TDTS 103

Enhancing the development of low-emitting products and materials

Summary

This Application Note describes how sampling technologies for thermal desorption that are typically used by test laboratories for screening products for chemical emissions can also provide manufacturers with tools that greatly aid the development of low-emitting products and materials, and thus compete in the expanding market for ‘green’ products.

Taking adhesives, flooring materials and a glazing spacer as examples, we show how Markes’ sampling equipment can be used to compare emissions between products, to assess the effect of manufacturing processes, and to troubleshoot problems arising during manufacture.

Introduction

The release of volatile and semi-volatile organic compounds (VOCs and SVOCs) from products and materials is increasingly subject to regulation in many countries. This, in conjunction with rising consumer awareness of the health risks of exposure to chemical emissions indoors, is driving demand for improved assessment and labelling of products.

These new regulations have a large impact, with manufacturers of a wide variety of products being in the front line, together with their suppliers. These include manufacturers of flooring, furniture, wood-based products, insulation materials, coatings, adhesives and sealants, toys, domestic goods and cleaning products, among others[1].

The majority of these regulations require products to be tested for emissions of volatile and semi-volatile organic compounds (VOCs and SVOCs). Formal product certification is carried out by accredited laboratories using reference tests. These involve the product being placed in a 100–1000 L chamber, with vapour sampling onto sorbent tubes, and analysis by thermal desorption–gas chromatography/mass spectrometry (TD–GC/MS). The length of time needed for these tests (3 or 28 days in Europe and 10–14 days in the USA), and the stringent conditions that need to be maintained (23°C and 50% relative humidity) make these tests both expensive and time-consuming.

Consequently, there is demand from industrial laboratories for simpler sampling methods that allow the rapid assessment of chemical emissions as part of routine quality control and during product development. Two such methods are direct desorption, and dynamic headspace extraction using a micro-chamber. Used in conjunction with TD–GC(MS), these allow meaningful chemical emissions data to be collected in industrial laboratories, enabling manufacturers to develop and evaluate low-emission, high-value materials and compete in the expanding market for ‘green’ products.

In this Application Note we use four examples to illustrate the benefits of being able to carry out material emissions screening in-house:

- Comparing cured and uncured adhesives
- Comparing an adhesive with a competitor’s product
- Assessing the effect of manufacturing processes on the final emission profiles of flooring tiles
- Troubleshooting – determining the cause of the failure of a glazing spacer.

Background

In the examples discussed below, two sampling methods were used – direct desorption, and dynamic headspace extraction using Markes' Micro-Chamber/Thermal Extractor™.

Direct desorption [2]

This process is suitable for homogeneous samples. Small pieces of the material are placed into an empty TD sample tube (Figure 1), if necessary being held in place by plugs of quartz wool. The tube is then placed directly into the TD unit for desorption and analysis.

Figure 1: Direct desorption of a solid sample.

Micro-Chamber/Thermal Extractor [3]

Markes' Micro-Chamber/Thermal Extractor (Figure 2) is a compact unit with four or six small cylindrical chambers, suitable for sampling chemical emissions from larger samples, or from materials that are not entirely homogeneous.

Figure 2: Markes' Micro-Chamber/Thermal Extractor.

The chambers are held at room (or elevated) temperature under a flow of pure air or nitrogen, with the vapours released from the sample being trapped on sorbent tubes connected to the outlet of each chamber. A constant flow of gas is maintained through each micro-chamber 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 Micro-Chamber/Thermal Extractor can be used for measuring emissions from both bulk samples and from the surface of planar samples (*e.g.* flooring tiles):

- **Bulk materials** are placed in one of the chambers, and the headspace vapours are dynamically extracted onto a sorbent-packed tube by a flow of heated air or gas (Figure 3a), ready for the thermal desorption stage.
- **Surface-only emissions** of flat samples can be studied using spacers that raise the sample up and ensure that only its upper surface is exposed to the flow of gas. Vapours emitted by the sample surface are swept onto a sorbent-packed tube as described above (Figure 3b).

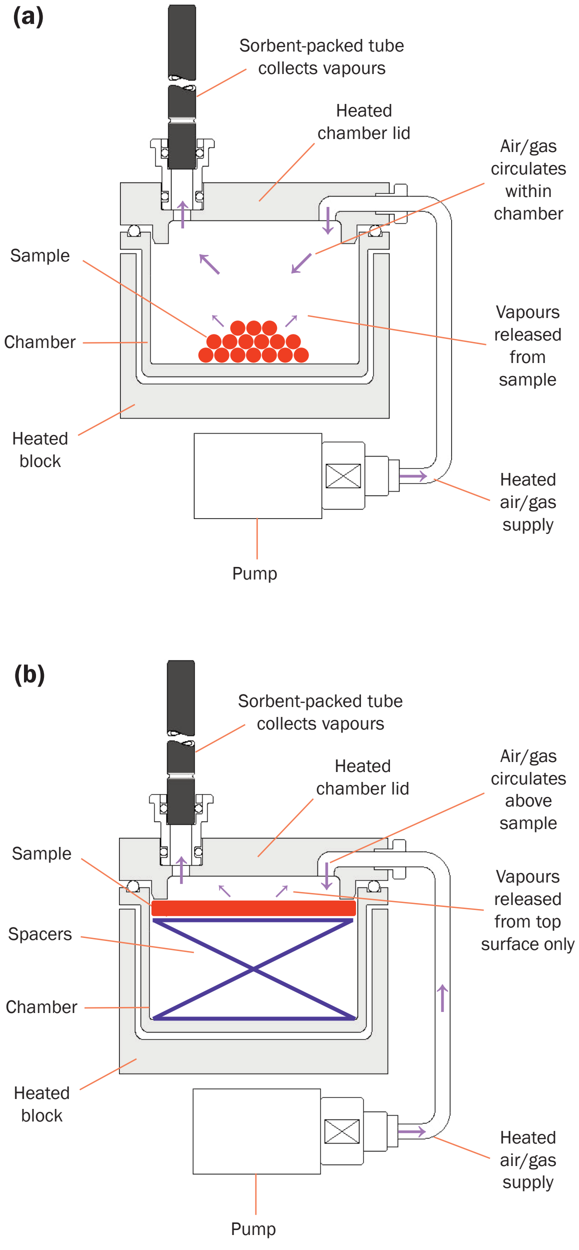

Figure 3: Operation of the Micro-Chamber/Thermal Extractor for sampling emissions of volatile chemicals from (a) bulk samples, and (b) the surfaces of flat samples.

Experimental

Adhesives and glazing spacer

TD (using the Micro-Chamber/Thermal Extractor):
Instrument: UNITY™ 2 (Markes International)
Sample: 0.65 g of each adhesive per chamber
Chamber temp.: 26°C for ambient sampling; 40°C for elevated sampling
Extraction time: 30 min
Sampling flow: 50 mL/min dry nitrogen
Sampling tubes: Glass tubes packed with 200 mg Tenax® TA (35/60 mesh)
Flow path temp.: 180°C
Trap type: U-T12ME-2S (material emissions trap)
Pre-purge: 1 min at 20 mL/min to split
Primary (tube) desorption: 320°C for 10 min, 40 mL/min trap flow, no split flow
Pre-trap-fire purge: 1 min at 50 mL/min trap flow, 20 mL/min split flow
Secondary (trap) desorption: 5°C trap low, 320°C trap high, heating rate ~100°C/min, hold time 5 min, split flow 20 mL/min
Overall TD split: 21:1

TD (using direct desorption):
Instrument: UNITY 2 (Markes International)
Sample: 80 mg of glazing spacer placed in a glass sorbent tube
Flow path temp.: 180°C
Trap type: U-T12ME-2S (material emissions trap)
Pre-purge: 1 min at 20 mL/min to split
Primary (tube) desorption: 185°C for 10 min, 40 mL/min trap flow, 40 mL/min split flow
Pre-trap-fire purge: 1 min at 40 mL/min trap flow, 100 mL/min split flow
Secondary (trap) desorption: 5°C trap low, 300°C trap high, heating rate ~100°C/min, hold time 5 min, split flow 100 mL/min
Overall TD split: 202:1

GC/MS:
Column: J&W DB-5, 60 m × 0.25 mm × 0.5 µm
Pressure: 16.2 psi constant pressure
Initial flow: 1 mL/min
Temp. programme: Micro-chamber sample: 40°C (5 min), 10°C/min to 320°C (20 min)
Direct desorption sample: 40°C (5 min), 10°C/min to 320°C (10 min)
Total run time: Micro-chamber sample: 53 min
Direct desorption sample: 43 min
Carrier gas: Helium
Mass scan range: m/z 35–350
MS source temp.: 230°C
MS quad temp.: 150°C
MS transfer line: 280°C

Flooring materials

TD (using the Micro-Chamber/Thermal Extractor):
Instrument: TD-100™ (Markes International)
Sample: Circular portion (4.5 cm diameter) of flooring tile cut to fit the chamber
Sampling temp.: 40°C
Equilibration time: 30 min
Extraction time: 30 min
Sampling flow: 50 mL/min dry air
Sampling tubes: Glass tubes packed with ~200 mg Tenax TA (35/60 mesh)
Flow path temp.: 180°C
Trap type: U-T12ME-2S (material emissions trap)
Pre-purge: 1 min at 20 mL/min to split
Primary (tube) desorption: 320°C for 10 min, 40 mL/min trap flow, no split flow
Pre-trap-fire purge: 1 min at 50 mL/min trap flow, 25 mL/min split flow
Secondary (trap) desorption: 5°C trap low, 320°C trap high, heating rate ~100°C/min, hold time 5 min, split flow 25 mL/min
Overall TD split: 26:1

GC/MS:
Column: J&W DB-5, 60 m × 0.25 mm × 0.5 µm
Pressure: 16.2 psi (constant pressure)
Initial flow: 1 mL/min
Temp. programme: 40°C (1 min), 20°C/min to 150°C, 4°C/min to 230°C, 20°C/min to 300°C (5 min)
Total run time: 35 min
Carrier gas: Helium
Mass scan range: m/z 35–350
MS source temp.: 230°C
MS quad temp.: 150°C
MS transfer line: 280°C

Results and discussion

Example 1: Comparing cured and uncured adhesives

A hot-melt solid adhesive was analysed in two forms – as the uncured pellets and after curing, both using the Micro-Chamber/Thermal Extractor. The chamber was set to 26°C, and in each case a total gas volume of 1.5 L was collected onto a sorbent tube packed with Tenax TA. These results are shown in Figure 4.

It is clear from the data that the curing process causes a reduction in the level of octane, but an increase in the emissions of long-chain hydrocarbons. The ability to compare samples before and after processing in this way allows manufacturers to optimise the curing process to minimise chemical emissions from the end product.

The Micro-Chamber/Thermal Extractor allows emissions screening at ambient and elevated temperatures. The latter can be used to simulate product applications at higher temperatures – *e.g.* evaluating the emission levels from car trim components inside a vehicle on a sunny day. To demonstrate the impact of temperature on product emissions, Figure 5 compares results from two samples of the uncured adhesive, one tested at 26°C and the other at 40°C. The increase in temperature results in a clear increase in chemical emissions, particularly of 2-(2-butoxyethoxy)ethanol.

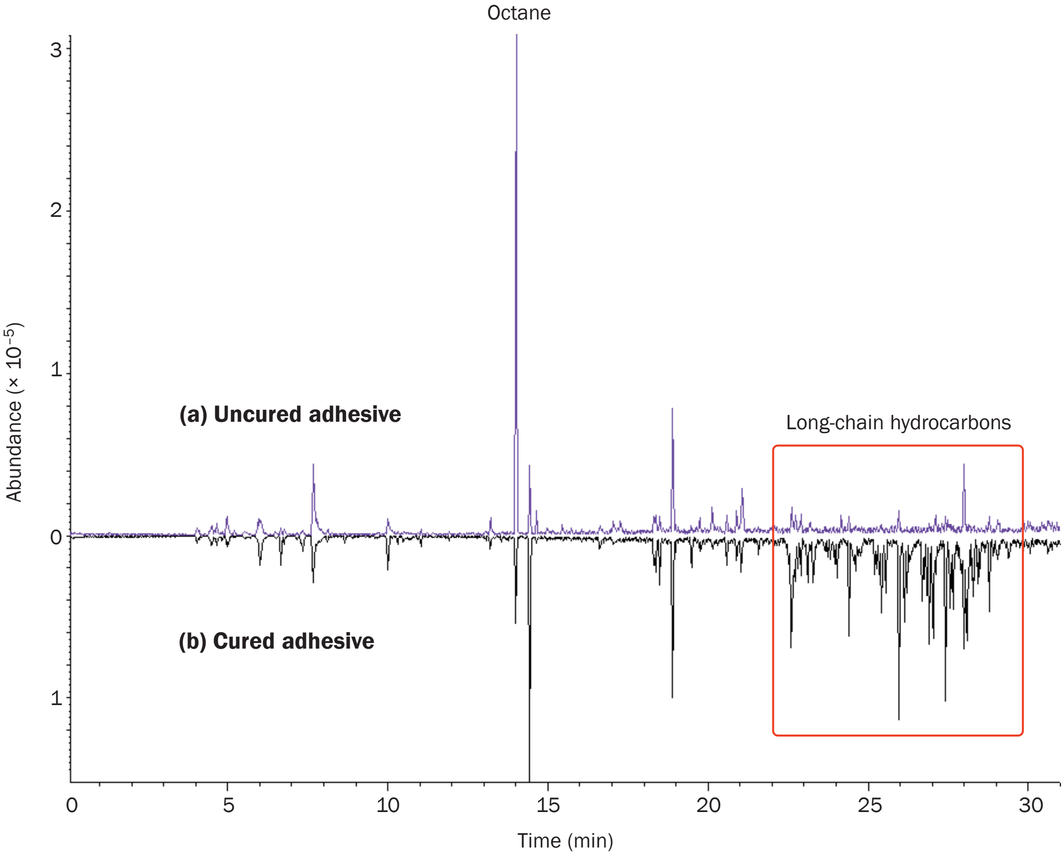

Figure 4: Comparison of the VOC profiles of an adhesive (a) before curing, and (b) after curing. Emissions were sampled using the Micro-Chamber/Thermal Extractor onto sorbent tubes packed with Tenax TA, and analysed by TD–GC/MS.

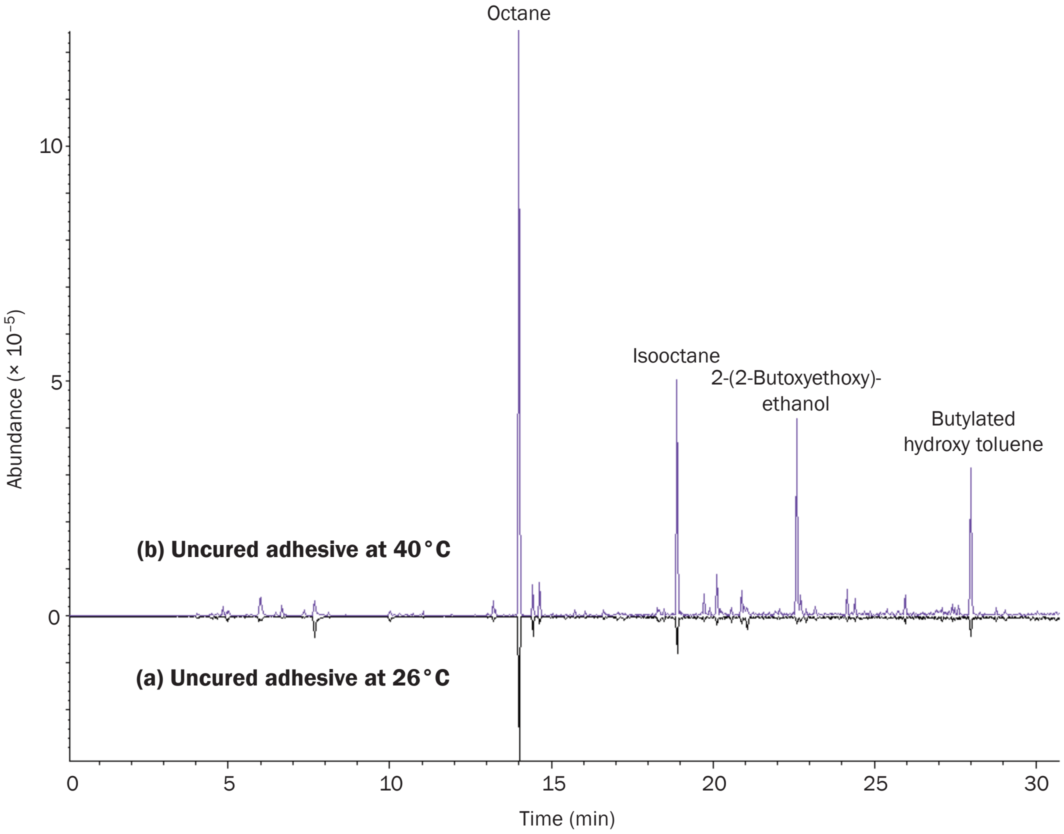

Figure 5: Comparison of VOC profiles of the uncured adhesive at 26 °C and 40 °C. Emissions were sampled using the Micro-Chamber/Thermal Extractor onto sorbent tubes packed with Tenax TA, and analysed by TD–GC/MS.

Example 2: Comparing an adhesive with a competitor's product

It is always interesting for manufacturers to compare emissions from their own products with those of similar materials from other suppliers. Such comparisons can also help identify particular chemicals or formulations that help products meet a particular customer requirement, or that make a product more environmentally friendly.

An example is shown in Figure 6, where the Micro-Chamber/Thermal Extractor was used to compare two brands of 'grab' adhesive (*i.e.* adhesives that bond instantly to a surface). In this case the main difference between the two products was the compound 2,2,6,6-tetramethyl-4-piperidinol, a light-stabilising agent only present in Adhesive B.

Example 3: Assessing the effect of manufacturing processes on the final emission profiles of flooring tiles

The power of thermal desorption to study emissions at different stages of the manufacturing process is shown by the following example. Chemical emissions were determined for three flooring samples with identical formulations but subjected to different treatments:

- Unlacquered
- Lacquered as normal (including a heat treatment cycle)
- Lacquered as above, but with an extra heat treatment cycle.

Circular sections of each tile, 4.5 cm in diameter, were cut to fit tightly inside the micro-chambers. Spacers were used to raise each sample within each micro-chamber, until the surface of the tile was pushed against the baffle projecting down from the micro-chamber lid. This ensured that emissions from the cut edges were excluded and just the VOCs released from the top surface were sampled. The chambers were heated to 40 °C and a total of 1.5 L of vapour collected.

The chromatograms for the three samples (Figure 7) are broadly similar, but display some differences in the levels of certain compounds, which could be of importance for product development. The amounts of seven key compounds are compared in Figure 8.

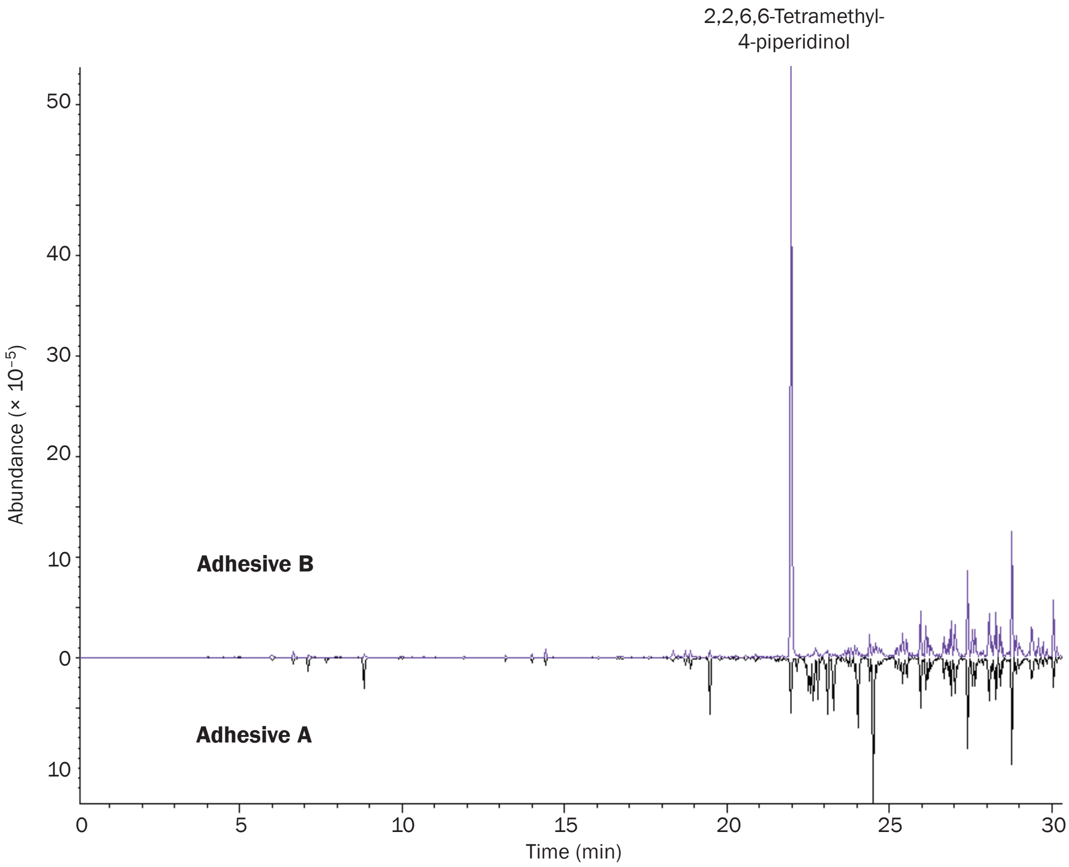

Figure 6: Comparison of two competing brands of 'grab' adhesives. Emissions were sampled (under identical conditions) using the Micro-Chamber/Thermal Extractor onto sorbent tubes packed with Tenax TA, and analysed by TD–GC/MS.

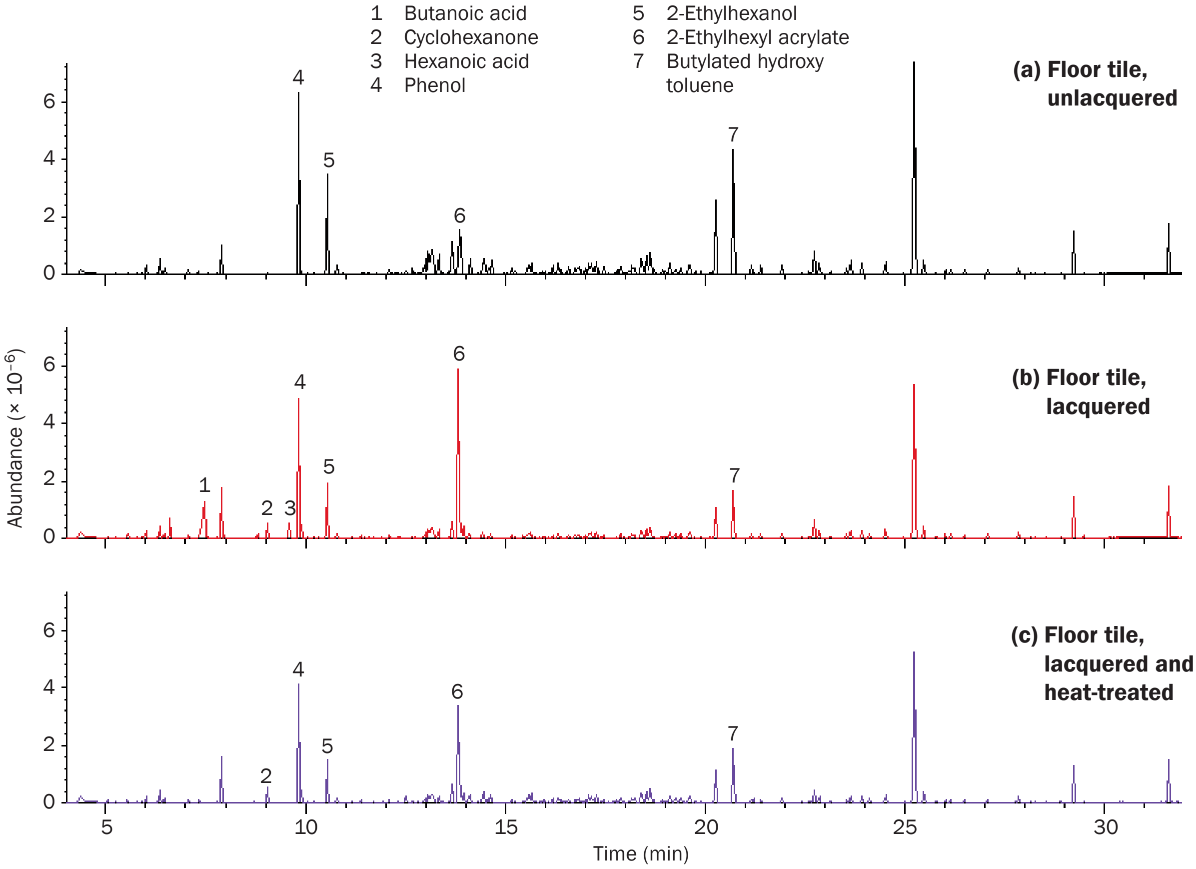

Figure 7: Comparison of VOC profiles for flooring samples with different treatments: (a) unlacquered; (b) lacquered as normal (including a heat treatment cycle); (c) lacquered as above, but with an extra heat treatment cycle. Emissions were sampled using the Micro-Chamber/Thermal Extractor onto sorbent tubes packed with Tenax TA, and analysed by TD–GC/MS.

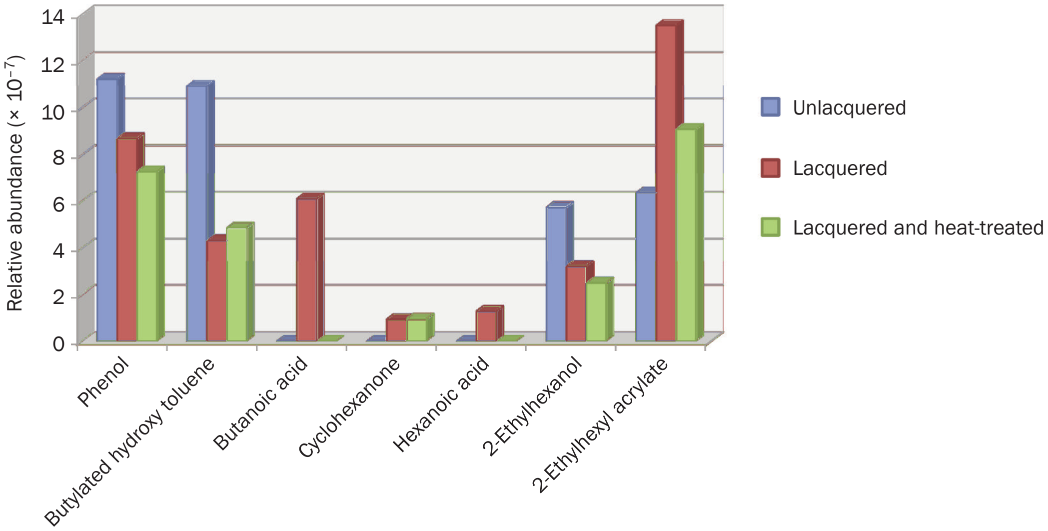

Figure 8: Comparison of relative abundance of the seven key compounds emitted by the flooring samples.

The lacquering process was shown to reduce emissions of phenol and 2-ethylhexanol by a small amount, and although the levels reduced further with another cycle of heat treatment, they did not fall by as much as expected. Lacquering also reduced the emissions of butylated hydroxy toluene, but surprisingly this effect was partly reversed by the heat treatment. Finally, although the lacquer was found to be entirely responsible for the emissions of odorous butanoic acid, these emissions were completely eliminated by the additional cycle of heat treatment.

Example 4: Troubleshooting – determining the cause of the failure of a glazing spacer

A plastic glazing spacer used in window manufacture was found to bubble badly when hot glue was applied to its upper surface. The spacer was a tube with a roughly rectangular cross-section, with its upper surface coated in foil, glued in place (Figure 9). The bubbling occurred underneath the foil, indicating high levels of chemical emissions (‘off-gassing’), either from the glue used to affix the foil, or from the plastic spacer itself.

An investigation was carried out to determine the source of the problem. The material was cut along the red dotted lines (Figure 9) to give two samples of the plastic, one foiled and the other non-foiled. A portion of each sample (80 mg) was then loaded into a glass tube for direct desorption at 185 °C.

The difference in the chromatograms is immediately obvious (Figure 10), with the primary off-gassing culprit being identified as dichloromethane. As the non-foiled sample released no dichloromethane, it was clear that the glue used to bind the foil to the plastic was the source of the off-gassing. This allowed the manufacturer to find a new adhesive to stop the problem from recurring.

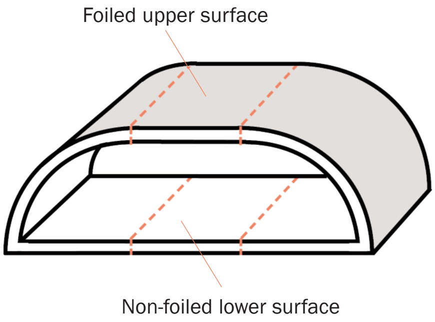

Figure 9: Cross-section of the glazing spacer. The red dotted lines indicate where the spacer was cut to provide foiled and non-foiled samples.

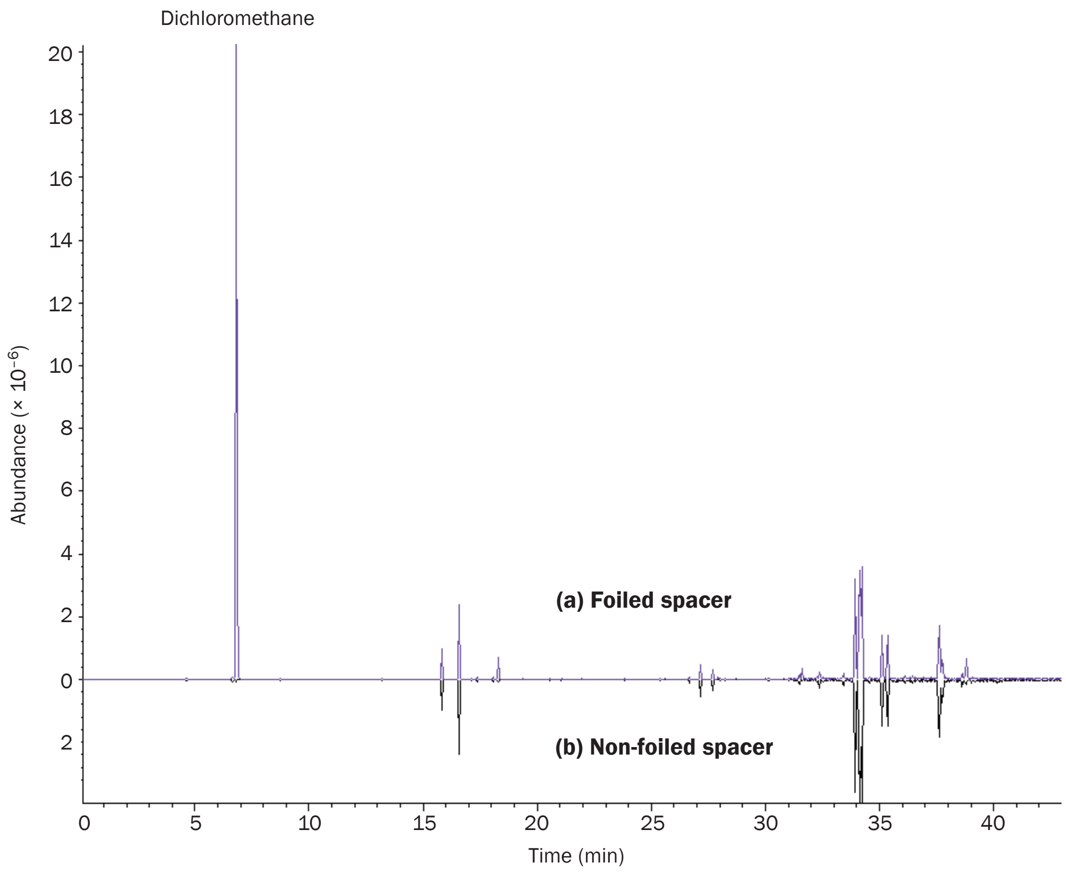

Figure 11: Comparison of the chromatograms for the (a) foiled and (b) non-foiled spacer samples. Emissions were sampled using direct desorption, and analysed by TD–GC/MS.

Conclusions

These examples have shown how valuable information on the amounts and nature of chemicals emitted by everyday products such as adhesives and flooring materials can be readily and quickly obtained, either using Markes' Micro-Chamber/Thermal Extractor, or direct thermal desorption.

The benefits of in-house product emission testing to manufacturers, both for routine checks of product quality and the development of low-emitting materials, have also been illustrated.

While it is true that regulations and increased consumer pressure are a burden for industry, it is also the case that increased consumer awareness of the importance of controlling chemicals is driving new markets for 'green' products. The ability to screen prototype materials and compare products against those of competitors is therefore valuable for any manufacturer keen to develop low-emission products and pursue this new business opportunity.

Trademarks

Micro-Chamber/Thermal Extractor™, TD-100™ and UNITY™ are trademarks of Markes International Ltd, UK.

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

References and notes

1. For information about the use of Markes' products to simplify compliance with construction product regulations, see Application Note TDTS 68.
2. For more information on the application of direct desorption to testing of material emissions, see Application Notes TDTS 40, 57, 59 and 65.
3. For more information on the Micro-Chamber/Thermal Extractor, and to download the brochure, visit http://www.markes.com/Instrumentation/Micro-ChamberThermal-Extractor-CTE.aspx.

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