MARKES
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TDTS

Thermal Desorption Technical Support

Note 93: Application of rapid micro-chamber tests (ISO 12219-3) for screening chemical emissions from plastic car trim components

Keywords:

Micro-Chamber/Thermal Extractor, car trim, plastics, 1,3-butadiene, styrene

Introduction

Despite its popularity, a major source of 'new car smell' is release of chemicals from car interior materials, *e.g.* plastic or wood trim, textiles, glues and sealants. Emitted volatile and semi-volatile organic compounds (VOCs and SVOCs) such as benzene, formaldehyde and phthalates may have a detrimental impact on vehicle interior air quality (VIAQ), and in extreme cases may pose a risk to the health of occupants.

With increasing awareness of VIAQ issues, it is becoming necessary for car manufacturers to monitor and control VOC and SVOC compounds released from interior trim components.

The ISO 12219 series for testing indoor air of road vehicles describes several methods for testing cabin air quality and measuring emission rates of VOCs and SVOCs from materials used in vehicle cabins. These include:

1. ISO 12219-1 Indoor air of road vehicles — Part 1: Whole vehicle test chamber -Specification and method for the determination of volatile organic compounds in cabin interiors
2. ISO 12219-2 Indoor air of road vehicles — Part 2: Screening method for the determination of the emissions of VOC from car trim components - Bag method
3. ISO 12219-3 Indoor air of road vehicles — Part 3: Screening method for the determination of the emissions of VOC from car trim components - Micro-scale chamber method
4. ISO 12219-4 Indoor air of road vehicles — Part 4: Method for the determination of emissions of VOC from car trim components - Small chamber method

While the larger-scale 12219-series tests take several hours, part 3 provides manufacturers with a convenient tool for rapid emissions screening (*i.e.* within minutes). It describes the use of micro-scale chambers which can accommodate small articles or representative samples of trim. Previous investigations comparing results from micro-scale chambers with emissions data obtained from larger chambers show strong correlation (Figure 1)[1–4].

Micro-chambers are ideal for in-house industrial applications such as:

- (S)VOC emission screening for routine quality control
- Evaluating prototype 'low-emission' materials/products during development
- Monitoring product uniformity/conformity between formal certification tests
- Comparing emissions from products within a range (*e.g.* different colours/patterns)
- Checking the quality of raw materials
- Troubleshooting customer complaints

Markes Micro-Chamber/Thermal Extractor™ (µ-CTE™) systems are a leading example of commercial micro-scale chamber apparatus. In this Application Note, we demonstrate the efficiency and reliability of Markes' µ-CTE in qualifying and quantifying the emission of residual monomer from polymer according to ISO 12219-3.

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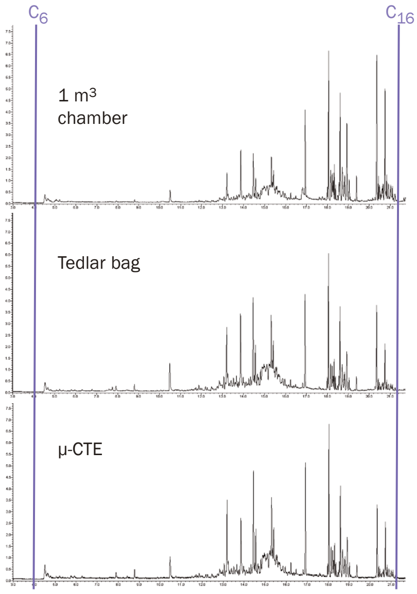

Figure 1: Correlation between chamber, Tedlar bag and µ-CTE emissions data (Data reproduced with the kind permission of Prof. Mangoo Kim, Kangwon National University, Korea[1])

Markes' micro-chamber equipment for ISO 12219-3

Markes offers two versions of the µ-CTE sampling instrument; a unit with four 114-mL chambers and another with six 44-mL chambers (Figure 2). Both versions of the µ-CTE are able to operate at ambient or elevated temperatures to allow the extraction of vapour-phase organic emissions from various types of car interior trim components, *e.g.* textiles, plastic polymers and sealants. Multiple test specimens can be readily evaluated from the same sample if required. Schematics of Markes' micro-chamber apparatus in operation for bulk and surface emissions testing are shown in Figure 3, and more information is given in the brochure.

Figure 2. Markes International Micro-Chamber/Thermal Extractor (µ-CTE) units

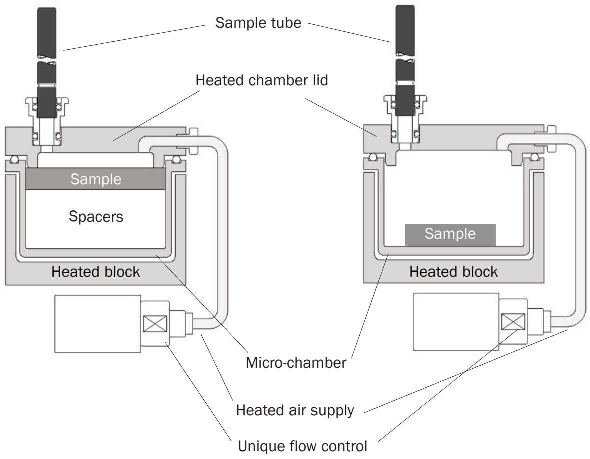

Figure 3. Schematics of µ-CTE apparatus in operation for bulk and surface emissions testing

The chambers of both µ-CTE units are constructed of inert-coated stainless steel to avoid interference and negate sink effects (see Markes' TDTS 67 for further information on blank TVOC levels). The chambers are supplied with a constant flow (up to 500 mL/min) of dry air or inert gas and, after equilibration, emissions are collected onto a connected sample tube. Thermal desorption (TD) sorbent tubes are used for retention of VOCs and SVOCs, and DNPH cartridges are used for formaldehyde.

Tenax® TA is the most commonly used sorbent for VOCs ranging in volatility from n-hexane to n-hexadecane. Tubes packed with 2 or 3 sorbents in series are available to extend this volatility range if needed. Analysis of the sorbent tube is then performed by TD with gas chromatography and mass spectrometry (GC/MS) according to ISO 16000-6[5].

Experimental

The polymer acrylonitrile–butadiene–styrene (ABS) is a thermoplastic resin widely used in the automobile industry, *e.g.* for interior trim, headlight housings and grilles.

Two irregularly shaped samples of ABS plastics (A and B) were obtained for bulk emission testing. Plastic A was cut into six pieces of roughly 2 cm^2 with a clean scalpel, ensuring that gloves were worn to reduce the risk of contamination. Plastic B was supplied in the form of moulded pieces that were small enough to fit directly into the chambers of the µ-CTE. The mass and exact area of each piece were recorded and they were placed into separate chambers. Care was taken to ensure that all samples were placed in the centre of the chamber

(Figure 4 and the right hand part in Figure 3), with the same surface facing upwards for each measurement.

A temperature of 65°C and a flow of helium at 50 mL/min were set, and the system was left to equilibrate for 20 min as per ISO 12219-3. A dual-bed sorbent tube comprising Tenax TA and Carbograph 5TD was then attached and emissions collected for 15 min. All tubes were analysed by TD-GC/MS using a similar procedure to that described in ISO 16000-6. A thick-film capillary GC column, designed for volatiles, was used in this case because of the specific interest in the very volatile component 1,3-butadiene. Other conditions are stated below.

TD

Instrument:	TD-100™ (Markes International)
Flow path:	140°C
Trap purge time:	1 min
Primary desorption:	8 min at 250°C
Focusing trap:	–10°C to 300°C, 4 min hold, 20:1 split
Trap type:	U-T12ME (Markes International)

GC/MS

Column:	DB-624, 30 m × 0.32 mm × 1.8 µm
Pressure:	4 psi, constant pressure mode
Initial flow:	2 mL/min
Temp prog.:	35°C (5 min) then 30°C/min to 230°C, hold for 2 min
Total run time:	13.50 min
Carrier gas:	He
Mass scan range:	25–300 amu
MS source temp:	230°C
MS quad temp:	150°C
Transfer line temp:	280°C

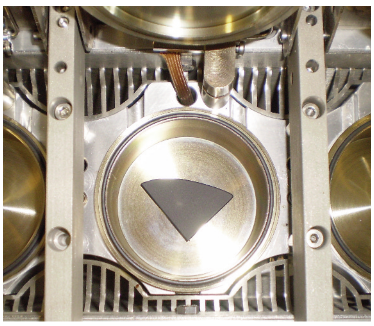

Figure 4: Samples were placed in the centre at the bottom of the micro-chamber to ensure a uniform flow of gas across the surface

The system was calibrated by introducing known volumes of standard gas into clean sorbent tubes.

Results

Data were calculated by integrating the extracted ion chromatograms using m/z 54 for 1,3-butadiene and m/z 104 for styrene (Figures 5 and 6).

Tables 1 and 2 detail the response and calculated specific emissions of 1,3-butadiene and styrene monomer from each sample of polymer. Figures 7 and 8 show the specific emissions of butadiene and styrene for each sample of plastic A and each sample of plastic B, and illustrate the reproducibility that can be achieved when using the µ-CTE for sampling.

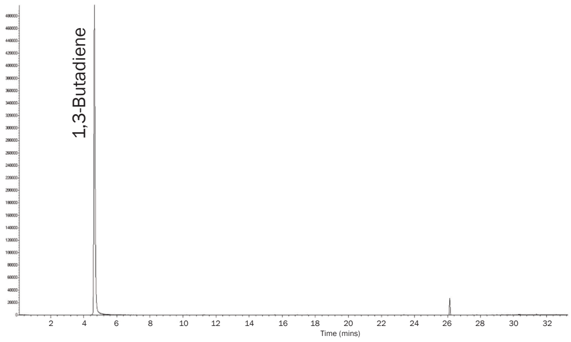

Figure 5: An extracted-ion chromatogram of m/z 54 (1,3-butadiene) obtained from polymer A

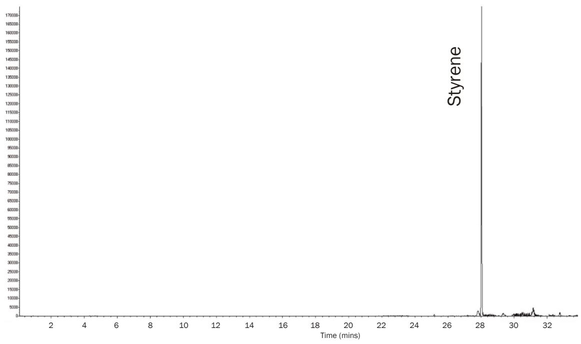

Figure 6: An extracted-ion chromatogram of m/z 104 (styrene) obtained from polymer A

Relative standard deviations (RSDs) of between 4.6% and 16.3% represent exceptional reproducibility within the context of materials emissions testing. Moreover, the figure of 16.3% includes one obvious outlier (see Table 2). Excluding this figure gives an RSD of 4.3%. Previous inter- and intra-lab studies using chamber equipment have shown RSDs in the order of 20–30% to be more common[6].

Plastic A	Butadiene		Styrene	
Sample area (cm²)	Mass of butadiene (pg)	Mass of butadiene (pg) per cm² sample	Mass of styrene (pg)	Mass of styrene (pg) per cm² sample
2.63	17.9	6.8	51.08	19.43
2.57	19.7	7.7	54.62	21.24
2.00	12.7	6.4	35.87	17.93
1.58	12.1	7.7	32.68	20.63
1.44	9.7	6.7	29.23	20.36
1.52	11.8	7.7	31.20	20.51
		RSD: 7.6%		**RSD: 5.4%**

Table 1: Surface emission results for sample A

Plastic B	Butadiene		Styrene	
Component mass	Mass of butadiene (pg) per component	Mass of butadiene/mass component	Mass of styrene (pg) per component	Mass of styrene/mass component
1.1586	3.20	2.76	4.47	3.86
1.1601	4.86	4.19	4.54	3.92
1.1563	3.52	3.04	4.38	3.79
1.1565	3.29	2.84	4.99	4.31
1.1563	3.53	3.05	4.61	3.98
		RSD: 16.3% or 4.3%		**RSD: 4.6%**

Table 2: Component emission results for sample B

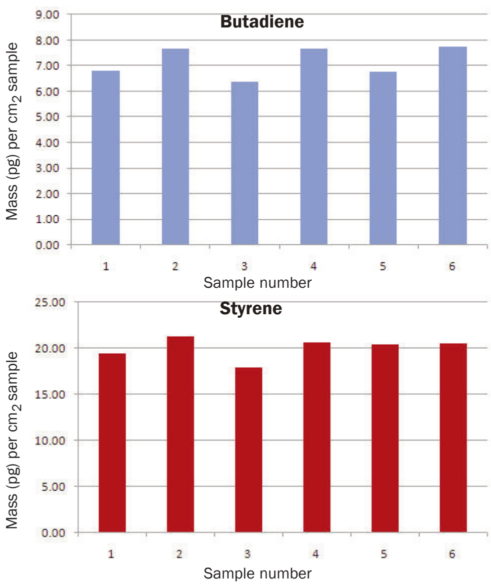

Figure 7: The area-specific emissions of sample A, demonstrating the reproducibility of the μ-CTE

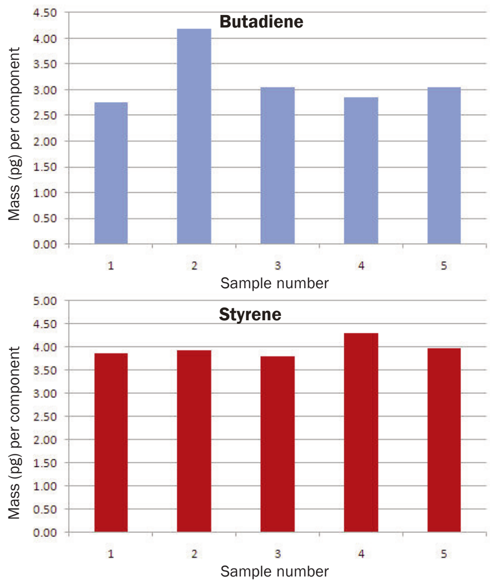

Figure 8: The component-specific emissions of sample B, demonstrating the reproducibility of the μ-CTE

Conclusions

Markes' µ-CTE provides industry with a fast, straightforward and efficient tool for materials emissions sampling in compliance with ISO 12219-3. The excellent reproducibility shown in this study further confirms the suitability of the µ-CTE for evaluating emissions of monomers and other volatiles from plastics, such as ABS, a terpolymer that is used to make car trim components.

References

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Trademarks

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

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