MARKES international

Thermal Desorption Applications Guide:

Defence and forensic

A comprehensive guide to using thermal desorption for homeland security, military and forensic applications

Introduction

Defence and homeland security

Although the 1997 Chemical Weapons Convention has been ratified by nearly all countries, the need to detect chemical warfare agents continues. This is increasingly to guard against their use by terrorist organisations, in addition to treaty obligations and military applications, such as decommissioning historic chemical agent stockpiles.

In the first section of this Applications Guide, we describe how thermal desorption (TD) can be applied to the detection of chemical agents. We describe both on-line monitoring of chemical agents, for rapid response to incidents in key civilian and military locations, and off-line tube-based monitoring of agent stockpiles and other materials.

Forensic

The detection of volatile and semi-volatile organic compounds (VOCs and SVOCs) is an important aspect of forensic science, as it can provide unequivocal evidence for the use or presence of incriminating materials.

In the second section of this Applications Guide, we describe how thermal desorption (TD) can be applied to forensic studies – from the analysis of shotgun propellant to the analysis of fire debris for accelerants.

For more information on any of the applications described, or to discuss how TD could benefit you, please contact our helpful and knowledgeable applications specialists at enquiries@markes.com, or by telephoning any of our regional offices (see back cover for details).

Throughout this Guide, this icon is used to indicate where you will find more details of the applications discussed (please note you will need to register with us to download our Application Notes, and may need to pay to download scientific journal papers).

What is thermal desorption?

Thermal desorption (TD) is a versatile pre-concentration technique for gas chromatography (GC) that is used to analyse volatile and semi-volatile organic compounds (VOCs and SVOCs) in a wide range of sample types.

By extracting organic vapours from a sample and concentrating them into a very small volume of carrier gas, 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 allowing full automation of sample preparation, desorption/extraction, pre-concentration and GC injection.

TD can be used:

- **On its own** – for example, for analysis of sorbent tubes or traps, or for direct desorption of materials.
- **In combination with other GC sampling techniques**, such as headspace or sorptive extraction, to enhance their performance.

TD is applied to a wide range of situations, comprehensively covered by our set of Applications Guides. The analyses described within have all been carried out on Markes' single-tube and 100-tube thermal desorbers (and related accessories) – as indicated in the "Typical analytical conditions" sections.

Launched in May 2016, Markes' new 'xr' series of instruments offer performance at least equal to earlier models, with the additional benefits of extended re-collection capability, wider analyte range, and improved reliability. See page 24 and our website for more details.

The exceptional versatility of Markes' TD technology is complemented by innovative accessories for sampling solids, liquids and vapours.

Contents

Image credit: DSTL.

Markes International gratefully acknowledges all customers who have provided experimental data for this Applications Guide.

On any page, please click on the page number
to return to this contents list.

Defence and homeland security

Detecting trace-level agents

Maximum sensitivity for highly toxic compounds

The very high toxicity of chemical agents demands detection at extremely low concentrations – often at the low-picogram level.

As a result, sample pre-concentration using TD is an essential component of any GC-based system for the detection of chemical agents. Whether monitored in near-real-time (see pages 7 and 8) or off-line using sorbent tubes (see pages 9–11), TD provides the high degree of concentration enhancement needed to detect these compounds at very low levels. The focusing traps in Markes' TD instruments desorb very efficiently, ensuring that sharp peaks are generated for optimum sensitivity.

Typical analytical conditions (for on-line monitoring of sarin):

Sample: Standard atmosphere.

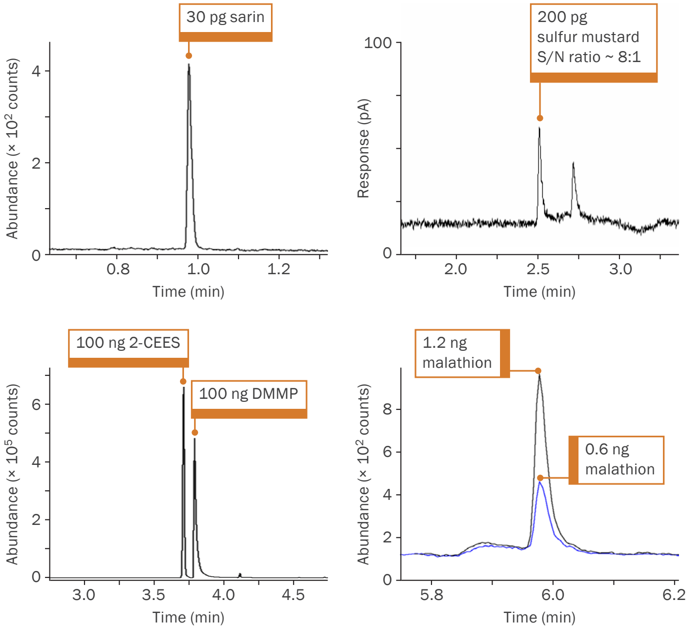
On-line sampling: 6 L, sampled at 600 mL/min every 10 min.

TD (TT24-7): Traps (CWA): Analytes trapped at 25°C, desorbed at 290°C (1 min). Split ratio: Splitless.

Analysis: GC–MS.

In all chemical-agent-monitoring scenarios, optimum TD–GC conditions depend crucially on the precise nature of the sample and the chemicals to be detected. Markes' experts are always on hand to offer advice on the best sampling and analysis conditions for specific circumstances.

Application Note 063



The sensitivity of Markes' TD systems is shown by analysis of sarin (GB), sulfur mustard (HD, here detected by GC–FPD), and three simulants – the sulfur mustard simulant 2-CEES (2-chloroethyl ethyl sulfide), the sarin simulant DMMP (dimethyl methylphosphonate) and the VX simulant malathion. See page 10 for analysis of free-VX.

Near-real-time monitoring

Topic continued on next page

Twin-trap sampling for complete data coverage

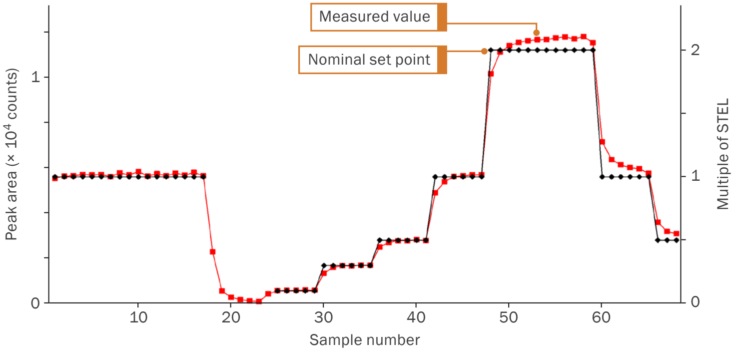
The recent rise in global terrorism has enhanced the need to monitor nerve agents at key civilian locations, such as government facilities and major transport hubs. Continuous near-real-time (NRT) monitoring using GC-based systems offers early alert in the event of a suspected chemical incident, and two key requirements for this are short cycle times and good peak shape.

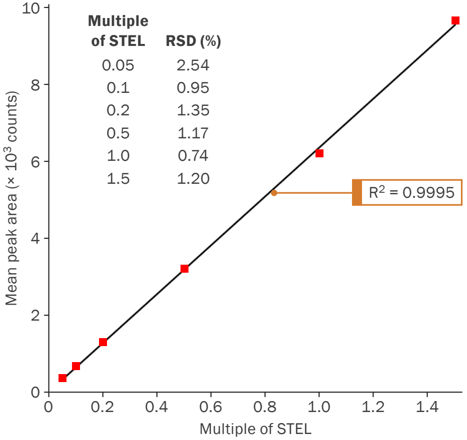
Markes' TT24-7 thermal desorber achieves 100% data coverage by using a pair of reciprocating narrow-bore focusing traps, which are cooled electrically to minimise cycle times and avoid the inconvenience of cryogen. Subsequent rapid heating of these traps efficiently desorbs the vapours directly into the GC, so providing optimum chromatography.

Typical analytical conditions:

Sample: Standard atmosphere.
On-line sampling: 6 L, sampled at 600 mL/min every 10 min.
TD (TT24-7): Traps (CWA): Analytes trapped at 25°C, desorbed at 280°C (1 min).
Split ratio: Splitless.
Analysis: GC–FPD or GC–MS.

Application Note 063





Multiple of STEL	RSD (%)
0.05	2.54
0.1	0.95
0.2	1.35
0.5	1.17
1.0	0.74
1.5	1.20

Airborne concentrations of sarin (GB) are closely tracked using the TT24-7 for near-real-time monitoring of a generated atmosphere. Note the excellent linearity at levels as low as 5% of the US short-term airborne exposure limit (STEL).

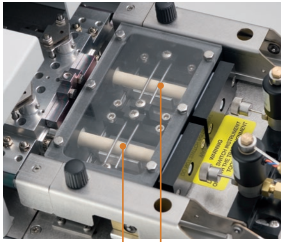
Near-real-time monitoring

Topic continued from previous page

Short cycle times for high-resolution time-profiling

For rapid response to chemical incidents – whether in civilian locations or in demil facilities – near-real-time monitoring systems need to have very short cycle times. Recognising this, the US Centers for Disease Control and Prevention (CDC) have stated that the entire sampling and analytical process for NRT monitoring should be complete within 15 minutes.

The TT24-7 uses twin, reciprocally-operated traps and efficient trap cooling after desorption of a sample, providing continuous coverage with minimum cycle times. In conjunction with fast GC systems, this allows cycle times of as little as 3 minutes. In addition, rapid trap heating rates combined with a reverse flow of carrier gas ensure efficient desorption – giving narrow peaks and optimum sensitivity.



Electrical cooling of the two focusing traps in the TT24-7 completely avoids the need for cryogen, making it ideal for continuous unattended monitoring.

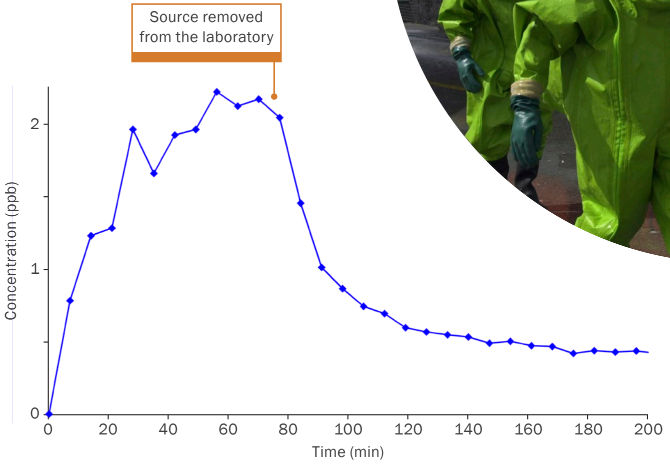
Typical analytical conditions:

Sample: Laboratory air, taken at a point 5 ft from a 2 cm^2 tissue spiked with 100 µL of methyl salicylate.

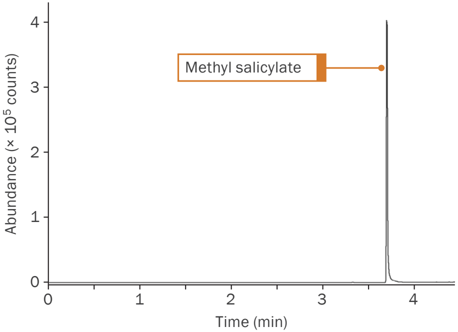
On-line sampling: 3.5 L, sampled at 500 mL/min every 7 min.

TD (TT24-7): Traps (CWA): Analytes trapped at 20°C, desorbed at 280°C (4 min). Split ratio: Outlet 20:1.

Analysis: GC–MS (SIM m/z 120).



The rapid rise and gradual decay of the sulfur mustard (HD) simulant methyl salicylate in laboratory air is clearly shown by this analysis using the TT24-7, which also ensures excellent peak shape.



Off-line screening

Topic continued on next page

Simultaneous screening of multiple agents at trace levels

For situations where concentrations need to be detected at general population limit (GPL) or airborne exposure limit (AEL) levels, off-line pumped-tube sampling provides the lowest levels of detection. However, many analytical systems struggle to monitor multiple compounds in one run.

The inherent compatibility of Markes' TD systems with a wide range of analyte volatilities, including reactive and 'sticky' compounds, makes it extremely useful for rapid screening samples for multiple chemical agents, even at ultra-trace levels. This has applications, for example, in cases where a number of chemical agents may be present in stockpiled or potentially contaminated material.

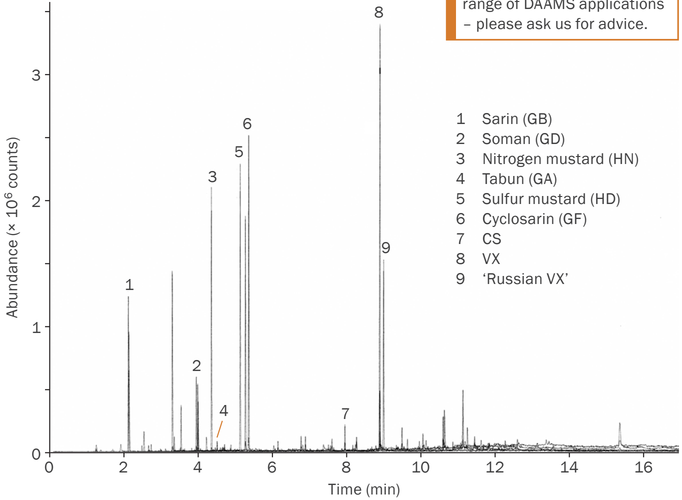
Typical analytical conditions:

Sample: Mixed standard, loaded onto a sorbent tube (5 ng per component).

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 300°C (8 min). Trap (CWA): Analytes trapped at 20°C, desorbed at 280°C (6 min). Split ratio: Outlet ~8:1.

Analysis: GC–MS.

Monitoring of airborne chemical agents is often carried out using the Depot Area Air Monitoring System (DAAMS). This employs metal or glass TD tubes of various dimensions, typically sampled for 6–24 hours. Markes supplies instruments and accessories suitable for a range of DAAMS applications – please ask us for advice.



Single-run analysis of a range of chemical agents at the 5 ng level is achieved using Markes' TD instruments.

Off-line screening

Topic continued from previous page

Detecting picogram quantities of free-VX

Some of the most challenging chemical agents to monitor are the ‘V-series’ nerve agents. Not only do they have extremely low airborne exposure limits (AELs), but they have high boiling points (e.g. 300°C for VX) and a strong tendency to react with any active sites in the sample flow path. These factors can result in low recovery, poor chromatographic peak shape and unacceptably high limits of detection. Consequently, some TD–GC monitoring methods involve derivatising VX to the more stable ‘G’ analogue before analysis, using silver fluoride pads. However, this process can be difficult to optimise, producing errors in quantitation.

This problem is addressed by Markes’ TD systems, which have a short, inert flow path that enables them to quantitatively monitor ‘free’ (underivatised) VX at sub-nanogram levels.

Typical analytical conditions:

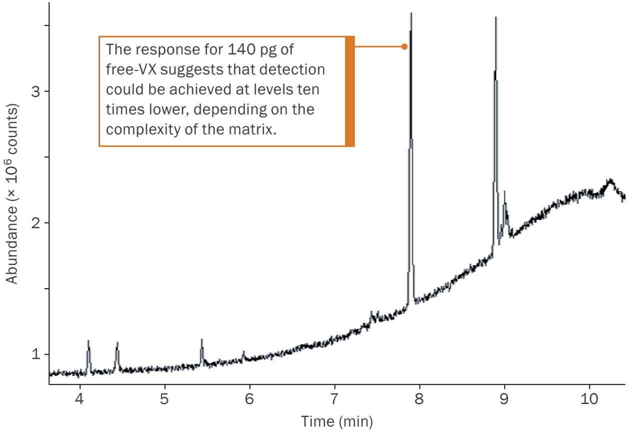
Sample: 140 pg VX, loaded on to a sorbent tube.

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 300°C (8 min). Traps (CWA): Analytes trapped at 20°C, desorbed at 300°C (3 min). Split ratio: Splitless.

Analysis: GC–FPD.

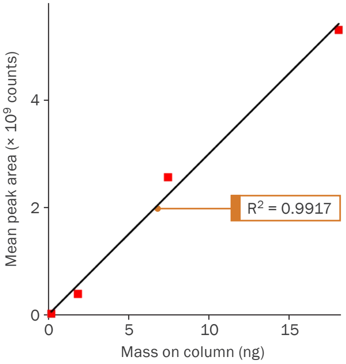
Markes’ compact TD systems – whether off-line or on-line – are easily accommodated within the tight confines of mobile laboratories. Importantly, low trap-purge flows and the availability of true splitless mode helps minimise gas consumption by the TD instrument.

Application Note 044



The response for 140 pg of free-VX suggests that detection could be achieved at levels ten times lower, depending on the complexity of the matrix.

Sorbent-tube sampling and TD–GC analysis allows detection of 140 pg free-VX. This would allow detection at the lower US AEL levels – for example the workplace limit (1 ng/m^3) and the general population limit (0.6 ng/m^3).



$R^2 = 0.9917$

Off-line screening

Topic continued from previous pages

Phosgene analysis using on-tube derivatisation

Phosgene has been used in the past as a chemical warfare agent, and also has many legitimate large-scale uses in the chemical industry, meaning that is is subject to manufacturing restrictions. There is therefore a need to monitor phosgene in both military and civilian locations, but GC analysis can be compromised by its susceptibility to hydrolysis.

To overcome this problem, a team at the UK's defence research laboratory sampled phosgene onto sorbent tubes spiked with a derivatising agent. Subsequent TD analysis of the resulting adduct gave a dramatic improvement in detection limit compared to solvent-elution methods. The authors also pointed out the benefit of the electronic pressure control, used with the Markes system, which allows constant carrier gas flow and a shorter GC run time.

Typical analytical conditions:

Sample: Laboratory air, spiked with phosgene at 4.4 ng/L. The subsequent blank run used clean laboratory air.

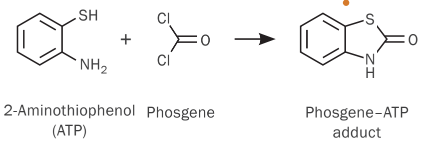
Pumped sampling: 1000 mL/min for 1 min (total volume 1 L).

TD (UNITY or TD100): Tube (Tenax® TA, loaded with 100 µg of 2-aminothiophenol and 100 µg of triethylamine, both in the vapour phase): Desorbed at 250°C (13 min). Trap: Analytes trapped at 10°C, desorbed at 225°C (3 min). Split ratio: Outlet 10 : 1.

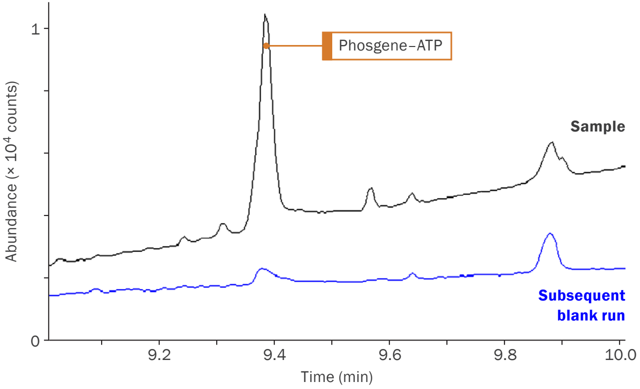
Analysis: GC–MS (SIM m/z 151, 123 and 96).

http://dx.doi.org/10.1016/j.chroma.2005.08.070

B. Muir, D.B. Cooper, W.A. Carrick, C.M. Timperley, B.J. Slater and S. Quick, Analysis of chemical warfare agents. III. Use of bis-nucleophiles in the trace level determination of phosgene and perfluoroisobutylene, *Journal of Chromatography A*, 2005, 1098: 156–165.



The authors found the derivative to be stable for up to 28 days on-tube – which is important because tubes often need to be shipped from the sampling location to the analytical laboratory.



On-tube derivatisation of phosgene with 2-aminothiophenol and TD–GC–MS analysis allowed detection at 0.44 ng on-column, with low levels of carryover in a subsequent blank run. *Data reproduced courtesy of DSTL, Porton Down, UK, and with permission from Journal of Chromatography A.*

Agents in complex matrices

Identifying chemical agents in diesel

Laboratories accredited by the Organisation for the Prohibition of Chemical Weapons (OPCW) have to regularly undergo proficiency testing to demonstrate their analytical capability. Included in such tests are analyses of chemical agents in complex ‘real-world’ matrices – which is a particularly difficult challenge.

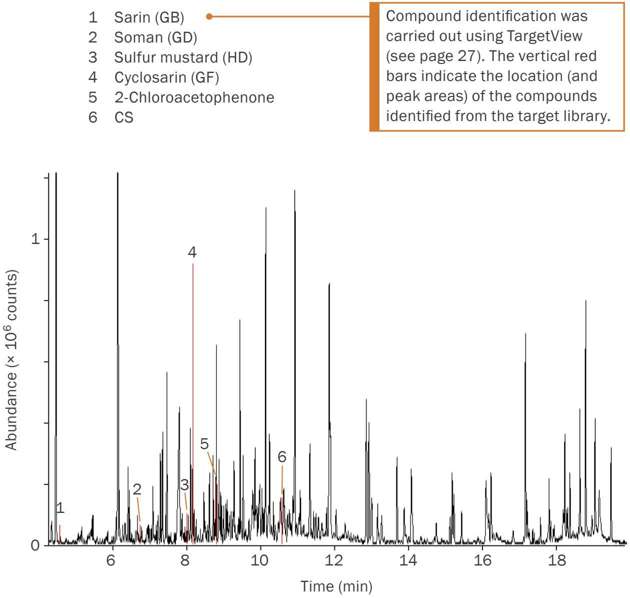
With a range of sampling options and the capability for full automation, TD is a versatile approach to the analysis of complex mixtures. Sensitivities for trace-level analytes are maximised by the use of splitless analysis, while higher concentrations can be handled by sample splitting at either (or both) the tube and trap desorption stages. Importantly for agent monitoring, the uniformly-heated valve and flow path in Markes’ TD instruments offer compatibility for reactive/labile species as well as the widest possible range of VOCs and SVOCs.

Typical analytical conditions:

Sample: A mix of chemical agents spiked into diesel (1 part in 7500), and loaded on to a sorbent tube.

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 300°C (3 min). Trap (CWA): Analytes trapped at 10°C, desorbed at 300°C (4 min). Split ratio: Outlet 20:1.

Analysis: GC–MS.



Compound identification was carried out using TargetView (see page 27). The vertical red bars indicate the location (and peak areas) of the compounds identified from the target library.

A worst-case agent-monitoring scenario is recreated here using a sample of diesel oil spiked with a mixture of chemical agents. Sharp peaks and efficient spectral deconvolution greatly improve the ability to identify the target analytes amongst numerous co-eluting diesel hydrocarbons.

Explosives in air

Inert systems for detecting explosives at low-nanogram levels

Monitoring air for explosives is important for both military and civilian security agencies – for the detection of airborne vapours at crime scenes, at possible arms storage locations, and from vehicles suspected of being used to transport weapons. However, the high boiling points and reactive nature of explosives requires that special attention must be paid to the inertness of the analytical systems.

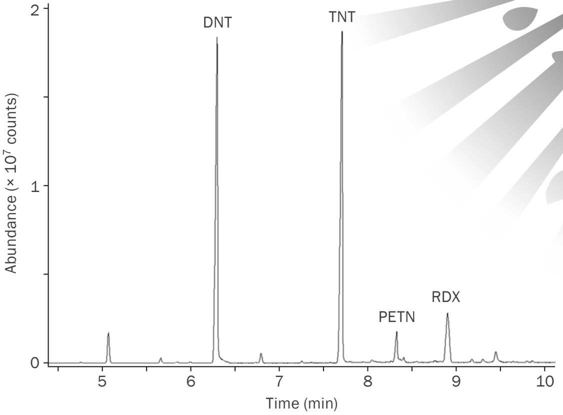
The heated valve and short, uniformly-heated flow path of Markes' TD systems are both fully passivated, and when used with appropriately inert sorbent-packed tubes and traps, reliable analysis of highly active compounds such as explosives becomes routine. In addition, rapid and highly efficient trap desorption ensures that even trace-level compounds produce sharp GC peaks.

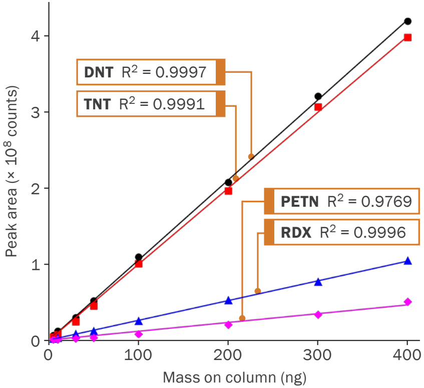
Typical analytical conditions:

Sample: Liquid standard, loaded onto a sorbent tube.

TD (UNITY or TD100): Tube (Quartz wool): Desorbed at 180°C (3 min) then 210°C (2 min). Trap (CWA): Analytes trapped at –10°C, desorbed at 190°C (2 min). Split ratio: Outlet 5.5:1. *A slow trap heating rate is advised with potentially explosive analytes.*

Analysis: GC–MS.





Analysis of trace-level DNT and TNT at low nanogram levels is now considered routine. As illustrated in this example, TD analysis is also compatible with the even more challenging pentaerythritol tetranitrate (PETN) and cyclotrimethylene trinitramine (RDX), if appropriate care is taken.

Permeation studies

Examining migration of chemical agents through protective materials

As well as the detection of chemical agents for homeland security and for the monitoring of military sites, a considerable amount of research has been undertaken to improve protective equipment used by military personnel. Part of this research investigates how chemical agents (typically in liquid form) interact with materials.

To assist in such work, Markes' Micro-Chamber/Thermal Extractor (μ-CTE) can be fitted with a permeation accessory that allows the migration of chemicals through materials to be studied in detail.

Typical analytical conditions:

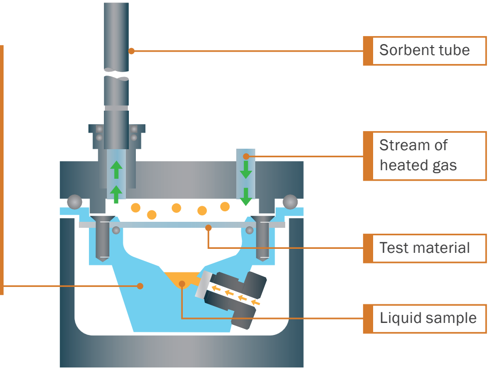
Sample: 5–20 μL of liquid methyl salicylate.

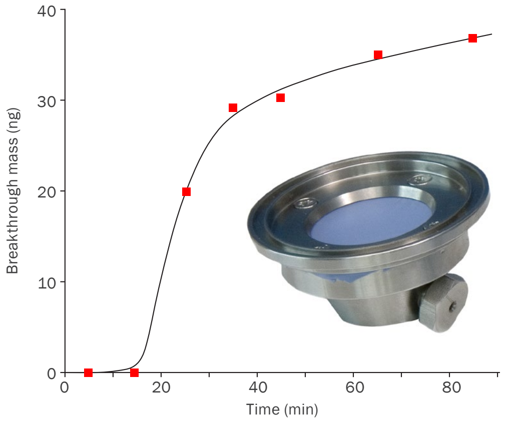
Dynamic headspace (Micro-Chamber/Thermal Extractor with permeation accessory): Flow rate: 50 mL/min for 10 min. Chamber temperature: 35°C. Sorbent tube changed approximately every 15 min.

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 300°C (5 min). Trap (Material emissions): Analytes trapped at 20°C, desorbed at 280°C (3 min). Split ratio: Outlet 5 : 1.

Analysis: GC–MS.

The permeation accessory fits securely inside the 4 or 6 cavities of the μ-CTE (in place of the usual sampling pots). A section of test material is secured in place, leaving a consistent 6 cm^2 exposed to the source of vapours in the well below. Vapours then diffuse through the material and are swept onto a sorbent tube in a stream of heated gas





The rate of permeation of methyl salicylate (a sulfur mustard (HD) simulant) through a nitrile rubber glove rises rapidly after ~15 minutes, and then levels off as a steady state is reached.

Forensic

Drug analysis

Minimising sample preparation to provide robust evidence

Chemical analysis of crime-scene materials can be vital in providing the proof needed by courts to achieve secure convictions. A key factor when deciding on the analytical methods used is the minimisation of sample preparation. This is because, as far as the legal system is concerned, it means that there is less risk of compromising data, and thus of evidence being challenged.

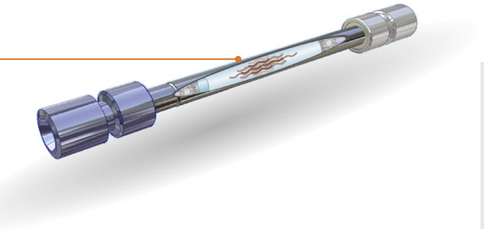
TD offers a considerable advantage over other GC sample introduction techniques for forensic applications because it requires little or no manual sample preparation. This is especially true for direct desorption, which simply involves positioning sample materials in empty TD tubes and dynamically extracting vapours directly onto a focusing trap. The trap is then rapidly heated to release the analytes into the GC system in a narrow band of gas.

Typical analytical conditions:

Sample: ~5 mg house dust from a UK crime scene, placed in an empty TD tube and secured between two plugs of quartz wool.

TD (UNITY or TD100): Sample: Desorbed at 150°C (10 min). Trap (Tenax® TA): Analytes trapped at 20°C, desorbed at 250°C (3 min). Split ratio: Outlet 16:1.

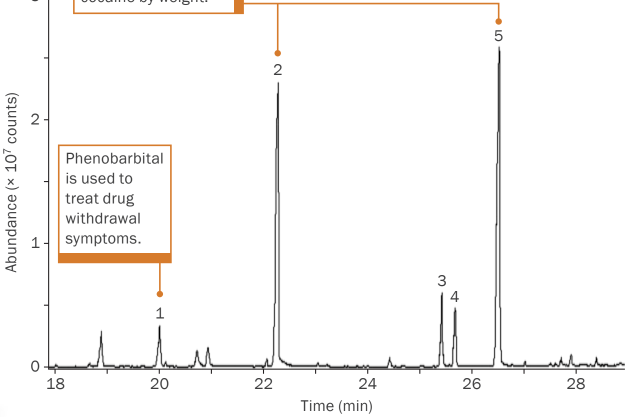
Analysis: GC–MS.



Samples for direct desorption are simply weighed directly into empty TD tubes or tube liners, supported by inert plugs of quartz wool.

Topic continued on next page

1 Phenobarbital
2 Cocaine
3 Acetylcodeine
4 Monoacetylmorphine
5 Heroin



Remarkably, the dust was found to be nearly 3% heroin and cocaine by weight.

Phenobarbital is used to treat drug withdrawal symptoms.

Drugs of abuse are easily identified in house dust using direct desorption followed by TD–GC–MS analysis. As well as benefitting from the versatility and sensitivity of Markes' TD systems, direct desorption is simple to carry out, and correspondingly easy to automate.

Topic continued from previous page

Enhancing sensitivity by combining headspace with TD

Confirmatory testing of seized substances by GC–MS techniques is widely used to assess their purity, and to identify counterfeit or synthetic drugs. Forensic analysis of drug-related crime-scene samples is also useful because it may identify impurities that allow their source to be traced.

Three main TD sampling techniques can be used to carry out such investigations. If samples are small, then direct desorption is ideal (see page 16). However, if larger samples are available, then headspace–TD offers enhanced sensitivity for trace-level impurities, by combining the larger sample sizes of headspace with the concentrating power of TD. In the example shown opposite, static headspace was used, but the Micro-Chamber/Thermal Extractor could also have been employed to dynamically release the headspace vapours (see page 20).

Typical analytical conditions:

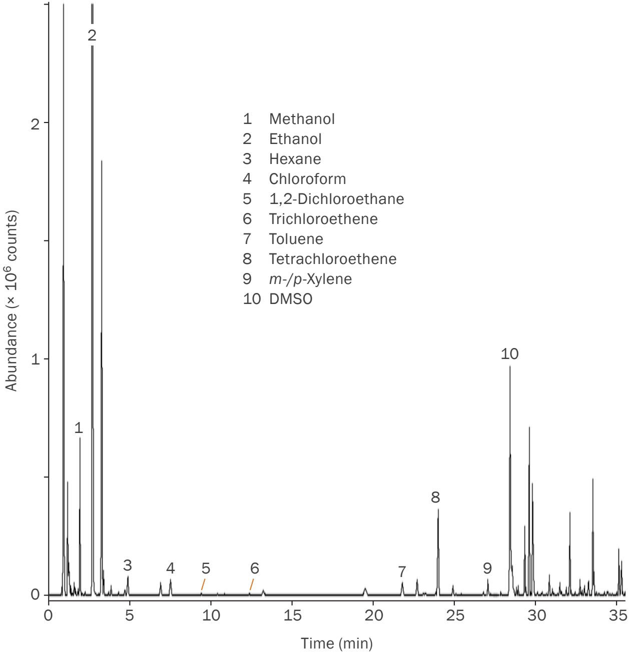
Sample: 0.5 g omeprazole tablet, dissolved in 5 mL DMSO.

Headspace: Equilibration: 45 or 60 min at 85°C.

TD (UNITY): Trap (Air toxics): Analytes trapped at 25°C, desorbed at 300°C (1 min). Split ratio: Outlet 6 : 1.

Analysis: GC–MS.

Headspace sampling can now also be carried out using Markes' HiSorb probes – see www.markes.com.



Analysis of high-abundance and trace-level residual solvents in the drug omeprazole illustrates the ability of TD to enhance the concentration and analyte volatility range of conventional static headspace techniques.

Body decomposition

Understanding cadaver VOCs in soil gas

In the aftermath of natural or man-made disasters, there is an urgent need to locate human remains, both for the sake of the victims' families and for public health & safety. However, training 'cadaver detection dogs' to do this is challenged by a lack of consistency between reported lists of cadaver VOCs, and a limited understanding of air–soil VOC partitioning. Establishing reliable methods for investigating soil VOCs has therefore become increasingly important.

An Australian research group have been addressing this issue by studying soil-borne VOCs near pig carcasses. Using a VOC-Mole sampler with TD–GC–MS, they were able speed up sampling and identify more compounds compared to methods such as solvent extraction.

Typical analytical conditions:

Sample: Soil air at 30 cm depth, adjacent to the abdomen of a pig carcass after 17 days of decomposition.

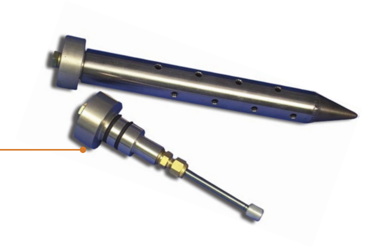
Pumped sampling (VOC-Mole): 100 mL/min for 30 min (total volume 3 L).

TD (UNITY or TD100): Tube (Tenax® TA–Carbograph™ 5TD): Desorbed at 300°C (4 min). Trap (Carbopack™ B–Carboxen™ 1000): Analytes trapped at –10°C, desorbed at 300°C (3 min). Split ratio: Outlet 21 : 1.

Analysis: GC–MS.

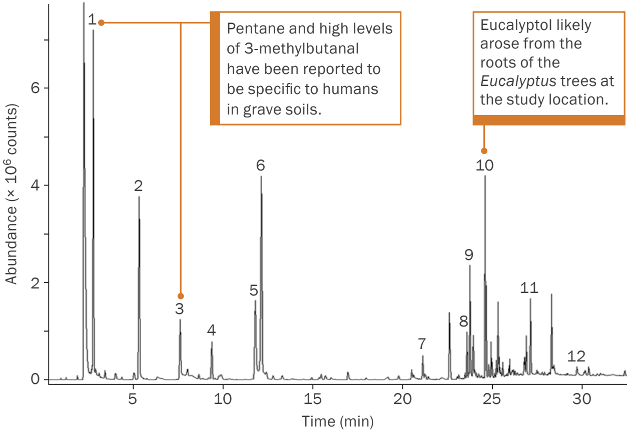
http://dx.doi.org/10.1371/journal.pone.0095107

S.L. Forbes and K.A. Perrault, Decomposition odour profiling in the air and soil surrounding vertebrate carrion, *PLOS One*, 2014, 9: e95107.



VOC-Moles are driven into the soil, and can be configured for pumped or passive sampling (shown).

1	Pentane	5	Cyclohexanone	9	Phenol
2	Butan-2-one	6	Dimethyl disulfide	10	Eucalyptol
3	3-Methylbutanal	7	Heptan-2-one	11	Indole
4	Pentan-2-one	8	Dimethyl trisulfide	12	*N*,*N*-Diethyl-4-methylbenzamide



Pentane and high levels of 3-methylbutanal have been reported to be specific to humans in grave soils.

Eucalyptol likely arose from the roots of the *Eucalyptus* trees at the study location.

Pumped sampling with a VOC-Mole onto two-bed sorbent tubes allows a wide range of VOCs to be collected from soil gas. *Data reproduced courtesy of Professor Shari Forbes and Dr Katelynn Perrault, University of Technology, Sydney, Australia.*

Accelerants in fire debris

Topic continued on next page

Easy grab-sampling of headspace vapours

The identification of accelerants in ignitable liquid residues (ILRs) from the scenes of fires can indicate that the fire was not accidental but the result of arson. Headspace sampling is widely used for such analyses because it is non-destructive, but sampling approaches that use small sorbent areas (such as micro-extraction) can result in preferential uptake of heavier compounds, creating skewed profiles.

Sampling headspace onto sorbent tubes with TD–GC analysis allows representative sampling of a wide range of compounds, overcoming this issue and offering a quick and analytically robust approach to the analysis of crime-scene residues. Importantly, TD is not limited to specific container sizes, which allows the sample size to be selected to maximise sensitivity and reliability.

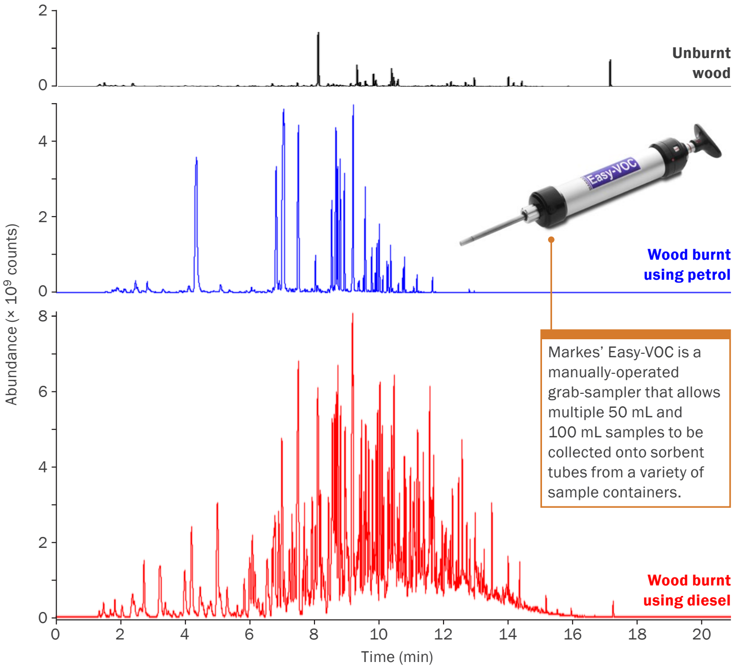
Typical analytical conditions:

Sample: Ten pieces of wooden dowel (5 cm long, 0.8 cm diameter), treated with diesel/petrol, burnt, and then placed in a non-emitting 1 L container.

Headspace (Easy-VOC): 5 × 100 mL, sampled successively.

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 280°C (10 min). Trap (Material emissions): Analytes trapped at –10°C, desorbed at 300°C (3 min). Split ratio: Inlet: 2:1, Outlet 34:1.

Analysis: GC–MS.



Markes' Easy-VOC is a manually-operated grab-sampler that allows multiple 50 mL and 100 mL samples to be collected onto sorbent tubes from a variety of sample containers.

Clear differences in the headspace profiles of wood samples exposed to different treatments are identified in this set of analyses. A useful advantage of TD is that it allows water to be selectively eliminated from the system before injection of the vapours into the GC, avoiding analytical interference.

Accelerants in fire debris

Topic continued from previous page

Facilitating analysis of unknown samples using TD splitting and re-collection

When analysing ‘unknown’ materials with a high volatile content – such as materials from the scenes of fires – 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’ and quantitatively re-collected onto a clean tube, during tube and/or trap desorption. 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 re-analysed under lower-split conditions to investigate minor compounds in more detail, if required.

Typical analytical conditions:

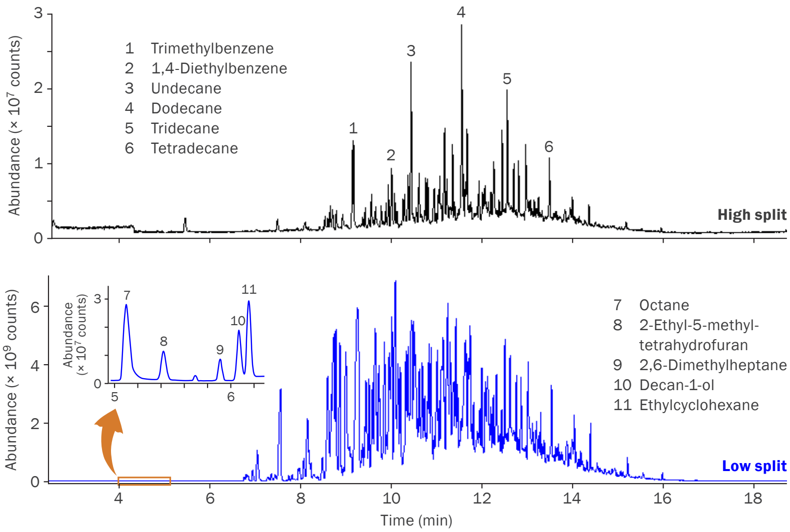
Sample: Burnt tea-towel, cut into 4 cm × 4 cm pieces.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 50 mL/min for 20 min. Chamber temperature: 40°C.

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 280°C (10 min). Trap (Material emissions): Analytes trapped at –10°C, desorbed at 300°C (3 min). Split ratio: Inlet: 2 : 1, Outlet 34 : 1 (low split) or 68 : 1 (high split).

Analysis: GC–MS.

The sampling pots of the µ-CTE are available with diameters of 4.5 or 6.4 cm.



High-abundance and low-level compounds from a single piece of burnt cloth are analysed in two consecutive runs with different split ratios, avoiding the risk of saturating the analytical system. In this case, the Micro-Chamber/Thermal Extractor (µ-CTE) was used for dynamic headspace sampling, allowing vapours from representative cloth samples to be taken.

Shotgun propellant

Reliable analysis of explosive residues

Detecting explosive residues in forensic samples presents a significant challenge to GC analysts, because these highly reactive compounds are very sensitive to any slight deterioration in system performance or inertness.

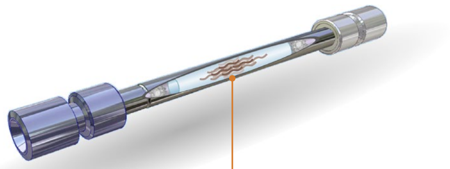
The heated valve and short, uniformly-heated flow path of Markes' TD systems are fully passivated, allowing highly active compounds such as explosives to be routinely analysed. In addition, rapid and highly efficient trap desorption ensures that even trace-level compounds produce sharp GC peaks. This is illustrated here by the analysis of shotgun propellant – enabling individual cartridges or weapons to be linked to specific crimes.

Typical analytical conditions:

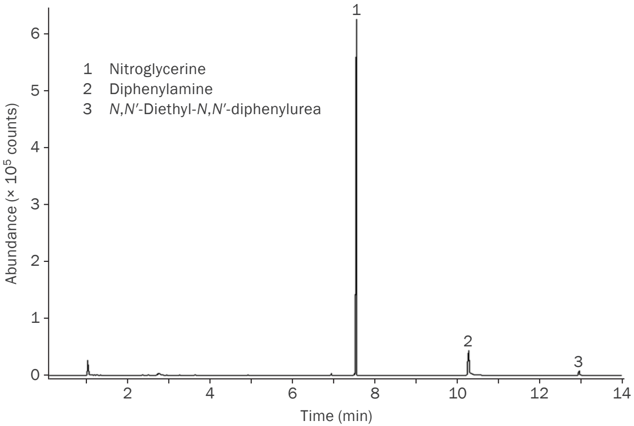
Sample: Small pellet of shotgun propellant, placed in an empty TD tube and secured between two plugs of quartz wool.

TD (UNITY or TD100): Sample: Desorbed at 160°C (3 min). Trap (CWA): Analytes trapped at 10°C, desorbed at 160°C (2 min). Split ratio: Outlet 11:1. *A slow trap heating rate is advised with potentially explosive analytes.*

Analysis: GC–MS.

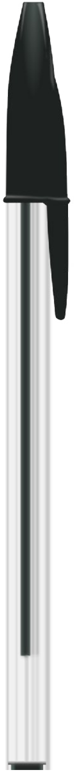


Samples for direct desorption are simply weighed directly into empty TD tubes or tube liners, supported by inert plugs of quartz wool.



Efficient analysis of firearm propellant – without matrix interference – is achieved using direct desorption to release volatile compounds from a small quantity of material, followed by TD–GC–MS analysis.

Ink



Detection of solvents and dye components on written materials by direct desorption

Forensic analysis of inks usually involves investigation of the organic dye components by solvent-extraction methods – but this makes it difficult to distinguish between inks with similar formulations and to tell how long ink has been on a particular document.

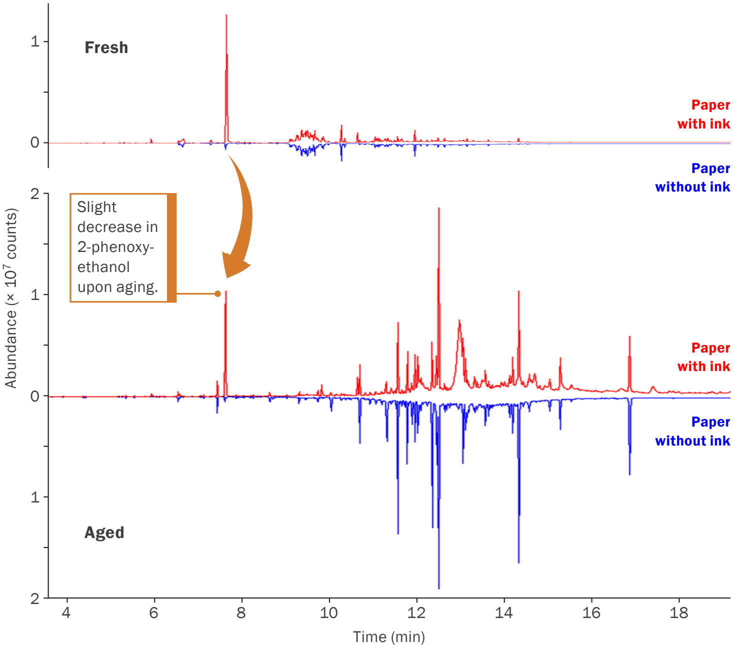
Direct desorption and TD analysis of inks on paper can be used to generate a ‘fingerprint’ that contains information on the solvents present as well as dye components. This can help to provide information on the age and source of the document, which is relevant to studies of authenticity as well as forensic investigations. It is important to note that the ability to detect such a wide analyte range in one run is due to the use of multi-bed traps – which is only possible because of the backflush operation of the valve in Markes’ thermal desorbers.

Typical analytical conditions:

Sample: Paper with and without ball-point pen writing, placed in an empty TD tube.

TD (UNITY or TD100): Sample: Desorbed at 100°C (15 min). Trap (General-purpose carbon): Analytes trapped at 25°C, desorbed at 350°C (3 min). Split ratio: Outlet 11:1.

Analysis: GC–MS.



Slight decrease in 2-phenoxy-ethanol upon aging.

Substantial differences can be seen between fresh and aged paper with and without ink. The solvent 2-phenoxyethanol is of note here because it is present in the majority of ballpoint pen inks, and because its slow evaporation rate means it can be used to estimate the age of a document.

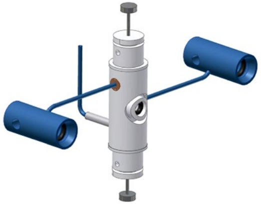
Relevant sampling and analytical techniques

Thermal desorption

Thermal desorption (TD) uses heat and a flow of inert gas to desorb volatile and semi-volatile organic compounds (VOCs and SVOCs) from sorbents or sample materials. Extracted vapours are swept onto an electrically-cooled focusing trap, which is then rapidly heated to inject them into a gas chromatograph (GC).

Markes International leads the world in TD technology. Key advantages include:

- **Analyte range** – Compounds ranging in volatility from acetylene to n-$C_{44}H_{90}$ *and* reactive species can all be analysed on a single TD platform.
- **Quantitative re-collection of split flows** enables repeat analysis and simple method validation, overcoming the historical 'one-shot' limitation of TD.
- **High sensitivity** – Two-stage desorption using sorbent tubes allows concentration enhancements of up to 10^6.
- **Wide dynamic range** – Two-stage desorption and sample splitting means that Markes' thermal desorbers can handle analyte concentrations ranging from part-per-trillion up to low-percent levels.
- **Sample compatibility** – As world leaders in TD technology, Markes offers an unmatched range of innovative and labour-saving sampling accessories for liquids, solids and gases.
- **Analytical quality** – The narrow-bore design of the focusing trap ensures that a highly concentrated band of vapour is introduced to the GC, allowing true splitless operation and optimising both resolution and sensitivity.
- **Reduced running costs** – Electrical cooling eliminates the cost of cryogen, and also avoids problems with ice formation.
- **Cleaner chromatography** – By circumventing the need for sample preparation, solvent artefacts are eliminated, while unwanted high-abundance components such as water can also be selectively removed.



Markes' patented inert valving enables C_2–C_{44} *and* reactive species to be analysed on a single thermal desorption system.

With options for automated analysis of 100 tubes or 27 canisters, and continuous on-line air/gas monitoring, Markes' TD systems allow you to expand laboratory capacity as demand grows.

For more on the principles, benefits and applications of TD, download Application Note 012.

For more on the the single-tube UNITY-xr™ thermal desorber and the multi-tube automated TD100-xr™ instrument, visit www.markes.com.

On-line sampling

On-line sampling – the collection of vapours directly into the focusing trap of the thermal desorber – is a useful approach to monitoring ultra-volatile compounds that are too volatile to be retained on sorbent tubes at ambient temperature. On-line TD systems are also valuable for continuous sampling and for near-real-time monitoring.

Two on-line monitoring systems are available from Markes:

- The **Air Server-xr™** samples air for a defined period of time and delivers it to the focusing trap of the UNITY-xr thermal desorber.
- The **TT24-7™** uses two focusing traps, working alternately, to sample and analyse air continuously.

The Air Server-xr (right) integrates with UNITY-xr.

The TT24-7 with cover removed to show the twin traps.

Whichever on-line system is chosen, the use of inert flow paths ensures compatibility with highly labile analytes such as sulfur compounds.

See pages 6, 7 and 8 for applications using on-line sampling.

For more on these products and to download the brochures, visit www.markes.com.

Pumped sampling

Pumped sampling onto sorbent tubes is a versatile option for simultaneous monitoring of multiple compounds, whether in the open air or contained within sampling bags (or other headspace containers).

Markes' backflush technology allows tubes to be packed with multiple sorbent beds, widening the analyte range detectable from a single sample.

Two accessories are available from Markes for pumped sampling onto TD tubes:

- **ACTI-VOC™** is a lightweight, compact low-flow pump specifically optimised for TD tubes, which can operate in constant-flow or constant-pressure modes.
- **Easy-VOC™** is a manually-operated grab-sampler that allows precise volumes of air or gas to be sampled directly onto sorbent tubes. By avoiding the need for batteries or electrical power, it is ideal for field sampling.

See pages 11 and 19 for applications using pumped sampling.

For more on these products and to download the brochures, visit www.markes.com.

Microchamber sampling

Markes' **Micro-Chamber/Thermal Extractor™ (μ-CTE™)** is a stand-alone sampling accessory for dynamic headspace sampling of organic vapours from a wide variety of materials. Operation is simple, with short sampling times (typically <60 minutes) and the capability to analyse up to four or six samples at once, depending on the model chosen.

Now available with humidifier accessory

The μ-CTE can be used for:

- Quality-control of chemical emissions from products and materials.
- Screening of products before long-term certification tests.
- Checking raw materials.
- Comparing products to those of competitors.
- Monitoring odour and emission profiles.
- Product troubleshooting and R&D.
- Kinetic studies such as shelf-life tests, or monitoring fragrance profiles as they change over time.
- Permeation tests.

The sampling pots of the μ-CTE have volumes of 44 or 114 cm^3, depending on the model chosen.

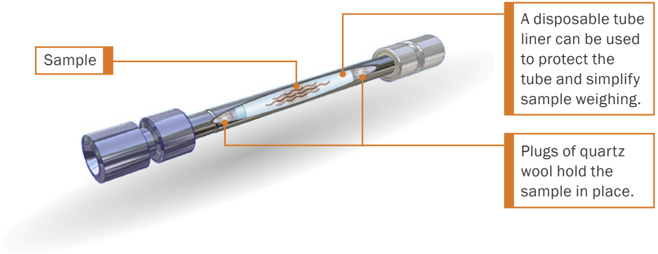
See pages 14 and 20 for applications using the μ-CTE.

For more on the μ-CTE and to download the brochure, visit www.markes.com.

Direct desorption

Direct desorption is a highly effective way of sampling organic vapours from homogeneous materials containing relatively high concentrations of volatiles.

A small quantity of the material is placed into an empty TD tube, and the tube placed in the thermal desorber. It is then gently heated in a flow of inert gas to dynamically extract headspace volatiles directly on to the focusing trap.



Direct desorption is a simple way of releasing organic vapours from a sample. It can use metal tubes, but glass ones are preferred by many analysts because it is easier to position the sample and monitor its state before and after analysis.

See pages 16, 21 and 22 for applications using direct desorption.

For more on direct desorption, see Application Note 009.

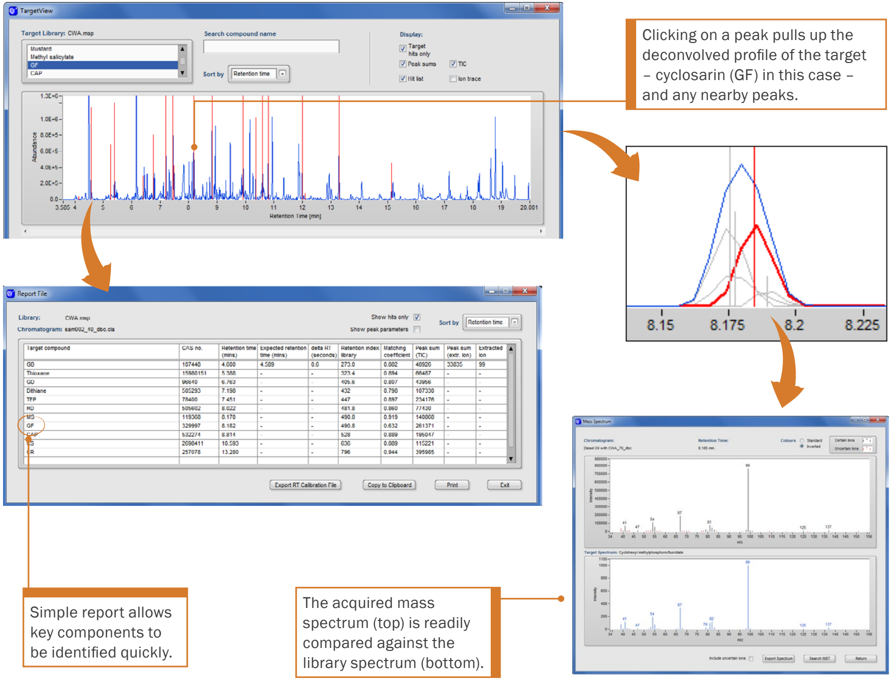
Compound identification software

TargetView™ is an easy-to-learn GC–MS software package that complements TD by making it easier to spot trace-level components in complex samples.

TargetView features:

- Automated screening of chromatograms for identification of targets and 'unknowns'.
- Dynamic baseline compensation (DBC) to remove column bleed and unwanted background interference.
- Advanced spectral deconvolution for cleaner spectra of co-eluting or masked compounds.
- Rapid creation of spectral libraries from various sources.
- Automated calculation of retention index values to assist compound confirmation.
- Compatibility with GC–MS file types from most major vendors.

For more on TargetView, visit www.markes.com.



Report File

Library: CWA.msp

Chromatogram: sam002_40_dbc.cla

Show hits only ☑

Show peak parameters ☐

Sort by Retention time

Target compound	CAS no.	Retention time (mins)	Expected retention time (mins)	delta RT (seconds)	Retention index library	Matching coefficient	Peak sum (TIC)	Peak sum (extr. ion)	Extracted ion
GB	107440	4.600	4.589	0.6	273.0	0.882	40926	33835	99
Thioxane	15980151	5.388	-	-	323.4	0.894	66487	-	-
GD	96640	6.763	-	-	405.6	0.807	43956	-	-
Dithiane	505293	7.198	-	-	432	0.798	107330	-	-
TEP	78400	7.451	-	-	447	0.897	234176	-	-
HD	505602	8.022	-	-	481.8	0.860	77430	-	-
MS	119368	8.170	-	-	490.8	0.919	140068	-	-
GF	329997	8.182	-	-	490.8	0.632	261371	-	-
CAP	532274	8.814	-	-	528	0.889	195047	-	-
CS	2698411	10.593	-	-	636	0.889	115221	-	-
CR	257078	13.280	-	-	796	0.944	395985	-	-

Clicking on a peak pulls up the deconvolved profile of the target – cyclosarin (GF) in this case – and any nearby peaks.

Simple report allows key components to be identified quickly.

The acquired mass spectrum (top) is readily compared against the library spectrum (bottom).

As shown in this analysis of chemical agents in a complex matrix, TargetView's interactive chromatogram (top left) allows you to delve into the results as much as you want – from a simple 'yes/no' confirmation that a particular compound is present, to detailed examination of elution profiles or comparison of mass spectra.

About Markes International

Since 1997, Markes International has been at the forefront of innovation for enhancing the measurement of trace-level volatile and semi-volatile organic compounds (VOCs and SVOCs) by gas chromatography (GC).

Our range of thermal desorption products has for many years set the benchmark for quality and reliability. By lowering detection limits, and increasing the options open to the analyst, our thermal desorbers greatly extend the application range of GC.

Our comprehensive portfolio of thermal desorption products includes instruments such as UNITY-xr and TD100-xr, a wide range of high-quality sorbent tubes, and innovative accessories that allow representative vapour profiles to be collected with minimal inconvenience.

As well as defence and forensic applications, Markes' products are used extensively in multiple routine and research scenarios – everything from food aroma profiling to atmospheric studies.

Markes is headquartered near Cardiff, UK, and also has laboratory and demonstration facilities in Cincinnati and Sacramento, USA, and near Frankfurt, Germany. Markes is a company of the Schauenburg International Group.

THE QUEEN'S AWARDS
FOR ENTERPRISE:
INTERNATIONAL TRADE
2015

ACTI-VOC™, Air Server™, Easy-VOC™, Micro-Chamber/Thermal Extractor™, μ-CTE™, TargetView™, TD100™, TD100-xr™, TT24-7™, UNITY™, UNITY-xr™ and VOC-Mole™ are trademarks of Markes International.

Carbograph™ is a trademark of LARA s.r.l.

Carbopack™ and Carboxen™ are trademarks of Supelco, Inc.

Tenax® is a registered trademark of Buchem B.V.

Analytical conditions presented in this document are intended as a guide only, and Markes International makes no guarantee that the performance indicated can be achieved under different circumstances.

MARKES international

L-0030 (011216-4)

Markes International

UK: Gwaun Elai Medi-Science Campus, Llantrisant, RCT, CF72 8XL **T:** +44 (0)1443 230935

US: 11126-D Kenwood Road, Cincinnati, Ohio 45242
2355 Gold Meadow Way, Gold River, Sacramento, California 95670 **T:** 866-483-5684 (toll-free)

Germany: Schleussnerstrasse 42, D-63263 Neu-Isenburg, Frankfurt **T:** +49 (0)6102 8825569

E: enquiries@markes.com **W:** www.markes.com

A company of the **SCHAUENBURG** International Group