TDTS 40

Direct desorption of VOCs and SVOCs from leather furnishings

Summary

This Application Note demonstrates the direct desorption of volatile and semi-volatile organic compounds (VOCs and SVOCs) from leather furnishings, in order to identify the cause of discoloration.

Introduction

Troubleshooting problems affecting textiles and other furnishings can be extremely challenging for the analyst. Issues such as discoloration, odour, unsatisfactory or uneven resistance to wear, and inadequate waterproofing can potentially be caused by a wide range of external factors, as well as by product treatment or processing.

One approach to such problems is to compare the VOC profile of a problem material to a control sample. Historically, VOCs and SVOCs have been studied using solvent extraction techniques (sometimes in combination with steam distillation to enhance concentration), followed by GC(MS) analysis. However, these extraction techniques lack sensitivity, are labour-intensive, and suffer from the presence of artefacts, difficulties in solvent selection, and masking of the compounds of interest.

A better approach is direct thermal desorption (TD) of VOCs and SVOCs from materials followed by GC(MS) analysis, which is both high-sensitivity and readily-automated. In this Application Note, the advantages of direct thermal desorption are demonstrated using the example of analysis of discoloration on leather upholstery.

Experimental

Three samples of cream-coloured leather were received:

- Sample 1 – Leather that had discoloured over time
- Sample 2 – A control sample from the same upholstered object, taken from an area adjacent to the discoloured patch
- Sample 3 – A control sample from the same upholstered object, taken from a different area.

In each case, two pieces of leather ~1.5 mm × 10 mm in size were cut from the samples using clean steel scissors (Samples 1A and 1B, 2A and 2B, 3A and 3B). The samples were inserted into empty stainless steel TD sample tubes. A stainless steel gauze inserted into each sample tube ensured the sample stayed in the correct position. Note that as this was not a quantitative assessment, samples were not weighed, though each sample was a similar size[1].

The samples were thermally desorbed, under helium, at a temperature that did not appear to change their physical properties – in this case 150°C. Analysis was by capillary GC/MS. Conditions are listed below:

TD (UNITY™):

Sample (primary) desorption:	150°C for 5 min
Desorption flow:	30 mL/min
Inlet split:	On. Split flow 30 mL/min (ratio 50:50)
Focusing trap:	Packed with quartz wool–Tenax® TA–Carbograph 1TD
Focusing trap temp.:	–10°C
Trap (secondary) desorption:	300°C, maximum heating rate, hold for 5 min
Column flow:	~2 mL/min
Outlet split:	On. Split flow 30 mL/min (ratio 14:1)
Flow path:	200°C

GC:

Column:	30 m × 0.32 mm × 1.0 mm bonded methyl silicone
Carrier gas:	Helium (14.5 psig, ~2 mL/min)
Temp. program:	60°C (5 min), 10°C/min to 280°C (5 min)

MS:

Scan mode:	45–350 amu
MS aux transfer line:	280°C
MS source:	230°C
MS quad:	150°C

Results and discussion

Figures 1–3 show the chromatographic profiles obtained from the two pieces of each of the three leather samples. Key components are identified using an MS library search in each case.

The similarity between the replicate analyses of each sample gives an excellent indication of the robustness of the method.

A major difference between the discoloured and control samples was immediately apparent. Three major phosphate components were detected in the control samples but not in the problem sample, and the 'envelope' of natural-oil-type components with retention times between 20 and 27 minutes was much less prominent in the control samples than in the discoloured sample.

1 Sulfur dioxide (?)
2 Diethylene glycol
3 1-Methyl-2-pyrrolidine
4 *tert*-Butylphenol
5 Octylphenol isomer
6 Chlorotriazine derivative
7 Heptadecanoic isomer
8 Fatty acid

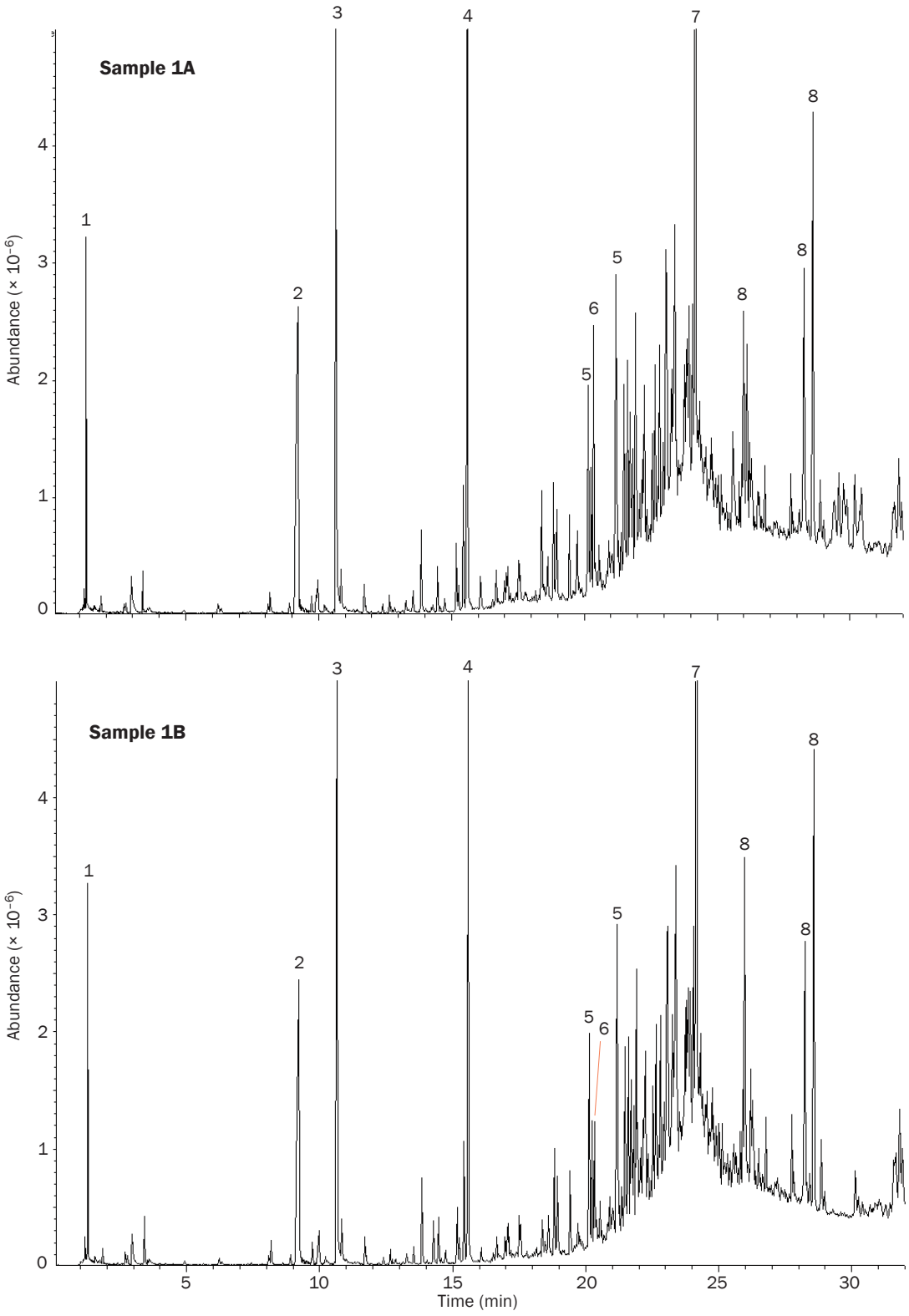

Figure 1: Desorption of the discoloured leather (Samples 1A and 1B).

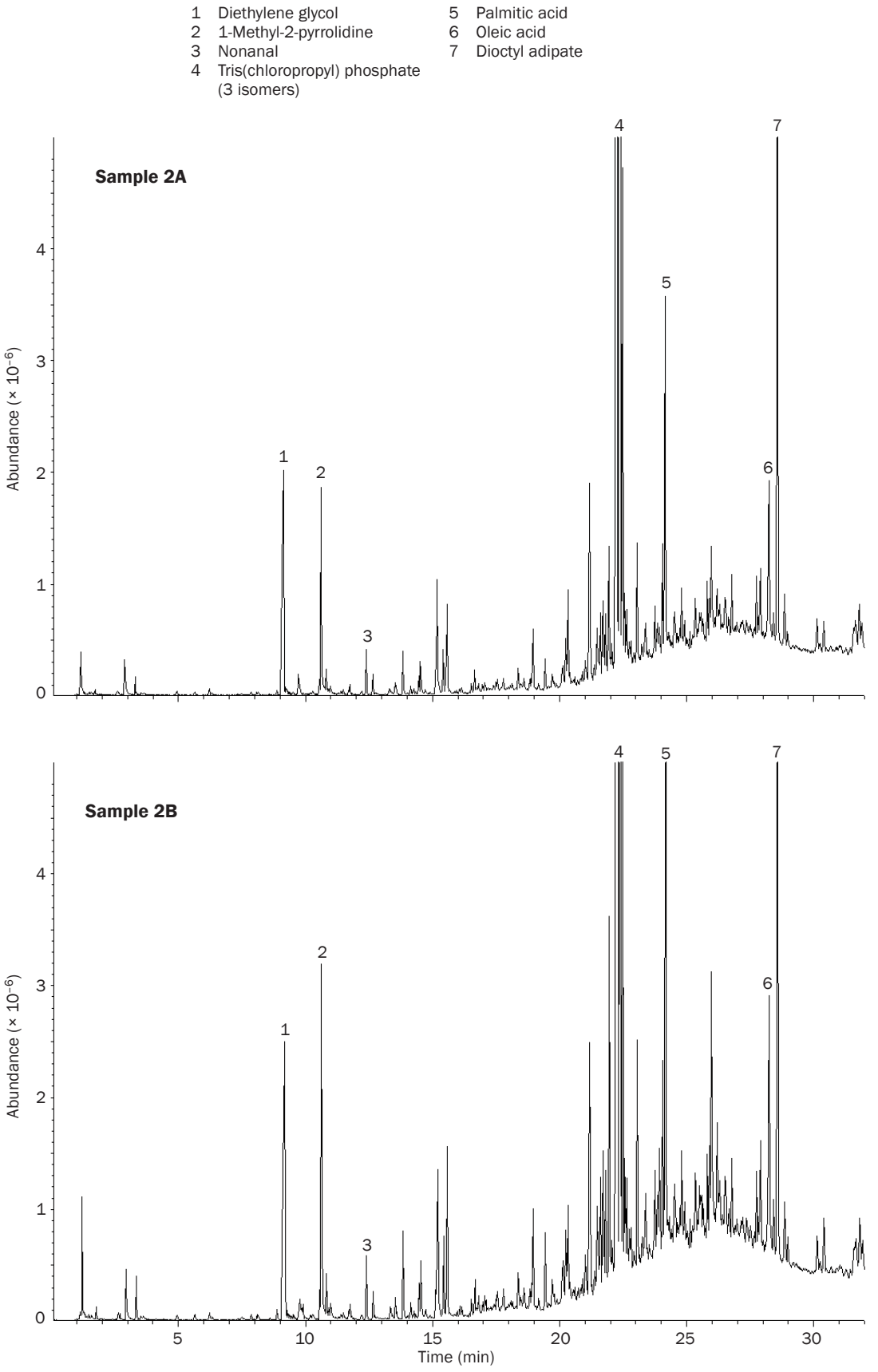

Figure 2: Desorption of the first set of control samples, taken from near the discoloured area (Samples 2A and 2B).

1 Diethylene glycol
2 1-Methyl-2-pyrrolidine
3 Nonanal
4 2-(2-Butoxyethoxy)ethanol
5 Tris(chloropropyl) phosphate (3 isomers)
6 Palmitic acid
7 Oleic acid
8 Dioctyl adipate

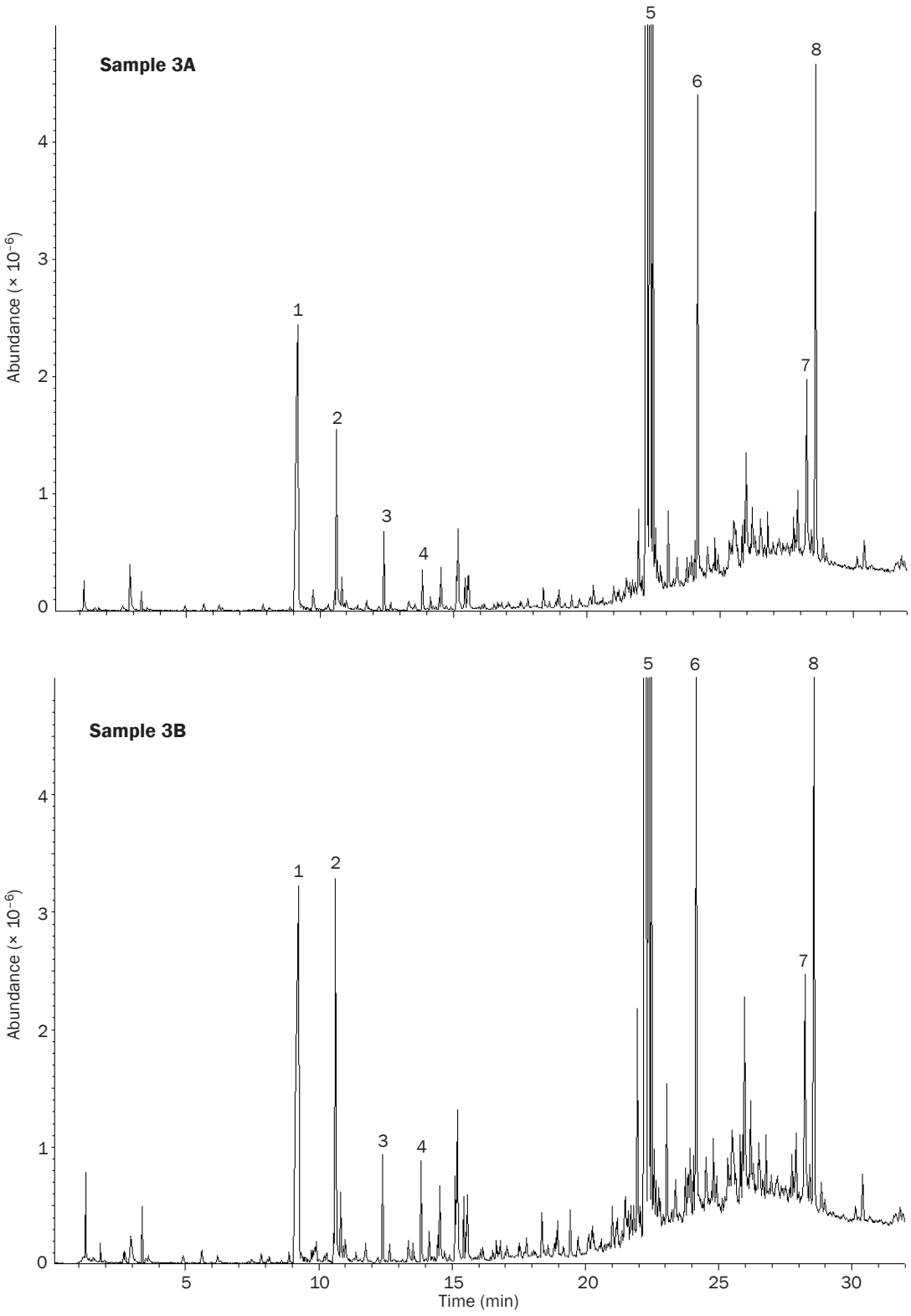

Figure 3: Desorption of the second set of control samples, taken from a different part of the different part of the upholstery to the discoloured area (Samples 3A and 3B).

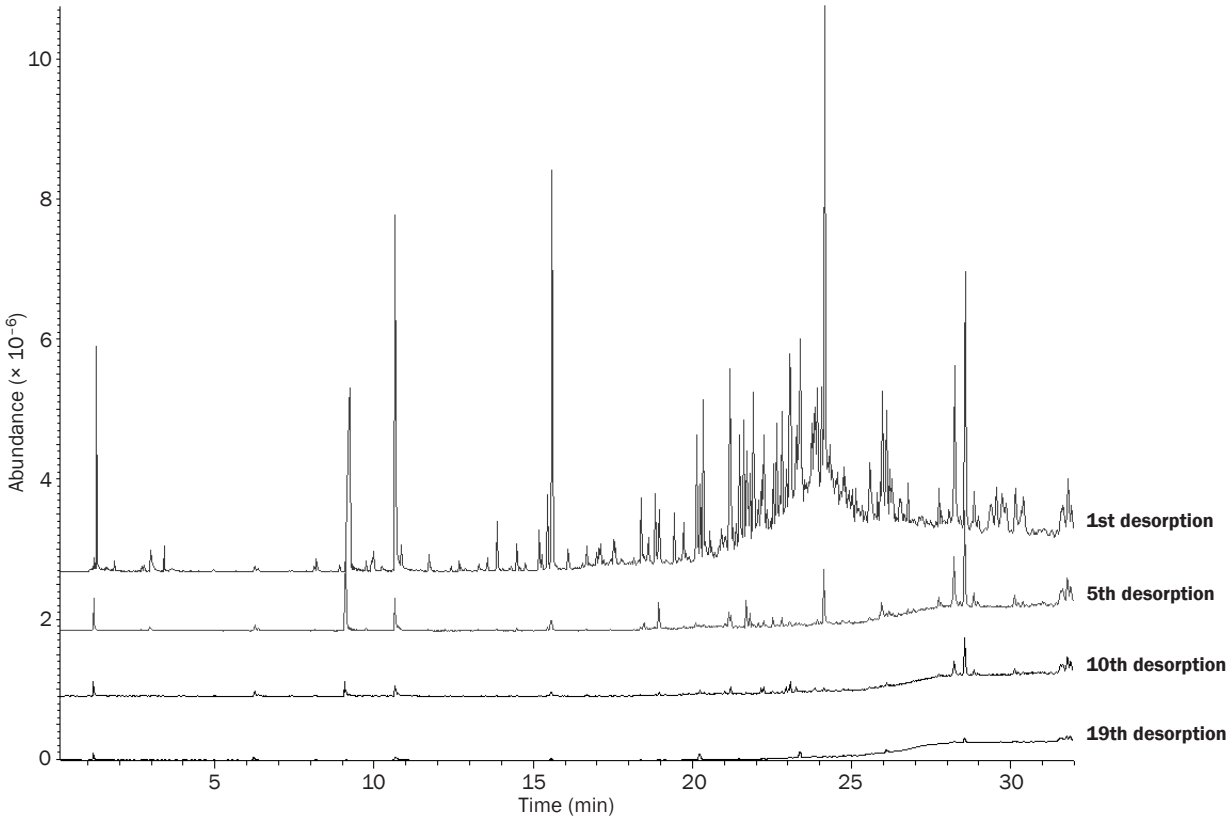

Figure 4: Sequence of repeat desorptions of one sample of the discoloured leather (Sample 1), demonstrating that exhaustive extraction is possible and that artefacts are not generated by the TD process.

The data appear to indicate that some process requiring a phosphate-based material (probably a soap or detergent) had not been evenly applied. If this was a cleaning process, it could also explain the higher concentration of natural oils in the discoloured sample.

Some of the components present in the natural oil 'envelope' (Figure 1) were found to be nitrogen-containing chemicals, substituted phenols and long-chain fatty acids. These are likely to produce dark-coloured degradation products over time if left at high concentrations, which could explain the discoloration.

A sequence of repeat desorptions of the sample of discoloured leather is illustrated in Figure 4. The fact that the concentration of volatiles and semi-volatiles reduces steadily over time demonstrates that quantitative analysis of the VOC and SVOC content of the samples is possible using this type of method. It also shows that compounds are not being generated by the TD process, but are inherent in the sample.

Notes

1. Samples must be weighed if the application requires quantitative measurement of the VOC content. See Application Note TDTS 9 for a more detailed discussion of this issue.

Trademarks

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

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