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TDTS

Thermal Desorption Technical Support

Note 69: The Micro-Chamber/Thermal Extractor - the innovative, rapid and cost effective approach for testing VOC emissions from materials

Keywords:

Materials; Microchamber; Emissions testing; Emission chamber; Correlation

Abstract

Emissions of (semi)volatile organic compounds ((S)VOCs) from materials can adversely impact indoor and in-vehicle air quality. National and international regulations/protocols, such as the European Construction Products Directive, German protocol for fire-resistant floorings (AgBB)[1] *and the Californian CHPS protocol for public school building programs (CHPS)*[2] *require the determination of materials emissions using conventional test equipment such as chambers/cells (Methods EN13419-1/-2/-3, ISO/EN 16000-6/-9/-10/-11, ASTM D5116-97, ASTM D7143-05 etc). This enables emissions to be evaluated under simulated real-use conditions and allows real-room concentrations to be estimated.*

Risk of toxic emissions can also be reduced by ensuring that the (S)VOC content of a material is kept inherently low. Direct thermal desorption/extraction (TD) may be used to measure (S)VOCs in a wide range of solid, resinous and liquid materials and eliminates complex liquid extraction steps. This process of thermally extracting the (S)VOCs is a technique that has been used over a number of years for analysis of a range of material types. It is already used by the paint industry (US EPA Method 311 for paints) for evaluating "low VOC" products and the German automotive industry for testing car trim components (Method VDA 278, 2001).

The recent development of a combined Micro-Chamber/Thermal Extraction system, comprising of six microchambers (up to 25 mm deep and ~50 mm in diameter), which allows rapid cost effective surface or bulk emissions testing on up to six samples simultaneously will be presented along with excellent correlation data with conventional emission chamber testing.

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Introduction

The most important methodology for materials emissions testing, for volatile organic compounds (VOC) or semi-volatile organic compounds (SVOC), requires test chambers or cells with vapour sampling onto sorbent tubes and thermal desorption (TD)-GC-MS/FID analysis. Correlation between data from chambers and cells is generally satisfactory (*i.e.* within 25% difference) for dry products**[3]**. Data from these types of emission tests allow manufacturers and users to compare products and to evaluate their potential impact on the indoor environment under simulated real use conditions. Relevant standard methods for such applications include ENV 13419-1, 2 (and 3), ISO 16000-9, 10 (and -11), ASTM D5116-97, ASTM D7143-05 and ASTM draft standard Work Item WK3368. Associated standard methods for analytical aspects include ASTM D6196-03, ISO 16017-1 and ISO 16000-6.

Alternatively, the characterisation of materials by their VOC or SVOC emissions/content, can be carried out by using direct thermal desorption**[4]**. Equilibrium headspace techniques are also occasionally used for volatile emissions**[5]**. These latter approaches are often used for quick volatile or semi-volatile content profiling/screening where the direct comparison of such results with emissions chamber/cell testing is difficult due differences in sample size and thermal conditions. However industry has, hitherto, been limited to such techniques for evaluating their products due to the prohibitively expensive costs associated with setting up and employing "in-house" emission chamber tests and the length of time involved for emissions chamber/cell tests to be performed. Addressing these issues, Markes have developed the Micro-Chamber/Thermal Extractor (µ-CTE™) to provide industry and researchers with a versatile tool for fast cost effective material emissions testing. The µ-CTE™ comprises six microchambers which allow bulk and surface emissions [(S)VOC] testing from up to six samples simultaneously. Bulk thermal extraction of volatile or semi-volatile compounds is a suitable technique for quick content profiling where compounds can be thermally extracted onto sorbent tubes at temperatures up to 120°C. Low temperature surface emissions testing simulates real use emissions analogous to emission chambers/cells testing. The objective of the following study was to compare the area specific emission rates determined from ambient temperature surface emissions testing using the µ-CTE in comparison with a 1m^3 conventional emission chamber (EC) operated in accordance with standard methods**[6]**.

Experimental

Experimental Design

The new Micro-Chamber/Thermal Extractor system (figures 1 & 2) comprises six micro-chambers (up to 28 mm deep and ~45 mm in diameter) which allow surface or bulk emissions to be tested from up to six samples simultaneously. When testing surface emissions; 12.82 cm^2 of sample surface area is exposed to the air/gas flow and the air/gas volume above the sample surface is 3.2 cm^3. The volume of the micro-chamber available for bulk emissions testing is ~ 44 cm^3. Conditioned Tenax or multi-sorbent tubes are attached to each micro-chamber and a controlled flow of air (10-500 ml/min) or inert gas is passed through all chambers. The µ-CTE is compatible with industry standard (89 mm long x 6.4 mm O.D.) sorbent tubes. Adaptors are also available for non-standard 6 mm O.D. sorbent tubes and aldehyde (DNPH) cartridges.

(S)VOC vapours are swept from the sample material in the microchamber and onto the attached sorbent tube. After sample collection, trapped vapours are thermally desorbed and analysed by GC(/MS) as *per* standard methods *e.g.* ISO 16000-6, EN/ISO 16017-1, ASTM D6196-03. Formaldehyde and other carbonyls can be measured using alternative sampling and analytical procedures (ISO 16000 parts 2 & 4, ASTM D5197 *etc.*). The thermal desorption (TD) analytical process is carried out offline allowing a fresh set of samples to be introduced to the µ-CTE, even while analysis of vapours emitted by the previous set of samples is being performed. TD focusing trap parameters (sorbent, temperature, gas flow) were selected such that target compounds were quantitatively retained while water and other, unwanted volatile interferents were purged to vent**[7]**. Subsequent rapid (backflush) desorption of the focusing trap thus transfers/injects only those volatile and semi-volatile compounds of interest, free of water

Figure 1: Micro-Chamber/Thermal Extractor (µ-CTE)

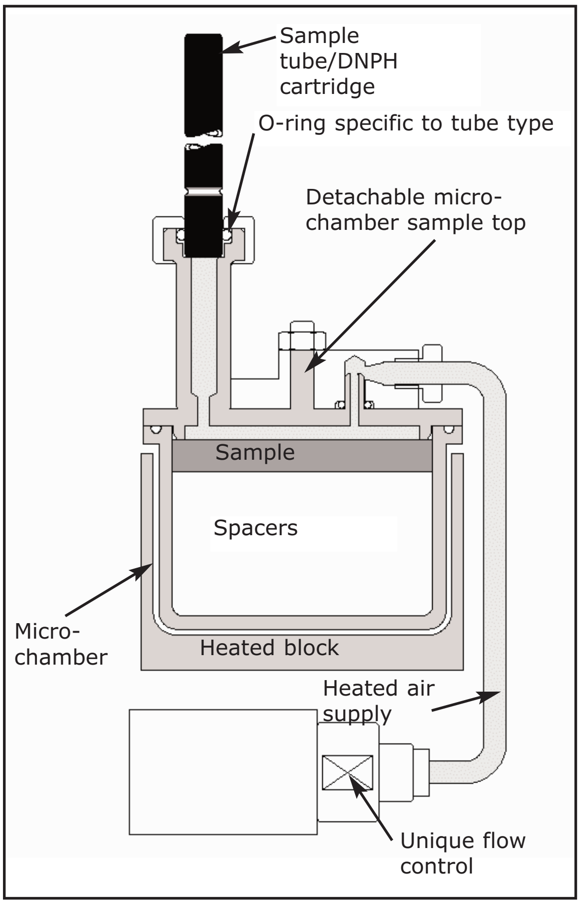

Figure 2: Microchamber schematic

and other unwanted volatiles. All experiments were carried out using an ULTRA-UNITY automated thermal desorber linked to a GC/MS system.

Sample Preparation

Micro-Chamber/Thermal Extractor

A homogenous PVC wall covering was chosen as the test material. It was prepared by cutting a sample disc ~ 45 mm diameter from a central section of the sample sheet in accordance with ENV 13419-3 and ISO 16000-11. The sample piece was pre-conditioned in a climate controlled room at 23°C and 50% relative humidity (RH) for a defined period of time (1 or 3 days) before being inserted into a single µ-CTE chamber. When pre-conditioning of the sample was not necessary the sample was immediately placed into a chamber. Up to six samples can be placed into the µ-CTE at any one time for simultaneous analysis. Once inside a µ-CTE chamber the sample was raised to the correct height, with the aid of a series of spacers, so as to provide 12.82 cm^2 of the sample surface area to be exposed to the air/gas flow. The air/gas volume above the sample surface was 3.2 cm^3. The innovative design of the µ-CTE means that no aluminum foil was required to seal the edges and the rear surface of the test material as is typically the case for conventional emission chamber testing.

Emission Chamber

A 1m^2 section of the same PVC wall-covering described in the previous section was prepared according to ENV 13419-3 and ISO 16000-11. The test piece was fixed onto a glass panel with the edges being sealed using aluminium sealing tape and the test piece immediately inserted into a 1m^3 glass emission chamber.

Experimental Conditions

A comparison of chamber conditions between the µ-CTE and the 1 m^3 emission chamber are depicted in Table 1.

Parameter	**μ-CTE**	**EC**
Sample Area (m^2)	0.001282	1
Chamber Volume (m^3)	3.2×10^{-6}	1
Load Factor (m^2/m^3)	400	1
Exchange rate (h^{-1})	1875	1
Gas Supply (L/min)	0.10	16.7
Chamber Temp. (°C)	23	23

Table 1: Experimental conditions for the μ-CTE and EC

Sampling

Emission Chamber

Emission chamber work was performed in accordance with ENV 13419-2; ISO 16000-10 where the area specific emission rate, (see Equation 1), was determined for day 3, as defined by the German AgBB scheme. Compounds were sampled onto Tenax sorbent tubes for 10 minutes at a flow rate of 100 ml/min.

Equation 1. For calculating area specific emission rates

$$SER_a = A\,{}^{n}/{}_{L}$$

where:

SER_a = area specific emissions rate

A = chromatogram peak area (normalized against sampling volume and an internal standard)

n = air exchange rate (h^{-1})

L = load factor (m^2/m^3)

Emission rates were determined for the total volatile organic compounds (TVOC) in the range of $n\text{-}C_6 - C_{16}$ and expressed as $A/m^2 * hour$.

Micro-Chamber Thermal Extractor

Test material was pre-conditioned in a climate controlled room (23°C and 50% RH) for a specified period (1 or 3 days) before being placed into a single μ-CTE chamber. Emissions from the test material were collected on to Tenax sorbent tubes for 10 minutes at 100 ml/min. SER_as for the test material were determined for up to 73 hours (3 days and 60 minutes).

Results and Discussion

Area specific emission rates were determined in triplicate and averaged for both the emissions chamber (red) and μ-CTE (blue) as depicted in figure 3. Emission rates were determined for up to three days for the μ-CTE while emission rates for the conventional emission chamber were determined for day three.

Area specific emissions rates determined from the μ-CTE, during the first hour of sampling, showed a rapid decrease. The initial rapid decay in the SER_a can be attributed to the loss of solvents adsorbed on the surface of the material. This phenomenon is explored in more detail later in this paper (see figure 6).

Generally speaking, emissions testing should be carried out after surface adsorbed solvents have been purged. Once this has happened, internal diffusion processes become the dominant mechanism of emission, the rate of change of SER_a slows and meaningful emissions data, for comparing different products/materials, can be collected. In the case of conventional emission chambers, additional equilibration time is also required, due to their large size, before vapour concentrations sampled from the chamber exhaust are representative of the emissions rate. According to the AgBB scheme and other test methods/protocols emissions testing using small chambers should be carried after 72 hours equilibration.

Figure 4 depicts SER_as for both the μ-CTE and the EC for the 72 hour test. The results illustrate excellent absolute correlation between the two techniques. The emission rates

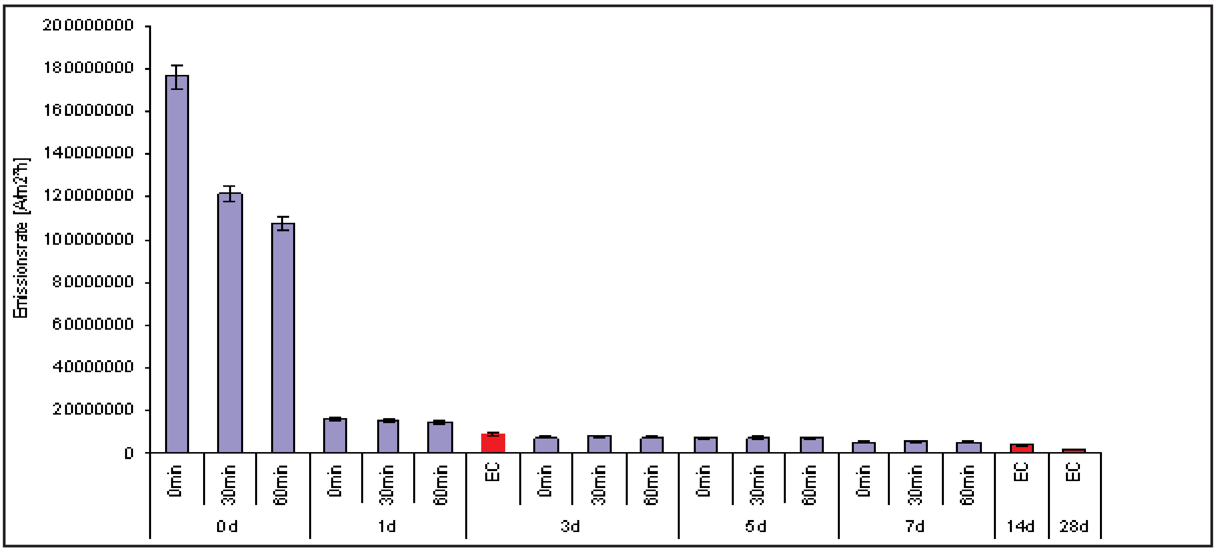

Figure 3. Calculated area specific emission rates for the emission chamber (red) and μ-CTE (blue) after different conditioning times

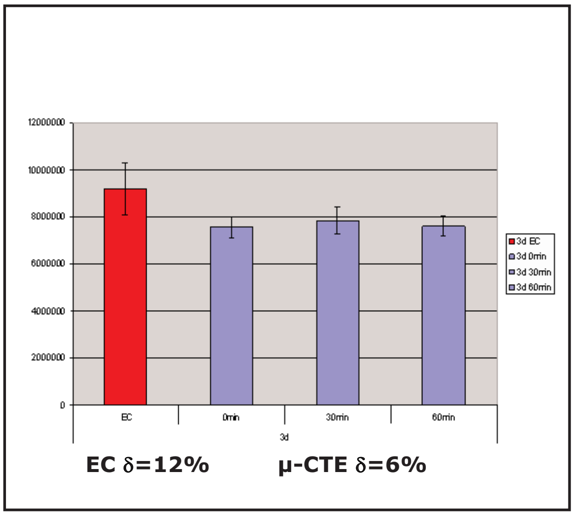

Figure 4: Calculated area specific emission rates for the emission chamber (red) and μ-CTE (blue) for day 3 illustrating the close correlation between the two techniques. The standard deviations (δ) for the respective techniques are also present

determined from the conventional emission chamber were ~15% higher than those obtained from the μ-CTE. The higher emission rates from the EC method were attributed to emissions from the aluminium sealing tape adhesive (used to secure the aluminium foil in the conventional emissions chamber) contributing to the TVOC observed.

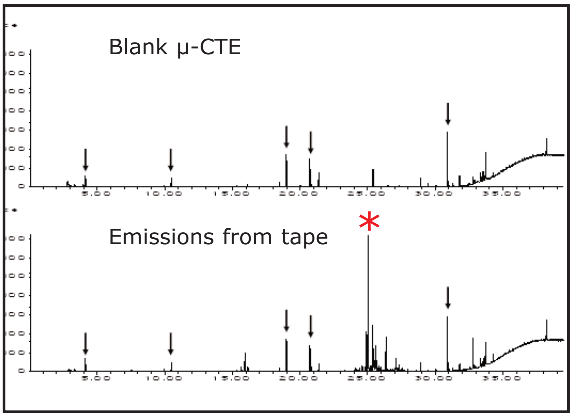

Figure 5: Comparison of blank μ-CTE with emissions from aluminium sealing tape

The effect that the aluminium sealing tape has on the total emissions measured by the small chamber was investigated by sampling some of the tape in the Micro-Chamber. The emissions were collected onto Tenax sorbent tubes for 10 minutes at 100 ml/min and ambient temperature and compared with a blank chromatogram of the μ-CTE chamber. The resulting chromatograms are depicted in Figure 5.

The top chromatogram in Figure 5 is the normal blank of the microchamber. The bottom chromatogram is from the same microchamber containing a very small section (~ 4 cm^2) of the aluminium tape. The arrows indicate the compounds used in the internal standard solution on the TENAX tubes. The additional peaks in the bottom chromatogram, indicated by the star, were attributed to emissions from the tape adhesive. This suggests that the tape adhesive contributed to the TVOC observed and the efficiency of the sealing tape was inadequate. Therefore, the tape's ability, in this instance, to prevent emissions from the rear surface and the edges of the test material contributing to the TVOC is questionable.

As shown in figure 4, results from the μ-CTE were seen to be more reproducible, relative to the conventional emissions chamber method. Results obtained from the EC method are often sensitive to parameters such as the orientation of the sample within the chamber and the way in which the test material has been prepared.

Results from an inter-laboratory study among 25 laboratories found that deviations of >50% can exist between EC testing for the same material[8]. Variation within the sealing efficiency of the foil used in the EC method will also contribute the observed deviation. These sensitivities imply the emissions chamber method relies heavily on the experience and expertise of the user in order to reproducibly obtain results with minimal deviation. The μ-CTE method always positions the test material at the same position in the chamber, relative to the carrier gas stream, and therefore results will not be sensitive to this parameter. Furthermore, due to the inherent sealing feature of the μ-CTE, the need to manually seal the edges and underside of the sample is made redundant. As a consequence, highly reproducible results from the μ-CTE are able to be obtained with little demand being placed on the experience/expertise of the user.

As discussed above, methods for emission chambers require the systems to equilibrate before vapour sampling can be conducted. The time required to establish equilibrium is dependent on the volume of the chamber, the volatility of the emitted compounds, and the air exchange rate and is usually specified as 72 hours in standard methods. When using the μ-CTE for surface emissions testing, the gas volume above the sample surface is 3.2 cm^3 and typical air exchange rates are 1000-2000. h^{-1}. This means that the time required establishing equilibrium is negligible and that vapour sampling can typically start as soon as surface adsorbed vapours have been swept away.

Figure 6 represents TVOC emissions from the PVC wall covering collected using μ-CTE during the first 240 minutes after sample introduction. As explained above, the initial rapid decay rate is indicative of adsorbed solvent being purged from the material surface during the first few minutes of testing. However figure 6 shows that a relatively steady emission rate was reached after ~20 minutes. This means that meaningful emissions data from the wall coverings could be obtained using the μ-CTE within only 20-30 minutes after placing the sample in the micro-chamber. Thus SER_a rates determined from a wall covering sample after 20-30 minutes equilibration in the μ-CTE should provide a valid indication of whether a high or low emission rate would be obtained from a conventional EC test after three days. This is confirmed by the findings of another study in which the μ-CTE was used to test emissions from polymer beads[9].

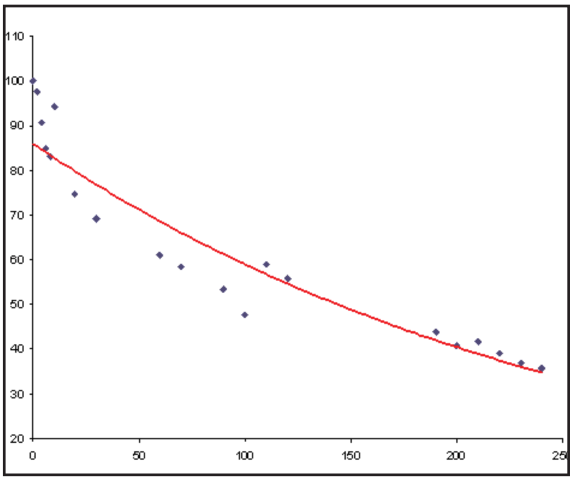

Figure 6: Emissions decay profile for PVC wall covering using the μ-CTE method. Emissions were observed for up to 240 minutes. Depicted are individual data points (blue) and a fitted exponential curve (red)

Conclusion

This study has shown that quantitative emission rates determined using the Micro-Chamber/Thermal Extractor correlated, in absolute terms, with those obtained using a 1 m^3 emissions chamber (72-hour test). Investigations also found that the reproducibility of the conventional emissions chamber method could be compromised by artefacts from the sealing tape and associated adhesive. It has also been shown that data obtained from the µ-CTE method was more reproducible than could be obtained from the emissions chamber method and less reliant on the expertise of the user.

It has also been shown that the µ-CTE method is capable of obtaining meaningful emissions data within 20-30 minutes.

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