; (b): Precision of μ-CTE chambers for ABS terpolymer samples, showing responses for 1,3-butadiene and styrene

Correlation with reference test methods for product emissions

Micro-chamber emissions data has been shown to correlate with results from reference methods that specify small chambers or cells. Correlation has been demonstrated in absolute terms (area-specific emission rate at three days)[2]. It has also been shown that fast emissions screening data obtained using the µ-CTE (*e.g.* on products within an hour of production) allows reliable estimation of longer-term results from small-chamber tests[2,3]. Data obtained within an hour of production can therefore be used to demonstrate continued compliance/ conformity with certification requirements. This *relative* correlation makes µ-CTE technology suitable for routine QC by manufacturers.

Example applications

Markes' µ-CTE is a versatile tool, compatible with a wide range of products and materials. Example applications are shown in Figures 8, 9 and 10.

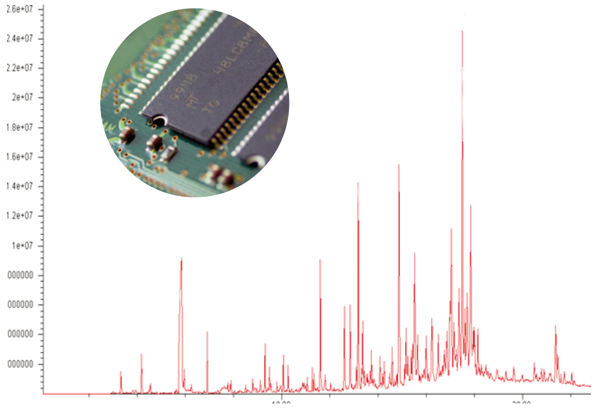

Figure 8: *Bulk emissions from a sample of printed circuit board (including electronic components) tested at 120ºC. Sample mass ~2 g with an area of ~10 mm²*

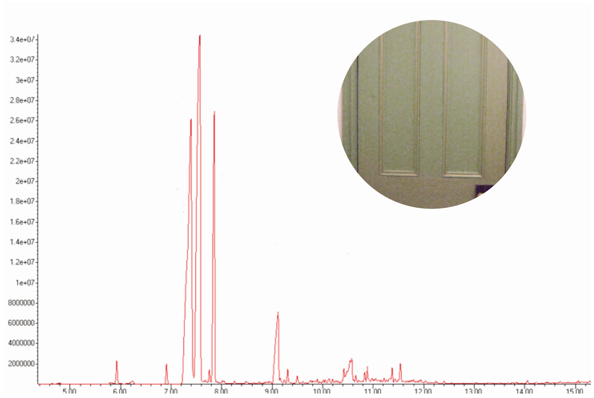

Figure 9: *Oil-based paint on wood composite cured for 17 h (µ-CTE conditions: 40ºC, 50 mL/min air flow, sampled for 30 min)*

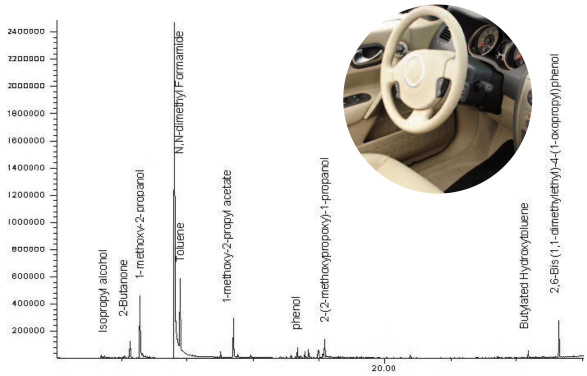

Figure 10: *Analysis of volatile and semi-volatile emissions from car trim materials. In this case, unusually stringent conditions were used (90ºC, 250 mL/min air flow and 30 min sampling time)*

Conclusions

Markes' µ-CTE has been demonstrated to be a rapid emissions screening tool that is suitable for routine QA/QC as well as for testing prototype products in research & development. Four or six samples can be processed for VOC emissions in less than 60 minutes using one µ-CTE unit.

For more information on the µ-CTE and related applications please contact Markes on enquiries@markes.com or call your local Markes distributor.

Trademarks

Micro-Chamber/Thermal Extractor™ and µ-CTE™ are trademarks of Markes International Ltd.

Tenax® is a registered trademark of Buchem B.V., Netherlands.

Carbograph™ is a trademark of LARA, Italy.

References

1. UK patent application 0501928.6
2. T. Schripp *et al.* (2007), A micro-scale device for testing emissions from materials for indoor use, *Analytical and Bioanalytical Chemistry*, **387**(5), 1907–1919.
3. G. J. Williams and M. Pharaoh (2009), *PARD Report: Correlation between the VDA 276 test and micro-chamber testing*, Issued by WMG, University of Warwick, UK.

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