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Overview

This paper reports the results of a detailed study of the performance of Markes' Micro-Chamber/Thermal Extractor (μ -CTE™) for low-cost, fast and meaningful materials emissions screening. The study was a collaborative programme between the Fraunhofer Willhelm Klauwitz Institute (WKI) and the University of Technology Braunschweig in Germany.

The objective of the study was to determine the degree of correlation between conventional emission test protocols (e.g. using 1 m³ emission test chambers) and the μ -CTE for wall coverings and polymers and to investigate the effect of various parameters on μ -CTE test results. The parameters evaluated included: temperature, air change rate and sample conditioning time.

Quantitative and qualitative correlation was observed between the μ -CTE and the 1 m³ emissions test chamber for ambient temperature area specific emissions rates after 72 hours.

To evaluate the potential of the μ -CTE as a tool for rapid materials emissions screening, (i.e. suitable for industrial quality control) two samples of a wall covering material were evaluated in the 1 m³ chamber for the standard 3 day (72 hours) emission test protocol (EN ISO 16000-9). After that time the ratio of VOC emissions from sample A to sample B was established as 4:1.

Subsequent rapid (20 minute) testing of emissions from these materials using the μ -CTE demonstrated the same ratio. This shows that rapid screening of VOC emissions can be carried out on materials within minutes of production using the μ -CTE and still provide a meaningful guide as to how that batch of product will perform in any subsequent standard 3-day emissions tests.

The paper also reports several fundamental performance characteristics of the Micro-chamber/Thermal Extractor unit including flow stability, ease of use and reproducibility. Computational fluid dynamic models were also used to predict air flow distributions within the device.



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

Trademarks

μ -CTE™ is a trademark of Markes International Ltd., UK.

A microscale device for measuring emissions from materials for indoor use

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Abstract Emission test chambers or cells are used to determine organic vapour emissions from construction products under controlled conditions. Polymeric car trim component emissions are typically evaluated using direct thermal desorption/extraction. The Microchamber/Thermal Extractor (μ -CTE, Markes International) was developed to provide both a complementary tool for rapid screening of volatile organic compound (VOC) emissions—suitable for industrial quality control—and a means for thermal extraction of larger, more representative samples of car trim components. To determine the degree of correlation between conventional emission test methods and the microchamber, experiments were carried out under different conditions of temperature, air change rate and sample conditioning time. Good quantitative and qualitative correlation was obtained for measurements at ambient temperature. Moreover, it was shown that ambient-temperature emissions data collected using the μ -CTE as rapidly as possible—i.e. with minimal or no sample conditioning time—nevertheless provided a

reliable guide as to how well that material would perform in subsequent 3-day chamber tests of VOC emissions. The parameters found to have the greatest influence on data correlation for experiments carried out at elevated temperatures were the sample mass (for bulk emissions testing) and the conditioning time. The results also showed that, within the constraints of inherent sample homogeneity, the μ -CTE gave reproducible emissions data, despite its small sample size/capacity relative to that of conventional chambers. Preliminary results of modelling the air flow within a microchamber using computational fluid dynamics showed a high degree of turbulent flow and two potential areas of still air which could cause sink effects. However, the experimental data reported here and in previous studies showed enhanced recovery of semivolatile components from the μ -CTE relative to a recovery from a 1 m³ conventional chamber. This indicates that if these areas of relatively still air are present within the microchamber, they do not appear to be significant in practice.

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Introduction

Over recent years there has been growing public awareness of indoor air quality. Most people spend 65% of their time indoors at home and 6% in transit [1, 2]; therefore the monitoring of the emissions of organic compounds from different products into indoor and vehicle cabin air is of high interest. Organic compounds used in the indoor environment are classified according to their volatility by the WHO [3] into very volatile organic compounds, volatile

organic compounds (VOC), semivolatile organic compounds (SVOC) and particulate organic matter or organic compounds associated with particulate matter. A working group of the European Community has presented a different definition for VOC, which is based on the retention time window in which a substance is eluted in gas chromatography [4, 5]. Different methods exist to identify and quantify organic emissions. Fast methods are normally based on direct thermal desorption (TD) or equilibrium headspace with gas chromatography (GC)/mass spectrometry (MS) or GC and flame ionisation detection (FID). However, in most cases, it is not possible to connect the emission-testing device directly with a gas chromatograph/mass spectrometer or a gas chromatograph/flame ionisation detector; therefore, a suitable adsorbent is necessary to collect the emitted organic substances and transfer them to the GC/MS or GC/FID analyser. Common general-purpose adsorbents for VOC are carbon blacks or the porous polymer Tenax TA (2,6-diphenyl-*p*-phenylenoxide) [6]. VOC retained by the sorbent are subsequently desorbed by solvent extraction or by heating the trap in a flow of carrier gas (TD). Analysis via TD/GC/MS or TD/GC/FID does require higher initial capital expenditure versus using solvent extraction; however, TD has significant advantages. Most notably it offers up to 1,000 times better detection limits because the collected VOC are not diluted by solvent. TD also offers shorter sampling and analytical cycle times and overcomes issues relating to the solvent peak masking some of the peaks of interest, thus allowing a wider range of compounds to be analysed. In addition, TD allows sorbent tubes/traps to be reused. An important limitation of TD has been that, until recently, it was limited to one-shot—i.e. it was not possible to repeat TD/GC/MS or TD/GC/FID analyses if something went wrong. This limitation has now been overcome by the advent of quantitative split re-collection for repeat TD analysis which is always associated with an inevitable reduction of analytical sensitivity.

Conventional methods to measure product emissions under controlled climatic conditions require emission test chambers/cells and are normally associated with relatively high expenditure of time and costs. A complementary quick emission test method would be very useful, especially for manufacturers wishing to pretest products before certification or as part of routine industrial quality control (QC).

Emission test chambers range in size from 80 to 0.003 m³. They are broadly classified into small scale (typically smaller than 1 m³) and large scale [7] (typically between 12 and 80 m³ [8, 9]). A common interior volume for an emission test chamber is 1 m³ and the interior is usually made of glass [10] or stainless-steel [11]. During the last decade the volume of chambers has been reduced to lower operating expense—for example the 51 L CLIMPAQ [12] and even a 3 L unit [13] have been reported. In line

with this trend, standard test methods have also been published [14, 15] for emission cells (e.g. the FLEC field and laboratory emission cell, which has an internal air volume of approximately 35 mL). Unlike emission test chambers, where samples are placed inside them, emission cells are placed on top of the emitting surface of a planar material so that it forms one “wall” of the air cavity. The main advantages of emission cells are the ease of use, the high loading factor (i.e. the small internal volume and relatively large emitting surface) and the associated improvement in analytical sensitivity. Other benefits include shorter equilibration times, higher sample throughput and better recovery of SVOC.

The Microchamber/Thermal Extractor (μ -CTE, Markes International) is a new device comprising small cylindrical chambers each with an interior volume of approximately 45 mL. By reducing the chamber volume, it was intended to reduce typical emission test times/costs but still generate meaningful emissions data—i.e. results that correlate with data from conventional emissions test chambers. The μ -CTE was not intended to replace standard emission test facilities. In fact it is a complementary tool intended to produce fast information about the composition and level of VOC emissions for industrial development of new, low-emission products/materials and QC.

Microchamber measurements have already been shown to provide a useful basis [16] for fast emissions screening prior to formal product certification. Moreover, since the device has only a small chamber volume and offers a relatively high loading factor, it has also been shown to offer enhanced sensitivity (relative to conventional chambers) for SVOC [17] which is due to reduced sink effects [18]. Even at trace levels, high-boiling compounds like plasticisers or flame retardants are of key interest owing to possible adverse health effects.

Experimental

The μ -CTE consists of six individual stainless-steel cylindrical chambers ($d=4.5$ cm), located in a heated block (ambient to 120 °C) (Fig. 1). All six microchambers are supplied simultaneously with the same, controlled flow of synthetic air via a restrictor. This means that the flow to the chamber units can be easily adjusted by changing the supply pressure. The relationship between air flow and supply pressure is almost linear. The device is equipped with two different restrictors allowing selection of a low-flow or a high-flow range (10–70 or 50–500 mL min⁻¹, respectively). The high-flow range was used exclusively during this project. Air enters each microchamber through the lid and is preheated to chamber temperature. The entire exhaust flow from each microchamber is passed through a

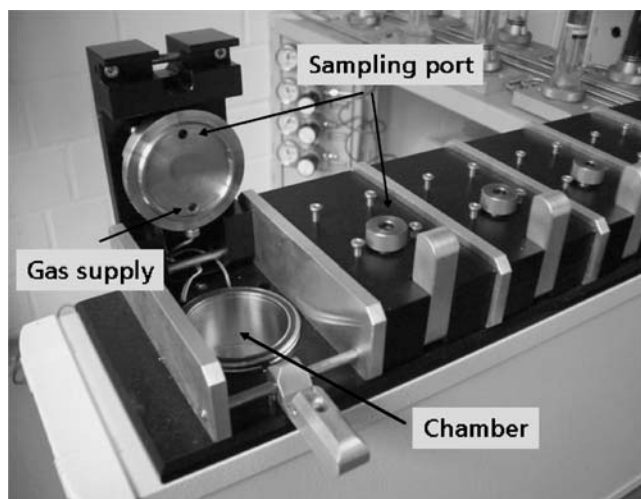


Fig. 1 The Micro-chamber/Thermal Extractor (μ -CTE) containing six stainless-steel units

sorbent tube (usually filled with Tenax TA), which is also attached to the lid. Experience with conventional stainless-steel emission test chambers has shown that it is best to avoid direct contact between the sample and the heated chamber wall in order to reduce carryover effects and contamination. Owing to the fact that the sample might cause an alteration of the surface of the chamber, an impact on the recovery rate or promotion of active sites cannot be excluded. The μ -CTE overcomes these limitations because each individual microchamber can be removed from the unit and cleaned.

Depending on the type of sample, two different testing modes are possible with the μ -CTE. First, the whole volume of the stainless-steel microchamber can be used for measuring bulk emissions (microchamber mode). Alternatively, spacers can be placed under a disk-shaped sample of the test material to raise the emitting surface up inside the microchamber until it reaches the circular collar which projects down, around the perimeter of the microchamber lid (Fig. 1). In this mode the sample surface forms one wall of a reduced-volume microchamber. This is referred to as cell mode. The properties of the μ -CTE in both of these modes are compared to those of a 1 m^3 emission test chamber in Table 1.

Reference emission measurements were carried out using 1 m^3 glass chambers (WKI, self-made) according to DIN EN ISO 16000-9 [19] plus a commercial 1 m^3 stainless-steel emission test chamber (model HCE 1000, Vötsch Industrietechnik, Balingen, Germany). For identification and quantification, known volumes of chamber air were sampled through stainless-steel tubes packed with 300 mg of Tenax TA using a FLEC air pump 1001 (Chematec, Denmark). The sampled Tenax tubes were subsequently analysed by TD (ULTRA-UNITY TD, Markes International) and GC (GC 6890N Network, Agilent Technologies)

Table 1 Comparison of Microchamber/Thermal Extractor (μ -CTE) properties (in microchamber mode, MCM, and cell mode, CM) with those of a conventional 1 m^3 emission test chamber (ETC)

	$V \text{ (m}^3\text{)}$	Maximum $n \text{ (h}^{-1}\text{)}$ sample diameter (mm)	Corresponding air flow rate (mL min^{-1})
μ -CTE (MCM)	4.45×10^{-5}	45	135–270
μ -CTE (CM)	3×10^{-6}	40	2,000–4,000
ETC	1	~800	0.5–1.0 ^a

^aTypical range

coupled with MS (MSD 5973, Agilent Technologies). The capillary column used for gas chromatography was a DB-1 MS ($60 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$). Analytes were identified on the basis of the mass spectra obtained. Peaks were quantified using the response factor for toluene.

Three different types of materials were tested—wall coverings (as an example of an indoor product), plus polyurethane foams and granular acrylonitrile–butadiene–styrene (ABS) plastic as examples of materials used in the automotive industry. Tests on the foam and plastic were carried out at $65 \text{ }^\circ\text{C}$ according to a standard method for emissions testing used in the automotive industry (see below).

Samples of the granular ABS plastic were weighed into the microchambers. Circular test specimens were cut from the polyurethane foam and wall coverings to fit into the microchambers. They were then wrapped in aluminium foil until they were placed into a microchamber. After a defined conditioning time, an adsorption tube was attached to the lid of the microchamber and the sampling flow was measured using a FlowTracker 1000 (Agilent Technologies) at the end of the sorbent tube. The sampled air volume passed through each tube was calculated from the sampling time and air flow. All flows were found to be stable over time (see “Results and discussion”) so additional measurement of the flow during sampling was not necessary.

The internal volume and the amount/area of the sample used are very different in a μ -CTE compared with those in a 1 m^3 emission test chamber. To achieve directly comparable vapour concentrations it would be necessary to use the same specific air flow rate q (cubic metres per square metre per hour). According to DIN EN ISO 16000, the specific air flow rate is calculated via the air change rate $n \text{ (h}^{-1}\text{)}$ and the loading factor L (area or mass per cubic metre).

$$q = \frac{n}{L} \quad (1)$$

Throughout this study, a loading factor of $1 \text{ m}^2 \text{ m}^{-3}$ and air change rates (n) of either 0.4 or 1 h^{-1} were used for surface emissions testing using the emission test chamber.

This gave area specific air flow rates (q) of 0.4 or 1 m³ m⁻²h⁻¹, respectively. To replicate these parameters exactly would require the μ -CTE to be operated at flow rates of 8 mL min⁻¹ ($n=160$ h⁻¹) or 21 mL min⁻¹ ($n=400$ h⁻¹). These flows are a result of the small volume of the μ -CTE in cell mode. The exposed sample surface area is 1.256×10^{-3} m² and the air volume 3.14×10^{-6} m³, thus giving a loading factor of 400 m² m⁻³. However, the flows mentioned are too low for convenient and quick operation of the μ -CTE so alternative q values in the range from approximately 5 to approximately 10 m³ m⁻²h⁻¹ have to be used.

Results and discussion

To obtain reliable quantitative results, the gas flow through the sorbent tube attached to the microchamber has to be stable. To estimate possible fluctuations in the gas flow during vapour sampling, a FlowTracker 1000 was used to monitor the flow constantly over 60 min. The dependence of the flow versus time is shown in Fig. 2. Small fluctuations are visible, but on the basis of the expected volume of 6.066 L (calculated from the measured flow at the start of the measurement), the actual volume of 6.032 L represents an error in measurement of 0.6%. Therefore, the restrictor provides sufficiently accurate flow control.

To assess the influence of heat conduction from the heated microchamber lids to the attached Tenax tubes, a series of tubes were each loaded with 1 μ L of a methanol solution containing compounds with different boiling points ranging from approximately 80 °C to approximately 300 °C (C-I, C-II and C-III) (Fig. 3).¹ These tubes were attached to microchambers, maintained at temperatures from 25 to 100 °C with an air flow of 200 mL min⁻¹. After 15 min the tubes were removed. For each temperature the experiment was carried out in triplicate. The tubes were then analysed, and the average and standard deviations are shown in Fig. 3. The results prove no clear deviations between the measured values for compounds C-II and C-III, but the most volatile compound (C-I) shows a significant loss at microchamber temperatures above 40 °C. This clearly demonstrates that heat was being transferred from the microchamber to the Tenax tube, causing breakthrough of the most volatile analyte. By measuring the temperature of the Tenax tube using a Pt-100 thermocouple, it was further shown that the Tenax tube reached a maximum temperature of 90 °C with the microchamber temperature set to 120 °C. As a consequence, the thermal insulation of each micro-

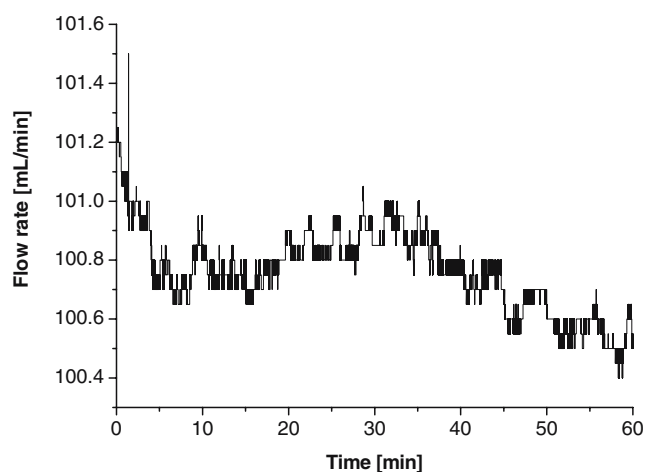


Fig. 2 Continuous measurement of the gas flow rate through a microchamber unit within 1 h

chamber-to-tube connector was improved by the manufacturer and repetition of the breakthrough experiment verified much reduced heating of the sorbent tube and no loss of VOC. After modification, compound C-I showed a peak area in GC/MS for sampling at 23 °C of $204,245 \pm 13,188$ ($n=12$) and at 65 °C of $209,996 \pm 10,273$ ($n=12$). This is a deviation of approximately 3%.

ABS plastic pellets

The first sample investigated was a granular ABS copolymer with a specific emission profile. Each polymer granule was roughly cubic in shape with an edge length of about 2 mm. This type of polymer is used in both computer monitors and in the automotive industry and emits VOC at elevated temperatures. Therefore, the method selected for comparative emissions testing was VDA 276 [20]—a standard used by the automotive industry to test emissions at 65 °C.

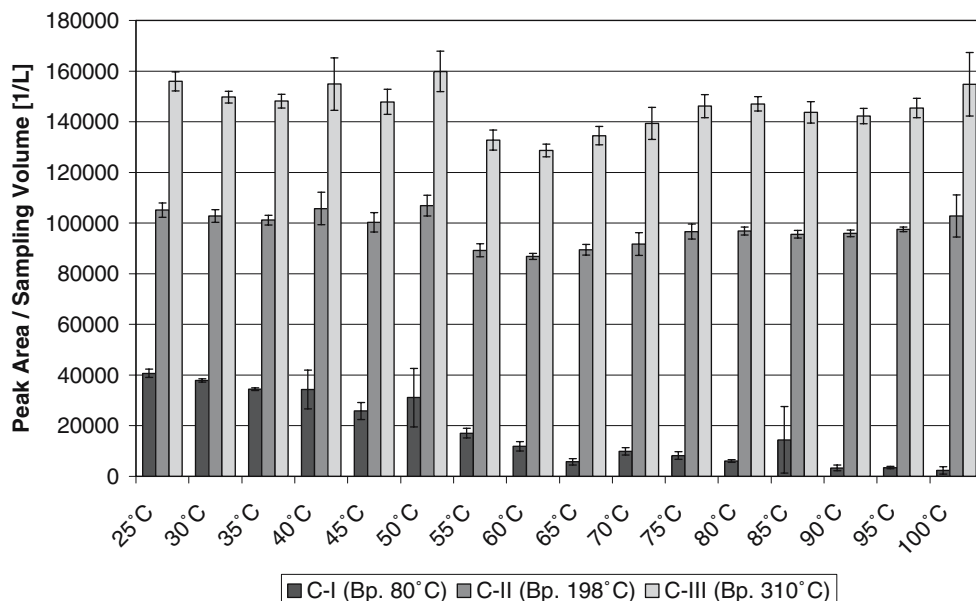
Measurements were carried out using a 1 m³ stainless-steel chamber at 65 °C with a mass loading factor of 2,700 g m⁻³. Vapour samples were collected after 2, 2.5, 4, 6 and 8 h. Comparative microchamber measurements were carried out using the μ -CTE in microchamber mode under different test conditions, for example equilibration times, sample amounts and air-exchange rates. Data were compared both qualitatively and quantitatively in terms of the mass-specific emission rate.

Figure 4, which shows chromatograms for 2.5 h equilibration in the emission test chamber and 1 min in the microchamber, demonstrates good qualitative correlation.

However, quantitatively, the microchamber showed a lower recovery of the most volatile compound (acrylonitrile) and better recovery of semivolatiles such as 2,4-di-

¹ The boiling points of the compounds used were 80 °C (C-I), 198 °C (C-II) and 310 °C (C-III). The particular compounds are not allowed to be mentioned by the authors because they are used for quality assurance in our laboratory.

Fig. 3 Influence of the chamber temperature on the loss of volatile organic compounds during microchamber measurements. The peak area are normalised by the sampled gas volume of three substances that are spiked onto the adsorption tube before start of the measurement



tert-butylphenol (4-DTBP). Low recovery of acrylonitrile is explained by heat transfer to the Tenax tubes from the prototype μ -CTE causing breakthrough of acrylonitrile during sampling, as described above. The improved recovery of SVOC (the 2,4-DTBP peak is twice as high from the microchamber as it is from the emission test chamber) illustrates the advantages of the microchamber in terms of reduced sink effects.

The results of the reference measurements in the stainless-steel emission test chamber at 65 °C are shown in Table 2.

Temperature and flow rate are easily adjusted in the μ -CTE; however, temperatures above 65 °C were not considered in case they fundamentally changed the emission mechanisms within the sample and the resultant VOC profile. The influence of flow rate was examined by testing

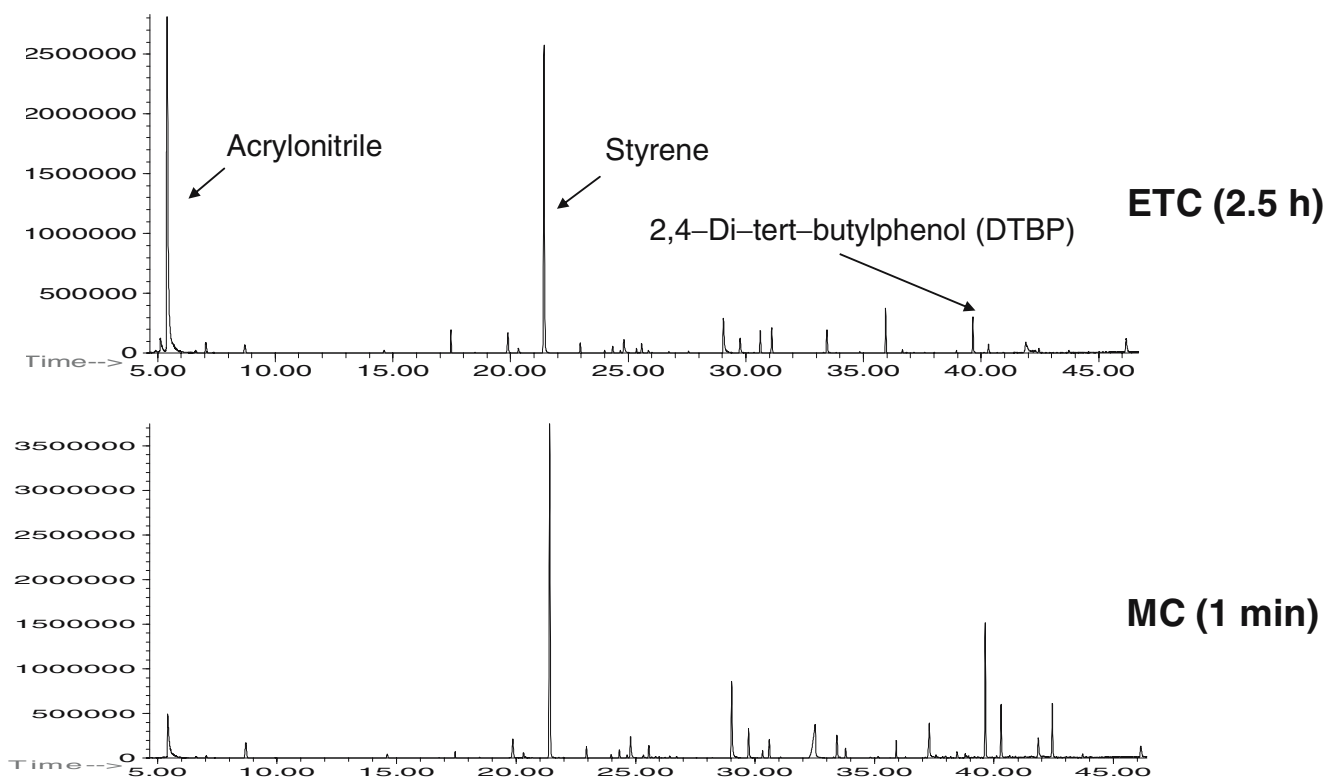


Fig. 4 Direct comparison of the chromatograms of an acrylonitrile-butadiene-styrene (ABS) polymer sample in the stainless-steel emission test chamber (ETC) and the microchamber (MC) at 65 °C

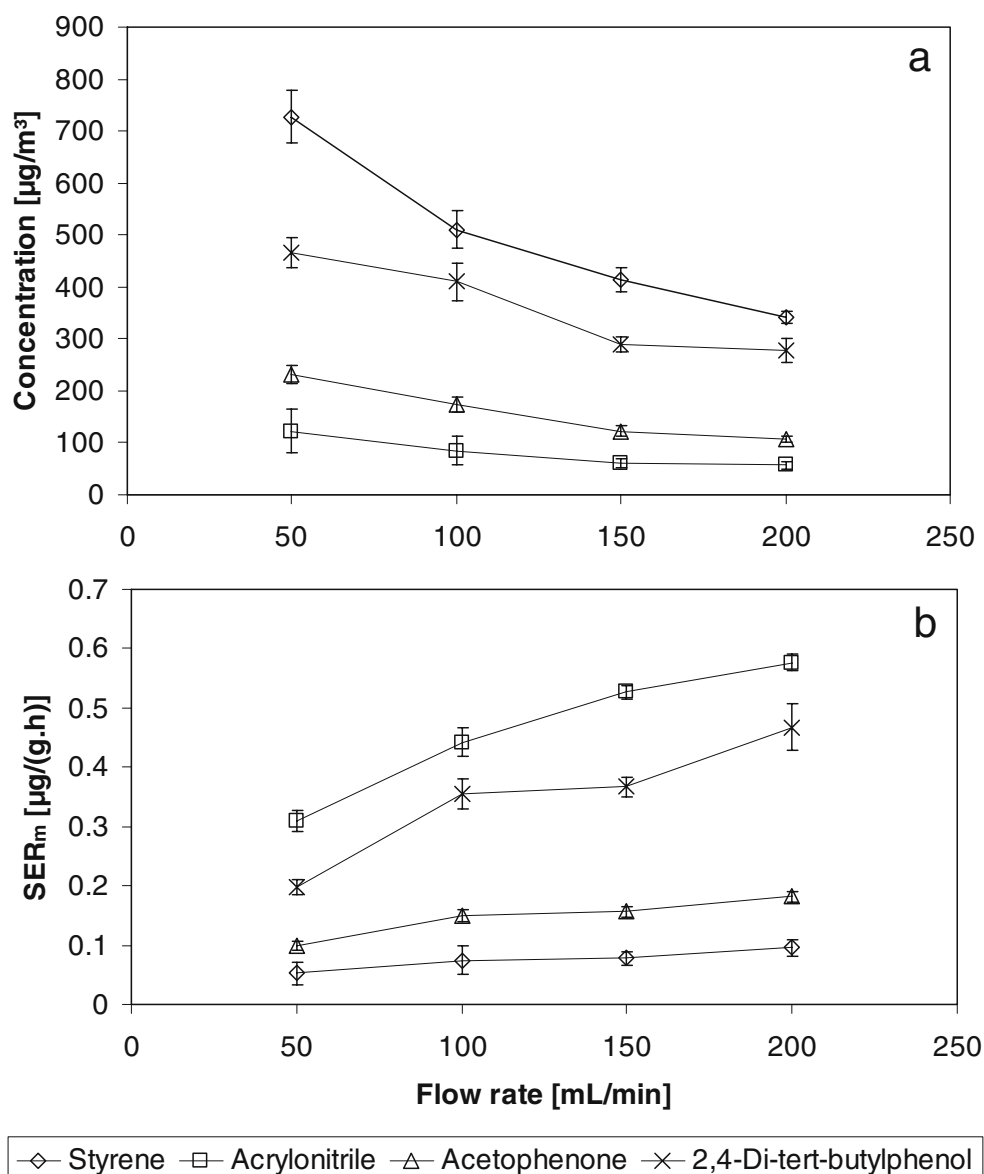
Table 2 Concentrations and mass-specific emission rates measured in a 1 m³ stainless-steel chamber test of an acrylonitrile-butadiene-styrene plastic granulate

	2 h		2.5 h		4 h		6 h		8 h	
	($\mu\text{g m}^{-3}$)	($\mu\text{g g}^{-1}\text{h}^{-1}$)	($\mu\text{g m}^{-3}$)	($\mu\text{g g}^{-1}\text{h}^{-1}$)	($\mu\text{g m}^{-3}$)	($\mu\text{g g}^{-1}\text{h}^{-1}$)	($\mu\text{g m}^{-3}$)	($\mu\text{g g}^{-1}\text{h}^{-1}$)	($\mu\text{g m}^{-3}$)	($\mu\text{g g}^{-1}\text{h}^{-1}$)
Acrylonitrile	3,020	0.44	3,196	0.46	3,052	0.44	2,366	0.34	2081	0.30
Styrene	1,371	0.20	1,411	0.20	1,374	0.20	1,154	0.17	994	0.14
2,4-Di- <i>tert</i> -butylphenol	125	0.02	225	0.03	162	0.02	113	0.02	64	0.01
Acetophenone	234	0.03	229	0.03	223	0.03	175	0.03	127	0.02

7 g of polymer beads in each microchamber using four different flow rates between 50 and 200 mL min⁻¹ at 65 °C. In each case, the same sampled volume (2.2 L) was collected. Every measurement was done in triplicate. The results are shown in Fig. 5. Excluding acrylonitrile, for reasons explained above, the emission rates in the μ -CTE

are higher than in the emission chamber at all flow rates. The mass-specific emission rate was shown to increase with flow, indicating that external diffusion (e.g. of surface-adsorbed VOC) may have been a significant emission mechanism under the test conditions selected. By increasing the air exchange in the chamber, we expect

Fig. 5 ABS polymer in the microchamber. Influence of the flow rate through the chamber on the concentration (a) and the emission rate SER_m (b) of four chosen compounds. Reference data of the emission chamber test are displayed in Table 2



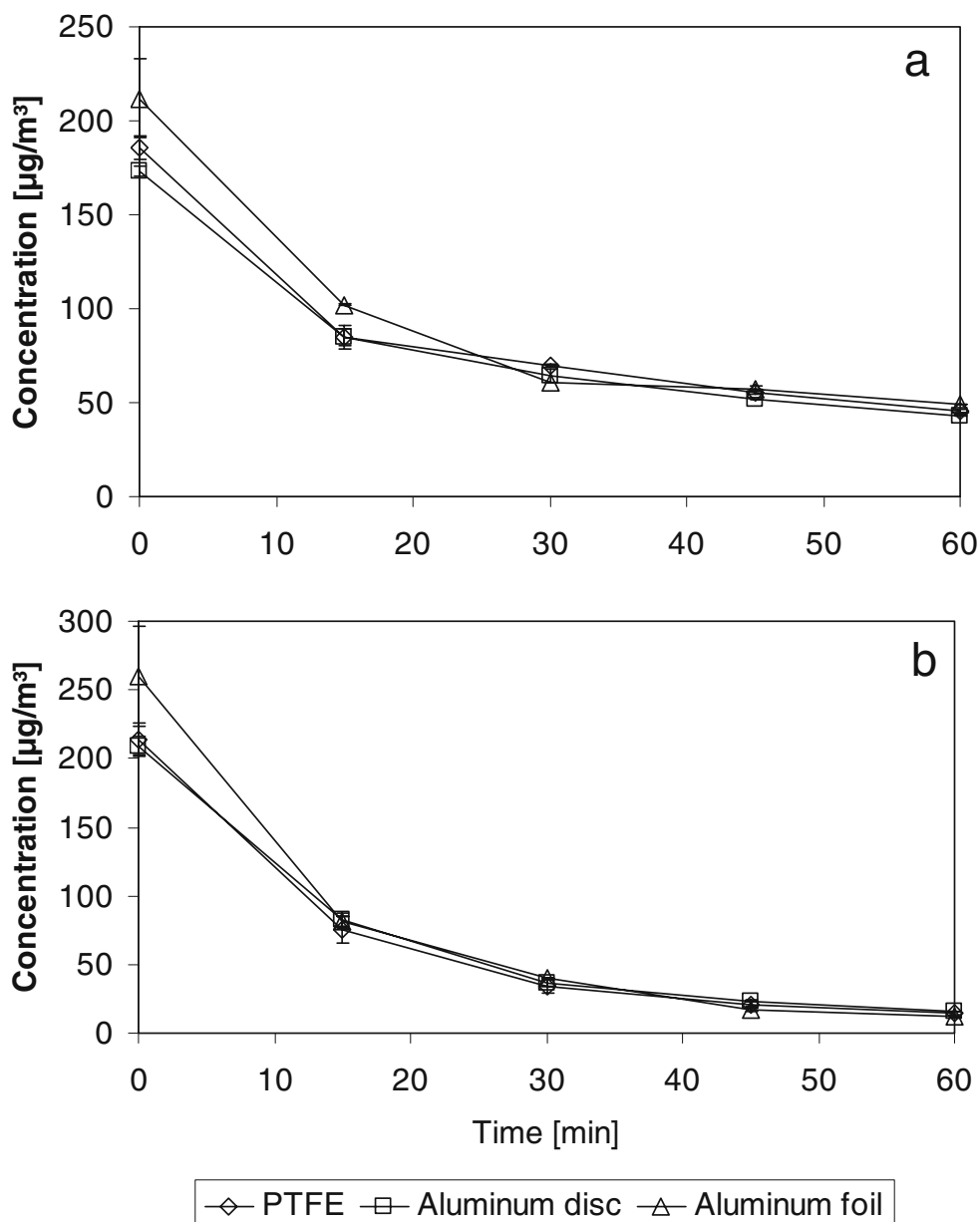
a change in the flow field (see “Computational fluid dynamic”). This may have an influence on the mixing in the chamber and lead to the measured increase in emission rate at higher air flows.

The conditioning time is a key issue for fast screening methods as it influences the overall length of the test and the degree of correlation with the test chamber data. The time necessary for conditioning the sample is dependent on the material and the sample size/structure and will need to be determined for each individual sample type. As shown in Fig. 6, 15 min conditioning was sufficient in the case of ABS polymer beads to allow emission rates to stabilise, independent of the choice of material used as the sample backing. The highest degree of correlation was

obtained for samples allowed to equilibrate for 30 min in the microchamber.

Although the stainless-steel surface of the microchambers is easy to clean, it is useful for high sample throughput to protect the chamber surface from direct contact with the sample by using a backing material. Markes International proposed the use of poly(tetrafluoroethylene) (PTFE) inserts or 1 mm thick aluminium disks. (Note that PTFE has been reported to act as a sink for VOC [21] in some cases.) The results for tests with PTFE, aluminium disks and aluminium foil are shown in Fig. 6. Both target compounds (styrene and 2,4-DTBP) show higher initial emission rates if aluminium foil is used to back the sample because it offers negligible thermal isolation from the microchamber wall. The relatively large thermal mass of

Fig. 6 ABS polymer in the μ -CTE. Investigation of appropriate conditioning times (up to 60 min) and the influence of the type of material selected as the sample backing. Results for styrene (a) and 2,4-di-*tert*-butylphenol (b) are shown



the other two backing materials means that there is a delay before the sample reaches the required temperature. However, after 20–30 min equilibration, the sample backing material can be seen to have no significant impact on the emission rate.

Another key consideration was that the standard deviation of the initial measurements (i.e. samples collected after minimal or zero conditioning time) was very high. This is because of the insulating nature of the polymer pellets themselves. Heat transfer is not very fast for polymer pellets which are not in direct contact with the microchamber wall. This is a particular issue for larger samples (masses) of polymer where the beads form a layer more than one bead thick (in this case at amounts above 3 g). In this case, beads in the upper layers have to be heated by radiation or the surrounding air, which takes more time. Use of a 15 min sample equilibration time helps to minimise uncertainty and improve reproducibility of emission data in such cases.

Another issue which can impact the reproducibility of emission data for larger samples of polymer is that if the beads are several layers deep in the microchamber, the granules in the lower layers will not be exposed to the full air flow. In this case, the surface air velocity over beads in the lower layers may be so low that internal diffusion rates are depressed. Measurements with different amounts of sample in the μ -CTE (data not presented) show that the mass-specific emission rate of the polymer decreases as sample mass increases [22]. With sample amounts ranging from 2 to 12 g, the emission rate of styrene decreases by 40%, while that of 2,4-DTBP decreases by 70%. The effect on lower-volatility compounds is also made worse by the fact that the “colder” granulate can act as a sink for higher-boiling compounds.

These issues should all be taken into account in order to optimise the degree of correlation between the μ -CTE and a conventional emission test chamber. In the case of this polymer granulate, using a sample mass of about 3 g, which forms a monolayer on the floor of the microchamber, minimises issues relating to heating rates, sink effects and variable surface air velocity, allowing good correlation to be obtained after a 15–30 min equilibration.

Wall coverings

Quick determination of total VOC emissions from wall coverings is currently achieved using static headspace analytic [23]. The main disadvantage of this method is that individual VOC emissions cannot be assessed because correlation between static headspace and emission test chamber methods is poor [24]. Given the good qualitative correlation between emission test chamber data and μ -CTE

results, the microchamber method will be a useful addition for rapid screening of wall covering emissions.

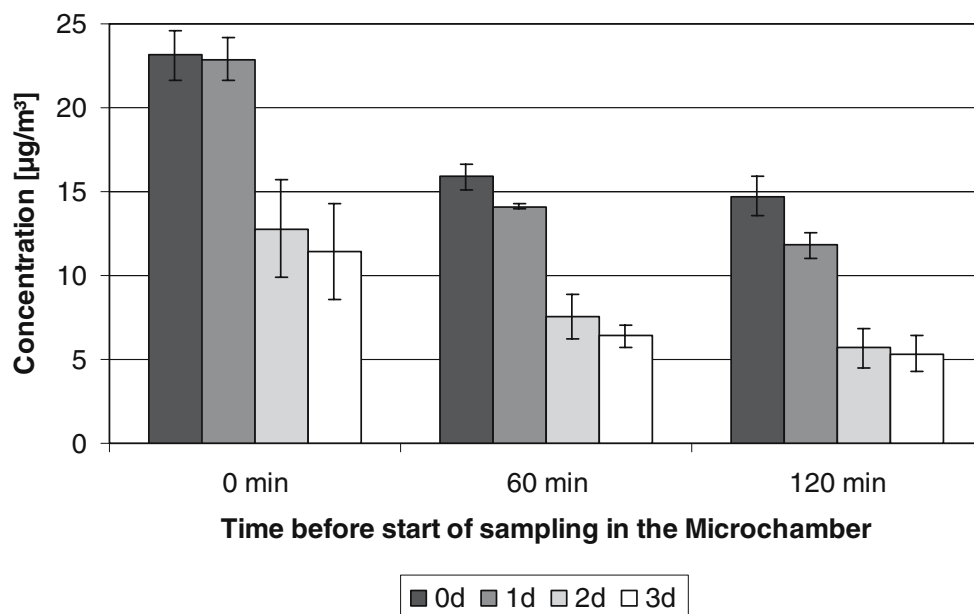
Many wall coverings are made of paper or fleece supported on foamed or compact poly vinyl chloride (PVC). Every wall covering examined in this study was uncoloured and unpatterned to reduce inhomogeneity issues. Typical emissions from these types of wall coverings include plasticisers and various aliphatic and aromatic solvents used during production and application of the PVC [25, 26]. Normally solvent emissions decrease rapidly over time because of their high volatility of solvents and because they are applied at the surface of the product. The rates of emission of other compounds, which are more “fixed” in the PVC matrix, decrease more slowly because they have to diffuse, internally, through the body of the polymer before vaporising.

To assess the applicability of the μ -CTE for precertification measurement of wall covering emissions, it was used to determine emission rates of an “assessable” compound—as defined by the German AgBB scheme [27] (Figs. 7, 8). The compound selected—2-ethylhexanoic acid (2-EHA), a known teratogen [28, 29]—is emitted by some PVC wall coverings because heavy-metal salts of 2-EHA are often used as a PVC additive. The 2-EHA concentration was measured immediately after removal of the sample packaging and after 1, 2 and 3 days, during which time the product was conditioned by leaving it unrolled within a climate chamber (23 °C, 50% relative humidity). Additional short-term conditioning was carried out by varying the time interval between putting the sample into the chamber and beginning vapour collection. The measurements were carried out using the μ -CTE in cell mode and with a gas flow of 100 mL min⁻¹. Every measurement was carried out in triplicate.

Figures 7 and 8 show how emissions of 2-EHA evolve over time for two different wall coverings named WC1 and WC2. Besides the decrease in emission over the 3 days, there is also a significant decrease (50–60%) within the 2-h conditioning time. This may indicate that there was a much lower air velocity on the surface of the sample in the climate chamber (corresponding to a real indoor environment) during the period of long term conditioning compared with the high air exchange/velocity in the microchamber. Overall, the measurements had standard deviations ranging from 1 to 25%, but nearly half of the measurements (11 of 24) had a relative standard deviation below 10%. Some variability in emissions data is expected with small samples of PVC wall coverings because there may be point sources of strong emissions on the product surface. Nevertheless the area of the sample used in the μ -CTE seems to be large enough to give reproducible results.

Parallel emissions measurements were carried out using a 1 m³ glass test chamber and 1 m² of each wall covering.

Fig. 7 Wall covering WC1 in the microchamber. Measured concentrations of 2-ethylhexanoic acid (2-EHA) using short- and long-term preconditioning. The average values of three measurements and their standard deviations are shown



The test was carried out according to requirements of the German AgBB scheme. For the first wall covering (WC1), the levels of 2-EHA, expressed in terms of vapour concentration in the chamber, were $49 \mu\text{g m}^{-3}$ (3 days) and $37 \mu\text{g m}^{-3}$ (28 days). For the second wall covering (WC2), the levels of 2-EHA were $200 \mu\text{g m}^{-3}$ (3 days) and $111 \mu\text{g m}^{-3}$ (28 days). The corresponding area-specific emission rates have the same numerical value because measurements were done at $q=1 \text{ m}^3 \text{ m}^{-2}\text{h}^{-1}$ (Table 3, Eq. (1)), i.e. the area-specific emission rates were 49 and $200 \mu\text{g m}^{-2}\text{h}^{-1}$ (at 3 days) for WC1 and WC2 respectively.

Emission rate data from the test chamber and microchamber cannot be compared directly in terms of vapour concentration (C_x) because the parameters used are differ-

ent (Table 3) However, the area-specific emission rates (micrograms per square metre per hour) should be the same or similar for any given test time. The parameters used to calculate the area-specific emission rates (SER_a) are found in Table 3 and Eq. (2):

$$\text{SER}_a = C_x q. \quad (2)$$

The q value for the microchamber, in cell mode, as used in these experiments, is $5 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$. The 2-EHA vapour concentrations determined for the 3-day test on each wall covering using the $\mu\text{-CTE}$ (60 min conditioning) were approximately 6 and approximately $34 \mu\text{g m}^{-3}$ for WC1 and WC2, respectively. This gives SER_a values of approximately 30 and approximately $170 \mu\text{g m}^{-2}$ for

Fig. 8 Wall covering WC2 in the microchamber. Measured concentrations of 2-EHA using short- and long-term preconditioning. The average values of three measurements and their standard deviations are shown

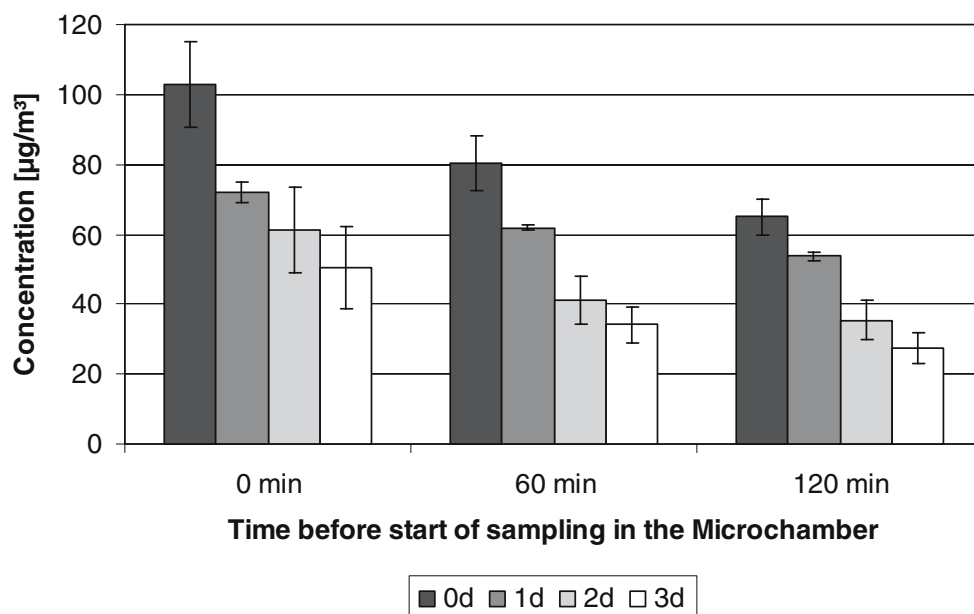


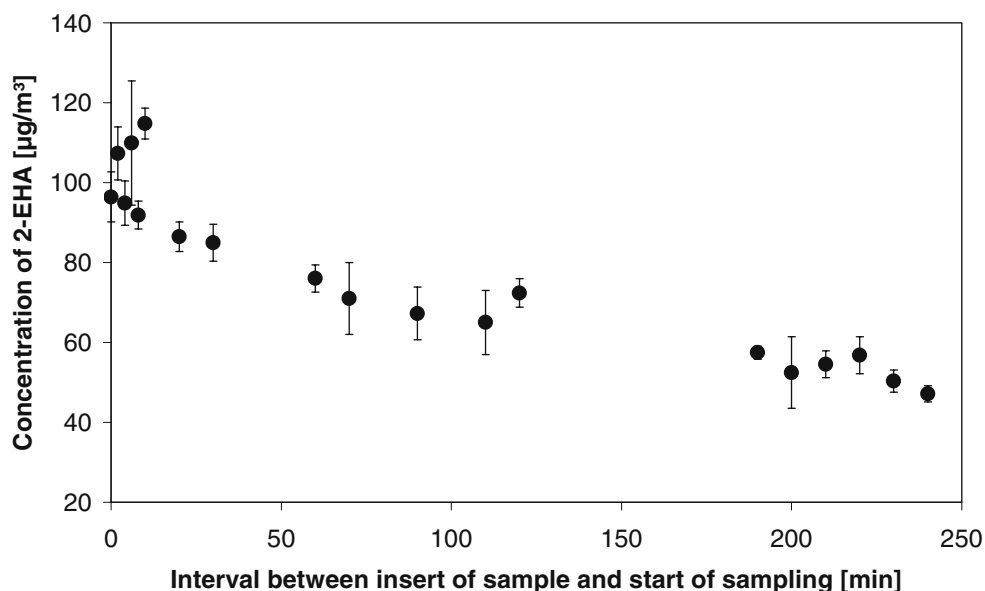
Table 3 Comparison of the testing parameters of a surface sample in the ETC and the μ -CTE in CM

	n (h ⁻¹)	A_{sample} (m ²)	V (m ³)	L (m ² m ⁻³)	q (m ³ m ⁻² h ⁻¹)
ETC	1	1	1	1	1
μ -CTE	2,000	1.256×10^{-3}	3.14×10^{-5}	400	5

WC1 and WC2, respectively. This shows good quantitative correlation for area-specific emission rate data for both wall coverings at 3 days between the conventional 1 m³ test chamber and the μ -CTE.

Although both WC1 and WC2 are covered with the same material (fleece), 3-day tests indicate that the emission strength differs by a factor 4. It is very interesting to note from Figs. 7 and 8 that the ratio of emissions between WC1 and WC2 as determined using the μ -CTE on day 0, (even without any conditioning/equilibration time) is consistent with that found in the 3-day tests—i.e. WC2 emissions are shown to be approximately 4 times higher than those of WC1 even when using the μ -CTE to test freshly unpacked product with no or minimal conditioning time. This is very significant with respect to the potential usefulness of the μ -CTE as a QC tool. It means that an industrial QC laboratory could use the μ -CTE to establish an acceptable (“control”) level of emissions for products/materials straight from the production line which subsequently go on to pass formal 3- and 28-day certification tests. This would then provide a benchmark against which all new batches of product could be tested, straight from the line or from development, giving the factory manager early warning of potential problems.

Fig. 9 Wall covering WC1 in the microchamber. Development of the concentration of 2-EHA within 4 h. The average values of three measurements and their standard deviations are shown



The difference in emission rate is a result of the two different types of PVC coating. The sample with the lower emission rate (WC1) was a foamed PVC wall covering, while the sample with the higher emission rate (WC2) used a more compact PVC material. The higher-emission, compact PVC wall covering was selected for another experiment on sample conditioning, this time with higher time resolution. In this case, the product was not conditioned for several days as previously, but was placed in the microchamber immediately after unwrapping and the emissions were monitored every few minutes. The results are shown in Fig. 9. Within the first 10–15 min, the concentrations measured fluctuated between 90 and 115 $\mu\text{g m}^{-3}$. After that, the emissions dropped at a steady rate.

It is also interesting to note that although the area of the sample used in a μ -CTE is nearly 1,000 times smaller than that used in the conventional emissions test chamber, analytical sensitivity is not compromised.

Polyurethane foams

Polyurethane foams are widely used in the interior of houses (e.g. for insulation) and automobiles (e.g. seat padding). Car trim components may be tested using emission chambers according to method VDA 276 at 65 °C. Samples for the μ -CTE were taken from each side of a cube of polyurethane foam using a stamping tool (diameter 5 cm). The tool was inserted into the foam to a depth of 5 cm. Two 1 cm-depth slices were then cut from this cylindrical “core” of the sample—one from the top and one from the bottom. The piece cut from the top (outer surface) of the core was called the “surface” sample and that from the bottom was referred to as the “core”

sample. Both were tested in the μ -CTE at 65 °C. A total of 12 core samples were prepared from the foam block in this way and were tested under the same conditions. Any deficiencies in sample packaging would show up as lower emissions from the surface samples. The three most important emitted VOC observed during TD/GC/MS analysis were isobornylacetate ($c_{\text{mean}}=41\pm6\ \mu\text{g m}^{-3}$), decamethylcyclopentasiloxane ($c_{\text{mean}}=487\pm37\ \mu\text{g m}^{-3}$) and 1,4-diazabicyclo[2.2.2]octane ($c_{\text{mean}}=948\pm149\ \mu\text{g m}^{-3}$). The last component is used as a catalyst. Siloxanes are used for controlling the foaming process.

To evaluate the reproducibility of emission tests using the μ -CTE, the results for the polyurethane foams were checked for their statistical distribution. Owing to the small number of data points ($n=12$) a Kolmogorov–Smirnov statistical test was used. The threshold value, that should not be exceeded, was 0.375 ($n=12$, level of significance 0.05). The results for the three compounds were as follows: isobornylacetate 0.177; decamethylcyclopentasiloxane 0.097; 1,4-diazabicyclo[2.2.2]octane 0.171. Therefore no significant deviation in the results could be observed. On the basis of this experiment it can be shown that emissions measurements carried out using the μ -CTE for homogeneous materials are very reproducible. Moreover, given that no difference was observed between emissions from the “surface” and “core” samples, it can also be seen that this sampling method is very robust provided the sample is wrapped according to DIN EN ISO 16000-11 [30].

The μ -CTE can therefore be used for testing emissions at elevated temperatures, as described in method VDA 276. A direct TD test method for small (approximately 30 mg) samples of car trim components is also described in method VDA 278 [31]. VDA 278 proposes a test temperature of 90 °C for VOC and 120 °C for semivolatiles. Testing

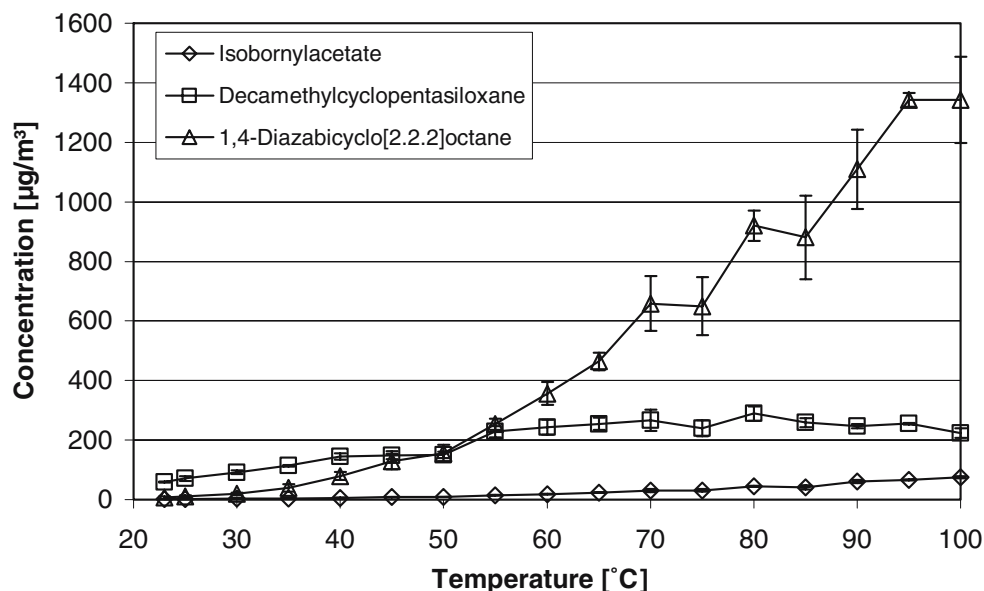
emissions at elevated temperatures can introduce its own problems. For example, the temperature should not be raised above any physical or chemical transition points in the material or (1) the material may lose its form, thus modifying the emitting surface and (2) molecules with a high molecular weight may diffuse to the surface of the material more easily, causing higher than expected emissions. Neither of these effects are generally observed during application of VDA 278, but they could be significant for some materials. Moreover, test data from these experiments are often simply used for comparison with product performance criteria set specifically for the VDA 278 test. In other words there is often no need to show correlation with emission test chamber measurements.

The μ -CTE was further used to test emissions from another polyurethane foam (Fig. 10) at temperatures from 20 to 100 °C. It is interesting to note that much higher standard deviations were observed for isobornylacetate at temperatures above 65 °C. This may be a result of some form of thermal degradation/transition of the polymer or of this particular analyte. Warming of the Tenax tube caused by heat conduction on the prototype μ -CTE unit (as described above) could also have contributed to this effect. These results emphasise the care that needs to be taken when carrying out emissions testing at elevated temperatures; whether using the μ -CTE, with a conventional test chamber or using direct TD/extraction.

Computational fluid dynamics

The small volume of the microchamber and the relatively high gas flow cause disturbances. The exact nature of the disturbances and the air velocity near the surface of the

Fig. 10 Polyurethane foam in the microchamber. Influence of the temperature on the vapour concentration of three chosen compounds



sample are important when correlating data between large chambers and the μ -CTE, especially in the case of materials where evaporation (external diffusion) is a primary mechanism of emission. Standard DIN EN ISO 16000-9 specifies the air velocity in the emission test chamber should be from 0.1 to 0.3 m s^{-1} in a distance of 10 mm over the surface of the sample [20]. Standard DIN EN ISO 16000-10 specifies the air velocity in the emission test cell should be from 0.003 to 0.3 m s^{-1} [14, 15].

To estimate the air velocity in the microchamber, simulations were done using a computational fluid dynamics code developed by the Institute for Computer Applications in Civil Engineering at the Technical University, Braunschweig. The simulation code is based on the lattice–Boltzmann method using the multi-relaxation-time model [32, 33]. The spatial discretisation was $256 \times 256 \times 216$, resulting in 14,155,776 grid points, of which 7,200,000 were located in the chamber. The geometry of the chamber was reconstructed with AutoCAD 2005 using the construction plan of the microchamber. The volume flow was $Q = 0.100 \text{ L min}^{-1}$ and the resulting inlet flow was $u = 0.150 \text{ m s}^{-1}$ (inlet cross section surface $A = 11.13 \text{ mm}^2$). The resulting cell Reynolds number was 2.319, so a simulation without a turbulence model was performed. The results are shown in Fig. 11. From these data, it appears that there are two vortices below the air inlet near the middle of the chamber. Furthermore, two spots (one near the lid and one immediately below the outlet) appear to have a very low air velocity. These indicate areas of low air mixing which could cause sink effects, though this was not corroborated by experimental data (see above), which in fact indicated that the μ -CTE appeared to be less prone to sink effects, particularly for semivolatiles, than conventional test chambers. Additional studies are needed to investigate this further. Obviously, the shape and the matrix of the sample will also influence air flow within the microchamber; therefore, surface air velocity could also be expected to differ from sample to sample. It is hoped to carry out further computational fluid dynamics calculations in the future to better understand flows within the μ -CTE when it is used in its different modes (microchamber mode and cell mode) and to assess the influence of the sample matrix.

Conclusions

The chromatographic data presented show good qualitative correlation between the μ -CTE and a 1 m^3 emission test chamber for all the samples studied. Quantitative correlation was also demonstrated for most VOC. Exceptions were explained either by breakthrough of very volatile analytes caused by heat transfer to the Tenax tube on a prototype version of the μ -CTE or by enhanced recovery of semi-

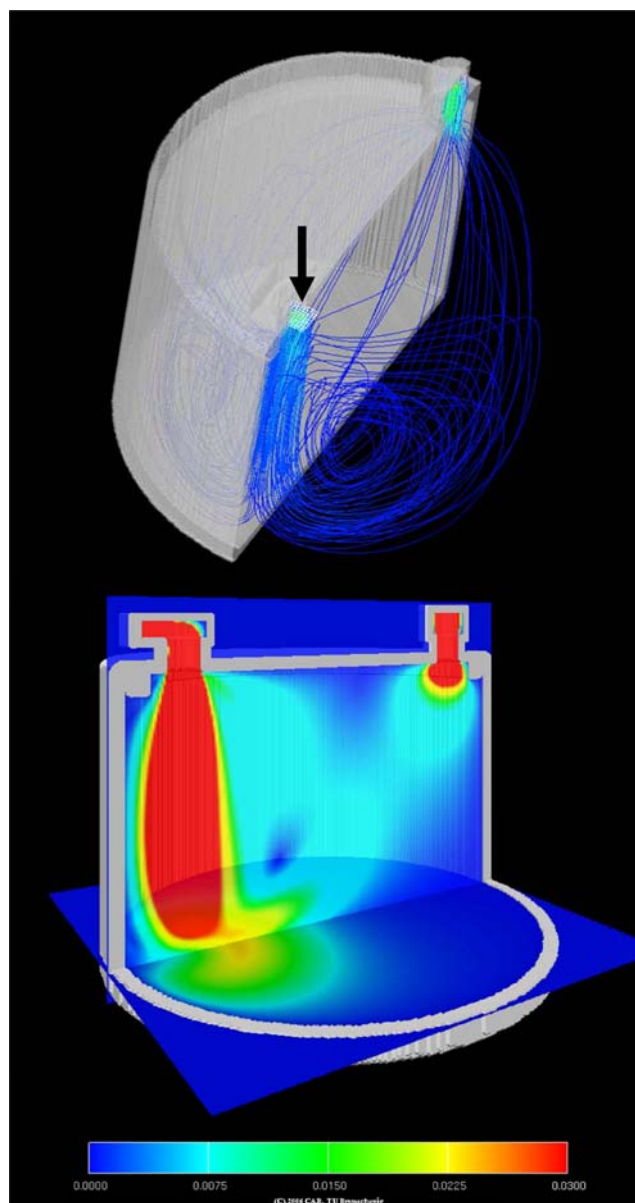


Fig. 11 Computational fluid dynamics calculation of the flow path (*top*) and the air velocity (*bottom*) in the microchamber. The air enters the chamber on the left (*arrow*). The scale of the air velocity is cut at 0.03 m s^{-1} for better visualisation of the flow characteristics

volatiles through the microchamber due to reduced sink effects.

Experiments carried out on freshly unwrapped samples, with little or no conditioning time, also showed that the μ -CTE should provide manufacturing with a suitable tool for rapid, meaningful screening of emissions on materials straight from the production line.

Computational fluid dynamics calculations indicate that the air velocity in the empty microchamber is below 0.1 m s^{-1} at a flow of 100 mL min^{-1} , but this is still within the limits of DIN EN ISO 16000-10 and should not impact area-specific emission rates where the primary emission mecha-

nism is internal diffusion. Moreover, experimental data did not show evidence of significant dead zones or sink effects. In fact the converse was true, with the μ -CTE showing better recovery of semivolatiles than the conventional 1 m³ chambers used in this study.

The size of the microchamber is so different to that of the 1 m³ emission test chamber that it is not practical to carry out experiments at the same specific air flow rate; therefore, vapour concentrations cannot be directly compared. However, comparable area-specific emission rates were obtained for a typical test time of approximately 45 min (depending on the sample matrix) in the microchamber.

In a 1 m³ emission test chamber, the time taken for vapour sampling is negligible compared with that spent conditioning the sample (72 h or 28 days); the same is not true for rapid emissions screening using the μ -CTE. In the case of the μ -CTE, the emission profile changes during vapour sampling and the emission measurement obtained will represent an average vapour concentration during the sampling time. This could lead to higher uncertainty. This effect is minimised by allowing a minimum conditioning period (e.g. 15–30 min) after placing the sample in the microchamber before the start of vapour collection.

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