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Application

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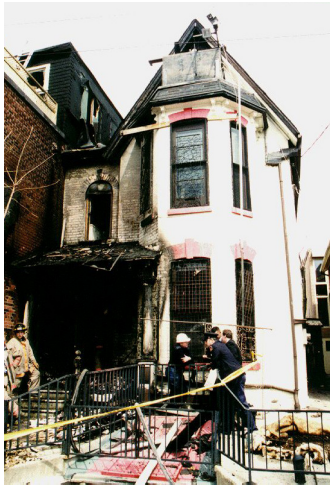
Application Note 134

Rapid forensic analysis of fire debris using headspace sampling onto sorbent tubes with TD–GC–MS

Summary

This Application Note describes the analysis of ignitable liquid residues (ILRs) from fire debris, using static or dynamic headspace sampling onto sorbent tubes, in conjunction with thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS). Key points demonstrated are the ease with which samples can be compared and conditions optimised, the benefits of sample re-collection for repeat analysis, and the very low levels of carryover (even for heavy petroleum distillates).



Introduction

Analysis of fire debris offers vital evidence to forensic studies, because the detection of accelerants in ignitable liquid residues (ILRs) can indicate that the fire was not accidental but the result of arson. Various methodologies are used for such analyses, and some of these are described in ASTM methods.[1–5]

The oldest method, direct solvent extraction,[1] as well as having the drawbacks of solvent use (such as cost and risk of sample contamination) involves the destruction of the sample. Methods that preserve the sample are therefore increasingly favoured, especially those using static[2] or dynamic[3] collection of sample headspace onto activated charcoal strips,[4] SPME fibres,[5] PLOT columns[6] or sorbent tubes.[7–9]

Sorbent tubes are the most versatile of these sampling methods, and are widely used for sampling headspace in many fields, in conjunction with thermal desorption (TD) pre-concentration and gas chromatography–mass spectrometry (GC–MS) analysis.

Key benefits of sorbent tubes for forensic applications are the low detection limits (due to the large sorbent area), and quantitative analysis of C_3 to C_{44} without analyte bias. There are also several practical advantages – the use of sorbent tubes completely eliminates the issues of solvent cost and disposal, they are much less likely than SPME fibres to be damaged due to operator error or incorrect storage, and automated sequential desorption of up to 100 tubes is easily achieved using modern instrumentation.

In this Application Note, we illustrate the advantages of sorbent-tube sampling and TD–GC–MS analysis for the investigation of ILRs in fire debris. Specifically, we highlight the ability of TD to interface with a variety of sampling devices – in this case, collection of static headspace vapours using a manually-operated pump, and dynamic sampling with a microchamber device.

Background to the sampling techniques

The **Easy-VOC™** (Figure 1) is a manually-operated pump that samples air/gas directly onto sorbent tubes, without the need for calibrated pumps or mass-flow-control equipment. Consequently, it is particularly suitable for field operation.

Sorbent tubes are pushed into the end of the Easy-VOC, and air/gas is drawn steadily into the tube over a period of several seconds. Air can be sampled in accurate aliquots of 50 or 100 mL, and larger volumes are easily collected by pulling a series of samples onto the same tube in quick succession. However, using relatively small gas volumes minimises water management issues, and reduces the risk of analyte breakthrough, allowing quantitative retention of more volatile compounds.

Figure 1: Easy-VOC pump, with sorbent tube attached ready for sampling.

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An alternative approach is to use the **Micro-Chamber/ Thermal Extractor™ (µ-CTE™)** (Figure 2). This is a compact, stand-alone unit that is widely used to sample chemical emissions from products and materials, to ease compliance with industry regulations. The µ-CTE operates on the principle of dynamic headspace sampling, which (as described in ASTM E1413[3]) is ideal when high sensitivity is required – for example, when looking for very low levels of accelerant.

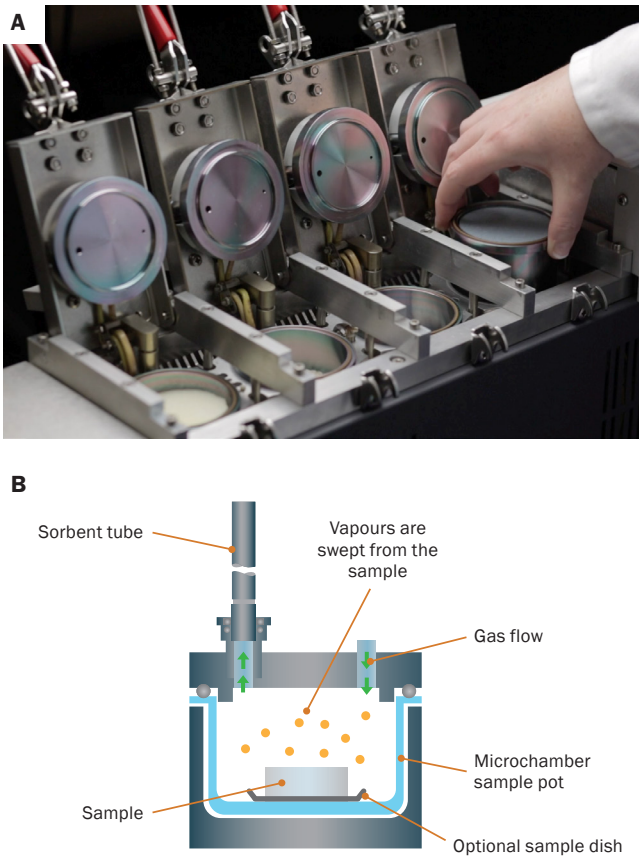

Figure 2: (**A**) The Micro-Chamber/Thermal Extractor (four- and six-chamber models are available). (**B**) Schematic showing operation for sampling from forensic samples.

Operation simply involves placing the samples into the chambers, using small glass or aluminium dishes if desired to avoid chamber contamination. The chamber lids are then closed, and a user-defined flow of pure air or nitrogen is applied, with the chambers usually being held at a slightly raised temperature to facilitate rapid sampling without compromising the integrity of the sample. After equilibration to ensure reproducible sampling and maximum analyte response, sorbent tubes are attached to the chamber outlets to trap the compounds released.

Samples collected onto sorbent tubes using either the Easy-VOC or the µ-CTE are analysed by **thermal desorption (TD)**. This is a versatile GC pre-concentration technology that is used to analyse volatile and semi-volatile organic compounds (VOCs and SVOCs) in a wide range of sample types. By concentrating organic vapours from a sample into a very small volume of carrier gas (Figure 3), TD maximises sensitivity for trace-level target compounds, helps to minimise interferences, and routinely allows analyte detection at the ppb level or below. It also greatly improves sample throughput, by combining sample preparation, desorption/ extraction, pre-concentration and GC injection. In this study we use the TD100-xr™ (Figure 4) for fully automated analysis of up to 100 sorbent tube samples.

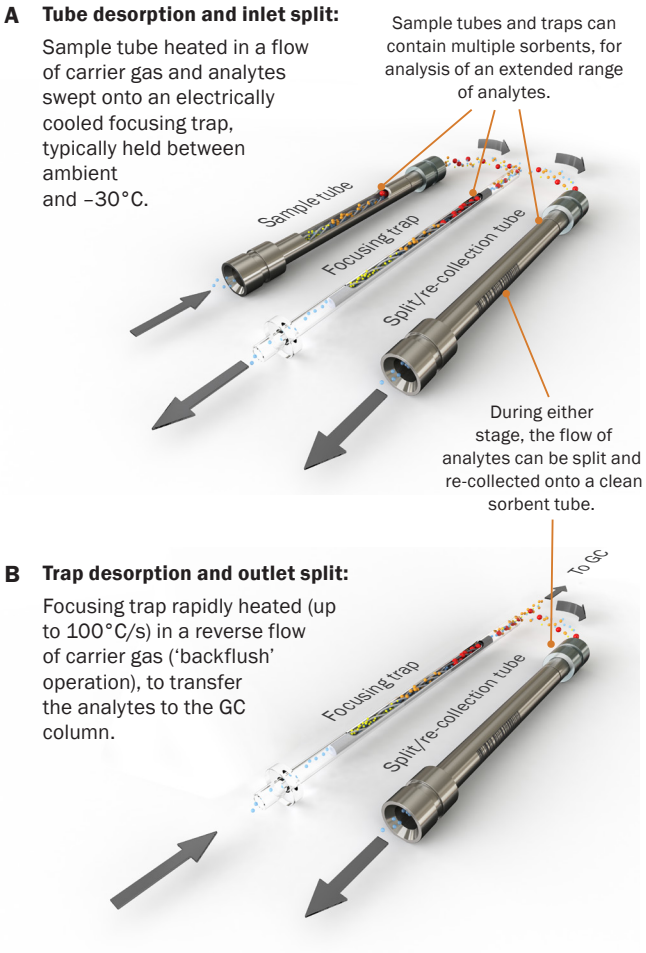

Figure 3: How two-stage thermal desorption works.

Figure 4: Markes' TD100-xr automated thermal desorber.

Experimental

Samples:
Measurements of residual ILRs were performed on (a) wooden dowel, cut into pieces 5 cm long × 0.8 cm diameter, soaked in diesel or petrol (gasoline) and then burnt; (b) cloth soaked in diesel, burnt and then cut into 4 cm × 4 cm pieces. The size of these samples ensured that they fitted easily into the headspace container and microchamber. Samples were analysed as soon as burning was complete.

Static headspace sampling:

Instrument:	Easy-VOC (Markes International)
Headspace container:	1 L, non-emitting
Sorbent tube:	Packed with Tenax® TA
Sample volume:	5 × 100 mL, sampled successively

Dynamic headspace sampling:

Instrument:	Micro-Chamber/Thermal Extractor (Markes International)
Gas:	Nitrogen (analytical grade 5)
Sorbent tubes:	Packed with Tenax TA
Equilibration:	5 min, no flow
Sampling flow:	50 mL/min
Sampling time:	20 min
Temperature:	40°C

TD:

Instrument:	TD100-xr (Markes International)
Flow path:	210°C
Cold trap:	'Material emissions' (part no. U-T12ME-2S)
Pre-purge:	50 mL/min (1 min), trap in line, 50 mL/min split
Tube desorb:	280°C (10 min), 30 mL/min trap flow
Inlet split:	30 mL/min
Trap low:	–10°C
Pre-trap-fire purge:	30 mL/min (1 min)
Heating rate:	Max
Trap high:	300°C (3 min)
Outlet split:	Low split 50 mL/min; high split 100 mL/min
Overall split ratio:	Low split 68.7:1; high split 135.3:1

GC:

Column:	BPX5™, 30 m × 0.25 mm × 0.25 µm
Oven ramp:	40°C (5 min), then 15°C/min to 300°C (5 min)
Constant flow:	Helium, 1.5 mL/min
Septum purge:	5.0 mL/min

Quadrupole MS:

Transfer line:	300°C
Ion source:	300°C
Mass range:	m/z 35–400
Scan time:	0.2 s

Results and discussion

1. Sample comparison

Different arson accelerants, when analysed by TD–GC–MS, give distinct 'fingerprint' profiles that allow rapid confirmation of the presence of absence of particular accelerants. To demonstrate this, Figure 5 displays the profiles of burnt wood previously treated with diesel or petrol, alongside a sample of unburnt wood, and sampled using the Easy-VOC. The three profiles are clearly very different, with the more complex mixture of compounds generated from the diesel-soaked sample immediately apparent.

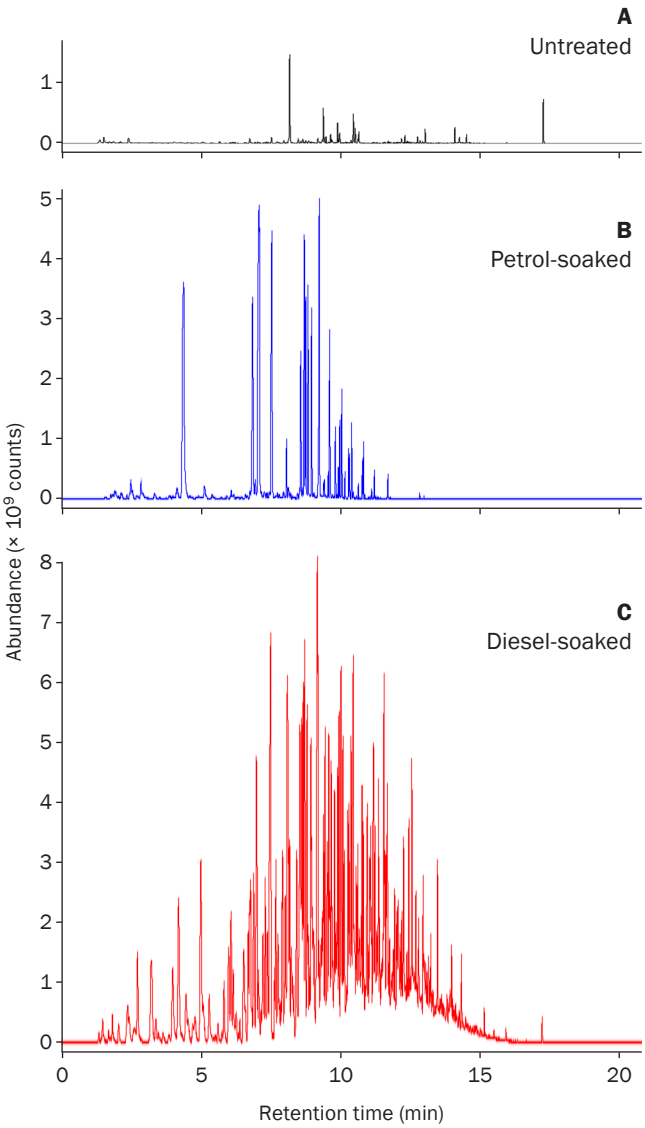

Figure 5: Total ion chromatograms of (**A**) untreated wood, (**B**) wood soaked in petrol and then burnt, and (**C**) wood soaked in diesel and then burnt. Sampling was carried out using the Easy-VOC with analysis by TD–GC–MS.

2. Assessment of sample carryover

One concern when running high-concentration samples containing semi-volatile organic compounds (SVOCs) is the risk of carryover (incomplete removal of analytes from the system flowpath, causing contamination of the next run). In the current study, carryover was assessed by running an empty tube immediately after the petrol-soaked and diesel-soaked wood samples (Figure 6). The area of the largest peak in the blank was then divided by the corresponding response in the sample run in order to obtain the percentage carryover.

The carryover values obtained were 0.050% for the petrol-soaked sample and 0.032% for the diesel-soaked sample. Both these values are very low, indicating the absence of 'cold spots' or surface reactivity in the flow path of the TD100-xr thermal desorber.

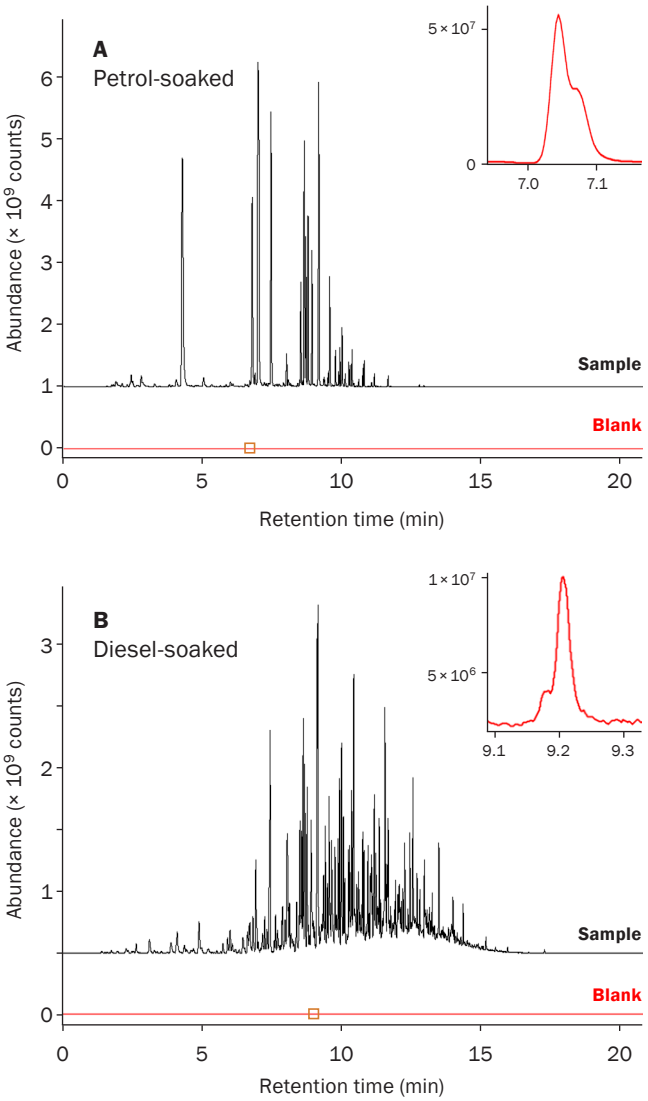

Figure 6: Overlaid total ion chromatograms and subsequent blank runs of (**A**) wood soaked in petrol and then burnt, and (**B**) wood soaked in diesel and then burnt. The small box and the insets show the highest peak in the blank run (used to generate the carryover values). Sampling was carried out using the Easy-VOC with analysis by TD–GC–MS.

3. Sample re-collection and repeat analysis

When analysing fire debris samples with potentially high volatile content, there is a danger of saturating the analytical system with high-abundance components. Markes' TD instruments assist in such scenarios by allowing a sample from a sorbent tube to be 'split', with a small proportion of the sample sent to the GC and the remainder quantitatively re-collected onto a clean tube. In an initial analysis, use of a sufficiently high split enables the sample loading to be assessed without risk of system overload. The re-collected portion can then be analysed under lower-split conditions, if required.

This 'High/Low' analysis is demonstrated in Figure 7, which shows analysis of burnt diesel-soaked cloth, with vapours sampled using the µ-CTE. After sampling, the sorbent tube was first analysed using a high split ratio (135:1) to achieve accurate responses from high-abundance components, and then re-run using a lower ratio (69:1) to investigate minor compounds in more detail.

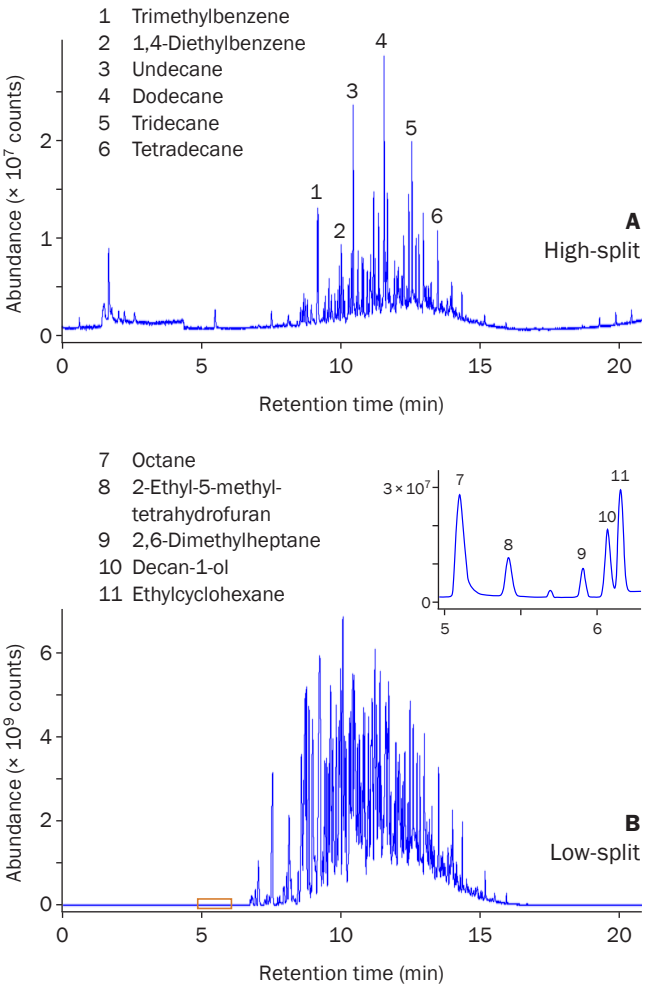

Figure 7: Total ion chromatograms of cloth soaked in diesel and then burnt, with analysis using (**A**) a split ratio of 135:1, and (**B**) a split ratio of 69:1. Key compounds are labelled, and the inset shows the identification of trace-level compounds in the low-split run. Sampling was carried out using the µ-CTE with analysis by TD–GC–MS.

This re-collection technology, which is standard in every Markes' TD system, also assists the construction of a robust portfolio of evidence. This is possible because the same sample can be run multiple times, either (a) using different conditions or detection techniques, or (b) under the same conditions to validate the method. In addition, analysis of re-collected samples conserves the original specimen and saves the analyst time, by avoiding the need to repeat the sampling process.

4. Effect of sampling time

The chromatographic fingerprint of a fire debris sample depends not only on the nature of the specimen but also the conditions under which it was sampled. Easy optimisation of the sampling method is therefore important, and is one of the benefits of the two TD-compatible sampling techniques outlined in this study. As an example, Figure 8 shows profiles from two pieces of diesel-soaked wood, both acquired using the µ-CTE and differing only in the length of time they were sampled (20 or 30 minutes).

The reproducibility of the µ-CTE method ensures that the profiles are easily recognised as containing the same accelerant. However, some of the more abundant compounds of interest are clearly overloaded in the profile for the 30-minute sample. It is therefore possible that in this case a sampling time of just 10 minutes would be sufficient to achieve positive identification of the accelerant.

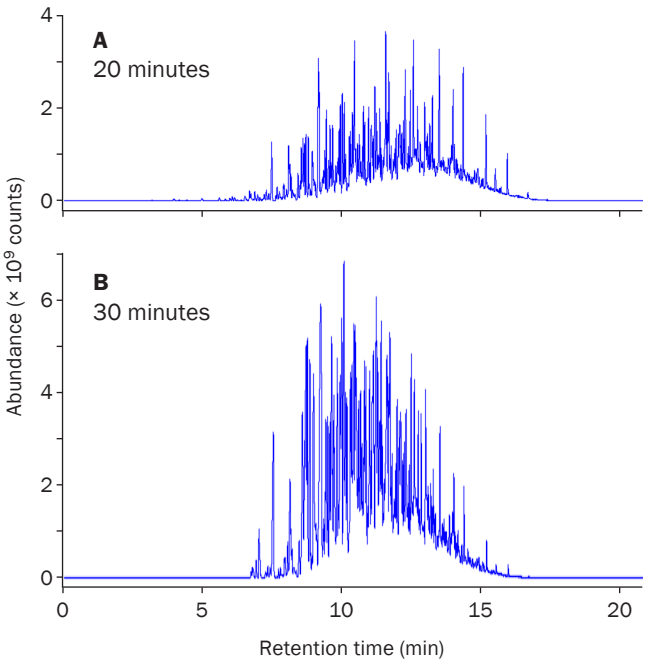

Figure 8: Total ion chromatograms of wood soaked in diesel and then burnt, using a sampling time of (**A**) 20 minutes and (**B**) 30 minutes. Sampling was carried out using the µ-CTE with analysis by TD–GC–MS.

Conclusions

In this study, we have shown how headspace sampling onto sorbent tubes, in conjunction with TD–GC–MS analysis, provides an analytically robust, easily optimised way of assessing vapour profiles from fire debris.

The key benefits of this approach in a forensic context are the high sensitivity associated with two-stage thermal desorption (TD), and the use of re-collection and repeat analysis to assist the generation of legally defensible evidence. This study also shows that Markes' TD100-xr thermal desorber is able to analyse ILRs without carryover of high-boiling components, which is reported to be an issue for instruments from other manufacturers.

From a practical standpoint, TD sampling tubes minimise manual handling and offer improved reliability compared to other techniques, such as SPME or activated charcoal strips. TD also offers the analyst a range of sampling options, including both static headspace and dynamic headspace, as outlined here. Static headspace sampling using the Easy-VOC is the ideal option for field scenarios, and is compatible with a variety of sample containers, while dynamic headspace sampling using the µ-CTE requires access to only electricity and gas/air, and provides enhanced sensitivity for optimum detection of trace-level compounds.

References

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Trademarks

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