Application

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Application Note 065

Automating measurement of VOCs and SVOCs in products and materials using direct thermal desorption–GC–MS

Summary

The application of direct thermal desorption for measurement of residual volatiles in materials used in car trim and consumer products is demonstrated using four examples – PVC foam, polyurethane-based artificial leather, real leather and water-based paint samples (both dried and liquid).

Introduction

The release of volatile and semi-volatile organic compounds (VOCs and SVOCs) from construction products and materials used in the home 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, spray polyurethane foam, coatings, adhesives and sealants, toys, domestic goods and cleaning products, among others. For discussion of the regulatory landscape in this area (with a focus on the EU's Construction Products Regulation), see Application Note 068.

The majority of these regulations require products to be tested for emissions of 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 to 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 microchamber. 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-emitting materials.

A number of voluntary labelling schemes that promote 'low VOC' products actually rely on product content testing rather than emissions testing in order to comply with the scheme. The European automotive industry adopts a similar approach to testing emissions from car trim components. Their standard method VDA 278[1] specifies direct desorption at elevated temperatures to assess VOCs and SVOCs (fogging components).

Traditional methodology for product content testing has required complex, multi-step sample preparation – for example, grinding of solids followed by solvent extraction, or steam distillation of resins. Such sample preparation methods are inherently time-consuming and subject to poor performance due to incomplete extraction, loss of volatiles and low sensitivity.

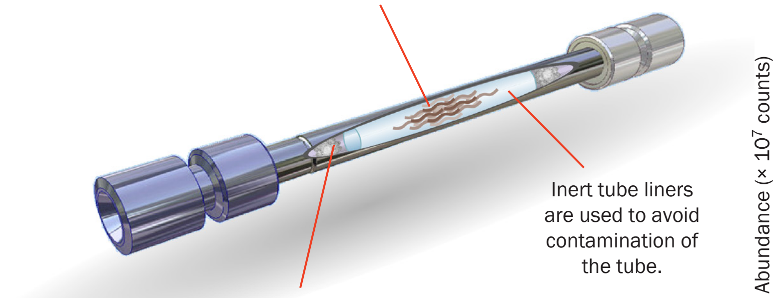
Direct thermal desorption (TD) offers an alternative, readily-automated approach for the determination of VOCs and SVOCs in materials, and has been applied to everything from fragrance in soap to solvents in pharmaceuticals. It can be applied to solids, resins, liquids and pastes, and involves heating the material in a flow of inert gas. Vapours eluted from the sample are focused on a sorbent-packed focusing trap, which is heated at 100°C/s to transfer the organics to the analyser as a narrow band of vapour, thus maximising sensitivity.

Methodology

Direct thermal desorption was evaluated for PVC foam, artificial leather, real leather and water-based paint. Various parameters were tried, including the exact procedure described in VDA 278.[1] The setup is shown in Figure 1. In all cases, care was taken to ensure that the sample did not block the gas flow through the sample tube.

Desorption parameters were selected so that complete or representative extraction of VOCs/SVOCs was achieved while matrix compounds were left in the sample tube. Focusing trap parameters (sorbent, temperature, gas flow) were selected so that target compounds were quantitatively retained while water and other unwanted volatile interferents were purged to vent. Subsequent rapid (backflush) desorption of the focusing trap thus transfers/injects only the compounds of interest.

- **Solid samples** can be weighed into empty tubes.
- **Resin or cream samples** can be smeared around the inner walls of inert tube liners.
- Small aliquots (~5 µL) of **liquid samples** can be introduced onto plugs of quartz wool.



Inert tube liners are used to avoid contamination of the tube.

Some direct desorption methods cite the use of quartz wool plugs to support the sample in the centre of the tube, but care should be taken in such cases because it can act as a sorbent for some semi-volatile organic compounds.

Figure 1: Preparation of solid, liquid and resin/cream samples for direct desorption.

Desorption parameters were selected so that complete or representative extraction of target compounds was achieved without decomposing or degrading the sample matrix. All experiments were carried out using Markes' automated thermal desorption systems with GC–MS.

Using the thermal desorber, split flows were quantitatively re-collected onto clean sorbent tubes, allowing a simple check on method performance/analyte recovery, as described in ASTM D6196[2] (see also Application Note 024). The new software used to control Markes' TD100-xr™ thermal desorber and the other members of the 'xr' series also facilitates automated pre-loading of an internal standard onto a focusing trap, for enhanced quantitation.

Results and discussion

1. PVC foam and artificial leather by VDA 278

Three ~30 mg samples of a PVC foam sheet and artificial leather based on polyurethane resin were evaluated for VOCs and fogging compounds respectively (Figures 2 and 3), following VDA 278.

Note that VDA 278 does not attempt to achieve complete extraction, but generates a representative profile of VOCs or 'fogging' compounds, allowing comparison of similar products.

The ability of Markes' instruments to quantitatively re-collect split flows, with subsequent re-analysis, can be used to check for loss of the type of high-boiling analyte observed during the VDA 278 'fogging' test. A phthalate standard (containing diethyl phthalate to dinonyl phthalate) was loaded onto Tenax® TA tubes then desorbed, re-collected and re-analysed to check for analyte bias (Figure 4). Good recovery was observed across the volatility range.

See Application Note 059 for further examples of materials analysis using VDA 278.

1 Toluene
2 2-(1-Methoxy)propyl acetate
3 2-Ethylhexan-1-ol
4 1-Methyl-2-pyrrolidone
5 2-(Butoxyethoxy)ethanol
6 Decan-1-ol
7 Butylated hydroxy toluene

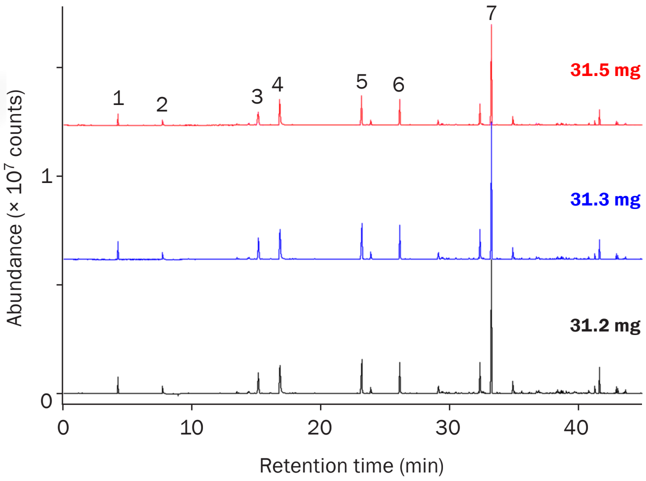


Figure 2: VOC analysis of PVC foam sheet.

1 2,6-Di-*tert*-butyl-4-*sec*-butylphenol
2 Dimethyldecanedioic acid
3 2-Hexyldecan-1-ol
4 Bis(pentamethylpiperidin-4-yl) sebacate
5 Diisodecyl phthalate
6 Di-n-decyl phthalate

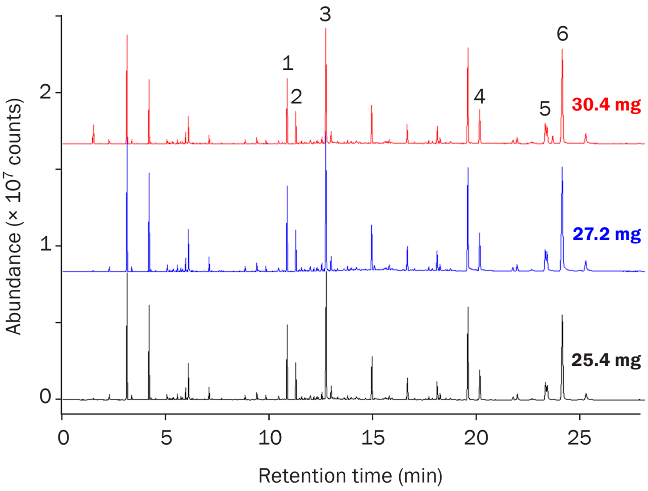


Figure 3: FOG analysis of artificial leather.

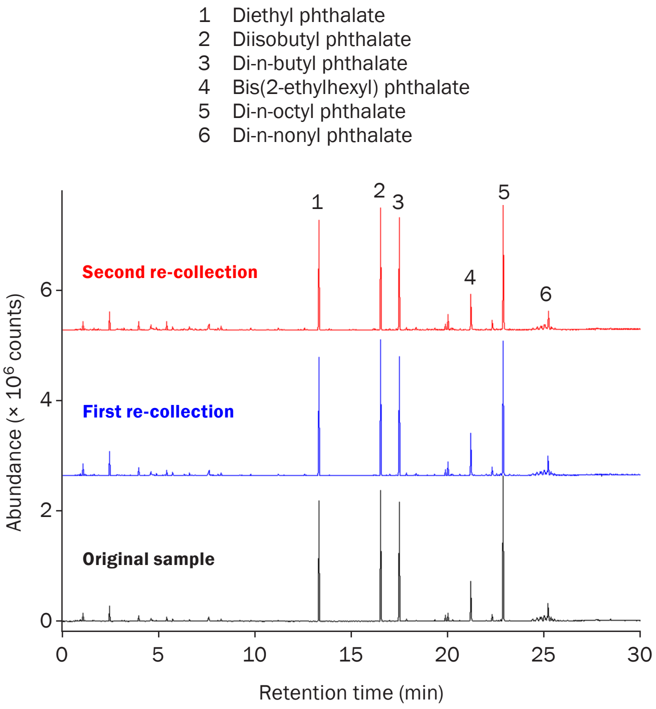


Figure 4: Original and repeat TD–GC–MS analyses of a phthalate standard to check recovery.

2. Troubleshooting discoloration of leather

White leather upholstery was found to be turning yellow in patches. Small sections of leather (~1.5 mm × 10 mm) from the discoloured and white areas were thermally desorbed (150°C for 5 min) and the TD–GC–MS data compared. It was immediately evident that detergent residues, present on the white leather, were absent from the yellowed leather, and that the yellowed leather had high levels of natural oils (Figure 5).

See Application Note 040 for full experimental details.

3. Complete desorption of VOCs and SVOCs from dried and liquid water-based paint

Direct thermal desorption was used for complete extraction of the volatile content of dried paint (220°C for 10 min – Figure 6) and wet paint (200°C for 10 min – Figure 7). Repeat desorption demonstrated >99% recovery of all analytes across the volatility range in one run.[3]

See Application Note 057 for full experimental details, including a demonstration of linearity.

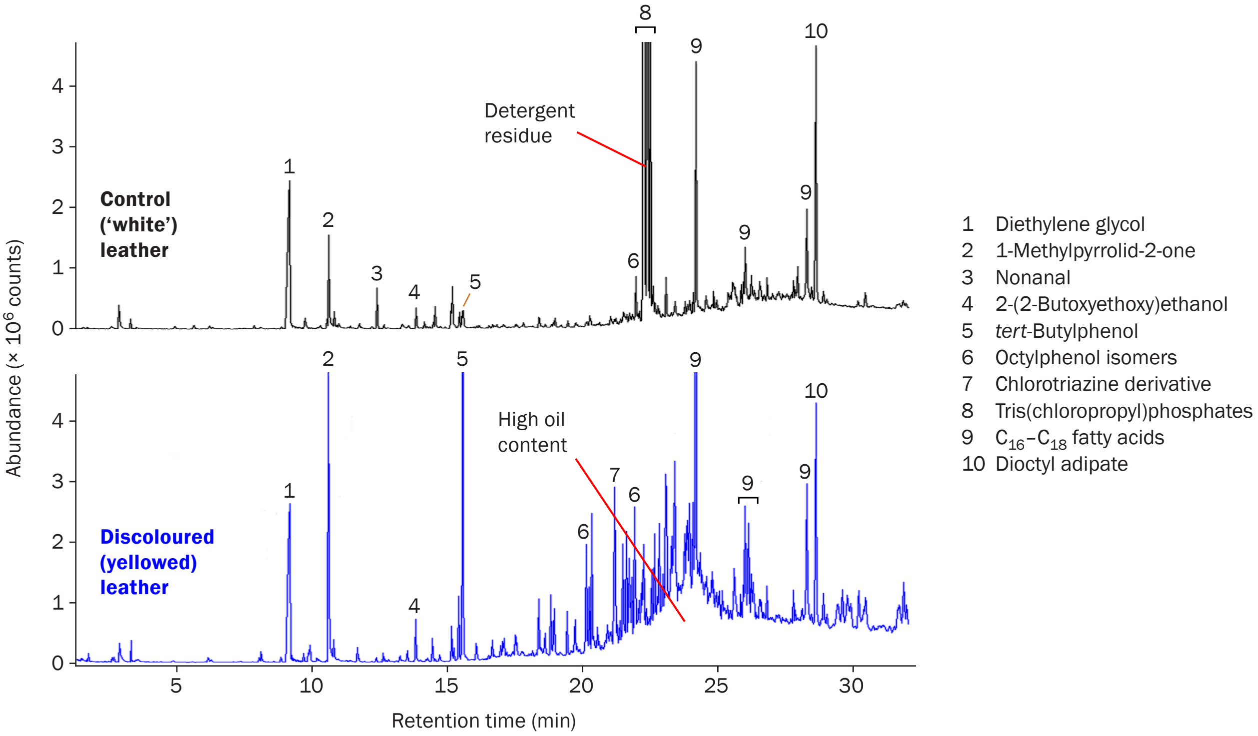


Figure 5: Direct desorption of leather to determine cause of discoloration.

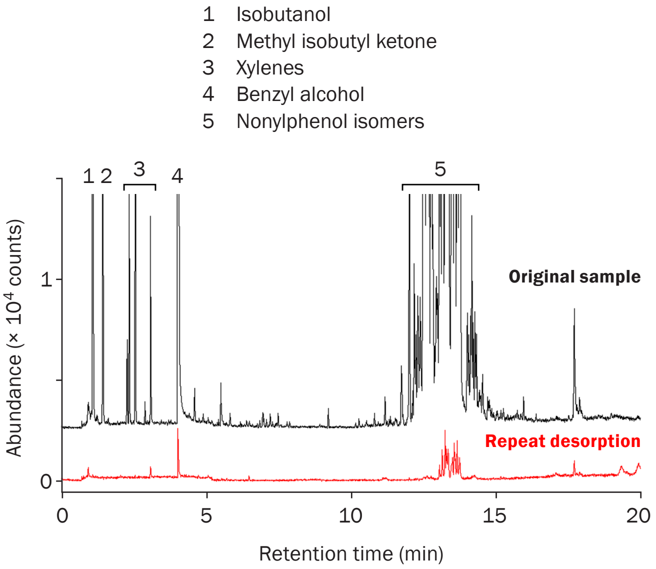


Figure 6: Direct desorption of a 2 mg paint flake, with re-desorption demonstrating minimal carryover.

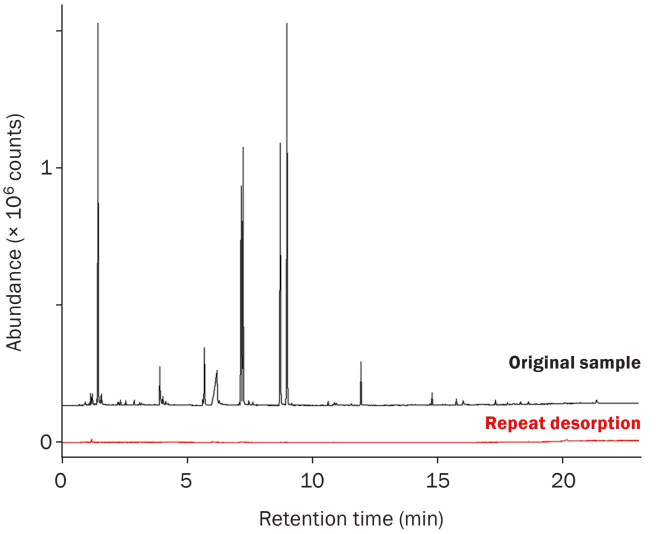


Figure 7: Direct desorption of 3.3 mg of water-based paint, with re-desorption demonstrating minimal carryover.

Conclusions

These examples demonstrate that direct TD is compatible with many material types, and can be used for both complete extraction and representative profiling of the volatile content of a material. Simultaneous analysis of VOCs and SVOCs is readily achieved provided that, as here, the focusing trap is desorbed in backflush mode.

By eliminating manual sample preparation, automated TD makes it possible for volatile content testing to be carried out as part of a routine industrial QA/QC procedure. However, there are limitations to direct thermal desorption, the main one being that it is only compatible with small samples, which for many materials may not be representative of the whole. Data obtained using direct desorption also cannot be directly correlated to that obtained using emissions chambers.

In such scenarios, Markes' Micro-Chamber/Thermal Extractor™ (µ-CTE™) offers a more versatile option, by allowing sampling from larger pieces of material at usually slightly elevated temperature, to allow rapid yet comprehensive emissions profiling. The µ-CTE also generates data that can be correlated with that produced by emissions chambers. Full details of the µ-CTE can be found in Application Note 067.

References and notes

1. VDA 278: Thermal desorption analysis of organic emissions for the characterization of non-metallic materials for automobiles, Verband der Automobilindustrie, 2011, www.vda.de/en/services/Publications/vda-278-thermaldesorption-analysis-of-organic-emissions.html.

2. ASTM D6196: Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for VOCs in air (and material emissions chambers), ASTM International, 2015, www.astm.org/Standards/D6196.htm.

3. Note that Markes' TD technology is compatible with simultaneous VOC and SVOC analysis because the focusing trap is desorbed in a reverse flow of carrier gas to that used during the trapping process, *i.e.* in backflush mode (see Application Note 064). SVOCs are thus quantitatively retained and released from weak sorbents in the front of the trap, while more volatile components are quantitatively retained and desorbed from stronger sorbents at the rear of the trap.

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