

Thermal Desorption: A Practical Applications Guide



III. Defence and Forensic

2nd Edition

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Introduction to Markes International Ltd

Formed in 1997, Markes International is world leader in the development and manufacture of analytical thermal desorption (TD) instrumentation and associated sampling equipment for measuring VOCs and semi-volatiles in air & materials.

Markes has pioneered major TD innovations such as quantitative re-collection for repeat analysis (**SecureTD-Q™**), **TubeTAG™** RFID tube labels, **DiffLok™** enabling technology for robust tube automation and cryogen-free analysis of multiple canister air samples. All these innovations feature in Markes' well known modular range of TD instruments: **UNITY™**, **ULTRA™**, **Air Server™** and the most recent addition, the **TD-100™**. Other ground-breaking TD products from Markes International include the twin-trap **TT24-7™** for continuous, online air monitoring, and unique sampling accessories such as the **Micro-chamber/Thermal Extractor™** and **HS5-TD™** for liquid and solid samples.

Markes' TD units can be seamlessly combined with all major brands of GC and GC/MS to provide trace or high level monitoring solutions.

What is analytical TD?

Analytical thermal desorption is a sample introduction technique for GC and GC/MS, which uses heat and a flow of inert gas, rather than an organic solvent, to extract/desorb analytes from the sample media, delivering them directly to the gas chromatograph. Since the early 1980s, TD has provided the ultimate versatile sample introduction technology for GC, by combining selective concentration enhancement with direct extraction into the carrier gas and efficient transfer/injection, all in one fully automated and labour-saving package.



Markes International Ltd, UK headquarters

Overview

Thermal desorption is now recognised as the technique of choice for environmental and workplace air monitoring. Relevant standard methods include: ISO/EN 16017, EN 14662 (parts 1 & 4), prEN 13649, ASTM D6196, US EPA TO-17 and NIOSH 2549. The same principles apply to air monitoring for defence applications.

TD is also routinely used for monitoring volatile and semi-volatile organic compounds ([S]VOCs) in products and materials. Examples include forensic analysis of suspect materials, product emissions testing, and food, flavour & fragrance profiling.

This publication presents several real-world applications in defence & forensics. Accompanying publications cover the application areas of:

- Chemical emissions from products & materials
- Food, flavour, fragrance & odour profiling
- Environmental monitoring and occupational health & safety

Defence & forensic applications for TD

TD is used extensively for forensic science and chemical defence.

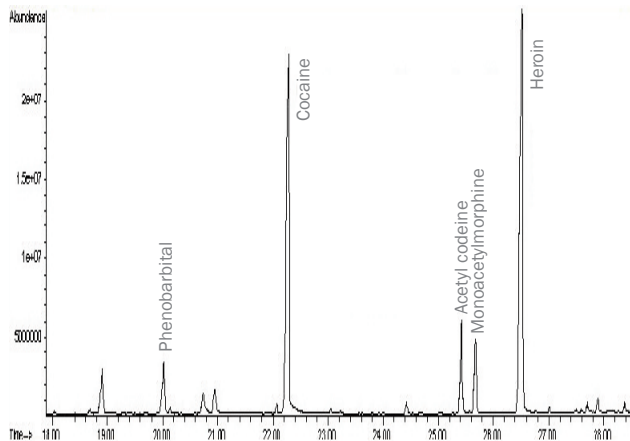
Key forensic applications include:

- Detection and forensic analysis of drugs of abuse
- Arson residue analysis for accelerants
- Detection of trace explosive vapours
- Shotgun propellant
- Forensic analysis of inks, paper and paint

The wide range of TD applications in chemical defence includes monitoring agent destruction, battlefield protection and civil defence (counter-terrorism).



Detecting drugs of abuse in house dust



Direct desorption of house dust, indicating the presence of drugs of abuse such as heroin and cocaine



Background:

Many real-world samples can be tested for traces of illicit drugs using direct thermal desorption/extraction with GC/MS. In this example, gentle direct desorption was used to detect drugs of abuse in house dust collected from a UK crime scene. High levels of heroin and cocaine, plus traces of other drugs, were identified.

Direct TD eliminates sample preparation, making it a simpler technique and reducing the risk of contamination. In addition, direct desorption of a pure drug sample facilitates detailed analysis of impurities, allowing the source of the drug to be traced.

Markes' TD systems offer splitless or multi-split operation to accommodate both trace and high level analytes. Quantitative re-collection of split flows also provides repeat, confirmatory analysis.

Typical analytical conditions:

Sampling: Small amount of house dust placed inside glass tube, secured between two plugs of quartz wool

TD system: UNITY 2 or TD-100

Primary desorption: 10 mins at 150°C

Trap: U-T1HBL-2S (High boilers)

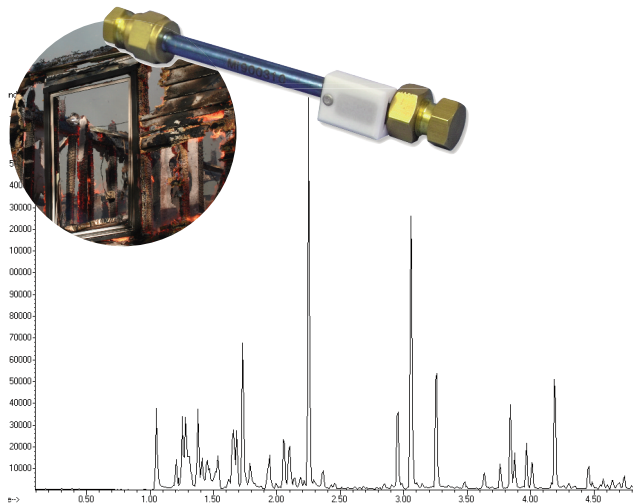
Split: 10 mL/min

Analysis: GC/MS

Reference: TDTS 58 (The application of TD-GC(MS) as a tool in forensic investigations)



Arson residue analysis: Gasoline vapours



Headspace analysis indicates the presence of gasoline accelerant in this case



TubeTAG starter kit (left) & RFID-tagged sorbent tube (top)

Background:

In suspected arson cases, it is often necessary to identify the fuel accelerant that was used to start the fire. A representative sample of debris is typically collected from the scene in a nylon bag and then returned to the laboratory. The bag and contents are gently heated to help release fuel vapours into the headspace of the bag. A measured volume of headspace is then withdrawn through a TD sorbent tube using a gas syringe. The tube is then analysed by TD-GC(MS), allowing the VOC profile of the fire debris headspace to be analysed for fuels/accelerants.

Quantitative re-collection coupled with TubeTAG™ electronic tube labels means that Markes TD systems ensure failsafe tracking of forensic samples through a sequence of repeat analyses.

Typical analytical conditions:

Sampling: ~100 mL of headspace from the sample bag transferred to a Tenax® TA tube.

TD system: UNITY 2 or TD-100

Primary desorption: 5 mins at 280°C

Trap: U-T2GPH-2S (General purpose [hydrophobic])

Split: 30 mL/min

Analysis: GC/MS

Reference: TDS 58 (The application of TD-GC(MS) as a tool in forensic investigations)

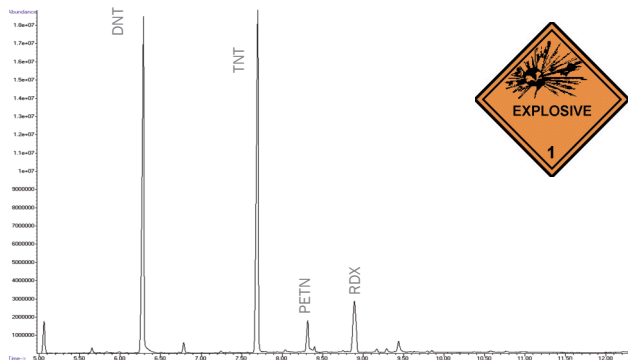
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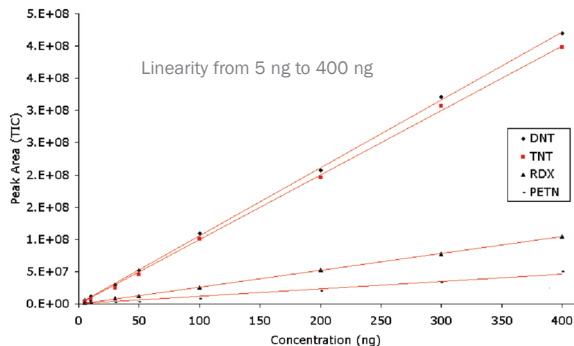
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Detection of trace levels of explosive vapours



Detection of explosives at low ng levels illustrates the inertness of the series 2 UNITY flow path



Background:

Both military and civilian security agencies require equipment on which to monitor air for explosives. Thermal desorption is used for the detection of trace explosive vapours in the air at crime scenes.

The high boiling point and reactive nature of explosives necessitates the use of inert sample tubes and TD instrumentation. The patented heated valve & short, uniformly-heated flow path of Markes TD systems are inert to accommodate these highly active materials.

Typical analytical conditions:

Sampling: Air drawn through Silcosteel® tubes packed with quartz wool and Tenax TA

TD system: UNITY 2 or TD-100

Primary desorption: 3 mins at 180°C followed by 2 mins at 210°C

Trap: U-T10CW-2S (Chemical weapons)

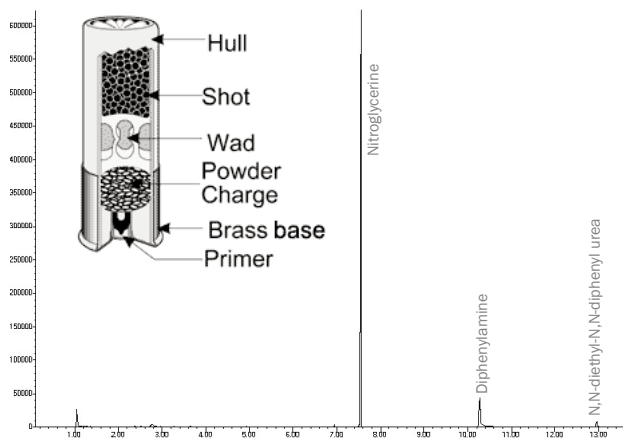
Split: 18 mL/min

Analysis: GC/MS

Reference: TDTS 58 (The application of TD-GC/MS) as a tool in forensic investigations)



Confirmation of shotgun propellant by direct desorption



Direct desorption of fine particles of firearm propellant



Background:

The composition of small particles suspected to be firearm propellant can be analysed by gentle direct desorption inside an empty, inert-coated TD tube. Volatile/semi-volatile components of interest are released into the carrier gas stream during the desorption process while solid residues remain in the sample tube. This allows clean analysis of the propellant without matrix interference, thus optimising detection limits.

Markes TD systems position tubes horizontally to minimise risk of solid samples shifting or falling out of the tube during direct desorption.

Typical analytical conditions:

Sampling: Small pellet of shotgun propellant placed inside an empty TD tube & supported by quartz wool plugs

TD system: UNITY 2 or TD-100

Desorption: Direct desorption at 60°C

Trap: U-T10CW-2S (Chemical weapons)

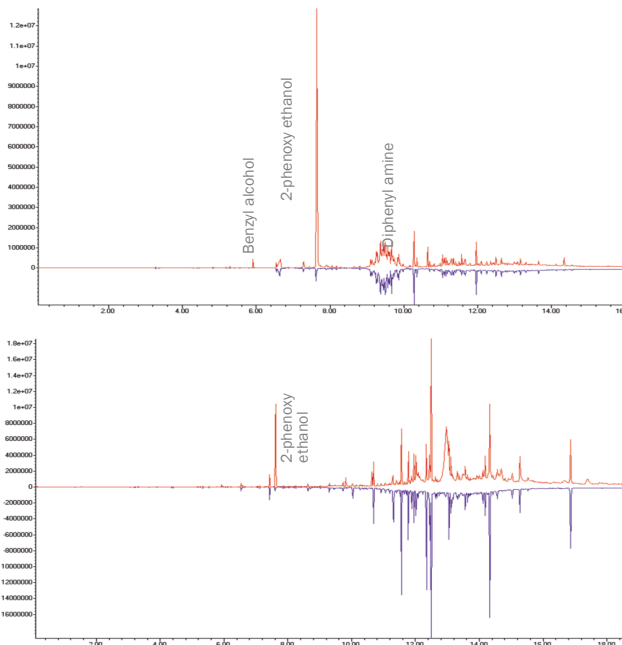
Split: 20 mL/min

Analysis: GC/MS



Reference: TDS 58 (The application of TD-GC/MS) as a tool in forensic investigations)

Forensic analysis of ballpoint pen ink



Paper with ink sample (red) vs blank paper (blue): Fresh (top) and aged (bottom)

Background:

Ink analysis is usually limited to comparisons of the organic dye components. However, 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 of paper samples with and without writing can be used to generate a comprehensive profile or 'fingerprint' of the ink comprising both solvents and dye components. This facilitates detailed forensic analysis, *i.e.* age, source, matches with other documents, *etc.*

The focusing trap of Markes TD systems accommodates multiple sorbents & desorbs in backflush direction to allow simultaneous analysis of components over a wide volatility range, *e.g.* volatile solvents *and* higher boiling ink constituents.

Typical analytical conditions:

Sampling: Direct desorption of paper sample

TD system: UNITY 2 or TD-100

Primary desorption: 15 mins at 100°C

Trap: U-T11GPC-2S (General purpose graphitised carbon)

Split: 20 mL/min

Analysis: GC/MS



Chemical Warfare Agents (CWAs)

Markes thermal desorption technology provides the ultimate pre-concentration and analytical solution for CWA applications. Military and civilian security agencies, as well as government scientists from across the world use Markes TD systems for monitoring:

- CWA stockpile sites
- Personal exposure of military personnel
- Agent destruction facilities
- Key civilian locations (counter-terrorism)

Relevant TD options from Markes International include both automated processing of offline sorbent tube samples and continuous, near-real time (NRT) online monitoring.



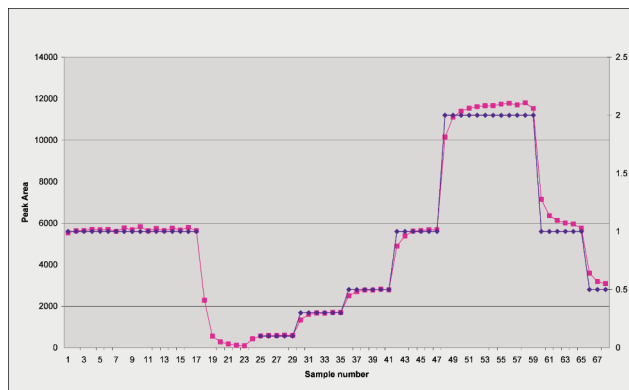
Offline, tube-based sampling is available for 3.5" (89 mm) x 6.4 mm O.D. 'standard' tube dimensions, or for 4.5" Depot Area Air Monitoring System (DAAMS) tubes (either standard [6 mm or 8 mm O.D.] or high flow [10 mm O.D. with 6 mm ends]).

Online, continuous sampling is achieved using the twin trap TT24-7 system. Both traps are electrically-cooled for optimum repeatability and to minimise cycle times. Split and splitless operation is available for maximum flexibility.



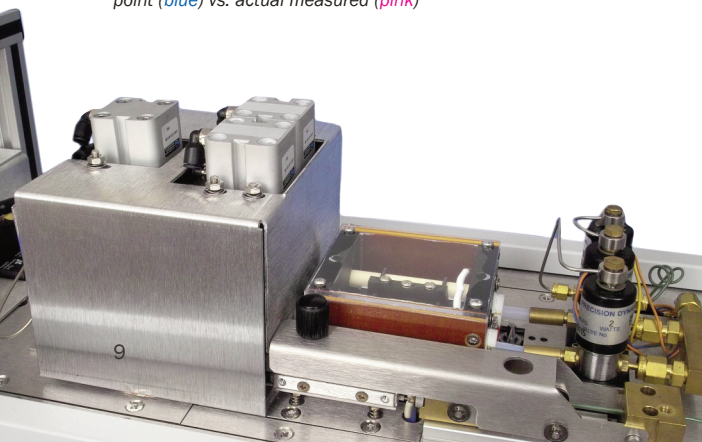
All TD systems described can be installed at-line in CW destruction facilities, in offline laboratories or in mobile labs/first responder vehicles.

TT24-7 performance: NRT analysis



Sample number

Using the TT24-7 for NRT monitoring of variable vapour concentrations of GB (sarin). Measured data tracks expected concentration closely. Nominal set point (blue) vs. actual measured (pink)



Background:

NRT monitoring of CWAs and other toxic chemicals offers early alert and identification in the event of a suspected chemical incident. It is also used for rapid (<15 mins) continuous air monitoring at agent destruction (“demil.”) facilities to protect the health and safety of plant personnel.

Both of these applications require a TD system with dual reciprocating traps such that sampling can continue on one channel, while the other is desorbed and analysed, so there is no down time or “blind spot”.

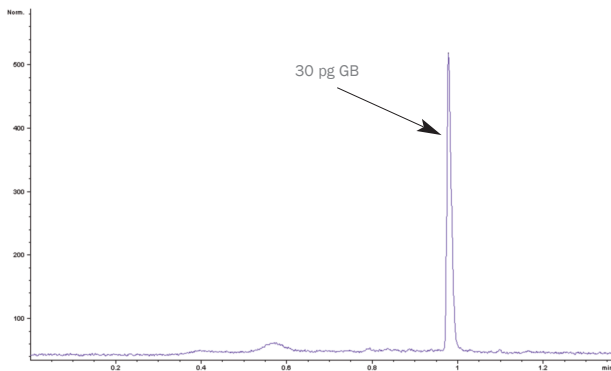
Using the TT24-7, air is sampled at ~500 mL/min for up to 10 minutes followed by rapid desorption and fast GC, MS or GC/MS analysis (*i.e.* <5 minutes). The TT24-7 tracks actual atmospheric concentrations closely with negligible time lag (see opposite).

Reference: TDTS 63 (Using the TT24-7 with twin electrically-cooled focusing traps for continuous monitoring of trace level toxic chemicals [e.g. CWAs] in air)



TT24-7 dual trap

Chemical warfare agents: Near real-time (NRT) online monitoring



Monitoring ultra-trace level CWAs using the TT24-7 NRT system with GC/FPD:
An illustration with GB



Background:

NRT monitoring of extremely toxic compounds such as the G-type nerve agents requires continuous, sensitive sampling and rapid online analysis. The TT24-7 traps desorb very efficiently, producing sharp peaks for optimum sensitivity.

15 minute cycle times can be comfortably achieved using the TT24-7, without compromising ppt-level detection limits.

The multi-mode sampling capability of the TT24-7 (*i.e.* continuous online operation and offline tube desorption) together with versatile split options make it a highly flexible TD system. It is ideally suited for monitoring strategically important areas for trace-level toxic contaminants.

Typical analytical conditions:

Sampling: 600 mL/min for 10 mins (6 L)

TD system: TT24-7

Trap low temp: 25°C

Trap high temp: 290°C for 1 min

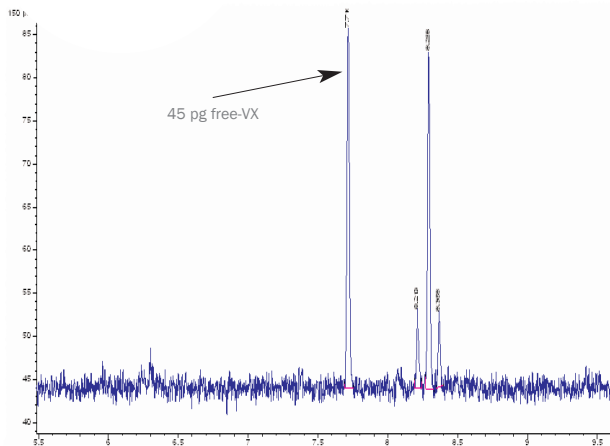
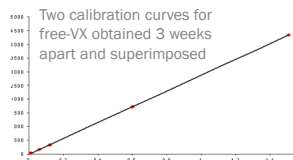
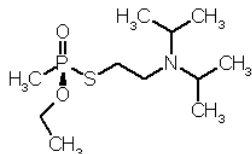
Splitless desorption

Column: 15 m x 0.25 mm I.D. DB1701

Analysis: GC/FPD

Reference: TDTS 63 (Using the TT24-7 with twin electrically-cooled focusing traps for continuous monitoring of trace level toxic chemicals [e.g. CWAs] in air)

Chemical warfare agents: Free-VX



Analysis of 45 pg of free-VX using sorbent tube sampling and offline TD-GC analysis. Reproducible calibration (inset) shows system stability

Background:

The nerve agent VX and its Russian equivalent (RVX) requires analysis of free (*i.e.* underivatised) VX/RVX at sub-ppt levels is very challenging because of the low volatility, reactivity & 'stickiness' of these compounds. VX and RVX are typically monitored by converting the compounds to their more stable G-analogues during sampling. However, the efficiency of the silver fluoride derivitisation process is less than 100% & diminishes over time, producing errors in quantification.

The short, inert flow path of Markes' TD systems makes them ideal for the most challenging CWA applications including analysis of free-VX at trace (sub-ng) levels.

Typical analytical conditions:

Sampling: 500 L air drawn through Silcosteel tube packed with quartz/Tenax TA

Tube desorption: 300°C for 8 mins

Desorption flow: 80 mL/min; no split

Trap: U-TRPCW (Chemical weapons trap)

Trapping temperature: 20°C

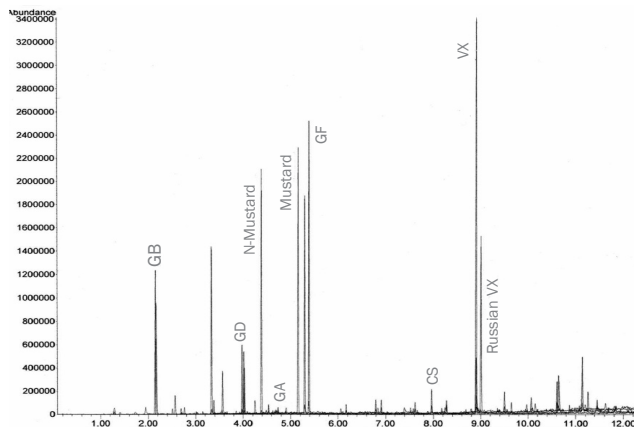
Trap desorption: 300°C for 3 mins; no split

Analysis: GC/MS or GC/FPD

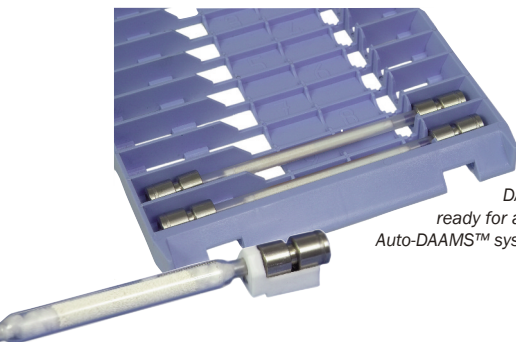
Reference: TDTS 44 (The analysis of free-VX from sorbent tubes at low and sub-nanogram levels)



Monitoring chemical warfare agents using offline sorbent (DAAMS) tubes



Analysis of mixed CW standard (5 ng level) by series 2 UNITY TD with GC/MS



Multiple, high-flow, 4.5" DAAMS tubes capped & ready for analysis on a Markes Auto-DAAMS™ system (capacity 100 tubes)

Background:

The ability to screen for multiple CW agents using a single TD-GC/MS method is extremely useful, having applications in both the military and civil defence arenas.

Where mixed CW material is stockpiled and/or destroyed there is a need to monitor the operational environment, both as a check on the exposure of plant operatives and for confirmatory analysis of online systems. Similarly, for civil defence, monitoring the location of any known or suspected chemical incident is essential to identify the specific agent released, so that correct remedial and decontamination procedures can be actioned.

TubeTAG™, an RFID-based tagging technology which attaches to standard or DAAMS tubes, enables every sorbent tube to be tracked through its operational lifetime. This greatly enhances analytical quality assurance for TD-GC/MS methods.

Typical analytical conditions:

Sampling: Air drawn through Silcosteel or glass CW (DAAMS) tubes

TD system: UNITY 2, TD-100 or Auto-DAAMS

Primary desorption: 8 mins at 300°C

Trap: U-T10CW-2S

Split: 15 mL/min (secondary desorption)

Analysis: GC/MS



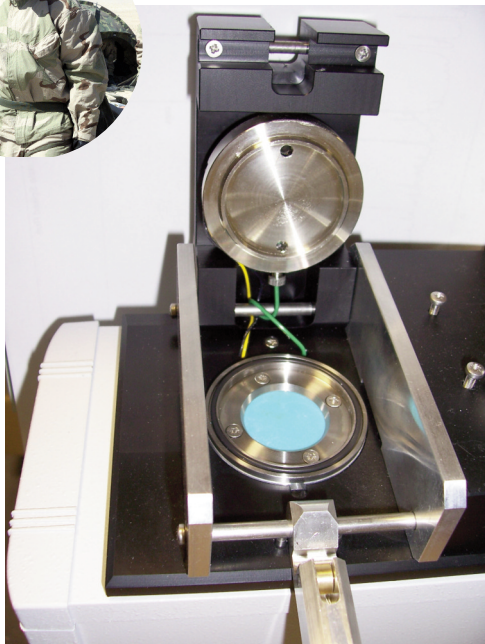
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Micro-Chamber/Thermal Extractor for decontamination & permeation studies



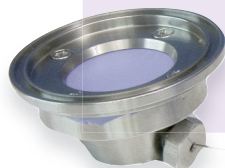
Permeation accessory installed in Markes' Micro-Chamber/Thermal Extractor

Background:

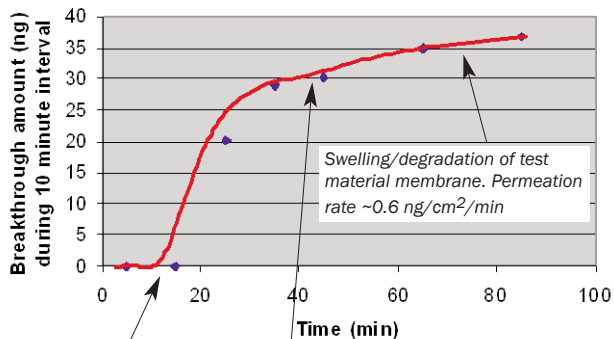
Markes supplies two variants of the μ -CTE™, which comprise either four (individual volume of 114 mL) or six (individual volume of 44 mL) micro-chambers operating up to 250°C and 120°C respectively. These are normally used for evaluating residual contamination and allow 4 or 6 samples to be tested simultaneously.

Once the samples have been introduced, each micro-chamber cell is purged with a controlled flow of inert gas. A TD tube attached to the exhaust of each micro-chamber traps any emitted or released organic vapours.

Studies on CWA permeation through protective fabrics & equipment can be undertaken using the permeation accessory module for the μ -CTE. This simply replaces of the micro-chamber cells. Agent/simulant is introduced to a small well at the base of the permeation accessory (*i.e.* the challenge side) and the purge gas passes over the top of the material. The exhaust is collected onto a series of conditioned sorbent tubes which are replaced at timed intervals & analysed offline. Online monitoring options are also available.

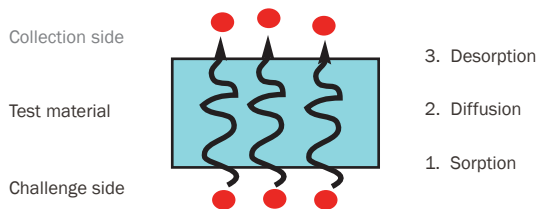


CWAs: Permeation of methyl salicylate through nitrile rubber



Breakthrough time ~15 mins Steady state permeation.
Permeation rate ~0.5 ng/cm²/min

The permeation process



Background:

A typical application for the μ -CTE permeation accessory is monitoring the breakthrough time of CW agents/simulants across a swatch of protective fabric or glove material. In this example, the simulant methyl salicylate has been used, and its permeation through a nitrile rubber glove examined.

In this case the sample tube was replaced every 10 mins and analysed using a Markes' TD system with GC/MS. The characteristics of the material, i.e. breakthrough time and permeation rate, can then be calculated.

Typical analytical conditions:

μ -CTE temperature: 35°C

Gas flow: 50 mL/min

Sampling: Every 10 mins onto a Tenax TA tube

TD system: Series 2 UNITY or TD-100

Primary desorption: 5 mins at 300°C

Trap: Quartz/Tenax TA/Carbopack X

Split: 5:1

Analysis: GC/MS

Reference: TDTS 34 (Monitoring trace-level high boiling compounds (triethylphosphate and methyl salicylate) in air)



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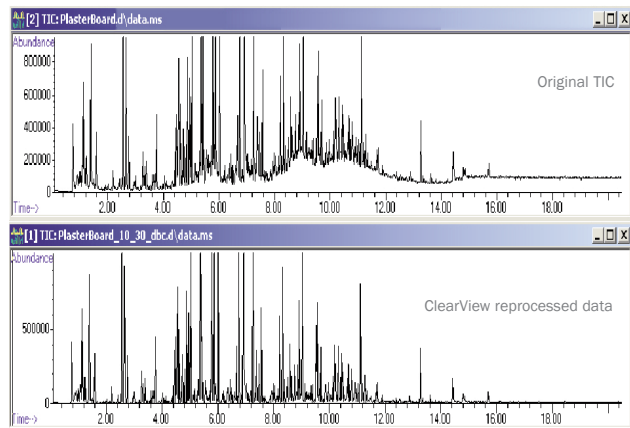
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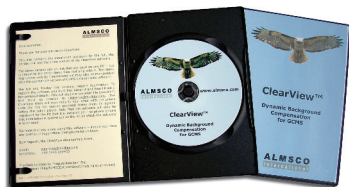
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CWAs: Finding trace target analytes in a complex background

Eliminating analytical background to improve detection of trace-components & minimise false positives.



Analysis of chemical warfare agents and simulants within a complex (diesel) matrix, illustrating the benefits of ClearView reprocessing



Background:

Accurate identification of constituent components can be extremely difficult within complex matrices or chromatograms with a high level of background interference e.g. from column bleed.

ClearView™ GC/MS data reprocessing software works on TIC data files to minimise non-peak-specific background ions. This results in a second data file for each run featuring improved signal-to-noise (sensitivity), more reproducible peak integration and a greatly reduced risk of false positives. ClearView uses a complex mathematical dynamic background compensation (DBC) algorithm to eliminate background ions without impacting peak-specific information.

The example opposite highlights the effectiveness of ClearView. It shows a mixture of CW agents and simulants diluted in diesel oil (1:750) and analysed by GC/MS. The complexity of the diesel oil matrix produces a classic 'hump' profile as shown in the original TIC. The ClearView reprocessed data has the unresolved, non-peak specific ions removed resulting in a flatter baseline and allowing enhanced data analysis.

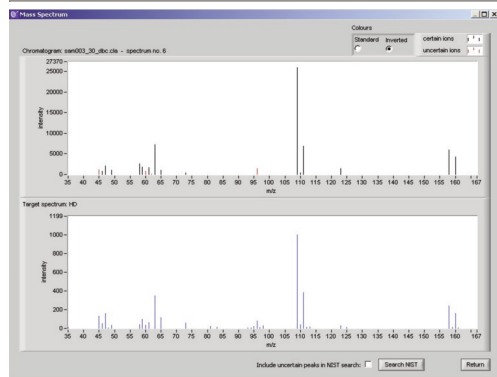
References: TDTS 83 & 85 (Enhancing TD-GC/MS methods for trace compound analysis using ClearView reprocessing software)



Chemical warfare agents: Finding trace target analytes in a complex background



Comparison of the spectrum of the identified peak with that found in the library for HD confirms detection of the CW agent, mustard gas



Background:

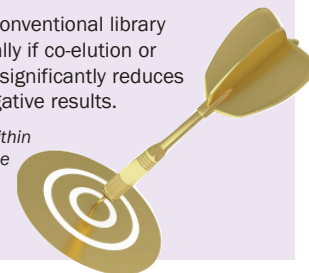
TargetView™ is a software program used to identify target compounds within complex GC/MS data files. TargetView uses a novel combination of spectral deconvolution and chemometrics (principal component analysis [PCA]) to identify target analytes. Target compounds are in collated libraries, which may extend to several hundred substances.

TargetView automatically reprocesses the TIC data file using a series of steps: First, non-peak specific background ions are removed using dynamic background compensation (ClearView). The processed data are then datamined for information on target compounds using spectral deconvolution and PCA. A report listing all identified target analytes, together with the degree of confidence and an indication of the amount of each compound present, is automatically generated.

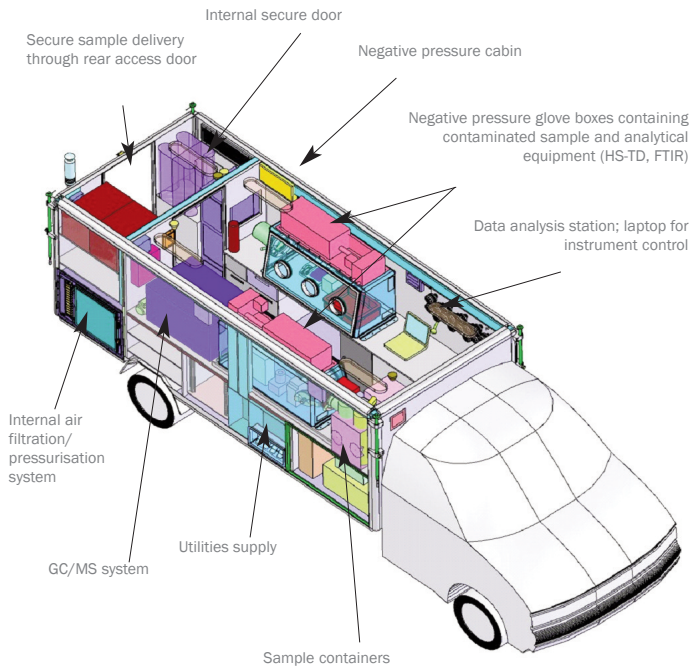
In this example, the CW/diesel mix TIC (described on page 15) was processed by TargetView using a library of CW agents for comparison. The nerve agent HD (mustard gas) is clearly identified from the complex matrix.

Compound identification using conventional library searching is error-prone, especially if co-elution or matrix effects occur. TargetView significantly reduces both false positive and false negative results.

Left: Analysis of CWAs & simulants within a complex diesel matrix illustrating the application of TargetView to identify the trace CWA, mustard (HD)



Transportable analytical solutions



Internal 3D schematic of a mobile laboratory

Background:

There is a growing demand within government and commercial agencies to operate mobile forensic laboratories. The technology within these vehicles must offer rapid and reliable qualitative/quantitative analysis from samples acquired in the field. Mobile labs are currently used by both military and civil defence organisations for deployment at sites of major chemical incidents.

Mobile laboratories may be equipped with both on- & offline TD-GC(MS) technology. This allows air samples to be drawn directly into the analyser if the vehicle can be deployed near enough to the site. Alternatively, air samples collected, for example onto sorbent tubes by suited personnel at the scene, can be taken back to the mobile forensic laboratory for fast turnaround offline analyses.

Markes' TD systems are installed in a wide range of mobile forensic laboratories as they fulfill the following key criteria:

- Small size (footprint/height)
- Ease-of-use, especially for operators wearing protective clothing
- Robustness
- Performance & versatility
- Low gas consumption



The Markes International advantage

Markes is the world leader in analytical thermal desorption and has pioneered important technical innovations such as SecureTD-Q (quantitative sample re-collection for repeat analysis), TubeTAG electronic labels for sorbent tubes and universal (multi-application) heated valve technology.

Markes' leadership in TD now extends to:

- The widest available product portfolio and application range
- Product quality and reliability
- Excellence in technical and applications support

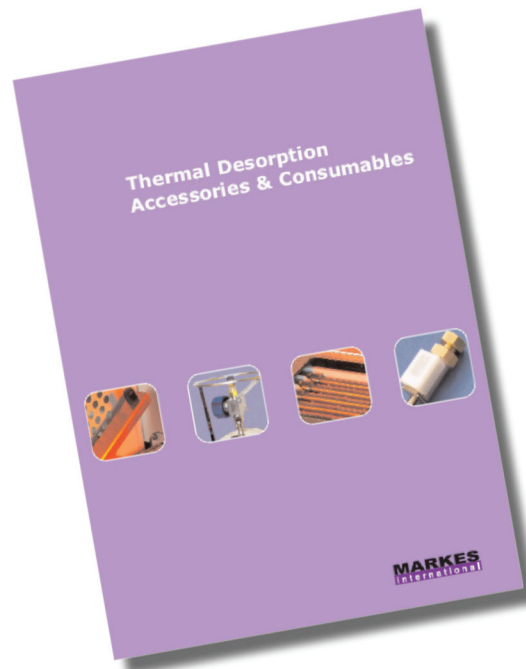
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For more information on Markes comprehensive range of thermal desorption instrumentation and sampling accessories request your free copy of Markes TD Accessories & Consumables catalogue

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