

## Thermal Desorption Technical Support

### ***Note 65: Automating the measurement of VOCs and semi-VOCs in building materials and car trim components using direct thermal desorption***

#### **Keywords:**

emissions chambers, PVC foam, artificial leather, fogging compounds, leather discolouration, dried paint, standard methods

#### **Introduction**

Concern is growing over emissions of VOCs and semi-VOCs from the materials used indoors and in vehicle cabins, due to their potential impact on human health/comfort. National and international regulations/protocols, such as the European Construction Products Directive, German protocol for fire-resistant floorings (AgBB 2004) and the Californian CHPS protocol for public school building programs (California 2004) require the determination of materials emissions using conventional test equipment such as chambers/cells (Methods EN 13419-1/-2/-3, ISO/EN 16000-6/-9/-10/-11, etc.). This enables emissions to be evaluated under simulated real-use conditions and allows real-room concentrations to be estimated.

However, conventional emissions testing requires considerable expertise to ensure production of meaningful/repeatable results, especially with respect to operation of emissions chambers. Although emission cells are much more compatible with industrial laboratories (See TDTS 72), tests still take over 24 hours if strict standard protocols are followed (ISI 16000-10, ENV 13419-2, etc.). If chambers are used, tests are expensive and lengthy to perform (typically 3-4 days per test) which makes them unsuitable for routine industrial QA/QC. One alternative way of minimising the risk from emissions is to ensure that materials do not contain significant concentrations of toxic/odorous compounds in the first place. A number of voluntary labelling schemes which promote 'Low VOC' products actually rely on product content testing rather than emissions testing in order to comply with

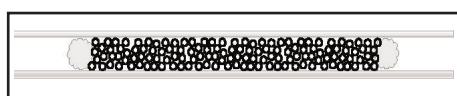
the scheme (e.g. those using US EPA Method 311 or similar procedures for paint). The European automotive industry, adopts a similar approach to testing emissions from car trim components. Their Method VDA 278 specifies direct desorption of materials, at elevated temperatures, to assess both VOCs and 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, etc. Such sample preparation methods are inherently manual/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 (S-)VOCs in materials and has been applied to everything from fragrance in soap to solvent in pharmaceuticals (See TDTS 9). 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 small electrically-cooled sorbent trap. This is subsequently heated at 100°C/sec, in a reverse flow of carrier gas, to transfer/inject the organics to the analyser (GC, MS or GC/MS) as a narrow, focused band of vapour thus maximising sensitivity. Key considerations to ensure optimum method performance include: simultaneous analysis of volatiles/semi-volatiles, quantitative recovery through the analytical system, repeatability and flexibility *i.e.* compatibility with multiple sample types.

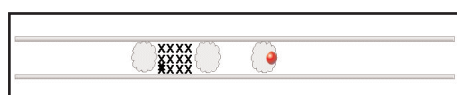
## Experimental

The utility of direct thermal desorption/extraction was evaluated for a range of materials. Various parameters were tried, including the exact procedure described in Method VDA 278. The types of materials tested included: PVC foam sheet, artificial leather (polyurethane resin), real leather, and dried & liquid water-based paint.

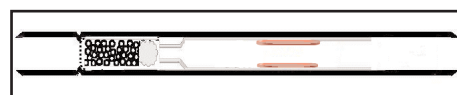
Samples of each material were weighed into empty glass or stainless steel thermal desorption sample tubes or into PTFE liners which were subsequently inserted into empty metal tubes. Solid samples were supported using clean quartz or glass wool plugs to ensure that the material stayed in the central portion of the tube. Resins or pastes were smeared around the inner walls of PTFE tube liners and aliquots of liquid samples (typically 2-10 µl) were deposited on clean quartz wool plugs inside PTFE tube liners (See figs 1-3). In all cases, care was taken that the sample did not block the gas flow through the sample tube.



**Figure 1: Solid samples weighed directly into empty TD tubes and supported with clean glass wool**



**Figure 2: Liquid samples loaded onto glass wool plug. Shown with optional Tenax bed**



**Figure 3: Resins or pastes smeared onto the inner walls of a PTFE tube insert. Shown with optional Tenax bed**

In the event that the maximum temperature of the sample matrix was unknown, a short bed (1 cm) of conditioned Tenax was placed at the front (desorption end) of the TD tube during the method development phase. This was to ensure that sample matrix components did not

migrate into the flow path of the thermal desorber and contaminate the system.

Desorption parameters were selected such that complete or representative extraction of (S-) VOCs was achieved while matrix compounds were left behind in the sample tube. 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 (See TDTS #s 26 and 51). Subsequent rapid (back-flush) desorption of the focusing trap thus transfers/injects only those volatile and semi-volatile compounds of interest, free of interference from matrix artifacts, water and other unwanted volatiles.

Desorption parameters were selected such that complete or representative extraction of (S-) VOC target compounds was achieved without decomposing or degrading the sample matrix. All experiments were carried out using a Markes ULTRA-UNITY automated thermal desorber (Figure 4) with GC/MS.



**Figure 4: ULTRA-UNITY automated thermal desorber for up to 100 tubes**

Quantitative recovery through the thermal desorber was evaluated using SecureTD-Q - quantitative re-collection for repeat analysis (See TDTS 24 and the SecureTD-Q brochure) as described in ASTM Method D 6196-03.

**PVC foam and artificial leather (PUR) by VDA 278** (see also TDTS 59): Three ~30 mg samples of a PVC foam sheet and an artificial leather were evaluated for VOCs and fogging

compounds respectively (Figures 5 and 6). The procedure followed method VDA 278 *i.e.* desorbing for 30 minutes at 90°C and for 60 minutes at 120°C respectively followed by GC/MS analysis.

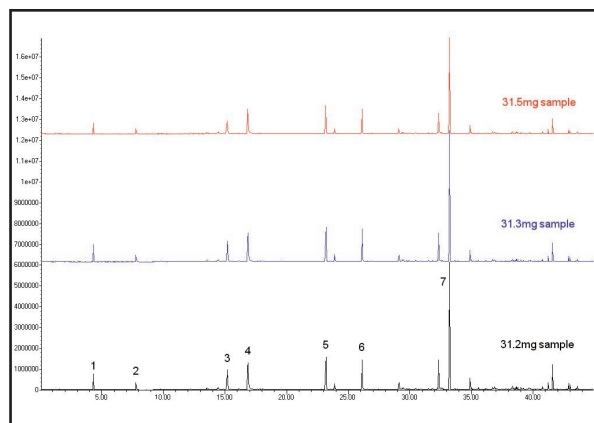


Figure 5: VOC analysis of PVC foam sheet

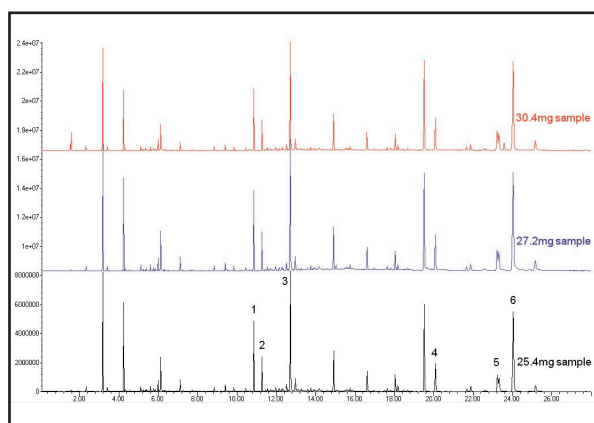


Figure 6: Fog analysis of artificial leather

Key compounds desorbed during VOC analysis of the PVC sheet are:

- 1) toluene
- 2) 1-methoxy-2-propylacetate
- 3) 2-ethyl-1-hexanol
- 4) 1-methyl-2-pyrrolidone
- 5) 2-(butoxyethoxy)-ethanol
- 6) 1-decanol
- 7) butylated hydroxytoluene

Key fogging compounds from the PUR artificial leather are:

- 1) 2,6-di-t-butyl-4-sec-butyl phenol
- 2) decanedioic acid dime. ester

- 3) 2-hexyl-1-decanol
- 4) bis (pentamethoxy-4-piperidiny) sebacate
- 5) di-i-decyl phthalate
- 6) di-n-decyl phthalate

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

The Markes TD system offers quantitative re-collection of split flow for repeat analysis and validation of analyte recovery as described in ASTM Method D6196. This procedure was used to check for loss of the type of high boiling analyte observed during the VDA 278 'fogging' test. A phthalate standard (di-ethyl to di-nonyl phthalate) was loaded onto Tenax tubes then desorbed, re-collected and re-analysed twice to check for bias (selective loss of one or other analytes) (Figure 7). Good recovery was observed across the volatility range.

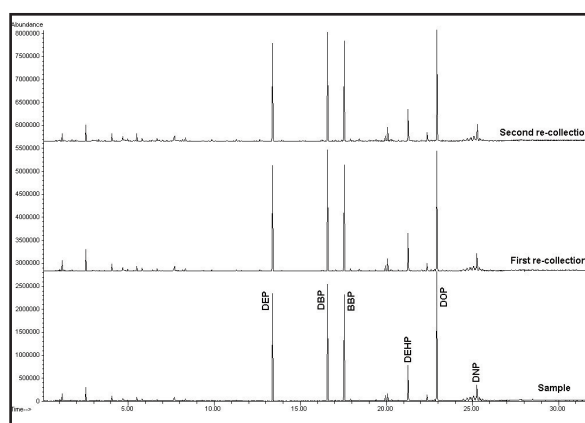
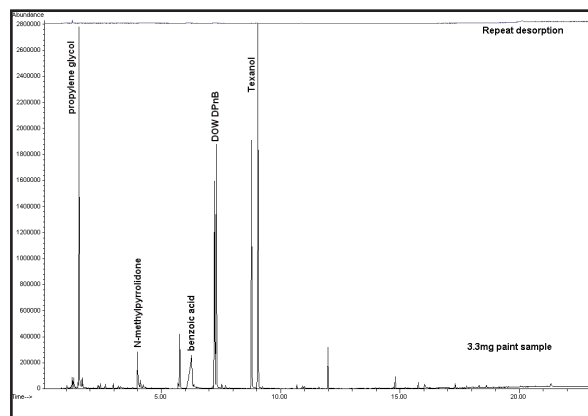
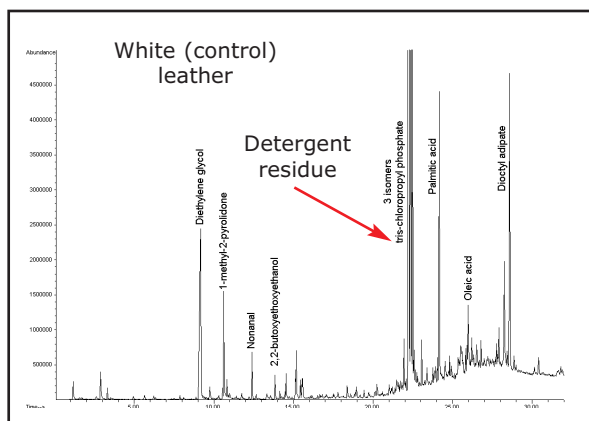


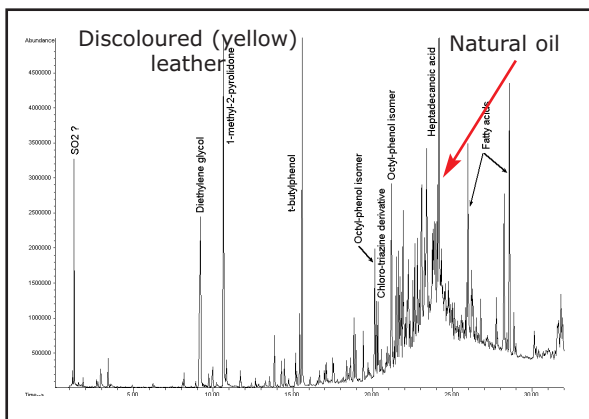
Figure 7: Original and repeat TD-GC-MS analyses of phthalate standard to check recovery

### Troubleshooting discoloration of leather

(See Also TDTS 40): White leather upholstery was found to be turning yellow in patches. Small sections of leather (~1.5 mm x 10 mm) from the discoloured and white areas were thermally desorbed (150°C for 5 mins) 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 8).

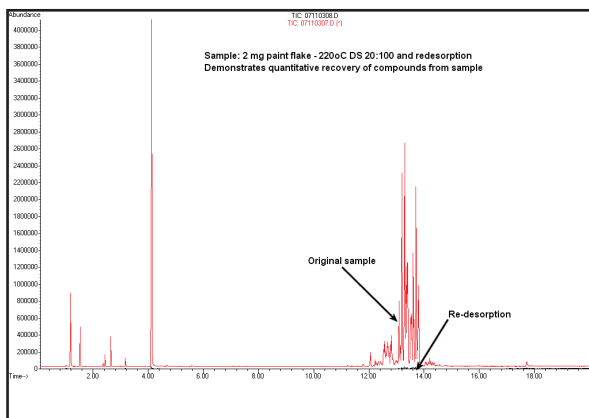


**Figure 10: Direct desorption of volatiles from 3.3 mg of liquid water-based paint**



**Figures 8(a) & (b): Direct desorption of leather to determine cause of discolouration**

**Complete desorption of (S-)VOCs from dried and liquid water-based paint** (See also TDTS 57): Direct thermal desorption was used for complete extraction of the (S-)VOC content of dried paint (220°C for 10 minutes - Figure 9) and wet paint (200°C for 10 minutes - Figure 10). Repeat desorption demonstrated >99% recovery of all analytes across the volatility range in one run.



**Figure 9: Direct desorption of volatiles and semi-volatiles from 2 mg of dry paint flakes**

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 TDTS #64). Semi-volatiles are thus quantitatively retained and released from weak sorbents in the front of the trap and volatiles are quantitatively retained and desorbed from stronger sorbents at the rear of the trap.

## Discussion

These examples demonstrate that direct thermal desorption is compatible with many material types and can be used for both complete (quantitative) extraction (Table 1) and representative profiling of the (S)VOC content of a material. Simultaneous (S)VOC analysis is readily achieved provided that, as here, the focusing trap is desorbed in backflush mode. By eliminating manual sample preparation, automated thermal desorption makes it possible for (S-)VOC content testing to be carried out as part of a routine industrial QA/QC procedure. Recent developments, such as quantitative re-collection for repeat analysis have also been shown to allow simple checks on method performance/analyte recovery. However, there are limitations to direct thermal desorption/extraction, especially in relation to quality control of materials emissions. Key issues include sample homogeneity (*i.e.* conventional sample tubes are only compatible with small sample sizes *e.g.* 100 mg of solids, or 5-10 µl of liquid. For many materials this may not be representative of the whole). It is also difficult to obtain a direct correlation



Peak Area	Amount			Isomer 2					Isomer 2				
	Peak Area	Amount	w/w %	Isomer 1	Isomer 2	Total	Amount	w/w %	Isomer 1	Isomer 2	Total	Amount	w/w %
3.3	39.47	39.67	1.20	23.41	28.6	52.01	52.36	0.18	28.42	45.86	74.28	74.53	0.16
8.1	123.64	123.84	1.53	64.92	77.53	142.45	142.80	0.18	71.98	114.22	186.2	186.45	0.16

**Table 1: Content of propylene glycol, DOW DPnB and Texanol in liquid paint**

between (S-)VOC data obtained using direct thermal desorption and conventional emissions testing. This is partly due to material heterogeneity and the small sample size, but other factors, such as the desorption of bulk materials (rather than surface only) plus the use of elevated temperatures, also play their part.

Markes has recently developed an automated Micro-Chamber/Thermal Extractor ( $\mu$ -CTE) (See Figure 11 and separate leaflet) to address these concerns. The new system comprises six micro-chambers (up to 25 mm deep and ~45 mm in diameter) which allow surface or bulk emissions to be tested from up to 6 samples simultaneously. A conditioned Tenax or other sorbent tube is attached to each micro-

chamber and a controlled flow of air passed through. A unique flow distribution system\* maintains a constant flow of air through each sample chamber, independent of sorbent tube impedance and whether or not a sorbent tube is attached. No pump or mass flow controller is required. Tests can be carried out at ambient or elevated temperatures (up to 120°C) and moderate temperatures (e.g. 40°C) can be used to approximate standard emissions testing and compensate for the relatively small sample size without affecting correlation with data from conventional chambers or cells). Total test time (equilibration and vapour sampling), for all 6 samples, is normally between 30 and 60 minutes, depending the temperature required.

The  $\mu$ -CTE does not fully comply with conventional emissions test methods (ISO/EN 16000-9/-10) but provides industry with an easy-to-use quality assurance tool for automated emissions testing. By generating data that correlates with conventional emissions tests it will also allow manufacturers to monitor product quality/uniformity in between formal certification tests by accredited laboratories.

The  $\mu$ -CTE also facilitates direct thermal desorption/extraction of bulk materials thereby allowing accurate measurement or representative profiling of the VOC/SVOC content of less homogenous materials.

## Summary

Thermal desorption is an invaluable analytical tool for materials testing and its ability to simplify and automate (S-)VOC content testing has been shown in this application note. TD is also used in specialist laboratories equipped with conventional chambers/cells for measurement of vapour-phase emissions trapped on Tenax tubes per standard methods



**Figure 11: Micro-Chamber Thermal Extractor system**

such as ISO 16000-6, ASTM D6196-03 and ISO 16017-1. The new ' $\mu$ -CTE' thermal desorption tool should further provide manufacturing industry with a means of carrying out cost-effective and automated in-house tests - generating data that correlates well with external product certification results produced using conventional emissions chambers/cells.

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\* UK Patent Application No. 0501928.6

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