Thermal Desorption: A Practical Applications Guide

III. Defence and Forensic

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Introduction to Markes International Ltd.

Formed in 1997, Markes International Ltd. is one of the world's leading suppliers of thermal desorption (TD) equipment for monitoring trace toxic and odorous chemicals in air, gas and materials. Serving fast growing markets from environmental health and safety to materials testing and from food / flavour / fragrance to defence / forensic, Markes' global customer base includes major industry, government agencies, academia and the service laboratory sector.

Markes has introduced several highly successful brands of TD instruments to the market including: UNITY™ – a universal TD platform for single tubes, the 100-tube ULTRA™ TD autosampler, the Air Server™ interface for canisters and on-line sampling, the **µ**-CTE™ Micro-Chamber / Thermal Extractor for materials testing, the TT24-7™ for continuous on-line monitoring and the TC-20™ multi-tube conditioner.

Markes also supplies a wide range of sampling accessories and consumables for all TD application areas.

What is TD?

Since the early 1980s, thermal desorption has provided the ultimate versatile sample introduction technology for GC / GC-MS. It combines 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 air monitoring and occupational health & safety. Relevant standard methods include: ISO/EN 16017, EN 14662 (parts 1 & 4), ASTM D6196, US EPA TO-17 and NIOSH 2549. Related applications include monitoring chemical warfare agents (CWA) in demilitarisation / destruction facilities & civilian locations (counter-terrorism).

TD is also routinely used for monitoring volatile and semi-volatile organic compounds (S)VOCs in products and materials. Examples include residual solvents in packaging & pharmaceuticals, materials emissions testing and food / flavour / fragrance profiling.

This publication presents several real world applications for thermal desorption in forensic science and monitoring chemical warfare agents (CWA). Accompanying publications cover the application areas of:

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

Forensic Applications for TD

Thermal desorption is extensively used for forensic science. Key applications include:

- Detection of drugs of abuse
- Arson residue analysis for accelerants
- Forensic analysis of drugs
- Detection of trace explosive vapours
- Shotgun propellant
- Forensic analysis of inks

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Chemical Warfare Agents (CWA)

Markes thermal desorption technology provides the ultimate pre-concentration and analytical solution for CWA applications. Military & civilian security agencies and government scientists from across the world are working with Markes TD systems for monitoring:

- CW 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 off-line sorbent tube samples (UltrA-UNITY) and continuous near-real time (NRT) detection (TT24-7). Systems can be installed at-line in destruction facilities, in off-line laboratories or in mobile labs for deployment to incident sites. Both on- and off-line TD systems offer rugged operation, quantitative recovery, optimum resolution / speciation (to minimise false positives) and lowest possible detection limits (ng/m^3 and below).

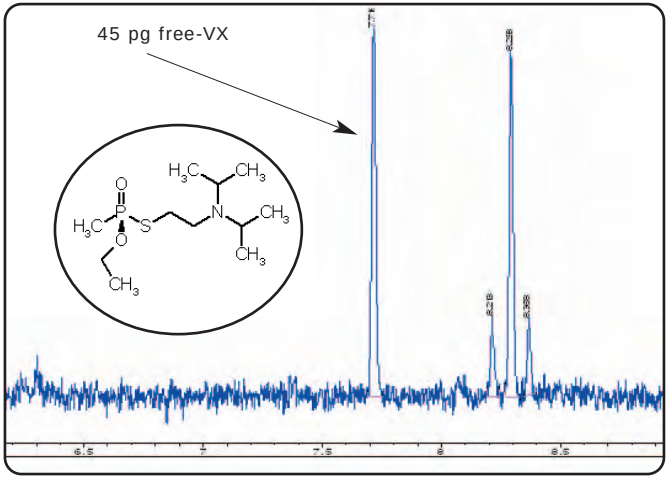
TT24-7

The transportable, near-real time TT24-7 TD system enables continuous on-line and at-line sampling and pre-concentration of airborne chemical agents. The enriched vapour sample is subsequently analysed by GC-(MS) or direct MS technology.

Continuous monitoring is essential to protect security agency personnel and the general public from potential exposure to highly toxic chemical agents.

The TT24-7 incorporates two, electrically-cooled (Peltier) large-capacity traps which are sampled sequentially at high flow rates (~ 500 ml/min), allowing efficient pre-concentration of trace-level agent in the shortest possible time (*i.e.* providing near real-time analysis).

Chemical warfare agents: Free-VX



Analysis of 45 pg of free-VX using sorbent tube sampling and off-line TD-GC analysis

Concentration: Sub-ppt vapour concentrations and pg levels on tube

Background:

The nerve agent VX and the Russian equivalent (RVX) (ethyl S-2-diisopropyl aminoethylmethyl phosphonothioate) are some of the most toxic CW compounds in existence today. The analysis of free (*i.e.* underivitised) VX/RVX at sub ppt levels is very challenging because of the low volatility, "stickiness" and high reactivity of these compounds. VX and RVX are typically monitored using off-line sorbent tubes sampling large (>500 L) air volumes with subsequent analysis by thermal desorption GC/FPD or GC/MS. However, the TD system used must be highly inert and uniformly heated. Markes UltrA-UNITY is ideal for the analysis of underivitised VX/RVX at trace levels.

Typical TD-GC conditions:

Sampling: Silcosteel™ CW tubes

TD system: UltrA-UNITY

Primary desorption: 8 mins at 300°C

Trap: Chemical weapons trap

Split: Splitless Analysis: GC-FPD

Reference: TDTS44 The analysis of free-VX from sorbent tubes at low and sub-nanogram levels

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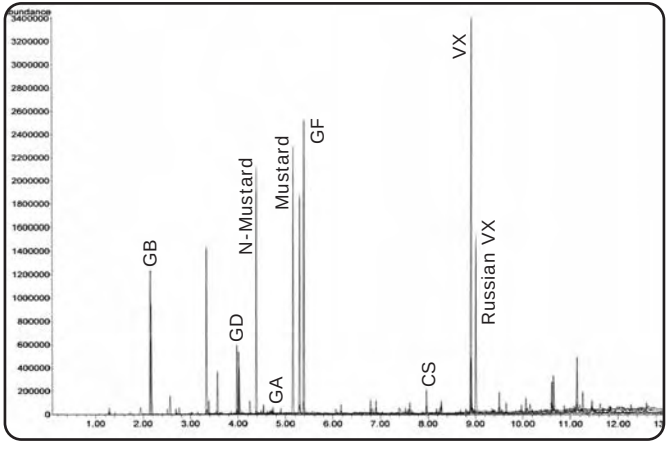
Chemical warfare agents: DAAMS tubes



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

Typical analytes:

GB, GD, GA, GF, CS, VX, RVX, mustard, N-mustard

Concentration: ppt to ppb levels (sub/low ng levels on tube)

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 defense 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 occupational health of plant operatives and for confirmatory analysis (DAAMS - Depot Air Analysis Monitoring Systems) of on-line 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.

Typical TD-GC conditions:

Sampling: Silcosteel CW tubes - manual pumps or automated sequential tube sampling (MTS-32™ - picture inset)

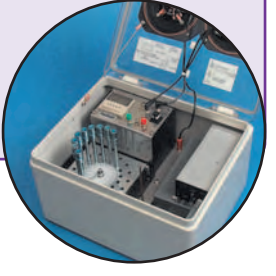
TD system: ULTRA-UNITY

Primary desorption: 8 mins at 300°C

Trap: Chemical weapons trap

Split: 15 ml/min (secondary desorption)

Analysis: GC-MS (SCAN)



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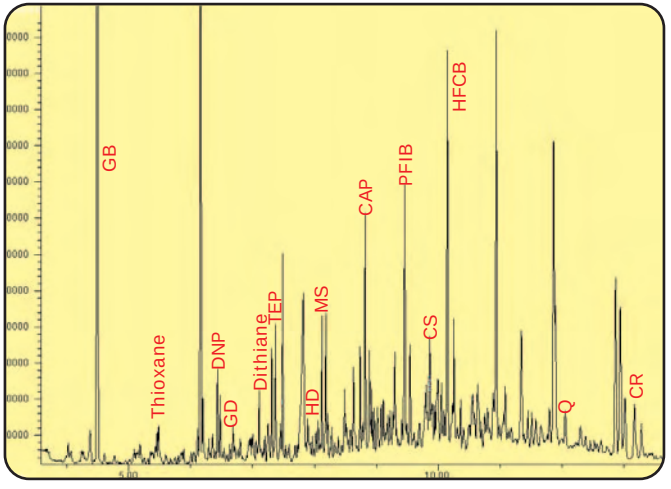
Chemical warfare agents: Trace target analytes in a complex background



CW test mix diluted to 2.5 ppm with diesel fuel and analysed with spectral deconvolution software

Background:

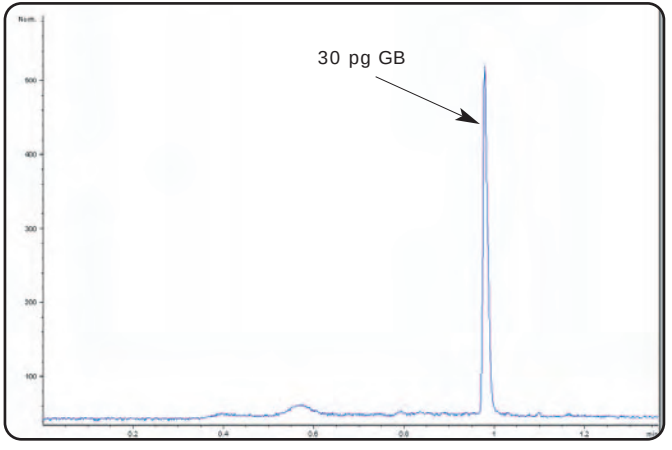
Analysing complex real air samples for the presence of trace CWA material can be very demanding as the background levels of other organic vapours (hydrocarbons, solvents, *etc.*) can be high relative to that of the target compunds. The risk is that this can cause high incidences of "false-positive" results which is problematical and potentially dangerous; for example, if it triggers large scale evacuations of public buildings. MS detection reduces this risk as it provides 3D data, including spectral information, for each compound.

In a recent development, retention time and spectral data can be further processed by a mathematical procedure (deconvolution) using software such as AMDIS which is provided by NIST in the USA. This identifies individual components in co-eluting / overlapping peaks and provides much greater confidence in the correct identification of trace target compounds thus eliminating false positives.

Typical TD-GC conditions:

As the previous page

Chemical warfare agents: NRT monitoring



Monitoring CW Agents using the TT24-7 NRT System with GC-FPD – An illustration with GB

Background:

Near Real Time (NRT) monitoring of extremely toxic compounds such as the G type nerve agents, requires continuous sampling with no time 'blind' spots and rapid on-line analysis. At trace levels, TT24-7 focusing traps desorb super-efficiently producing sharp peaks (opposite) for optimum sensitivity.

The NRT mode of operation is an absolute requirement for CW monitoring at military-stockpile sites or demilitarisation / destruction facilities and can also be used for continuous monitoring of civilian locations in case of terrorist attack.

Typical TD-GC conditions:

Sampling: Continuous monitoring

Sampling time / flow: 10 mins at 600 ml/min

TD system: TT24-7

Traps: Chemical weapons traps

Analysis: GC-FPD

Reference: TDTS63 Using the TT24-7 with twin electrically-cooled focusing traps for continous monitoring of trace level toxic chemicals (*e.g.* CW agents) in air

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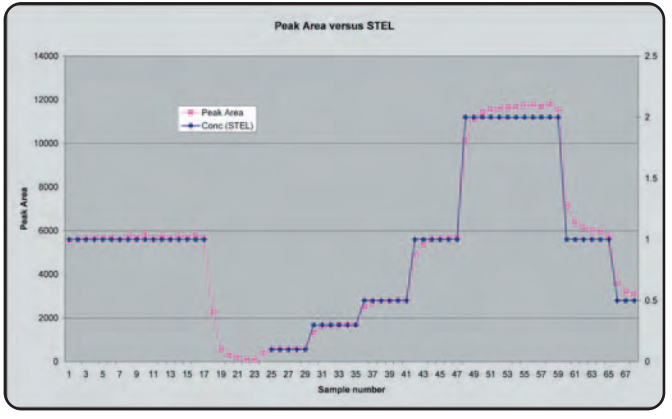
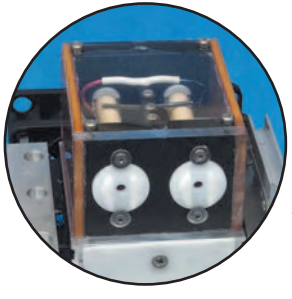
TT24-7 performance



TT24-7 data tracks atmospheric concentration exactly - Nominal set point (blue), actual measured (pink)



TT24-7 dual trap

Background:

NRT monitoring of chemical warfare agents and other toxic chemicals offers early alert and compound identification in the event of a chemical incident. Organisations, such as the Centre for Disease Control (CDC) in the USA, have defined parameters for 'NRT' monitoring including completion of the entire sampling and analytical process within 15 mins plus continuous sampling of air with no 'blind' spots. This requires dual reciprocating sampling traps such that sampling can continue on one channel, while the other is desorbed and analysed. Air is drawn into the system using either positive sample pressure or by vacuum pump at electronic mass flow controlled rates of ~500 ml/min for up to 10 mins. Sampling of each channel is followed by rapid desorption and fast GC, MS or GCMS analysis (*i.e.* < 5 minutes). The TT24-7 TD tracks actual atmospheric concentrations closely with negligible time lag (see opposite).

Reference: TDTS63 Using the TT24-7 with twin electrically-cooled focusing traps for continous monitoring of trace level toxic chemicals (*e.g.* CW agents) in air

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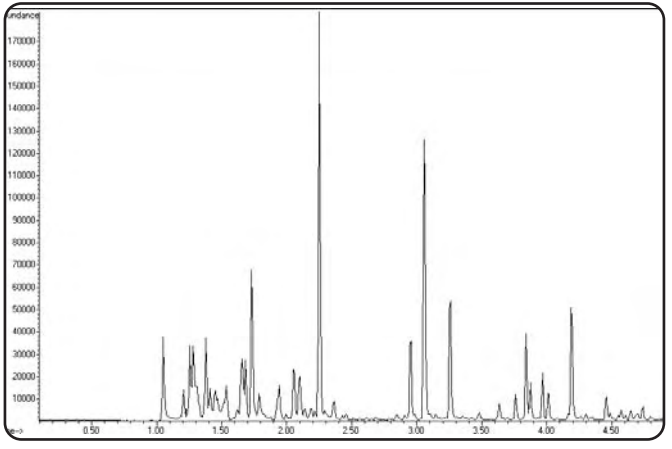
Arson residue analysis: Gasoline vapours



Sample of headspace from cloth soaked in petrol.

Typical analytes:
Hydrocarbons

Concentration: ppb to % levels

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 using a nylon bag, and then returned to the laboratory. The bag and contents are first heated (gently) to help release fuel vapours into the headspace of the bag. A small hole is then made in the bag allowing a measured volume of headspace to be withdrawn using a gas syringe and transferred into a thermal desorption tube for pre-concentration. The tube is then analysed by TD-GC-(MS) allowing the VOC profile of the fire debris headspace to be analysed for fuels / accelerants.

Typical TD-GC conditions:

Sampling: ~100 ml of headspace transferred to Tenax tube.

TD system: ULTRA-UNITY

Primary desorption: 5 mins at 280°C

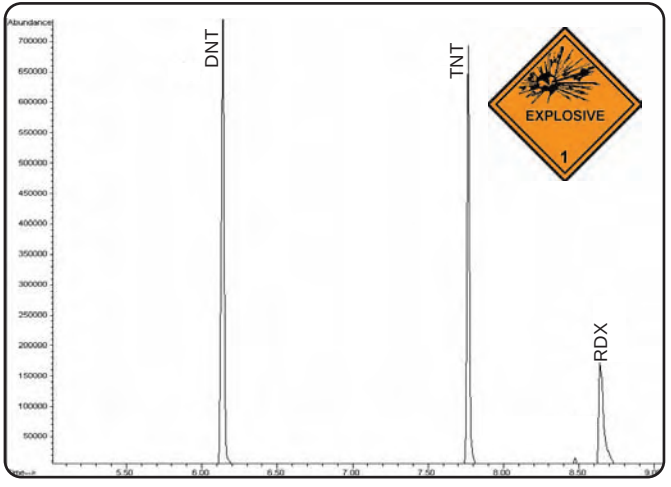
Trap: General purpose hydrophobic

Split: 30 ml/min

Analysis: GC-MS

Reference: TDTS58 The application of TD-GC(-MS) as a tool in forensic investigations

Explosive vapours



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

Typical analytes:

DNT, TNT, RDX

Concentration: Typically ppt to ppb levels of vapours in air

Background:

Both military and civilian security agencies need to monitor for explosives. Thermal desorption is used for monitoring trace explosive vapours in air at crime scenes, from possible arms storage locations and from vehicles suspected of being used to transport bombs or other weapons.

The high boiling point and reactive nature of explosives necessitates the use of inert sample tubes and sorbent materials.

Typical TD-GC conditions:

Sampling: Silcosteel tubes packed with quartz wool and Tenax TA™

TD system: UltrA-UNITY

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

Trap: CW trap

Split: 18 ml/min

Analysis: GC-MS

Reference: TDTS58 The application of TD-GC(-MS) as a tool in forensic investigations

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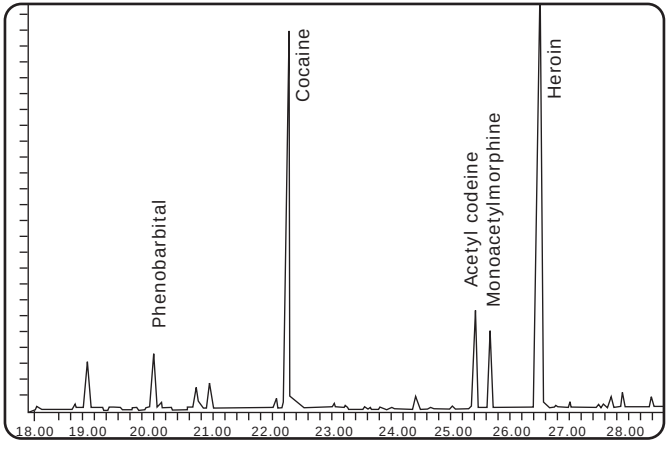
Direct desorption for detecting drugs of abuse in house dust



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

Typical analytes:

- Phenobarbital
- Cocaine
- Acetyl codeine
- Monoacetylmorphine
- Heroin

Concentration: ppb to %

Background:

Many real-world samples can be tested for proscribed 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 so reducing the risk of contamination. This technique is suitable for detection and identification rather than absolute quantification of the drugs. Direct desorption of a pure drug sample would also facilitate detailed analysis of impurities allowing the source of the drug to be traced.

Typical TD-GC conditions:

Sampling: Small amount of dust placed inside glass tube, secured between 2 plugs of quartz wool

Primary desorption: 10 mins at 150°C

Trap: High boilers trap

Split: 10 ml/min

Analysis: GC-MS

Reference: TDTS58 The application of TD-GC(-MS) as a tool in forensic investigations

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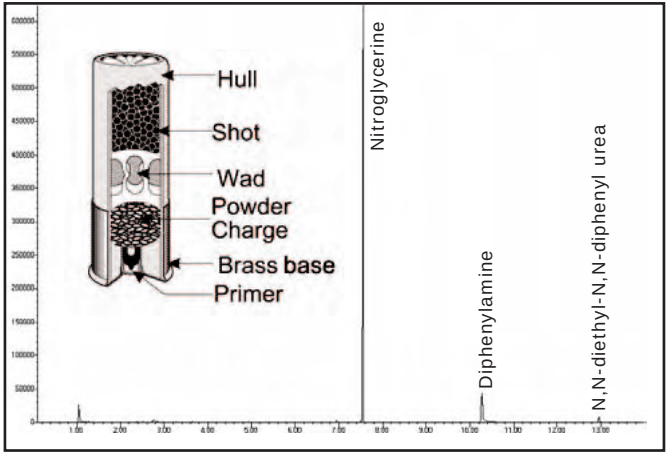
Shotgun propellant



Direct desorption of fine particles of firearm propellant

Analytes:

N,N-diethyl-N,N-diphenyl urea, diphenylamine, nitroglycerine

Concentration: ppm to % in particles

Background:

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

Typical TD-GC conditions:

Sampling: Small pellet of shotgun propellant placed inside an empty thermal desorption tube

Primary desorption: Direct desorption at 60°C

Trap: CW trap

Split: 20 ml/min

Analysis: GC-MS

Reference: TDTS58 The application of TD-GC-(MS) as a tool in forensic investigations

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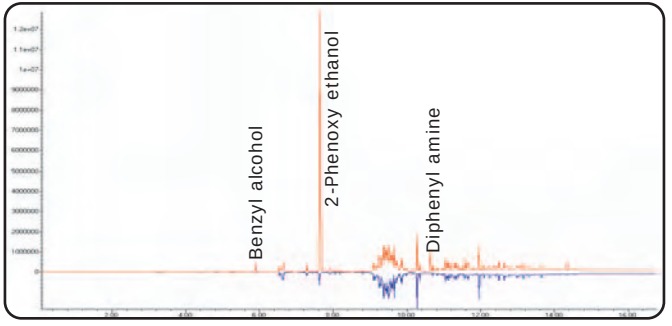
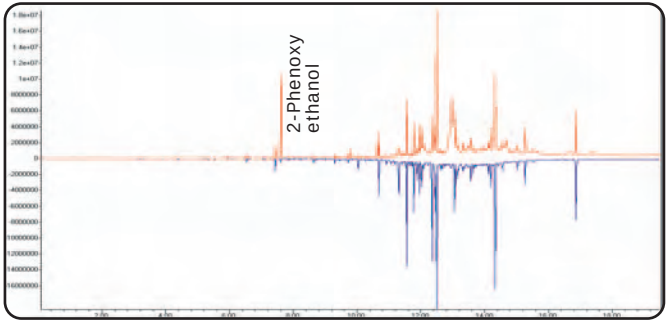
Forensic analysis of ballpoint pen ink





Black ink: fresh (top) and aged (bottom). The blue chromatograms are from blank paper

Analytes:
2-Phenoxy ethanol, benzyl alcohol, diphenylamine

Background:

In general, inks are composed of dyes in solvents and other materials that impart selected characteristics. Ink analysis is usually limited to comparisons of the organic dye components. However, this does not allow inks with similar formulations to be distinguished nor does it allow forensic scientists 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 / “fingerprint” of the ink comprising both solvents and dye components. This facilitates detailed forensic analysis of the ink used - age, source, matches with other documents, *etc.*

Typical TD-GC conditions:

Sampling: Direct desorption

TD System: UNITY

Primary desorption: 15 mins at 100°C

Trap: General purpose - graphitised carbon

Split: 20 ml/min

Analysis: GC-MS

The Markes International advantage

- Markes is the market leader in TD
- Unparalleled reputation for product quality and reliability
- Excellence in technical and applications support
- For further information on Markes comprehensive range of instruments, sampling accessories and consumables please use one of the contact numbers / email address below or browse the web site

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