TDTS 12

Analytical thermal desorption: History, technical aspects and application range

Summary

This Application Note, which replaces earlier editions of TDTS 11 and 12, summarises the history of thermal desorption (TD), and describes the technological advances that have led to it becoming the foremost sample introduction methodology for GC(MS).
A comprehensive overview of the applications of TD is given, followed by discussion of MS technologies that enhance its power and application range.

For more information, we recommend consulting Markes' Application Notes, which are referenced in the text. Of particular relevance are TDTS 5–7, 19–22, 26, 27 and 60. In addition, Markes' Applications Guides provide useful overviews of real-life solutions in the four key TD applications area.

Contents

1 Introduction

Thermal desorption (TD) is the most powerful and versatile of all gas chromatography (GC) sample introduction technologies. It is readily automated and serves to combine sampling/sample preparation, selective concentration and efficient GC injection in one fully-automated procedure. It is compatible with sampling and analysis of gas- (vapour-) phase organics trapped on sorbent media and allows concentration factors up to 10^6 to be comfortably achieved. It can also be used for direct gas extraction of volatiles and semi-volatiles from solid or liquid matrices.

Thermal desorption is generally used with GC, either on its own or in conjunction with a mass spectrometer (GC/MS). However, it can also be used with alternative vapour-phase analytical options including process mass spectrometers and sensors ('e-nose' technology). TD also provides the basis for many other GC sampling procedures – most notably purge-and-trap, sorptive-extraction, some forms of large-volume injection and headspace-trap.

The development of thermal desorption was fundamentally driven by the limitations and complexity of conventional GC sample preparation methods – liquid extraction, steam distillation, *etc.* It held out the promise of an alternative high-sensitivity/solvent-free gas extraction process that could be fully automated.

1.1 The principles of thermal desorption (TD)

In its simplest form, TD is a straightforward extension of gas chromatography. It involves heating sample materials or sorbents in a flow of inert 'carrier' gas, so that retained organic volatiles and semi-volatiles are extracted ('desorb') from the matrix and are transferred into the GC column in the carrier gas stream. As in GC, key method parameters include temperature, carrier gas flow rate, desorption time and sorbent (stationary phase) selection.

However, as soon as you move away from the simplest form of thermal desorption, the power and potential of the technique expands rapidly. It is possible, for example, to configure TD technology in multiple stages so that analytes are repeatedly extracted/desorbed into smaller and smaller volumes of gas, thus concentrating the compounds of interest and enhancing sensitivity/detection limits. Figure 1 illustrates a relatively conventional monitoring procedure whereby 100 L of air or sample gas are pumped through a sorbent sampling tube over a period of (say) 12 hours. Retained vapours are then desorbed in approximately 100 mL of carrier gas and subsequently refocused on a smaller ('cold') sorbent trap. Depending on trap design, this in turn can be quantitatively desorbed, with the analytes eluting in as little as 100 µL of gas, thus providing a million-fold enhancement in vapour concentration overall.

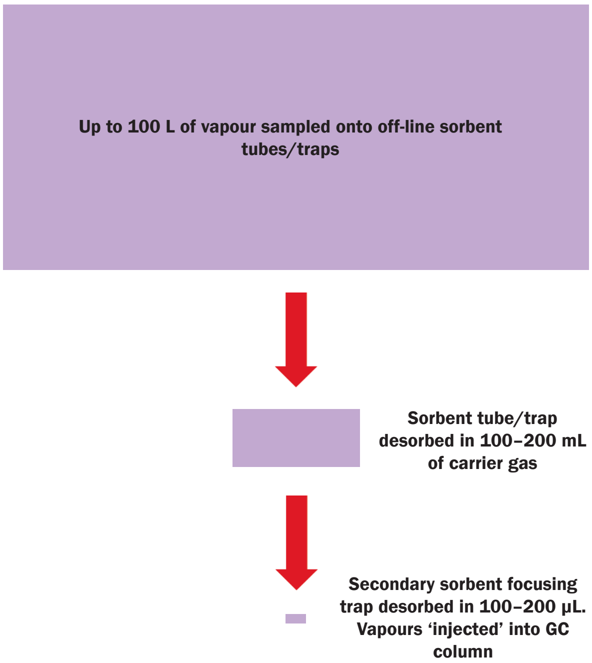


Figure 1: An illustration of the concentration potential of multi-stage thermal desorption.

Another advantage of thermal desorption is that it is often possible to quantitatively retain target compounds during one or more of the trapping stages while unwanted interferents, such as water and/or permanent gases, are selectively purged to vent. This allows compounds of interest to be transferred/injected into the GC analytical column with minimal interference.

1.2 Comparing TD with solvent extraction

The first and most obvious advantage of thermal desorption compared to solvent extraction is that it is possible to transfer 100% of retained analytes to the analytical system, whereas solvent extraction generally involves microlitre injections of millilitre extracts. This means that TD typically offers at least a 1000-fold enhancement in sensitivity compared to equivalent solvent extraction procedures for volatile organic compounds (VOCs). Other significant advantages are listed below. They include:

Increased extraction/desorption efficiency: Assuming appropriate selection of sampling and analytical conditions (sorbent, temperature and flow), it is usually very straightforward for TD methods to exceed 95% desorption efficiency[1] (in other words, for retained compounds to be stripped completely from the sorbent tube or trap and transferred quantitatively to the analytical system). This is because TD is a dynamic process, with gas continually purging compounds away from the sorbent or sample matrix as soon as they are released into the vapour phase by the rising temperature. In contrast, typical solvent extraction procedures are static, with analytes partitioning between the sorbent, solvent and vapour (headspace) phases. This limits desorption efficiency. Standard methods for solvent extraction therefore typically specify only 75% recovery[2].

Reproducible extraction efficiency: Static partitioning systems such as most solvent extraction procedures are also subject to increased variability of analyte recovery depending on the nature of the compounds of interest and the presence of interferences. The desorption efficiency of methods specifying charcoal sample tubes with CS_2 extraction for example, have been shown to fall as low as 20 or 30% for polar compounds in the presence of water[3]. This uncertainty is particularly problematic for air monitoring methods or measurements of industrial VOC emissions, as the analyst may not be aware of field/sample conditions such as high water content; moreover, poor recovery may lead to significant under-reporting.

Automation: Thermal desorption is inherently less labour-intensive than solvent extraction, requiring little or nothing in the way of manual sample preparation.

Reduced interference: Solvent interference can be a major consideration for liquid extraction methods. One of the reasons CS_2 was originally selected as the preferred solvent for many charcoal-based air sampling methods was that it gives little or no signal on a GC flame ionisation detector. However, nowadays, with the preference for MS detection, this advantage no longer holds. Common concerns include masking of peaks of interest, signal quenching (for components co-eluting with the solvent) and baseline disturbances. All these solvent interference issues make peak integration difficult and more prone to error.

Selective purging: Depending on the volatility of the compounds of interest, thermal desorption usually facilitates selective purging of sample interferences such as water or ethanol prior to analysis. Applications as diverse as monitoring VOC emissions from paint and characterising the aroma of whisky benefit from the selection of sorbents that quantitatively retain compounds of interest while allowing water, and in the latter case, ethanol, to purge to vent. Selectivity is usually only possible for solvent extraction procedures when there is a very significant volatility difference between the compounds of interest and the interferences.

Health & safety: Many common extraction solvents, such as CS_2, are toxic, odorous and present a significant potential health and safety hazard. Thermal desorption is inherently safer in this respect. TD–GC(MS) systems can generally be installed without ventilation equipment or fumehoods, provided all outlet points, including sample split lines, are configured with appropriate filters. In TD operation, wet chemistry procedures are confined to the preparation of liquid standards for spiking tubes when gas standards aren't available – see Section 6.

Reusable samplers and lower cost per analysis: Vapour samplers designed for solvent extraction are invariably one-shot only. For example, the charcoal tubes traditionally used for industrial hygiene monitoring comprise glass tubes with drawn/sealed ends that are broken during sampling and analysis. Pre-packed TD tubes (glass, stainless or coated steel) are typically about 10 times more expensive than charcoal tubes, but they can then be re-used at least 100 times. They are also automatically cleaned by the TD process. This generally reduces the sampling costs of TD methods to roughly a tenth of equivalent solvent extraction procedures.

2 The evolution of thermal desorption: Essential functions

The history of TD can be traced back to the mid-1970s. Scientists struggling with the limitations of conventional GC sample preparation methods began to experiment by packing standard GC injector liners with sorbent material. These sorbent-packed injector liners were used to sample a fixed volume of air or gas and were then dropped quickly into the GC inlet for desorption and transfer of analytes to the analytical column. The limitations of these primitive adaptations of conventional GC injectors are many and obvious (air ingress, volatile losses, variability, contamination from the outer surfaces of the liner, single stage,...), but the fact that it was attempted at all demonstrated the need for this technology.

Another early incarnation of thermal desorption was in purge-and-trap technology. The US Environmental Protection Agency (EPA) first developed purge-and-trap/GC-based test methods to measure volatile organic compounds in drinking water in the late 1970s in response to a number of serious environmental incidents. The most infamous of these related to Love Canal – an area of housing in Niagara City, New York, that had been developed on land used by the chemical industry in the 1940s and 1950s. An unusually high incidence of serious birth defects and other human health effects was ultimately linked to chemical waste that had been seeping into the drinking water supply underground. The 500-series purge-and trap methods produced by EPA at that time relied on volatiles being sparged from the water in a stream of pure nitrogen and trapped on a sorbent tube/trap. This was subsequently heated in a reverse stream of carrier gas to thermally desorb the organic chemicals of interest and transfer them to the GC analytical system in a standard TD-type procedure.

The first early commercial configurations of dedicated general-purpose thermal desorption technology were invariably based on desorption of a single tube or badge. The 'Coker cooker', designed by Environmental Monitoring Systems Ltd (UK) in the mid-1970s[4], was a popular example and accommodated samples or sorbents contained in ¼″ o.d. tubes. These early desorbers were very primitive by modern standards, typically offering only single-stage desorption and without any of the functions that would now be regarded as standard such as leak testing or pre-purging of air from the tube. However, within specific constraints (*e.g.* packed column only, stable compounds only, narrow concentration-and volatility ranges), they operated sufficiently well for routine applications such as workplace air monitoring in the petrochemical industry[4].

The most important early technical breakthroughs came from 'Working Group 5' (WG5) of the UK Health and Safety Executive's (HSE) 'Committee on Analytical Requirements' (CAR). HSE/CAR WG5 began with a chance meeting at a conference on workplace air monitoring in the late 1970s. Scientists including Richard Brown (then of HSE), Kevin Saunders (then of BP) and Jack Charlton & Brian Miller (then of ICI) found that they had a common interest in both diffusive (passive) sampling and thermal desorption. This group believed diffusive sampling would allow quantitative air monitoring without the complications and expense of personal sampling pumps[5]. At a series of meetings over the next couple of years, various other experts joined the team including Peter Hollingdale-Smith of Porton Down[6], David Coker of Exxon, and Nico van den Hoed of Shell. Between them WG5 evaluated the various available forms of diffusive monitor, and decided to standardise on axial samplers based on the ¼″ o.d. sorbent tubes used in the 'Coker cooker'. These were a practical size and were found to be least susceptible to air speed limitations[5,7]. They were also suitable for both pumped and passive sampling.

Thermal desorption was seen as an enabling technology for passive sampling because it offered approximately 1000 times better sensitivity than solvent extraction, which was more than enough to offset the slow sampling (uptake) rate of axial-form diffusive samplers (typically around 1 mL/min). WG5 also realised that TD overcame the toxicity and variability issues inherent in the charcoal/CS_2 extraction methods in use at that time. Once they had fixed on a sampler design, WG5 then set about outlining a specification for the world's first automated thermal desorber. The TD functionality requirements that came out of these discussions in the late 1970s are still relevant today. They include two-stage TD operation, the necessity of certain pre-desorption checks (stringent leak testing, pre-purging of air to vent) and robust automation.

2.1 One- or two-stage desorption

With standard sampling tubes containing 100 mg to 1 g sorbent (depending on density), WG5 realised that single-stage thermal desorption (Figure 2) would be inherently limited. Tens of millilitres of gas are required for complete extraction of a standard tube, which rules out capillary chromatography, and compromises resolution and analytical sensitivity even with packed columns.

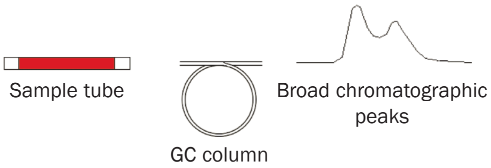


Figure 2: Single-stage thermal desorption.

Initial attempts to address this issue involved some sort of capillary cryofocusing device (either on-column or in cooled GC inlets such as 'programmable temperature vaporisers' – PTVs) positioned inbetween the sorbent tube and analytical system (Figure 3). Analytes desorbed from the primary sorbent tube were refocused/concentrated in a short length of cryogen-cooled narrow-bore tubing (typically 1 mm internal diameter or less). Heat was then applied to release the compounds into the analytical system in a small volume of carrier gas.

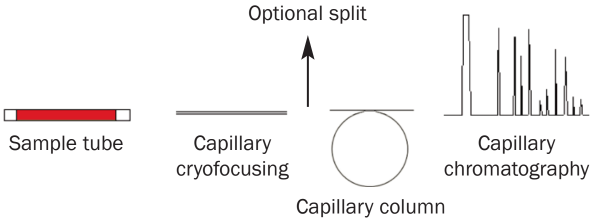


Figure 3: Two-stage thermal desorption incorporating capillary cryofocusing.

Early TD configurations which harnessed capillary cryofocusing included the Chrompack CTC unit. The CTC produced excellent peak shape even under splitless conditions, and it therefore offered exceptional sensitivity. However, the limitations of capillary cryofocusing quickly became apparent. Key concerns included ice blockage, incomplete retention of very volatile compounds[8], loss of high-boilers due to aerosol formation[9] and high running costs (systems consumed up to 6 L of liquid nitrogen per hour in operation[10]). More importantly, because capillary-cryofocusing devices were connected directly to the GC column, it made it difficult to implement essential pre-desorption checks such as leak testing.

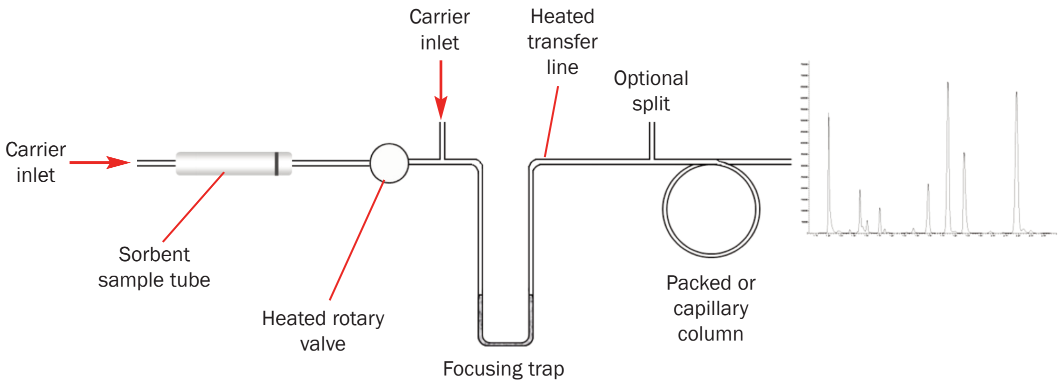


Figure 4: Two-stage thermal desorption incorporating sorbent focusing trap and heated valve.

Ultimately, Peter Higham (then of PerkinElmer) designed the ATD 50 unit using the WG5 specification and addressed all these issues. Introduced in 1981, the ATD 50 incorporated a small, Peltier- (electrically-) cooled, sorbent-packed focusing trap (Figure 4). The combination of sorbent packing and modest focusing temperatures (minimum: –30 °C) was a real breakthrough. It offered quantitative retention of a wide range of compounds including very volatile species, such as the lightest gasoline components[11], SF_6 and N_2O [12], without the cost and inconvenience of liquid cryogen. The steel focusing trap also had a wide enough internal diameter (~3 mm) to prevent ice plug formation, yet it could be heated at rates approaching 60 °C/s to allow rapid (capillary-compatible) desorption/injection with minimal split and good sensitivity. Another breakthrough was the inclusion of a rotary valve in the flow path of the desorber (Figure 4). This isolated the sorbent tube from the GC, allowing both stringent ‘stop-flow’ leak testing and pre-purging of air to vent prior to desorption of every tube.

2.2 Automation

TD automation requires tubes to be kept sealed both before and after desorption to minimise risk of artefact ingress from laboratory air and to prevent loss of analytes over periods of (say) 1 or 2 days. Caps are essential because sample losses from poorly sealed tubes can be very significant. The ATD 50 addressed this issue by using stainless steel ‘analytical’ caps incorporating a ball valve. It wasn’t an ideal solution, involving several O-rings in direct contact with the sample flow path, but at least the caps could remain on the tubes throughout an entire sequence (no uncapping or recapping required), thus providing a robust solution for the time.

TD–GC applications expanded rapidly after introduction of the ATD 50. Apart from personal exposure assessment[11–13], examples included residual solvents in drugs[14], and ambient air monitoring[15–17].

2.3 Multiple splitting

‘Multiple’ or ‘double’ splitting was not part of the original WG5 specification, but was introduced as an enhancement to the ATD 50 in around 1985 (Figure 5). It allowed the transfer of analytes from the tube to the trap to be carried out split or splitless, and likewise the subsequent transfer/injection of analytes from the secondary (focusing) trap to the GC column. It brought some significant benefits in terms of application versatility. Total split ratios up to 10,000:1 could accommodate milligrams of individual analytes, while ng- or pg-level samples could still be analysed with negligible split or no split at all.

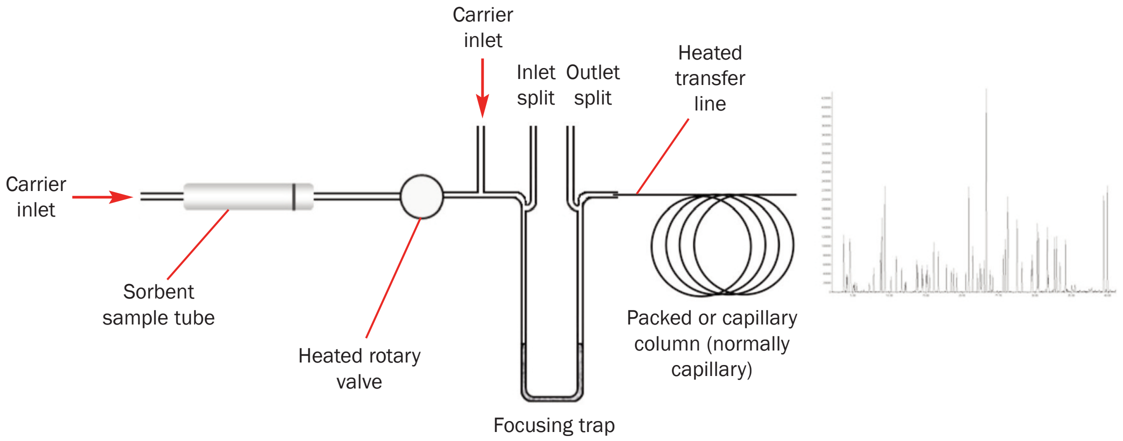


Figure 5: Two-stage thermal desorption, as shown in Figure 4, but incorporating double splitting capability.

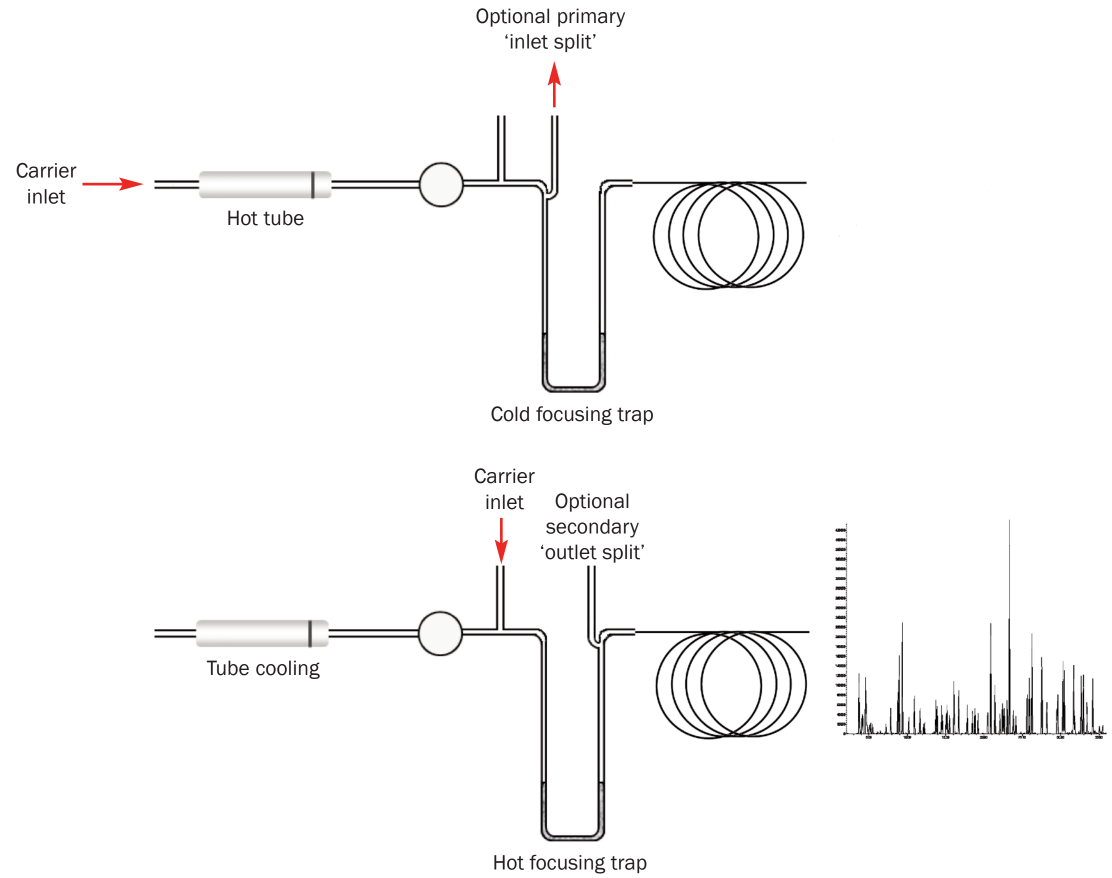


Figure 6: An illustration of gas flow during the two stages of thermal desorption with double splitting.

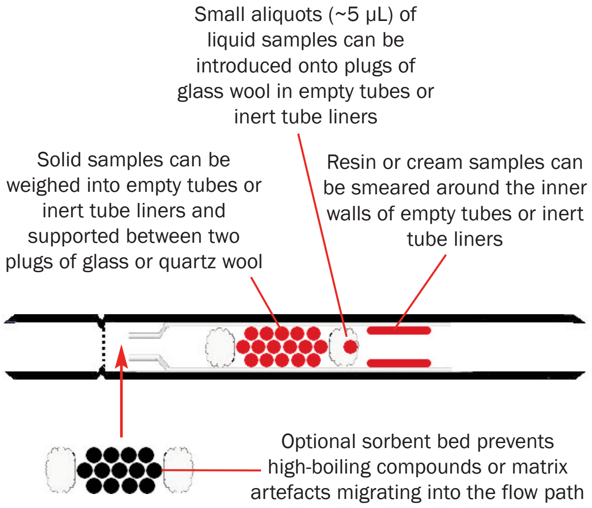
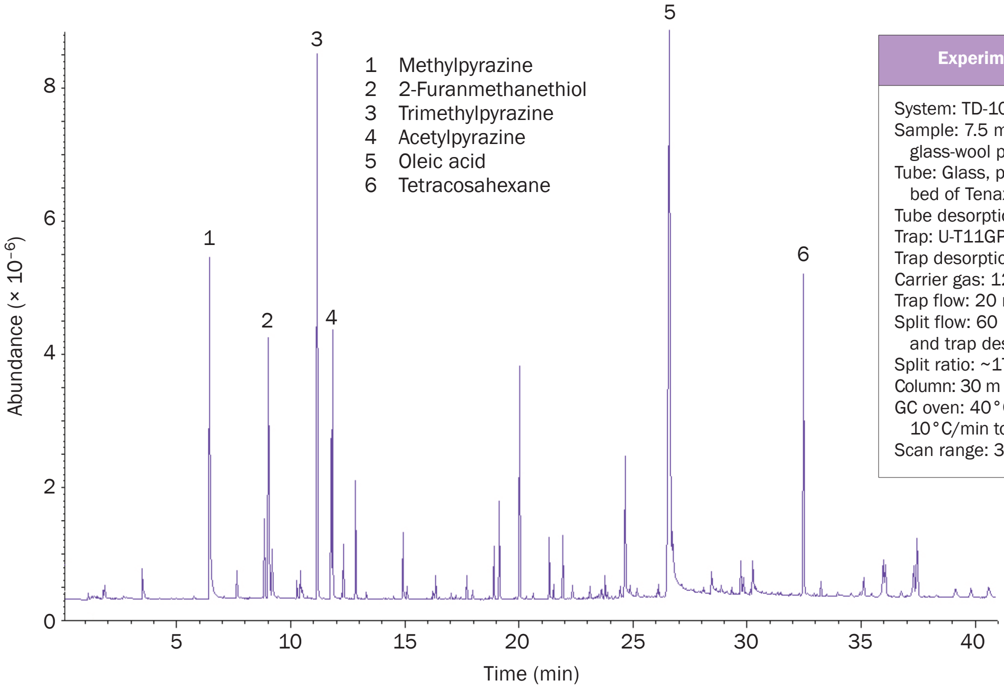


Figure 7: An illustration of sample preparation for direct desorption of materials.

It may seem odd to want such high split ratios for thermal desorption applications, but it must be remembered that sensitivity is not the only advantage that TD offers – many laboratories simply prefer to use thermal desorption because it offers a higher degree of automation and eliminates the need for hazardous solvents such as CS_2. In fact, many industrial air monitoring applications benefit from (or even require) a significant split ratio. For example, when sampling a compound of nominal molecular weight 100 at 100 mL/min over a full 8-hour shift (sample volume 48 L) a vapour concentration of 5 ppm would mean collecting ~1 mg of that compound. An overall split ratio of at least 2000:1 would be advisable in this case in order to prevent overload of high-resolution capillary GC columns and detectors.

As well as offering application flexibility, the introduction of double splitting enhanced the process of two-stage thermal desorption. Analytical objectives during primary (tube) desorption are complete removal (extraction) of retained vapours from the sample tube combined with quantitative trapping of the compounds of interest on the secondary (focusing) trap. If the sample is sufficiently large to allow implementation of a split during primary desorption, it helps achieve both objectives – it allows a relatively high carrier gas flow to be maintained through the hot sample tube during desorption while at the same time allowing a lower flow to be maintained through the cold focusing trap, thus aiding analyte retention. Application of a second split during subsequent trap desorption then boosts the gas flow through the trap when it is being heated and desorbed (Figure 6).

Implementation of double splitting enabled the first serious expansion of TD into direct desorption of materials (Figure 7). Relevant application examples include solvents in paint, residual monomer in polymer, natural oils (Figure 8), and volatiles in dried vegetable products such as tobacco or spices[14,18,19].



Experimental conditions

System: TD-100™–GC/MS.
Sample: 7.5 mg sesame oil on a glass-wool plug.
Tube: Glass, packed with a 1 cm bed of Tenax® TA.
Tube desorption: 10 min at 300°C.
Trap: U-T11GPC/Tenax at 30°C.
Trap desorption: 320°C for 5 min.
Carrier gas: 12 psi He.
Trap flow: 20 mL/min.
Split flow: 60 mL/min (during tube and trap desorption).
Split ratio: ~170:1.
Column: 30 m × 0.25 mm × 0.25 µm.
GC oven: 40°C (1 min hold), then 10°C/min to 300°C (10 min hold).
Scan range: 33–350 amu.

Figure 8: Direct thermal desorption of a sesame oil sample employing double splitting.

3 The evolution of TD technology

3.1 The limitations of early systems

While the ATD 50 represented state-of-the-art TD technology in its day, new thermal desorption application requirements began to emerge that highlighted the limitations of these early systems. Key concerns included:

- Forward-flow trap desorption meant analytes had to pass through the entire sorbent bed of the focusing trap. This limited the volatility range of components that could be analysed simultaneously
- Flow path and desorption temperatures: The ATD 50 operated with a flow path maximum of 150°C and maximum desorption temperatures of 250°C and 300°C for the tube and trap respectively. This was hot enough to allow complete recovery of compounds up to n-C_{26} (b.p. ~400°C)[20]. However, there was growing interest in measuring the vapour concentration of higher-boiling semi-volatiles such as PCBs, phthalates and multi-ring PAHs
- Inertness: the predominantly stainless steel flow path of early systems caused the degradation of many reactive VOC species
- Internal standard addition had become an accepted part of automated GC procedures generally, and TD users were beginning to demand this option
- Whole-air sampling: There was growing interest in ultra-volatile compounds such as C_2 hydrocarbons and freons, which are not quantitatively retained by conventional sorbent tubes at ambient temperatures. At the same time, demand for semi-continuous, near-real-time monitoring of urban air pollutants with known adverse health effects (specifically C_2 to C_9 hydrocarbons originating primarily from vehicle exhaust emissions[21,22] – so-called 'ozone precursors') was also increasing. This led to thermal desorption technology being adapted to allow the controlled introduction of whole-air or gas samples directly into the cooled focusing trap[23] – see Section 3.7.

To address these limitations and respond to the new demands, thermal desorption technology began to evolve rapidly from the early 1990s. The most significant changes were made in the following areas:

3.2 Optimisation of the focusing trap

While electrically-cooled/sorbent-packed focusing traps remain the most robust and versatile platform for two-stage thermal desorption, the technology has been refined considerably since 1981. Key considerations include construction material, internal diameter, sorbent bed length, cooling efficiency, heating rate and desorption efficiency. Packed with a sorbent bed 60 mm long and 2 mm in diameter, Markes' TD focusing traps represent the state of the art. They are constructed of

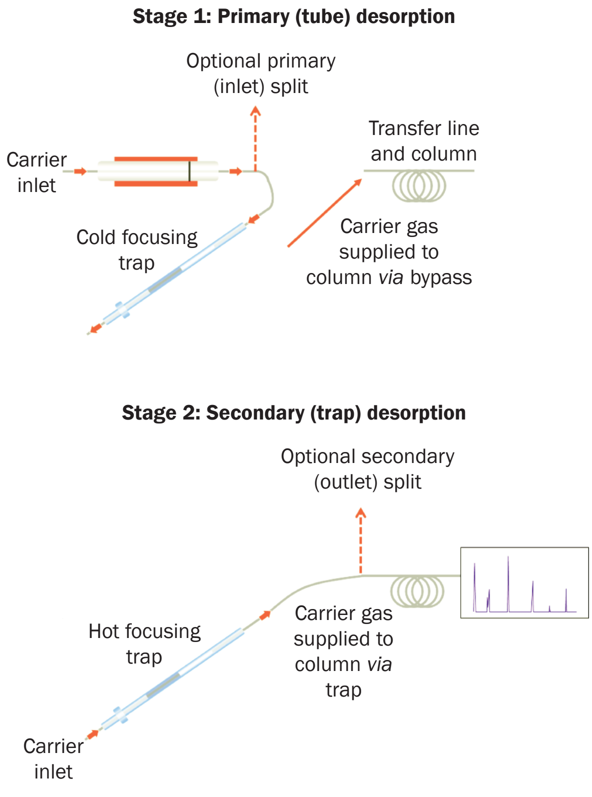


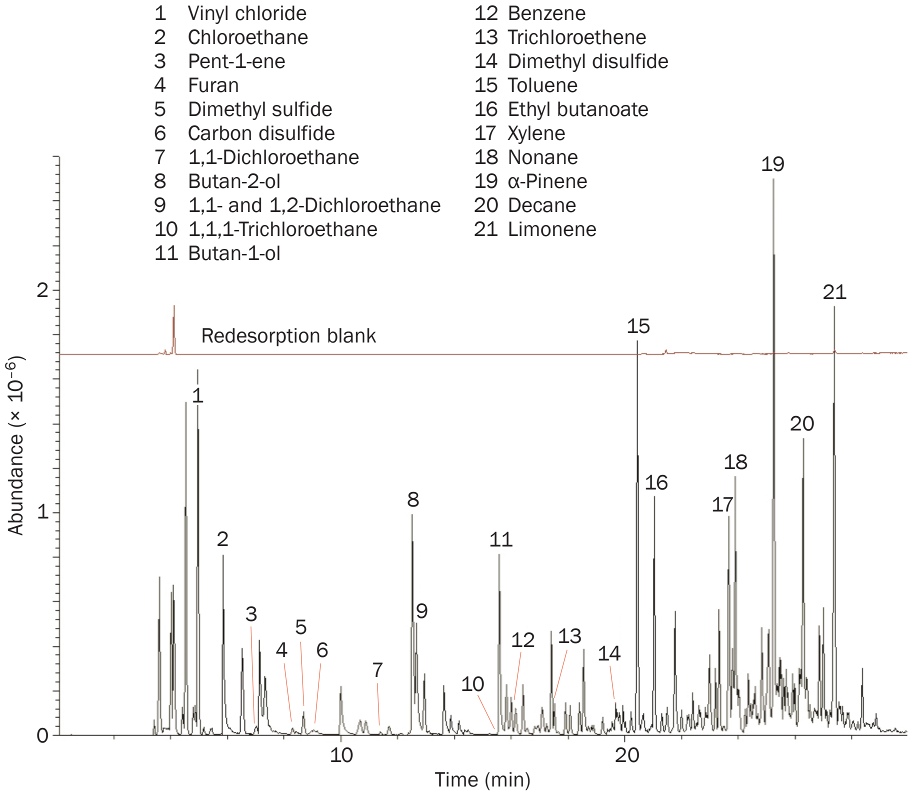
Figure 9: Illustration of two-stage thermal desorption, incorporating backflush of the focusing trap.

inert quartz and have a wide enough bore to prevent ice blockage, yet can be heated at rates up to 100°C/s to allow efficient desorption at flows down to 1.5 mL/min for optimum sensitivity. The focusing trap is configured in 'backflush' mode, so that analytes enter and leave the trap from the same end (Figure 9). This extends the analyte volatility range (see TDTS 64). Examples of results that can be routinely obtained for air monitoring using the latest TD trapping technology are presented in Markes' Applications Guide on environmental applications – see examples given in Figures 10 and 11.

Trapping performance has also been optimised considerably over recent years. Markes' latest focusing trap technology allows the entire 60 mm sorbent bed to be cooled to –30°C without liquid cryogen, thus significantly improving the retention of ultra-volatile organics from air/gas samples, compared to earlier systems – see TDTS 16 and 87, and also Figure 12.

3.3 The evolution of heated valve technology for thermal desorption

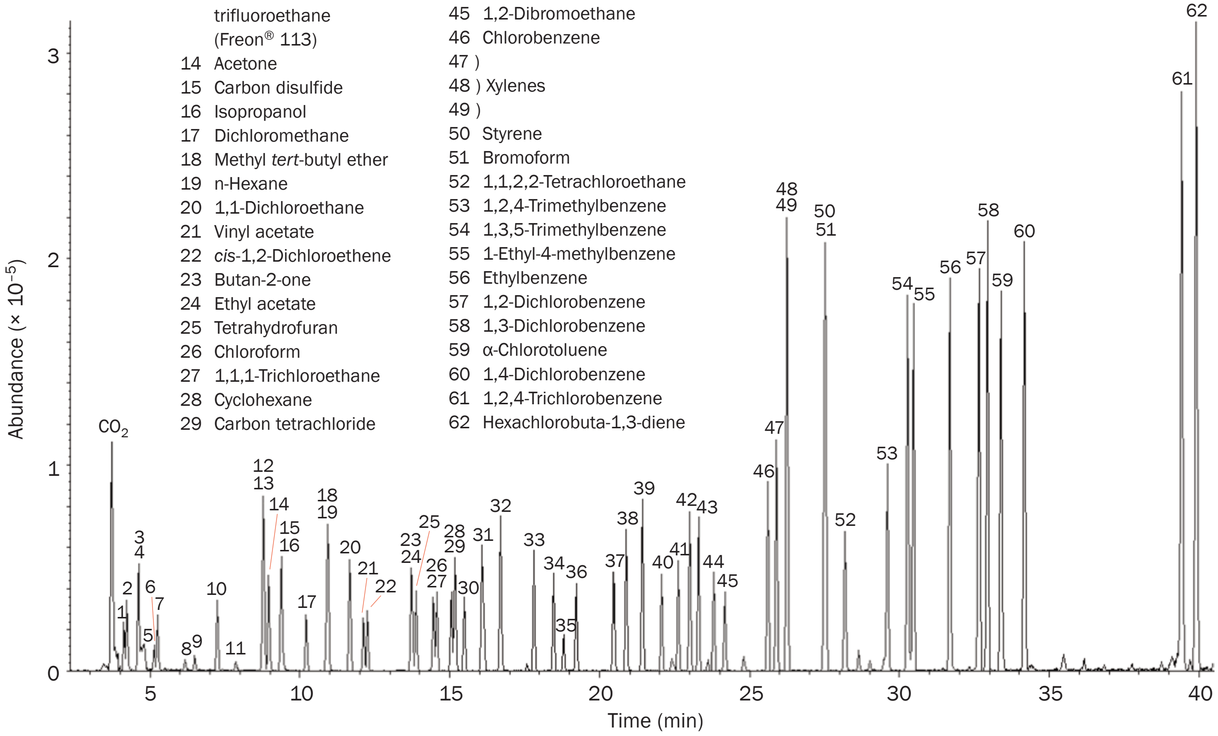
The essential functions of leak testing and pre-purging of air to vent, plus the more recent requirements for backflush desorption, dry-purging and internal standard addition (to the sampling end of the tube), have all reinforced the need for valving in the TD sample flow path. Rotary valves are still widely used in commercial TD



Experimental conditions

System: ULTRA-UNITY™–GC/MS.
Tube: Silcosteel, packed with Tenax–UniCarb™.
Tube desorption: 5 min at 200°C.
Trap: Multi-sorbent ('sulfur') trap at –15°C, split flow 20 mL/min; trap flow 20 mL/min.
Trap desorption: 220°C with 80 mL/min split flow.
Flow path: 120°C.
Column: 60 m × 0.25 mm × 1.4 µm.
GC oven: 40°C to 225°C at 10°C/min.
Scan range: 35–260 amu.

Figure 10: 100 mL landfill gas with trace target analytes and many major components identified.



1	Propene
2	Dichlorodifluoromethane
3	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon® 114)
4	Chloromethane
5	1,2-Dichloroethane
6	Buta-1,3-diene
7	Vinyl chloride
8	Bromomethane
9	Chloroethane
10	Trichlorotrifluoroethane
11	Ethanol
12	1,1-Dichloroethene
13	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon® 113)
14	Acetone
15	Carbon disulfide
16	Isopropanol
17	Dichloromethane
18	Methyl *tert*-butyl ether
19	n-Hexane
20	1,1-Dichloroethane
21	Vinyl acetate
22	*cis*-1,2-Dichloroethene
23	Butan-2-one
24	Ethyl acetate
25	Tetrahydrofuran
26	Chloroform
27	1,1,1-Trichloroethane
28	Cyclohexane
29	Carbon tetrachloride
30	Benzene
31	n-Heptane
32	Trichloroethene
33	1,2-Dichloropropane
34	1,4-Dioxane
35	Bromodichloromethane
36	*trans*-1,3-Dichloropropene
37	4-Methylpentan-2-one
38	Toluene
39	*cis*-1,3-Dichloropropene
40	*trans*-1,2-Dichloroethene
41	1,1,2-Trichloroethane
42	Tetrachloroethene
43	Hexan-2-one
44	Dibromochloromethane
45	1,2-Dibromoethane
46	Chlorobenzene
47	)
48	) Xylenes
49	)
50	Styrene
51	Bromoform
52	1,1,2,2-Tetrachloroethane
53	1,2,4-Trimethylbenzene
54	1,3,5-Trimethylbenzene
55	1-Ethyl-4-methylbenzene
56	Ethylbenzene
57	1,2-Dichlorobenzene
58	1,3-Dichlorobenzene
59	α-Chlorotoluene
60	1,4-Dichlorobenzene
61	1,2,4-Trichlorobenzene
62	Hexachlorobuta-1,3-diene

Experimental conditions

System: UNITY™–CIA–GC/MS.
Trap: Multi-sorbent ('air toxics') trap at 25 °C.
Trap desorption: 40 °C/s to 320 °C.
Flow path: 140 °C.
Column: 60 m × 0.32 mm × 1.8 µm.
GC oven: 40 °C to 230 °C at 5 °C/min.
Scan range: 35–300 amu.

Figure 11: Splitless analysis of 1 L × 1 ppb 62-component air toxics standard in a canister.

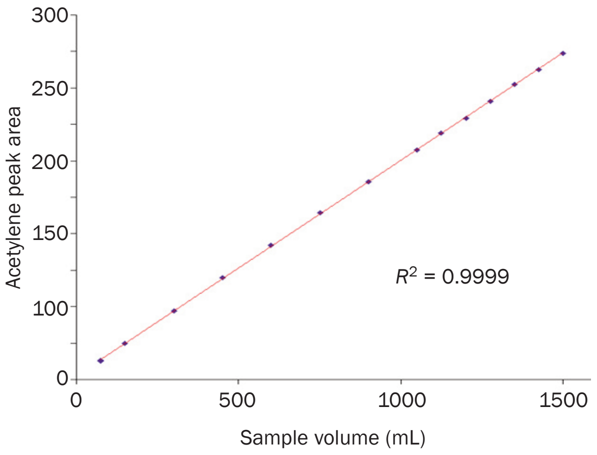


Figure 12: Cryogen-free retention of ultra-volatile analytes from large volumes of air/gas: illustration with acetylene.

systems, but concerns regarding cold spots and temperature limitations led Markes to develop inert, low-volume valving specifically for thermal desorption. Using this TD-specific valve means TD-100™ and UNITY™ 2 systems are compatible with high-boiling semi-volatiles (*e.g.* up to n-C$_{40/44}$ – see TDTS 53 and Figure 13) yet still allow flow path temperatures to be set low enough for quantitative recovery of the most labile species. Thiols and CS (tear) gas for example, work best with TD flow path temperatures at or below 125 °C[24].

3.4 Tube sealing for automation

Early attempts to overcome the sorption and artefact limitations of the original ATD 50 analytical tube seals involved caps that were removed and replaced by the thermal desorber during automatic operation. These incorporated PTFE-coated O-rings to reduce friction and make the automatic uncapping/recapping processes as

Experimental conditions

System: UNITY™ 2 TD–trace GC/FID.
Tube: Stainless steel, packed with quartz wool and graphitised carbon black.
Tube desorption: 10 min at 370 °C with 40 mL/min flow.
Trap: Multi-sorbent (quartz–carbon black) trap at 0 °C.
Trap desorption: 370 °C with 30 mL/min split flow and 3 mL/min constant column flow.
Flow path: 210 °C.
Column: 30 m × 0.25 mm × 0.25 µm.
GC oven: 100 °C (1 min hold) to 325 °C at 15 °C/min.

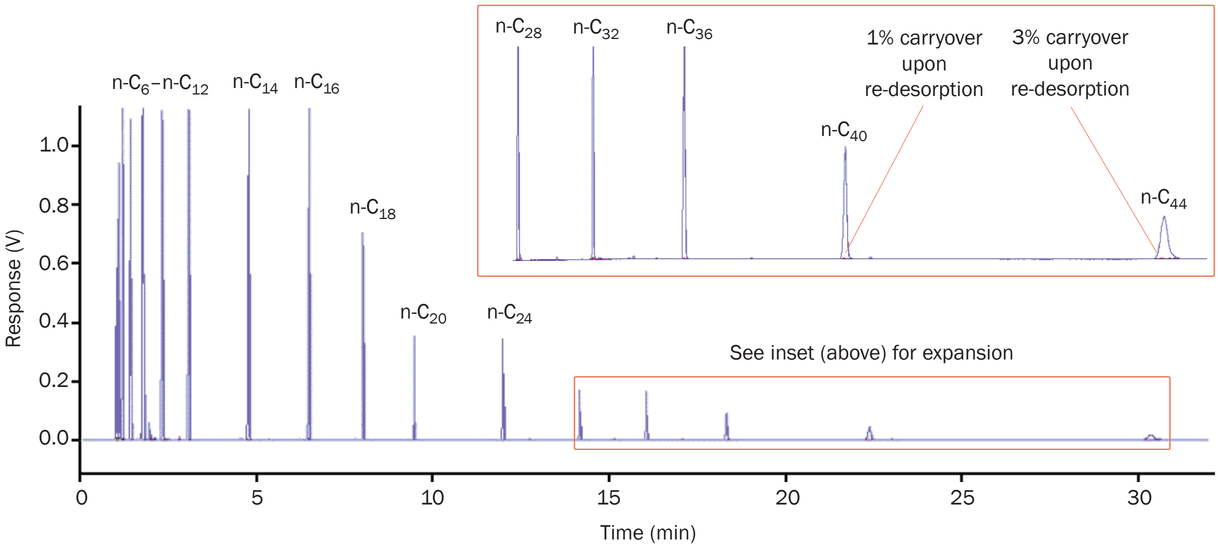


Figure 13: Analysis of a sorbent tube loaded with 2 µL of an n-C_6 to n-C_{44} hydrocarbon standard (500 ng/µL) using 2-stage TD with a valve and with trap desorption in backflush mode.

reliable as possible. However, they were shown to be prone to significant loss of volatiles over time[25]. Markes' introduction of DiffLok™ capping technology, which incorporates a very long, narrow gas flow path, provides a much more robust solution. This patented 'diffusion-locking' mechanism reduces analyte losses and artefact ingress to negligible levels, even over extended periods (*e.g.* a week) but still allows gas to flow unimpeded when pressure is applied. This means that the integrity of sampled and clean (desorbed) tubes can be rigorously maintained without complicating the TD automation process – *i.e.* without the need to uncap/recap tubes.

3.5 Re-collection of split flow

An inherent drawback of all early thermal desorption systems was that the technique was 'one-shot' – if anything went wrong during the analytical procedure, no sample remained to repeat the test. Quantitative re-collection of TD sample split flow was first reported by Jan Kristensson in 1988[14,26]. Kristensson's initial implementation involved adapting a standard TD system of the time, and was therefore unavoidably cumbersome. Nevertheless, it showed the potential of split-flow re-collection for overcoming the inherent one-shot limitation of traditional TD technology and for confirming analyte recovery and test results.

The first commercial implementation of quantitative split flow re-collection for TD was developed in 1998 by a team led by Peter Higham, then lead mechanical engineer at Markes International. They configured the new Markes heated valve so that both primary tube desorption ('inlet') split flow and secondary trap desorption ('outlet') split flow were directed to the same 're-collection' tube (Figure 14). This overcame the old one-shot limitation of thermal desorption for the vast

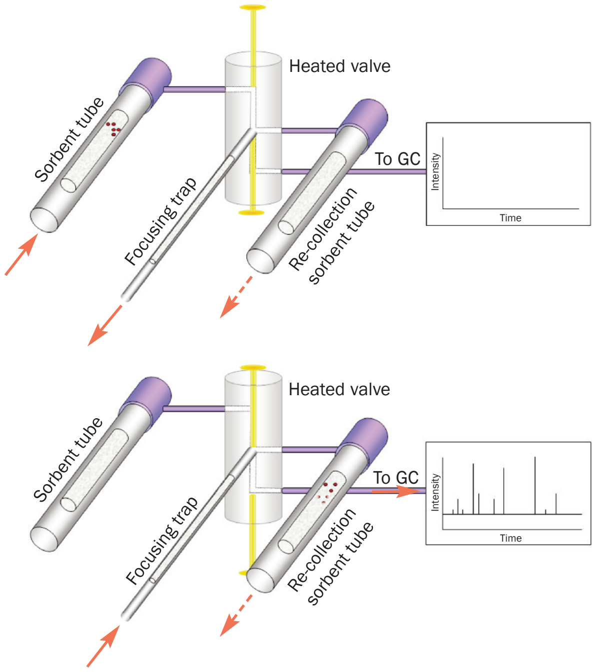


Figure 14: Operation of two-stage thermal desorber with integrated low-volume TD-specific valve and the capability to re-collect primary and/or secondary split flow on the same tube.

majority of applications – *i.e.* all single-split and double-split methods. Furthermore, because re-collection involved analytes passing through an extended version of the TD flow path, carrying out a short sequence of repeat analyses on a single standard allowed selective losses of one or more analytes (relative to split ratio or to other more stable/volatile compounds in the mix) to be readily identified.

Quantitative sample re-collection is now a TD function that has become accepted as a standard requirement, and is referenced in many international standards as an important approach to method validation[27,28].

3.6 Electronic control of flows and pressures

While GC systems with conventional liquid injectors have benefitted from electronic pneumatic control of carrier gas and split flow for many years, most two-stage TD procedures present a significantly more difficult technical challenge. This is because the route (flow path) by which carrier gas is supplied to the column alters depending on the phase of operation. For example, at the start of trap desorption, the flow to the column switches from a simple bypass line to pass through the very different impedance of a sorbent focusing trap. The trap then heats, thus changing the impedance once again. Maintaining a stable electronically-controlled carrier gas pressure or flow to the head of the GC column under these conditions requires very robust closed-loop feedback.

Despite this complexity, Markes pioneered implementation of both precise electronic pneumatic control of carrier gas flow/pressure and electronic mass flow control of desorption and split flows for TD. This enhanced complex analyses by stabilising ('locking') peak retention times independent of split flow, trap impedance, *etc.* (Figure 15). Without electronic pneumatic control of carrier gas, late-eluting components would be subject to significant retention time variation if the analytical conditions changed.

3.7 TD innovations for whole-air/gas sampling (canisters/bags and on-line monitoring)

Recent advances in thermal desorption technology for whole-air/gas monitoring have included optimisation of cryogen-free focusing trap technology for retention of ultra-volatile components (see Section 3.2), the development of reciprocal twin-trap system configurations for continuous on-line operation (the TT24-7), extended sequencing capabilities (more channels) and improved general analytical performance (linearity, reproducibility, reduced carryover, *etc.*).

On-line air/gas monitoring systems tend to be installed on industrial plant or in environmental field monitoring stations, and are thus often required to operate unattended for extended periods of time. High liquid cryogen consumption was a major limitation for the earliest on-line TD–GC systems[10], but this was addressed as soon as the first Peltier-cooled systems became

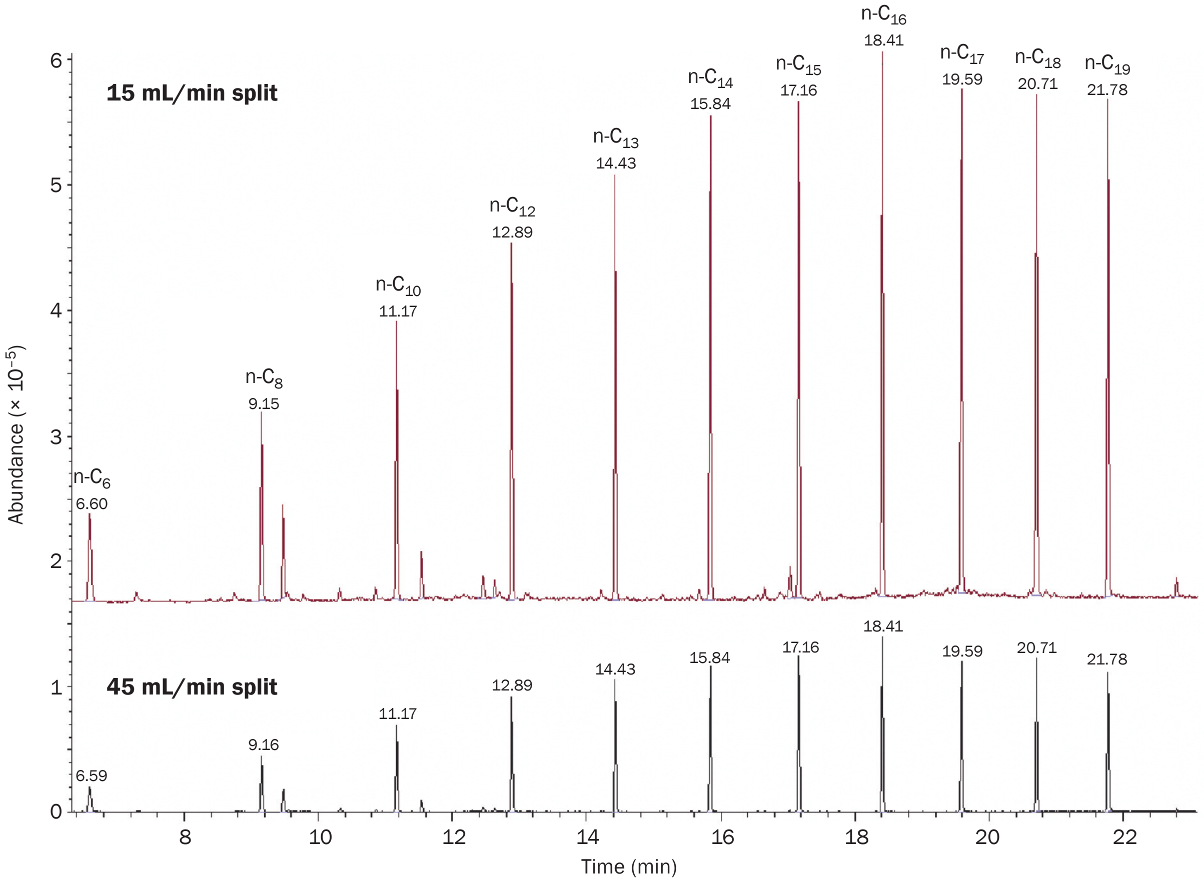


Figure 15: Using electronic carrier gas control to stabilise TD–GC(MS) retention times under different analytical conditions.

available for on-line work[23]. More recently, the optimisation of trap performance has played a major part in extending the compatibility of cryogen-free on-line TD technology even further, to include trace greenhouse gases such as ultra-light perfluorinated compounds (see TDTS 87).

TT24-7 systems, which incorporate two reciprocally-operated traps, offer on-line monitoring without any sampling 'blind spots'. These are often targeted at very hazardous applications, for example in counter-terrorism or for monitoring particularly dangerous chemical processes – see Section 14.

The first widely used standard method for air monitoring using canisters was published by the US EPA in 1991 and involved cryo-focusing[29]. Automated analytical technology for whole-air/gas containers such as canisters or bags has been slow to evolve since then. This situation is finally beginning to change, and most modern canister standards[30,31] now specify (or at least include) the option of cryogen-free sorbent trapping. Improved trap performance, better designed (more uniformly heated) sample flow paths and extended purging have also served to reduce carryover[32] and make modern canister-based autosamplers more versatile and productive than their predecessors. Markes' CIA *Advantage*™ technology is a good example.

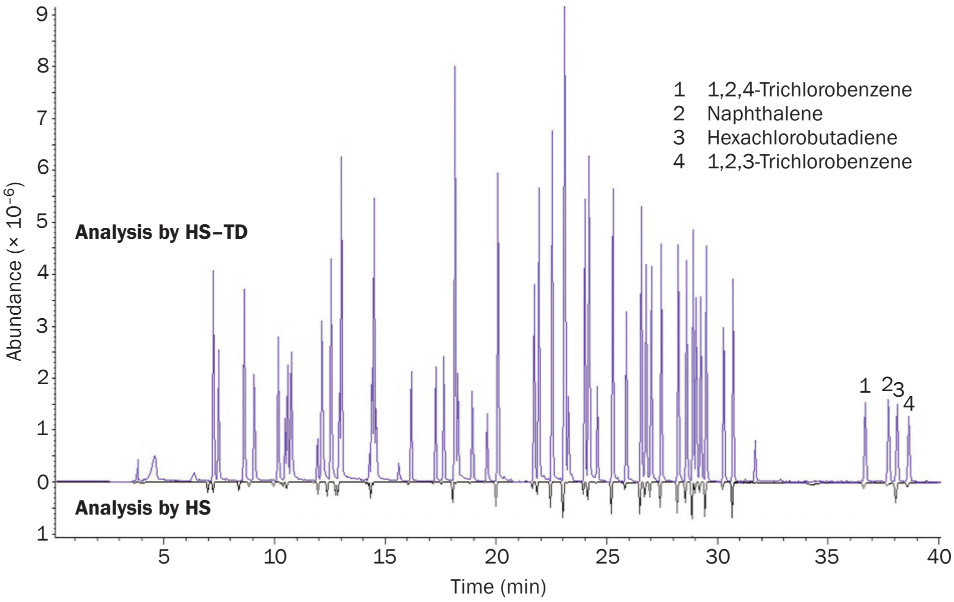
4 Sampling options and the role of TD as a front-end technology for GC

Sampling options associated with thermal desorption have conventionally included vapour-monitoring, *via* sorbent tubes/traps, canisters and bags[7], and direct desorption of homogeneous liquids or solids (see TDTS 9 and Figure 7). However, thermal desorption is also the primary interface for many other GC 'front-end' technologies, namely purge-and-trap[33,34], large-volume injection, sorptive extraction and headspace–trap or headspace–TD (HS–TD).

4.1 Headspace–TD

Traditional equilibrium headspace technologies for GC are fundamentally static systems. They rely on target compounds partitioning reproducibly between the sample matrix and the vapour (headspace) phase under fixed conditions of temperature and pressure, so that analyte concentrations in the headspace are representative of analyte concentrations in the sample matrix. Aliquots of headspace vapour in the order of 1 mL volume are typically transferred to the GC either *via* a simple syringe or using rather more sophisticated mechanisms such as gas loop or pressure balance.

The addition of a focusing trap turns headspace into what is essentially a stepwise dynamic process. It allows larger volumes of headspace vapour to be collected/focused over a longer period of time. Markes' HS–TD systems allow the headspace vials to be repressurised and resampled repeatedly (in multiple cycles) before the focusing trap is finally thermally desorbed to 'inject' all the retained vapours in one go. The main advantages of HS–TD *versus* conventional static headspace procedures are a 10–100-fold increase in sensitivity (depending on analyte volatility and the number of cycles), an extended volatility range (conventional static headspace is intended to preferentially increase the concentration of volatiles at the expense of higher-boiling matrix components) (Figure 16) and selective pre-purging of interferences (water, ethanol, *etc.*). In effect, it allows headspace procedures to approach purge-and-trap sensitivity levels but with the practical advantages of disposable vials, no foaming, and minimal risk of aerosol formation[35].



Experimental conditions

System: HS-5TD™–GC/MS.
Trap: Multi-sorbent ('air toxics') trap at 25°C.
Vial temp: 40°C.
Headspace cycles: 10 vial sampling cycles at 50 mL/min.
Trap purge: 3 min.
Trap desorption: 40°C/s to 320°C with 5 mL/min split.
Flow path: 150°C.
Column: 60 m × 0.25 mm × 1.4 µm.
GC oven: 40°C (5 min), 5°C/min to 180°C (10 min) then 20°C/min to 240°C.
Scan range: 29–400 amu

Figure 16: 200 ppb purgable VOC standard in drinking water analysed by conventional HS–GC/MS (black) and HS–TD–GC/MS (blue).

4.2 Solid-phase (micro-)extraction (SP(M)E) or sorptive extraction (SE) for GC

Sorptive extraction is available in various commercial formats comprising fibres, bars and Markes' SPE-tD cartridges. All are coated with sorbent or stationary phase – most commonly polydimethylsiloxane (PDMS). The technique is principally applied to higher-boiling organics in the liquid phase and is thus a good complement to headspace-trap – see TDTS 88 and Figure 17. Organic compounds partition between the sample matrix and the stationary phase on the SP(M)E/SE device at a given temperature. The sampled cartridge/fibre is then rinsed, dried and analysed using thermal desorption (or solvent extraction) with GC(MS).

Sorptive extraction is most commonly used for screening (rather than absolute quantitation) because the limited range of predominantly non-polar coatings is not compatible with all analytes. Furthermore, the partition system can be very sensitive to variations in sample conditions – humidity, analyte concentration, matrix composition, time, temperature, *etc.* Nevertheless, SP(M)E/SE provides a useful extraction tool for complex samples and is widely used for routine drug screening and for monitoring persistent organic pollutants in foods, beverages and other products derived from natural sources[36].

4.3 Large-volume injection

Large-volume injection technology is also frequently based on TD. Some of the earliest studies of groundwater and soil contamination, for example, described 'Adsorption/Thermal Desorption' and involved injecting several millilitres of water onto Tenax tubes before they were subsequently dried and analysed by TD–GC(MS)[37]. Modern implementations are typically built on similar principles, albeit in more automated and integrated configurations.

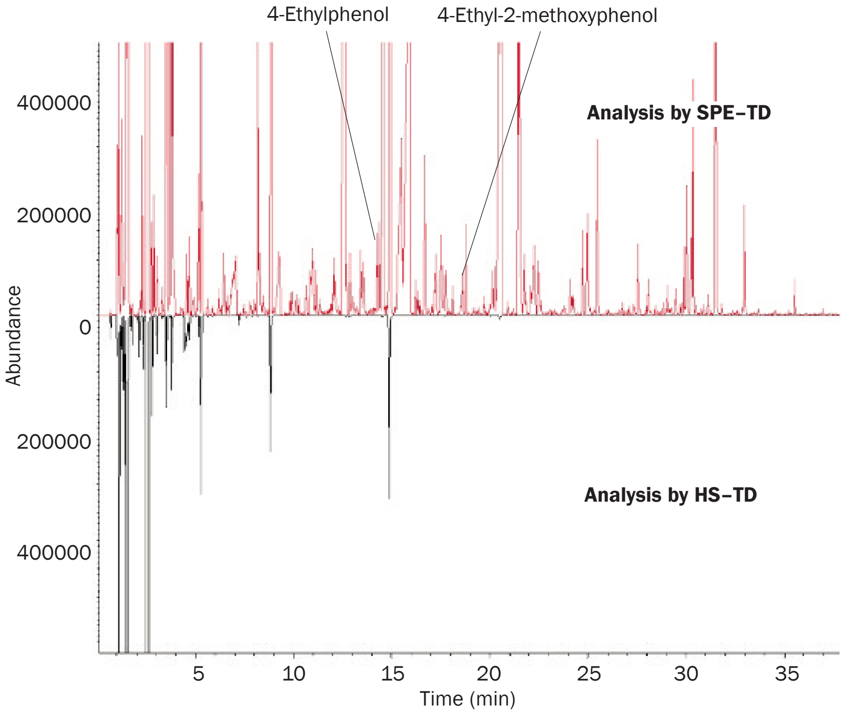
4.4 Stand-alone sampling accessories

Numerous specialist 'stand-alone' sampling devices have also been introduced for thermal desorption over recent years[38]. Key examples are presented in Markes' series of Applications Guides. They include alveolar breath samplers such as the Bio-VOC™ [39,40], materials emission testing equipment such as FLEC® and the Micro-Chamber/Thermal Extractor™ [41–43], and soil probes like the VOC-Mole™ [44,45].

4.5 Summary of the versatility of TD

The multiple roles played by thermal desorption in GC sample introduction are best illustrated diagrammatically (Figure 18). In its various manifestations, TD offers compatibility with gas-, liquid- and solid-phase samples and with GC-compatible organic analytes ranging in volatility from C_2 hydrocarbons and freons to n-C_{40} and 6-ring PAHs. Key TD applications include: air/gas monitoring (including fugitive industrial emissions), materials characterisation, odour and aroma profiling, civil defence, product quality control, and testing chemical emissions from everyday products released into indoor air.

In many respects, high-performance TD systems can be thought of as versatile, readily-automated, programmable split/splitless GC injectors. The desorption efficiency of the focusing trap should equate to that of a well-designed liquid inlet for GC in terms of peak shape, compatible boiling range, stability, longevity, *etc.* In other words, the



Experimental conditions

Parameters used in both runs:
Trap: Multi-sorbent ('general purpose') trap at 25°C.
Trap desorption: 300°C with 20 mL/min split.
Column: 30 m × 0.25 mm × 0.25 µm.
Scan range: 35–300 amu.
HS-TD analysis: 2 HS vial sampling cycles at 50 mL/min.
Vial temp: 50°C.
Trap purge: 3 min.
Flow path: 140°C.
GC oven: 40°C to 160°C at 5°C/min.
SPE-TD analysis: SPE-tD™ cartridge (hollow tube coated inside and out with PDMS).
Desorption: 180°C for 5 min with 50 mL/min carrier gas flow.
Flow path: 200°C.
GC oven: 40°C, 5°C/min to 160°C then 10°C/min to 320°C.

Figure 17: Analysing organic components in red wine using HS–TD (bottom trace) and SPE–TD (top trace) with GC/MS.

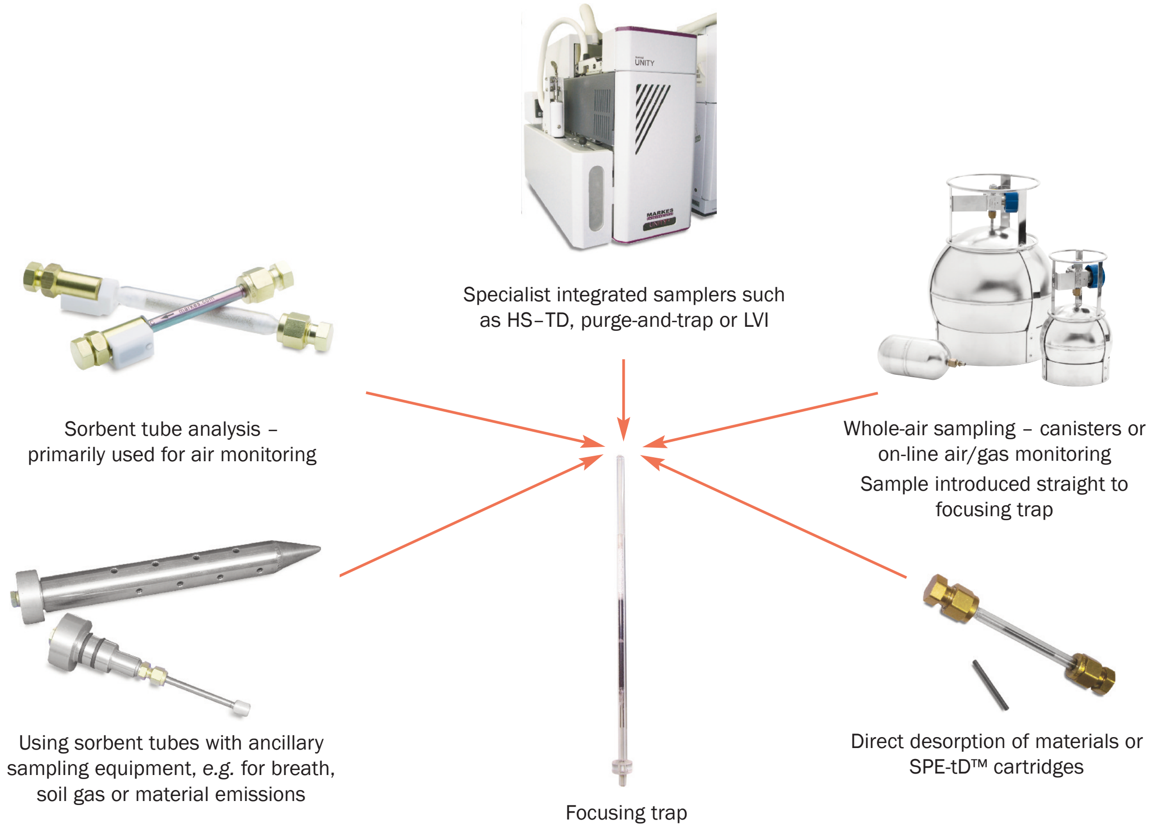


Figure 18: GC(MS) sample introduction options supported by thermal desorption.

performance of the thermal desorber should allow it to be interfaced directly to the analytical column, using a simple heated transfer line, without any additional form of injector or focusing device.

5 Method development and optimisation

The fundamentals of TD method development and optimisation have remained essentially the same since the advent of backflush desorption of the focusing trap. While more detailed information is provided in TDTS 21, the following general guidelines may be useful:

5.1 Sampling

As with any measurement procedure, it is essential to make sure that samples are collected correctly. Considerations for optimising sorbent selection for on- or off-line collection of air/gas samples, with and without specialist sampling accessories (breath, material emissions, *etc.*) are presented in TDTS 5, 20 and 27 (amongst others). While the selected sorbents must be strong enough to prevent breakthrough and loss of any target compounds during sampling, they must also be weak enough to allow quantitative recovery of all the analytes of interest at safe temperatures during the desorption phase – *i.e.* at temperatures that don’t exceed the stability limits for the sorbent or compounds of interest. It is also useful to minimise the retention of interfering compounds, such as permanent gases and water during the sampling process – *e.g.* by selecting hydrophobic sorbents. Similarly, use of canisters, bags or unheated, on-line air/gas manifolds must be restricted to vapours that can readily be recovered from ambient temperature containers/streams – this typically means compounds more volatile than n-C$_{9/10}$ (see TDTS 80).

Headspace–TD and sorptive extraction applications have been extensively reported[35,36], and associated optimised sampling conditions for headspace–TD and sorptive extraction are presented in relevant publications, including TDTS 78, 88, 91, 94 and 96. The direct desorption of materials also requires some specific considerations. General guidelines are given below.

5.2 Optimising the analytical procedure

General considerations: As described in Section 1.1, TD is essentially an extension of gas chromatography, with key parameters including temperature, gas flow, time and sorbent (stationary phase) selection. While thermal desorption parameters vary widely from application to application, it is possible to apply some general rules that aid the development of robust methods.

It is usually best to start by considering the analysis as a whole: What are the objectives? What are the target compounds and likely interferences? What is the expected concentration range? What range of analyte masses should be allowed to reach the column and detector to best ensure optimal GC performance and required detection levels?

In the case of sorbent tubes, it is usually (but not always) necessary to desorb everything that has been trapped/collected on the primary sample while at the same time quantitatively retaining the compounds of interest on the focusing trap. Key considerations at this stage include the volatility range of compounds of interest, the maximum temperature of the sorbents and the likely presence of interferences. If it is possible to adjust the trapping/focusing parameters so that compounds of interest will be quantitatively retained for the duration of primary (tube) desorption while unwanted interferences (CO_2, water, ethanol for example) are purged to vent, then this is a big bonus.

Once primary desorption is complete, the objective of secondary (trap) desorption is invariably to completely desorb everything retained by the trap and transfer it to the GC analytical column, usually in as small a volume of carrier gas as possible.

Temperature: Selection of optimum and flow path temperatures is usually straightforward, taking into account both the volatility and thermal stability of the compounds of interest and the temperature limits of the tube and/or trap sorbents concerned. One commonly misunderstood factor is that the energy required to break the sorbent–sorbate bond and release retained analytes into the gas stream is much higher than that required to keep analytes in the vapour-phase as they pass through the empty narrow-bore tubing that comprises the rest of the TD system flow path. In fact, provided the rest of the TD flow path is uniformly heated, inert and narrow-bore, desorbed compounds will remain comfortably in the vapour-phase in the stream of carrier gas at temperatures well below that required for tube or trap desorption. This is intuitive to most gas chromatographers: just as analytes would be expected to elute from a 30 metre coated capillary column at a temperature well below their boiling point, so compounds will elute very readily from the short, uncoated, narrow-bore internal flow path of a TD at surprisingly moderate temperatures. For example, re-collection and repeat analysis (Figure 14) was used to validate recovery of the hydrocarbon standard shown in Figure 13 through an automated TD system. The experiment was carried out with the TD flow path and transfer line set at only 210 °C. Results demonstrate negligible losses of n-C_{40} (b.p. ~550 °C) and are shown in Figure 19[46,47]. It is important to understand this, because it allows relatively low flow path and transfer line temperatures to be set for most applications, thus enhancing recovery of reactive species[24].

Flow and split ratio selection: The power of gas flow to enhance the thermal desorption process is commonly underestimated. Increasing flow can be a very useful alternative to raising temperatures – for example, when analysing reactive compounds such as explosives and/or to minimise artefacts when using less stable sorbents such as Chromosorb® 106 or PoraPak™ N. As a general rule, doubling the desorption flow approximately halves the desorption time.

Typical flow rates used in thermal desorption are in the order of 20–200 mL/min for tube desorption, 10–100 mL/min for whole-air sampling, 2–50 mL/min through the cold trap during focusing and 2–100 mL/min during secondary (trap) desorption.

Implementation of sample splitting often directly benefits the thermal desorption process by allowing tube and/or trap desorption flows to be set higher than (and independently of) focusing or GC column flows respectively – see above. It also extends the applicable concentration range. Whole-air/gas sampling methods, headspace–TD, and other procedures that transfer unconcentrated analytes directly into the focusing trap, are all generally restricted to selection of a single split, *i.e.* during desorption of the focusing trap. This limits split ratios to between zero and approximately 200:1 in these

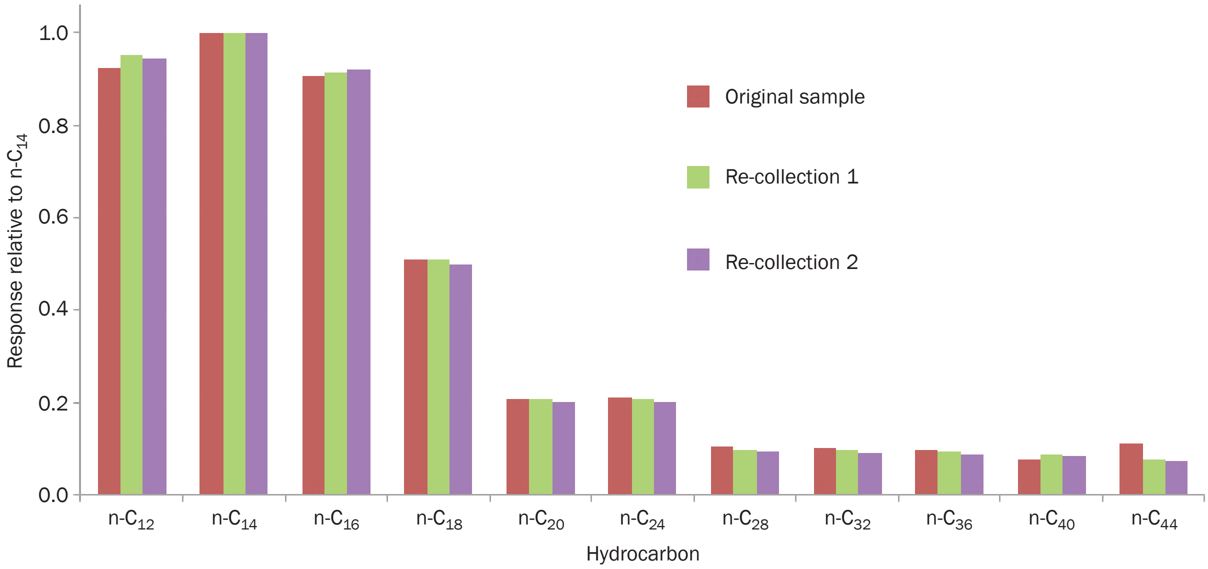


Figure 19: Quantitative recovery of high-boiling hydrocarbons validated using quantitative re-collection of thermal desorption split flow and repeat analysis. Experimental conditions as for Figure 13.

cases. However, all two-stage TD procedures, including tube desorption, direct desorption, large-volume injection and sorptive extraction–TD, benefit from the option of double splitting. In this case the overall split ratio is the product of the two individual split ratios, and milligram-level samples can be reduced to a few hundred nanograms on-column[19].

Minimising interferences: Thermal desorption offers several opportunities for selective elimination of common GC interferences such as permanent gases, water[48] and, when applicable, volatiles such as methanol, ethanol and acetic acid. Common options include selective retention during sampling/focusing, dry-purging or pre-purging prior to desorption and, occasionally, the use of specific devices such as a Nafion dryer, *e.g.* for on-line monitoring of very volatile non-polar compounds such as freons or 'ozone precursors' (see TDTS 26).

5.3 Direct desorption

Key considerations for direct desorption of materials or sorptive extraction cartridges are presented in TDTS 9. They include:

- Ensuring the flow path through the tube is not blocked by sample material or the SP(M)E/SE sampling device
- Ensuring the material/device is positioned securely in the central, heated portion of the sample tube not in the relatively cooler zones at either end of the tube
- Understanding the objective, *i.e.* is it the intention to carry out complete extraction of the volatiles of interest (*e.g.* for residual solvent studies) or simply to obtain a representative VOC profile (*e.g.* for characterising the aromas released by products derived from natural sources)?
- Understanding the nature of the sample matrix – maximum temperature, water content, *etc.*

For many solid and liquid samples, direct thermal desorption allows both interfering volatiles and unwanted higher-boiling matrix components to be excluded from the analysis. In these cases, TD effectively combines sample preparation/clean-up and selective extraction into one fully-automated process, thus extending the lifetime of capillary columns and other GC(MS) system components.

6 Calibration and validation

Thermal desorption procedures are generally calibrated using external standard methods with the optional addition of a gas-phase internal standard such as deuterated toluene or bromofluorobenzene – see TDTS 7.

Theoretically, gas-phase standards should be used for calibrating vapour-monitoring applications, but they can be expensive and/or difficult to obtain at appropriate concentrations. For example, certified cylinders of ppb-level hydrocarbons for calibrating ozone precursor systems retail at upwards of US$3000.

Reliable gas standards are also notoriously difficult to generate. Static standard atmospheres are prone to analyte losses through surface sorption, condensation and dissolution into any liquid water present inside the container, even the thinnest surface film. (*N.B.* Many of these same issues afflict air/gas samples collected in modern canisters.) Dynamic standard-atmosphere generation methods are much more reliable and are described in several papers[49–51]. However, there are very few laboratories in the world that have sufficiently sophisticated apparatus, including continuous monitoring equipment, to produce low-concentration (low ppm) standard atmospheres that are truly traceable to primary standards.

The most important international standard thermal desorption methods therefore describe external standard calibration using liquid solutions[27,28,52,53]. Standard solutions are prepared so that injection of small volumes (typically 0.2 to 2 µL) introduces the same analyte masses that are expected to be retained by (or loaded into) the TD tube during sampling. The preferred injection method involves introducing the liquid standards through what is essentially a simple unheated GC injector which is connected to the sampling end of the sorbent tube as if it was the injector end of a ¼″ packed column – see TDTS 7. Carrier gas flows are typically set to something in the order of 100 mL/min, and the syringe is usually inserted through the septum and into the 'injector' so that it just touches the sorbent-retaining material within the tube (gauze, frit, quartz/glass wool *etc.*). Analytes vapourise rapidly in the fast flow of carrier gas, and reach the sorbent in the vapour phase, as they do during sample collection.

After the aliquot of standard has been introduced in this way, tubes are typically left *in situ* with the carrier gas flowing for up to 5 minutes to allow selective purging of solvent (typically methanol) if applicable. Calibration of very light components is similar but involves gas standards and gas syringes. If calibration is required over a wide volatility range using multiple standards, liquid standards containing higher-boiling stable components are introduced first, with gas standards of the lightest compounds being loaded last.

Note that with two-stage thermal desorption, it is not usually important to load standards onto tubes packed with the same sorbents that will be used for vapour sampling. This is because the critical 'analytical' injection is the second (trap) desorption. It is more important to make sure the standard loading and calibration procedure is simple/robust and to use selective purging if possible to eliminate the carrier solvent.

For obvious practical reasons, if the nature of the analytes means it is not possible to use a solvent that can be selectively purged prior to analysis, it is usually best to minimise injection volumes (*i.e.* to <0.5 µL) and to choose a solvent that gives a sharp, well-resolved peak under the analytical conditions selected.

Traditional methods for validating analyte recovery through a thermal desorption system were complex and tedious. Users were generally recommended to carry out a multi-level calibration using the thermal desorber and then set up an equivalent liquid injection system (same column, column flow, split ratio, *etc.*) and repeat the process[52]. Aside from the time required, it is difficult to exactly match column and split flows for two such different GC injection systems, especially in the case of double-split TD methods. The latest international standard methods for thermal desorption have therefore begun to recommend the use of quantitative re-collection for repeat analysis as an alternative approach – see TDTS 24 and Figures 14 and 19.

7 An introduction to thermal desorption applications

Having concentrated thus far on describing the necessary functions for thermal desorption and how to optimise methods, we can now begin to address the application range. But first, it is worth briefly considering its limitations.

Most thermal desorption systems do not provide the best GC interface option for:

- Inorganic gases such as O_2, O_3, N_2, CO_2, NO_x, SO_x and NH_3 (there are notable exceptions including N_2O, H_2S and SF_6, which can all be conveniently monitored using TD methods)
- Methane: This is hard to trap quantitatively, even on the most efficiently cooled sorbent traps. However, it is often present in such abundance (relative to other organic vapours) that it can typically be monitored without pre-concentration, *e.g.* using conventional flame ionisation detectors
- Organic compounds that are not compatible with conventional GC analysis
- Non-volatiles, *i.e.* compounds less volatile than n-$C_{40/44}$, didecyl phthalate or 6-ring polyaromatic hydrocarbons (PAHs)
- Organics retained in a thermally unstable sample matrix.

Apart from this limited number of exceptions, thermal desorption can enhance/facilitate a wide range of GC applications, especially those that present a 'challenge' to conventional inlet technology, *i.e.* liquid autosamplers, static headspace or gas sample valves. Suitable analytes include any GC-compatible organic compounds within the constraints listed above.

8 Air monitoring

Air monitoring is the first application everyone thinks of in connection with thermal desorption, but it is a broad field which can be subdivided into several distinct areas[7,38]. The following text summarises these different areas and presents some topical examples.

8.1 Workplace air monitoring

Monitoring personal (inhalation) exposure to toxic chemicals for compliance with workplace health & safety regulations was one of the very first applications of thermal desorption. Samples are typically collected using pumped or diffusive sorbent tubes according to various national and international standard methods[27,52,54–56]. Time-weighted average measurements, *e.g.* over an 8-hour shift, are then assessed against threshold limit values (TLVs), sometimes called 'Occupational Exposure Limits' (OELs), to check compliance. While vast improvements in workplace health & safety have been implemented in most industrialised countries over recent years, the developing world still struggles to keep personal exposure levels below safe limits. Additional information on chemical toxicity has also led to the continued re-evaluation and reduction of many limit levels, thus driving the ongoing need to monitor personal exposure at lower and lower concentrations.

There are many excellent publications reporting on use of analytical thermal desorption for occupational hygiene[57,58]. One important point is that best practice typically requires average monitoring results to be well below prescribed limit levels (*e.g.* one tenth). This is because differences in behaviour between individuals generate such a wide range of results (for example, over 1 or 2 orders of magnitude[1]) that it is only when the average falls well below the OEL that it is safe to assume no workers are being exposed to unsafe levels.

Related TD applications include biological monitoring – *i.e.* measuring chemical concentrations in the blood, urine, or breath of workers as a means of assessing their chemical exposure *via* all possible routes (ingestion and skin absorption, as well as inhalation[40,59,60]). Generally speaking, subjects prefer to provide a breath sample, rather than blood or urine, and another benefit of this non-invasive approach is that it doesn't require trained medical personnel[40]. With sufficient data, guideline 'acceptable breath concentration' levels can be set for specific processes or tasks. However, results are more typically interpreted in relative terms – *e.g.* to make sure exposure levels don't increase over time or to identify anomalies across a group of workers all supposedly doing the same job. Guidance notes are available to help interpret breath monitoring data for some common skin-absorbed compounds[61].

8.2 The diagnostic potential of breath analysis

While perhaps not a mainstream air monitoring application, there is also increasing interest in the diagnostic potential of VOCs in breath[39,62]. Many metabolic processes and disease states produce specific indicative VOCs or patterns of VOCs – *e.g.* diabetes and stress. The diagnostic potential of breath has been extensively studied for lung/respiratory conditions (lung cancer, asthma, TB, *etc.*)[39,62–65], and has even been investigated for gut disorders and mental health conditions.

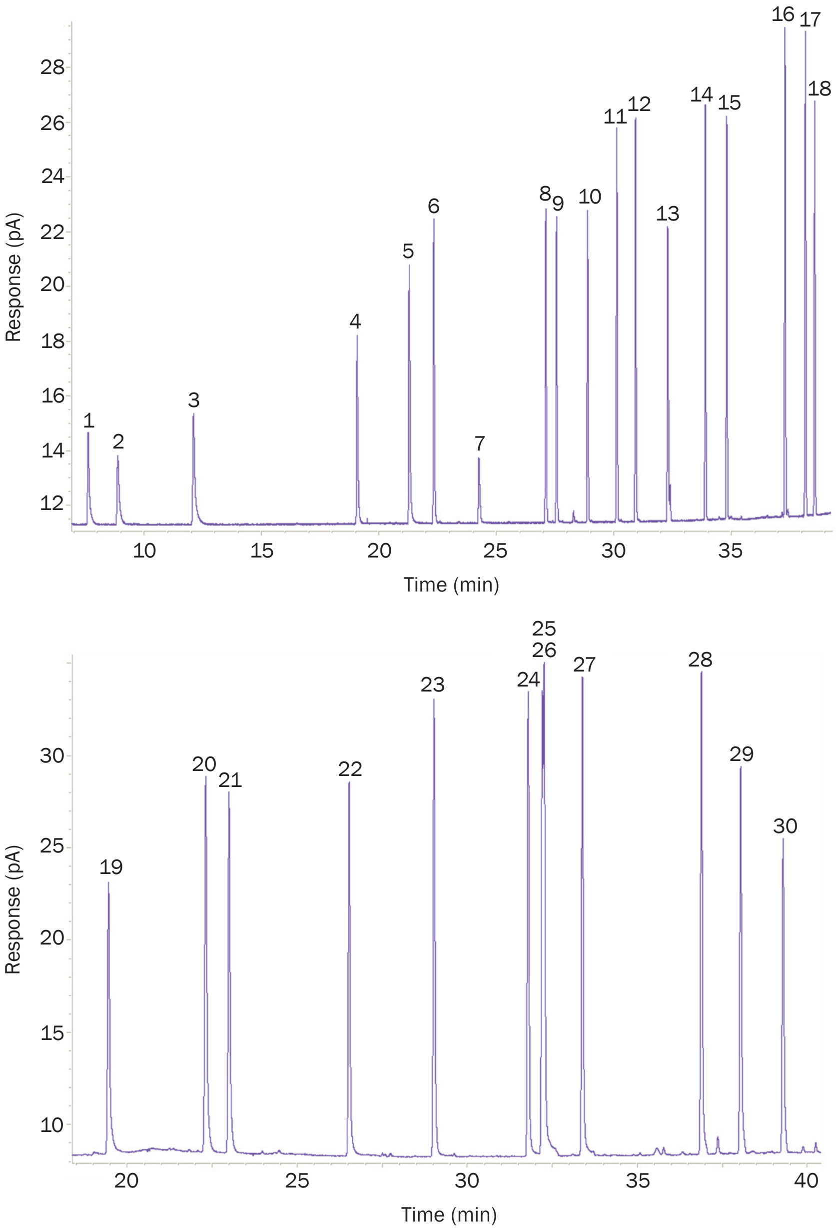
Other applications for monitoring VOCs in breath have included:

- Investigations of the permeability of human skin to volatile halogenated species at elevated (bath/shower) temperatures[60]
- Studies of halitosis or breath odour[66]
- Identification of compounds that can be used as reliable indicators of smoking[67,68].

8.3 Ambient outdoor and indoor air monitoring

TD–GC/MS has been the analytical method of choice for ambient air monitoring applications for over 20 years. A wide variety of sampling options are applied to this field depending on monitoring objectives. On-line or near-real-time monitoring systems are used for round-the-clock monitoring of key pollutants such as ozone precursors[22–24,69,70] in urban air (see TDTS 16 and Figure 20) and odorous sulfur compounds (hydrogen sulfide, methane thiol, dimethyl sulfide, dimethyl disulfide) near landfill sites and sewage treatment works[71,72] (see TDTS 32). Off-line sampling options include both sorbent tubes[73,74] and whole-air sampling into canisters[75] (see TDTS 80). Applications for whole-air sampling options such as canisters include the more volatile 'air toxic'[76] species and ultra-volatile trace greenhouse gases – CF_4, C_2F_6, SF_6, *etc.*[77] (see TDTS 87). Generally speaking, most indoor and outdoor air monitoring applications are more conveniently sampled using pumped sorbent tubes[7,17,27,38,54,76,78–81].

Some detailed studies of air pollution in large cities have been carried out using diffusive sampling onto sorbent tubes. The low cost of passive (diffusive) sampling facilitates the collection of large numbers of samples, allowing accurate mapping of pollution isopleths (Figure 21)[82].



Experimental conditions

System: UNITY™-Air Server™–GC configured with Deans switch.
Trap: Multi-sorbent ('ozone precursor') trap at –30°C.
Trap desorption: 40°C/s to 325°C.
Flow path: 80°C.
Columns: 60 m × 0.25 mm × 1.0 µm; 50 m × 0.32 mm × 8 µm.
GC oven: 30°C (12 min), 5°C/min to 170°C, then 15°C/min to 200°C.
Deans switch at 17.5 min.

1	Ethane
2	Ethene
3	Propane
4	Propene
5	2-Methylpropane
6	n-Butane
7	Acetylene
8	*trans*-But-2-ene
9	But-1-ene
10	*cis*-But-2-ene
11	2-Methylbutane
12	Pentane
13	Buta-1,3-diene
14	*trans*-Pent-2-ene
15	Pent-1-ene
16	2-Methylpentane
17	Isoprene
18	n-Hexane
19	Benzene
20	2,2,4-Trimethylpentane
21	n-Heptane
22	Toluene
23	Octane
24	Ethylbenzene
25	*m*- and *p*-Xylene
26	
27	*o*-Xylene
28	1,3,5-Trimethylbenzene
29	1,2,4-Trimethylbenzene
30	1,2,3-Trimethylbenzene

Figure 20: On-line monitoring of 'ozone precursors' (C_2 to C_9 hydrocarbons) using TD–GC with dual column/Deans switch configuration and dual FID.

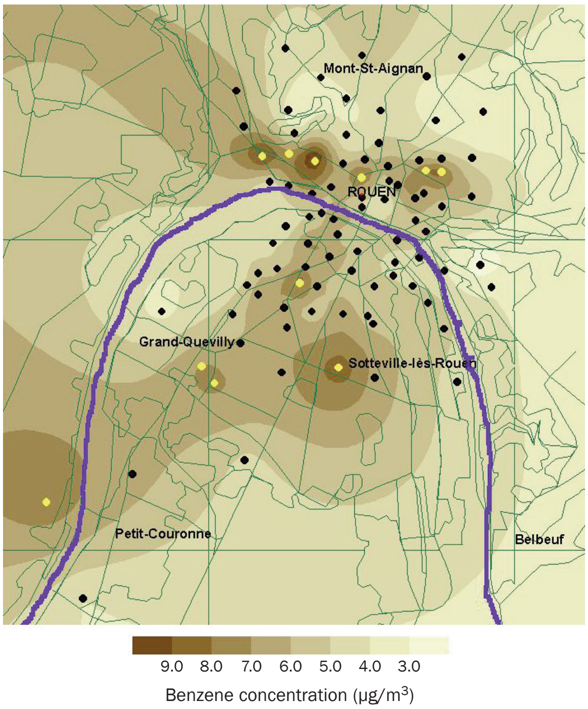


Figure 21: Mapping criteria pollutants in urban air around Rouen, France, using diffusive sampling over a 5-day period.

8.4 Industrial (fugitive) emissions

Thermal desorption has always been popular for monitoring around the perimeter of industrial plants as a check on the impact of industrial emissions. Again, the simplicity of diffusive monitoring means that 10 or 20 samplers can be cost-effectively deployed around a site, allowing accurate mapping of pollution/contamination levels under different wind and weather conditions[83].

While most bulk organic vapour measurements in industrial emissions (stack or flue gases) are made using sensors (continuous emission monitoring (CEM) technology), lower-level toxic organics are measured using sorbent tubes with either solvent extraction or thermal desorption. Key test methods have included EPA Methods 0030, 0031 and 5041A in the US, and EN 13649 in Europe[84]. While originally restricted to solvent extraction, EN 13649 is currently being revised to include thermal desorption, in response to demand from industry.

8.5 Atmospheric research

Recent fears about the impact of air pollution on climate and the stratospheric ozone layer have led to numerous national and international research projects into atmospheric pollution. Investigated issues have included global background pollution (monitoring some of the cleanest air on earth[85,86]), atmospheric chemistry, biogenic emissions[87,88], and measurements of air–seawater interactions[89].

These studies typically involve vapour concentration measurements at ppt or even ppq concentrations, requiring the best available TD–GC technology coupled with high-sensitivity MS detection (*e.g.* negative-ion chemical ionisation (NCI), triple-quadrupole, time-of-flight). Preferred sampling options include pumped sorbent tubes or canisters[86], depending on target analyte range.

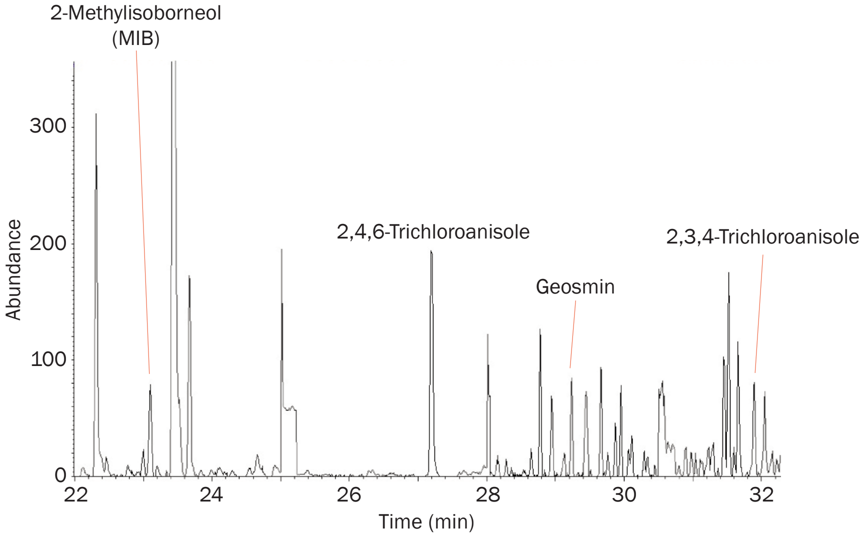
8.6 Soil gas and vapour intrusion into buildings

As the human population continues to expand, there is increasing pressure to redevelop disused industrial land rather than build on 'greenfield' sites. However, as in the case of the infamous Love Canal incident mentioned in Section 2, there is always concern that the residue from old chemical processes, or leaks from disused chemical/fuel storage tanks, may remain in the soil. Redevelopment of industrial land therefore requires detailed assessment and remediation of any identified contamination. Even after remediation (clean-up), long-term monitoring of soil gas, or air from inside buildings that are developed on the site, may be required to make sure that the risk from any residual pollution remains low. Occasionally it is necessary to adapt building construction to minimise risk of vapour intrusion – for example, by installing impermeable membranes in the basement.

The US has led the way in this field, and many related monitoring methods are now under development, for example within ASTM. Cited soil gas (or 'under-slab') sampling approaches include using canisters (limited to compounds more volatile than n-$C_{9/10}$) and active or passive sampling onto sorbent tubes (compatible with a wider volatility range). In both cases, analysis is by thermal desorption[7,90–92].

8.7 Water odour

A few odorous organic compounds – *e.g.* geosmin, 2-methylisoborneol and the trichloroanisoles – are responsible for a high proportion of complaints about drinking water quality. They are typically detectable down to 10 ppt by the human nose, and while they don't present an actual health hazard at these levels, their musty, earthy smell is a real concern to consumers. Conventional GC sampling methods such as static headspace or purge-and-trap do not offer sufficient sensitivity for this demanding application, and it is one of the areas where sorptive extraction or HS–TD (headspace–trap) have recently been found to present a potentially useful automatic alternative. Detection limits in the order of 1–2 ppt have been reported[35] (Figure 22).



Experimental conditions

System: HS-5TD™–GC/MS.
Trap: Multi-sorbent (‘general purpose’) trap at 25°C.
Vial temp: 45°C.
HS-TD analysis: 10 HS vial sampling cycles at 50 mL/min.
Trap purge: 2 min.
Trap desorption: 50°C/s to 300°C splitless.
Flow path: 160°C.
Column: 60 m × 0.25 mm × 0.25 µm.
GC oven: 50°C (2 min), 5°C/min to 175°C, then 20°C/min to 260°C.
SIM ions: Group 1: 95, 108, 135; Group 2: 195, 197, 210, 212; Group 3: 112, 182.

Figure 22: 5-ppt-level odorants in drinking water analysed by TD–GC/MS (SIM).

8.8 Monitoring tracer gases

Tracer gases typically comprise perfluorinated compounds such as sulfur hexafluoride or perfluoromethylcyclohexane, because they don’t occur naturally and are readily detected at low levels by GC methods (*e.g.* by using electron capture detection or GC/MS in NCI mode). Sources of tracer gases are placed in various locations in buildings or vehicles. On- or off-line TD–GC methods are then used to monitor the tracer gas concentrations as they change over time, thus allowing ventilation efficiency to be evaluated. Both passive and active sampling methods have been applied[93,94].

It is interesting to note that halogenated organic compounds are now known to play a key role in ozone depletion (*i.e.* damaging the ozone layer) and to have very high global warming potential (5000 to 10,000 times more than that of CO_2). They also have a long half-life in the atmosphere. SF_6, for example, can now be detected around the planet at ~6 ppt and Freon® 113 at around 75 ppt (Figure 23). While these levels do not present any immediate or significant environmental risk, scientists are nevertheless concerned to make sure their research does not contribute to global pollution levels. Use of tracer gases has therefore been minimised over recent years.

For more information on all TD applications relating to environmental monitoring, see Markes’ Applications Guide I.

Experimental conditions

System: TD-100™–GC/MS; GC–BenchTOF-dx™.
Tube: Stainless steel, packed with carbon black and carbon molecular sieves.
Tube desorption: 10 min at 320°C.
Trap: Multi-sorbent (‘air toxics’) trap at +25°C.
Trap desorption: 320°C at 40°C/s with 5 mL/min split.
Flow path: 140°C.
Column: 60 m × 0.32 mm × 1.8 µm.
GC oven: 35°C to 230°C at 5°C/min.
Quad MS: 20–300 amu (scan).
SIM ions: Group 1: 56, 67, 93, 151; Group 2: 57, 78, 106; Group 3: 58, 91, 117.
Masses acquired using TOF-MS: 20–300 amu.

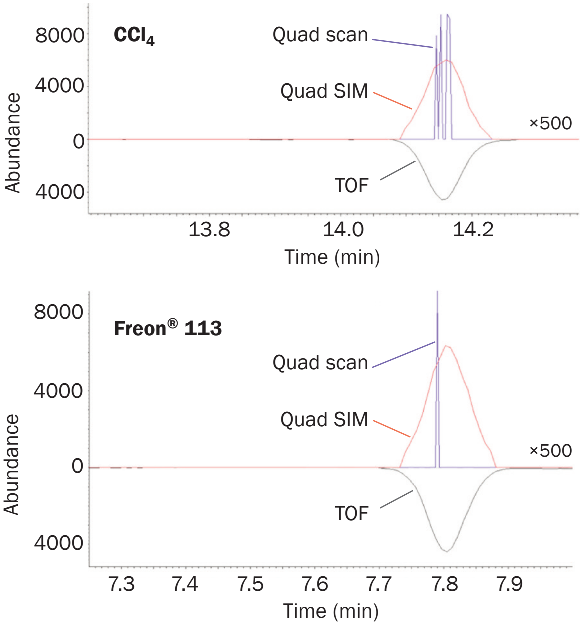


Figure 23: Comparison of TD–GC/MS data obtained for the analysis of carbon tetrachloride and Freon® 113 in 200 mL forest air. Blue: Quad scan data. Red: Quad SIM data. Black: TOF data. Quad data (scan and SIM) are expanded by a factor of 500 relative to the TOF data.

9 Chemical emissions from everyday products

Fears relating to global warming have also driven new regulations relating to the energy performance of buildings[95]. Unfortunately, this well-intentioned legislation has had the unwanted side-effect of significantly reducing building ventilation levels and impacting indoor air quality. Whereas air change rates in north European or US housing stock were traditionally in the order of 1 or 2 per hour, this has been reduced to 0.2 air changes per hour or even lower in some new homes/offices[96,97]. Reports of adverse health effects have therefore led to increased focus on controlling the sources of pollutants, including chemical emissions from products used indoors[98]. Construction products, decorative materials, car interior trim components, furniture and cleaning products have all come under the spotlight. Even natural materials that have been used for centuries in traditional housing may compromise air quality when installed in modern air-tight dwellings.

Experimental conditions

System: Micro-Chamber/Thermal Extractor™ with TD-100™–GC/MS.
Chamber temperature and flow: 50 °C and 100 mL/min dry air.
Equilibration time: 20 min.
Vapour sampling time: 15 min, onto a stainless steel tube packed with Tenax® TA.
Tube desorption: 5 min at 280 °C.
Trap: Multi-sorbent quartz–Tenax–Carbograph™ 5TD trap at +25 °C.
Trap desorption: 300 °C with 30 mL/min split flow.
Flow path: 150 °C.
Column: 60 m × 0.25 mm × 0.5 µm.
GC oven: 40 °C to 225 °C at 10 °C/min.
Scan range: 35–300 amu.

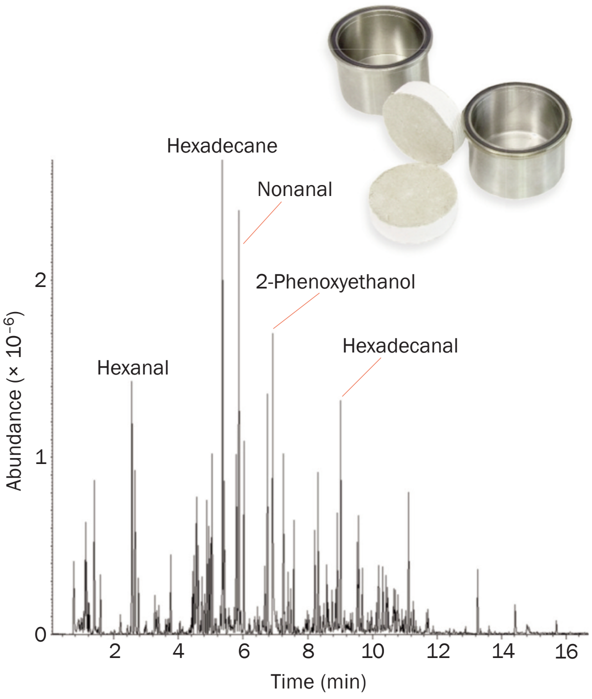


Figure 24: Screening chemical emissions from plasterboard (dry wall) using test chambers/micro-chambers or emission cells with sorbent tubes and TD–GC/MS.

New regulations[99–101], test protocols[102–104] and analytical methods[105–107] have been developed to address these concerns. Those relating to vapour-phase organic chemicals predominantly specify use of sorbent tubes with subsequent TD–GC/MS analysis[28,108] [*].

Reference methods for material emissions testing generally specify small environmental chambers (typically 20–1000 L volume) or test cells, both of which can be used to evaluate chemical emissions from products and materials under simulated real-use conditions. Samples are usually prepared so that only the surface exposed to the indoor environment is exposed in the test chamber or cell. Pure humidified air is then driven into the chamber under specified conditions of temperature, humidity, time, *etc.* After a given period, the exhaust air is sampled and analysed as described above to measure the area-, mass- or component-specific chemical emission rate. Tests are usually carried out over an extended period (typically 3, 7, 14 or 28 days) to simulate airborne concentrations soon after product installation or building occupation – see TDTS 55, 56 and 70–72.

Faster emission screening methods using micro-chambers have been developed recently[111,112] to complement long-term reference tests and to provide industry with a practical tool for routine in-house use (see TDTS 67–69, 89 and 90). Micro-chambers are also used in combination with sorbent tubes and TD–GC/MS to measure emitted organic vapours (Figure 24) or with DNPH cartridges and subsequent HPLC analysis for formaldehyde emissions.

There are numerous publications and reports describing emission tests from construction products and car trim[113,114]. Other everyday products which are commonly subjected to emissions testing include furniture, furnishings and toys (Figure 25). Note that, even though the toy emission profiles shown in Figure 25 were obtained at relatively low temperatures (40 and 90 °C respectively) they still show emission of significant levels of key SVOCs – including phthalates, several of which are now designated 'Substances of Very High Concern' under REACH[†], and bisphenol A, which is a known endocrine disruptor.

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[*] Formaldehyde is the primary exception to this. It can be analysed by TD–GC(MS), but is so reactive and prone to hydrolysis that it is very difficult to store in its free state. Most reference methods therefore specify sampling using cartridges impregnated with dinitrophenylhydrazine (DNPH). This reacts with the formaldehyde to form a more stable derivative, which is then analysed by solvent extraction and HPLC[109,110]

[†] REACH: European Directive [2006/121/EC] on the Registration, Evaluation, Authorisation and restriction of CHemicals.

Experimental conditions

System: Micro-Chamber/Thermal Extractor™.
Chamber temperature and flow: 40 °C and 100 mL/min flow (top chromatogram); 90 °C and 50 mL/min flow (bottom chromatogram).
Equilibration time: 20 min.
Vapour sampling time: 15 min in each case.
Similar analytical conditions to Figure 24.

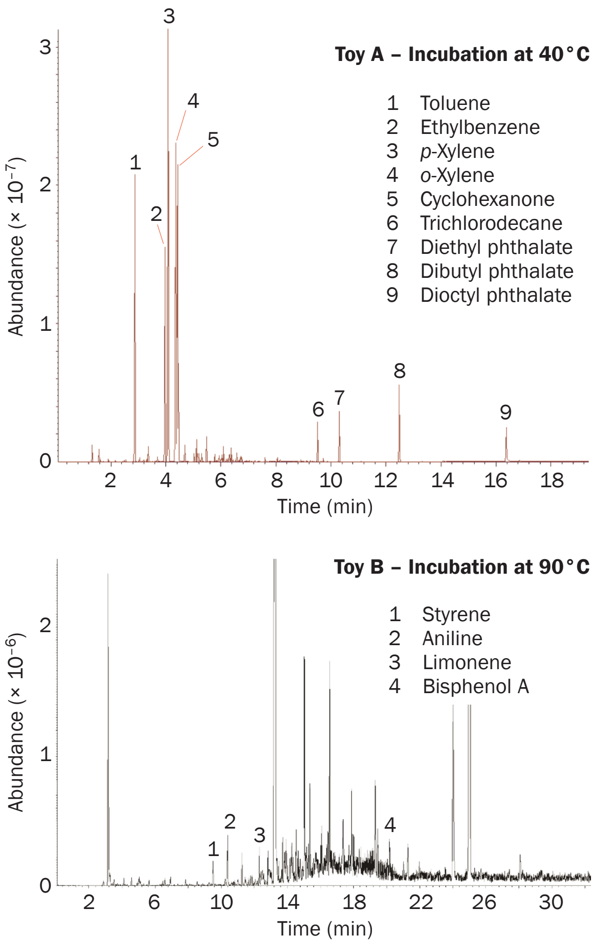


Figure 25: Screening volatile and semi-volatile chemical emissions from children's toys.

Emissions testing is now being implemented more widely within the manufacturing industry to ensure consumer safety and to take advantage of market demand for low-emission products. Specific applications include quality control of production, development of new low-emission product ranges, monitoring raw materials, and comparison against best-in-class competitors. Similar procedures are used for quality control of volatile and semi-volatile chemical emissions from sensitive electronic components such as PC hard-drives.

For more information on TD applications relating to chemical emissions from materials, see Markes' *Applications Guide II*.

10 Chemical warfare agents and civil defence

While in many ways a simple extension of air monitoring, use of thermal desorption for detection of extremely toxic chemical agents is now considered a field in its own right. Example applications include:

- Monitoring agent storage and destruction facilities – to ensure the safety of personnel and protect the nearby environment
- Continuous monitoring of critical civilian locations – transport hubs, key government buildings, *etc.*
- Studies of decontamination technology and protective coatings, *e.g.* paints designed to prevent agent from penetrating into the fabric of buildings or machinery to simplify decontamination in the event of a chemical attack
- Battlefield protection – using sorbent tubes with TD–GC(MS) to evaluate protective equipment – *e.g.* monitoring the permeation of agent through masks and clothing
- First responders – teams equipped with mobile laboratories and trained to be the first on the scene in the event of a major chemical incident.

Many of the most toxic chemical warfare agents present a major analytical challenge, because of the low detection limits required (*e.g.* 0.0006 µg/m^3 for general population exposure) and because of the reactivity and/or 'stickiness' of the compounds themselves.

Early TD technology was not compatible with many of the highest-boiling or most reactive CW agents. VX, for example, was traditionally monitored by sampling the air

Experimental conditions

System: UNITY™ 2 TD–GC/FPD.
Tube: Silcosteel packed with Tenax® TA.
Tube desorption: 8 min at 300 °C.
Trap: Multi-sorbent quartz–Tenax trap at +20 °C.
Trap desorption: 300 °C (splitless).
Flow path: 200 °C.
Column: 30 m × 0.25 mm × 0.5 µm.
GC oven: 60 °C to 250 °C at 20 °C/min.
FPD: 250 °C, H_2 150 mL/min, air 110 mL/min, N_2 55 mL/min.

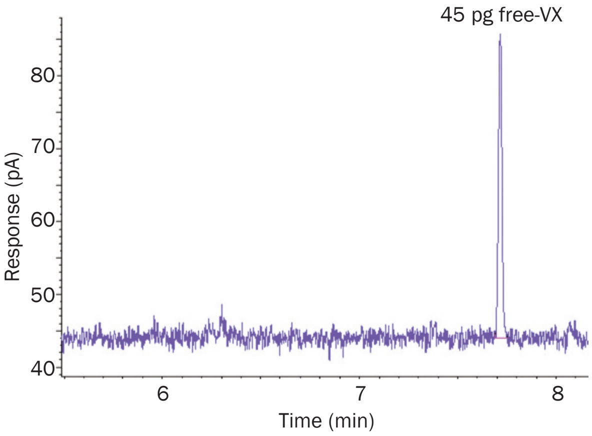


Figure 26: TD–GC/FPD analysis of 45 pg free-VX on-tube.

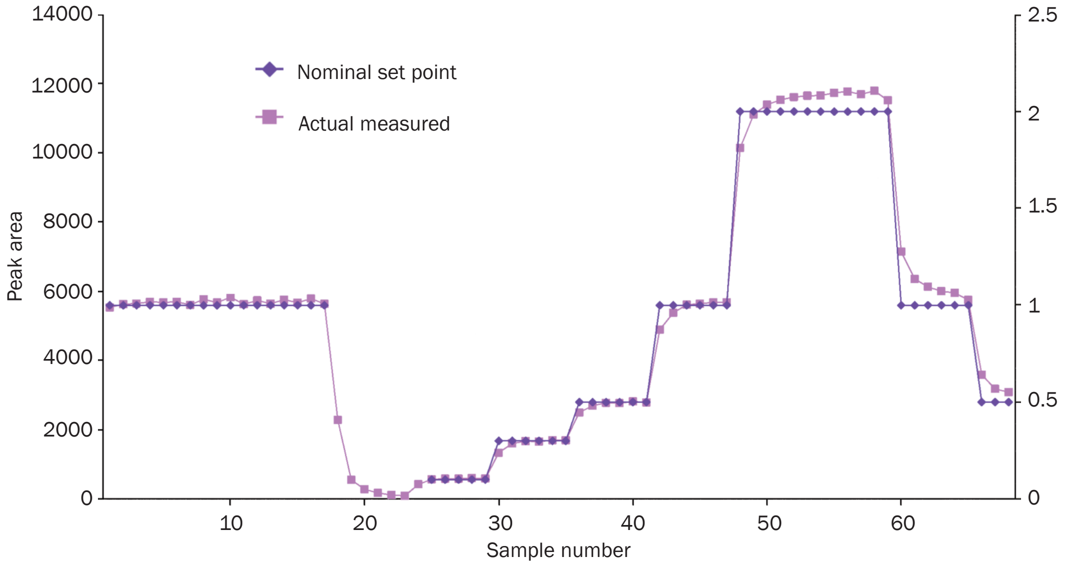


Figure 27: Using twin-trap thermal desorption equipment (Markes' TT24-7™) for continuous, near-real-time monitoring of the chemical warfare agent sarin (GB) in a dynamically generated standard atmosphere (see reference 54).

through silver fluoride pads to produce the more volatile 'G-analogue'[115]. However, the performance of this conversion process was rarely 100% efficient and tended to diminish as the pads aged, leading to risk of under-reporting. The latest on- and off-line thermal desorption technology is compatible with free-VX even at the lowest levels (Figure 26), thus removing the need for derivatisation and reducing analytical uncertainty.

Much of the impetus for developing twin-trap TD configurations also came from chemical agent monitoring applications. Twin-trap systems allow air or gas streams to be sampled continuously, thus generating near-real-time data without any unsampled time or 'blind spots'. While air is being drawn into trap A, trap B is desorbed and analysed. Once trap B has cooled, it can be switched to sampling, thus allowing trap A to be desorbed. Data shown in Figure 27 illustrates continuous monitoring of the chemical agent sarin (GB) using one such system. Typical applications for this kind of technology include continuous monitoring of government buildings against terrorist attack and process monitoring at agent destruction ('demil') facilities to ensure the safety of site personnel.

For more information on TD applications relating to chemical agents, see Markes' Applications Guide III.

11 Direct desorption of residual volatiles

TD–GC/MS is now widely applied for measurement of residual volatiles and VOC content. As described in TDTS 9, many relatively dry and homogeneous materials can be conveniently weighed into empty sample tubes or tube liners (Figure 7) for analysis by gas extraction (dynamic headspace) process. Direct (thermal) desorption works best with materials that have a high surface area to mass ratio (powders, granules, fibres, or films). The power and simplicity of direct TD relative to conventional static (equilibrium) headspace methods is that no additional dissolution or salting-out steps are required, and that it does not rely on partition coefficients or equilibria. Furthermore, complete (or nearly complete) extraction is often possible in one run, thus simplifying calibration.

Another advantage of direct thermal desorption is that it can be applied to much smaller sample sizes (*e.g.* 2 or 3 mg rather than the 2 or 3 g often required for conventional headspace). This makes it suitable for some forensic applications (see Section 13) and for measuring residual solvents when sample amounts are limited, *e.g.* prototype pharmaceuticals.

A lot of direct desorption applications fall under the general header of manufacturing QA/QC. Materials suitable for this approach include:

- Pharmaceutical powders and medicinal ointments – see TDTS 91 and Figure 28[15]
- Soap powders
- Textiles and treated leather – see TDTS 40 (Figure 29)
- Paints and adhesives – see TDTS 57
- Polymers in powder, granule, film or fibre form[15]
- Packaging materials[116]
- House dust[117].

For more information on TD applications relating to direct desorption, see Markes' Applications Guide II.

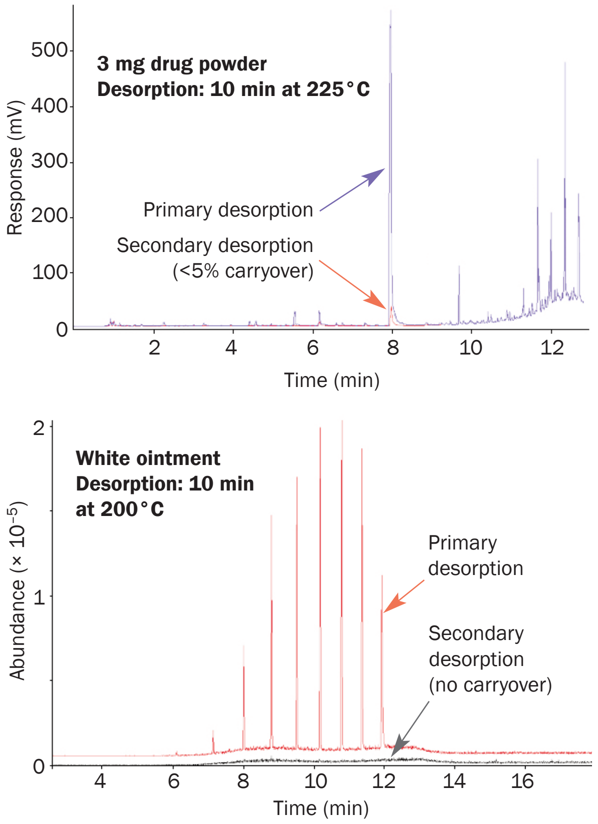


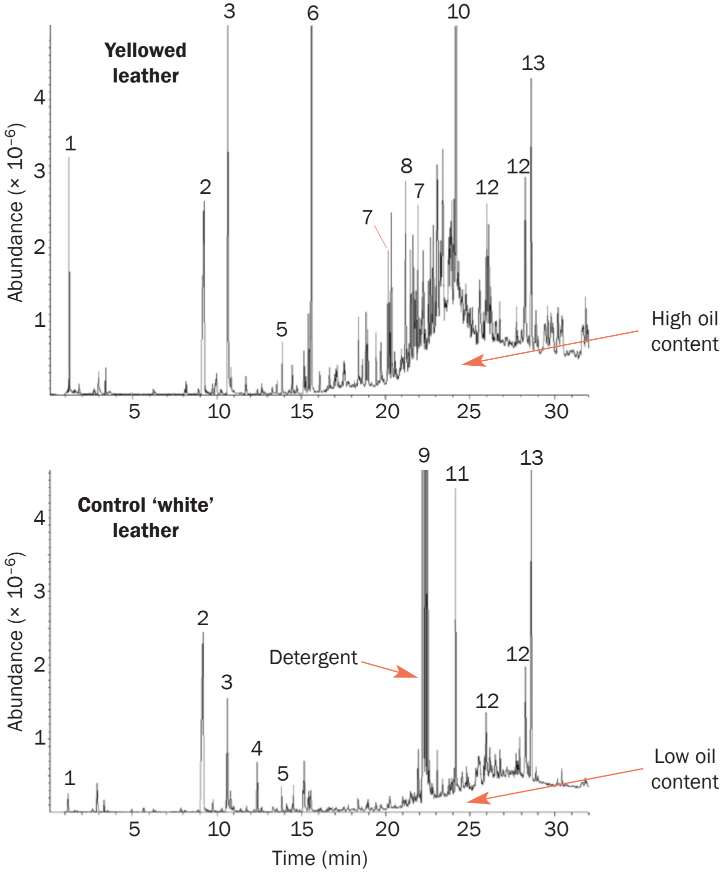
Figure 28: Direct desorption of residual solvents and/or active ingredients from pharmaceutical preparations.

12 Food, flavour, fragrance and odour profiling

Direct thermal desorption can also be applied to the characterisation of aroma and fragrances. Relevant applications include the profiling of dried foodstuffs, such as spices, instant coffee, cocoa powder and tobacco. In this case, the intention is not to get complete extraction but to obtain a characteristic chromatographic profile. Temperatures are typically kept low to prevent denaturing the sample.

Direct TD (dynamic headspace) fulfils a different purpose than conventional equilibrium headspace for this type of work. Whereas standard headspace selectively concentrates the most volatile constituents, thermal desorption allows analysis of a wider, more representative profile of the overall aroma (odour), including both volatile and less volatile components. The technique is also very sensitive, accentuating even minor differences in composition (*e.g.* 5% less of one ingredient and 10% more of another), thus allowing very precise quality control[118,119].

HS–TD and sorptive extraction (see Section 4.2) complement direct thermal desorption by providing tools that can be used to study organic volatiles and semi-volatiles in drinks such as wine, beer, fruit juices (see TDTS 88 and 94) and food extracts[35,120,121]. When applied together, these approaches provide a comprehensive profile of organic chemicals in products derived from natural materials (Figure 17).



1	Sulfur dioxide
2	Diethylene glycol
3	1-Methyl-2-pyrrolidone
4	Nonanal
5	2-(2-Butoxyethoxy)ethanol
6	*tert*-Butylphenol
7	Octylphenol isomer
8	Chlorotriazine derivative
9	Tris(chloropropyl) phosphate (3 isomers)
10	Heptadecanoic acid
11	Palmitic acid
12	Fatty acids
13	Dioctyl adipate

Experimental conditions

System: Direct TD–GC/MS using a UNITY™ system.
Sample: 1.5 mm × 10 mm sections of control and discoloured leather.
Desorption: 150 °C for 5 min.
Flow: 60 mL/min carrier gas (split 50:50).
Trap: Tenax®/Carbograph™ 1 at –10 °C.
Trap desorption: 300 °C with 30 mL/min split flow and 2 mL/min column flow.
Flow path: 200 °C.
Column: 30 m × 0.32 mm × 1.0 µm.
GC oven: 60 °C (5 min hold) to 280 °C at 10 °C/min.
Scan: 45–350 amu.

Figure 29: Direct desorption of discoloured and control samples of white leather. The control sample shows detergent residue and much lower levels of natural oils.

Conventional on- or off-line sorbent sampling modes of thermal desorption are also extensively applied to monitoring fragrance, aroma and odour profiles in air.

Overall, this is a growing field with many interesting applications and research opportunities. Many examples are included in Markes' Applications Guide IV. Highlights include:

- Accelerated food shelf-life studies, sometimes using similar micro-chamber technology to that applied to material emissions testing (see TDTS 95)
- The composition of air freshener profiles and the kinetics of fragrance decay
- Identification of crop emissions, plant species and plant health[122–124]
- Monitoring flavour/aroma quality in genetically modified foods[125]
- Studies of insect–plant interactions and pheromones[126]
- Identifying moulds, fungi and bacteria[127]
- Tracking sources of taint and off-odour
- Studies of human body odour and bad breath[128,129].

For more information on TD applications relating to food, flavour, fragrance and odour profiling, see Markes' Applications Guide IV.

13 Forensic applications

The big advantage of thermal desorption as a GC sample introduction technology for forensic applications is that it requires little or no manual sample preparation. This is important for forensic science because it means that there is less risk of compromising data and thus of evidence being challenged in court. Relevant application examples are as follows:

13.1 Accelerants in fire debris

Thermal desorption is often used to determine the presence or absence of 'accelerants' (*i.e.* fuels such as gasoline or kerosene) in burnt residue from the scene of suspected cases of arson[130]. Typically the fire debris is collected in inert containers like metal cans or nylon bags. Pumps or large gas syringes are then used to draw the headspace vapours through well-conditioned sorbent tubes. The volume of vapour sampled varies considerably because the only objective in this case is to determine whether or not accelerants are present. Small volumes (20–50 mL) are therfore sufficient if the sample smells of fuel.

Thermal desorption offers several advantages over conventional static headspace methods for this application. Firstly, it is not limited to specific container sizes (*e.g.* headspace vials). Thus it allows larger, more representative samples of the fire debris to be analysed, giving enhanced sensitivity and better reliability. Moreover, the presence of significant quantities of liquid water in many fire residue samples can present a challenge to detection of trace levels of higher-boiling accelerants using conventional HS. In comparison, the dynamic sampling process of TD allows both selective elimination of water and enhanced detection of less volatile compounds.

13.2 Drugs of abuse

Many drug-related GC/MS applications benefit from the versatility of thermal desorption. Examples include direct desorption of house dust from the scene of a crime (Figure 30), direct desorption of bank notes[131] and detection of amphetamine 'factories' by monitoring the air for indicative solvents. The example shown in Figure 30 is interesting, not only because the levels of drugs were so high in this case (the dust was found to be nearly 3% heroin/cocaine) but also because phenobarbital, an anti-epileptic treatment for dogs, was identified at the same time. *Were the police able to use this finding to narrow their investigations to drug dealers who'd recently visited the local vet?!*

Experimental conditions

System: Direct TD–GC/MS using an ULTRA-UNITY™ system.
Sample: ~5 mg dust in glass tubes supported by quartz wool plugs.
Desorption: 150°C for 10 min.
Flow: 50 mL/min carrier gas.
Trap: Quartz–Tenax® at +20°C.
Trap desorption: 40°C/s to 250°C with 30 mL/min split flow and 2 mL/min column flow.
Flow path: 150°C.

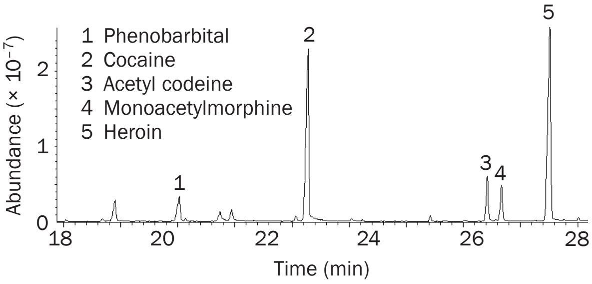


Figure 30: Direct desorption of proscribed drugs in house dust.

Sorptive extraction combined with TD–GC/MS also provides a convenient analytical approach for detecting proscribed substances in biological fluids[132].

13.3 Explosives and shotgun propellant residues

Explosive vapours present a significant challenge even to conventional GC(MS) analysis. These highly reactive compounds are very sensitive to any slight deterioration in system performance – injector activity, column age, detector contamination, *etc.* It is therefore a testament to the performance of Markes' TD technology that two-stage thermal desorption of trace-level DNT and TNT is now considered routine, and that even more challenging compounds such as RDX and PETN can be detected at trace levels (Figure 31). Use of thermal desorption to detect and characterise ('fingerprint') residual propellant on spent shotgun cartridges has also been reported, and can be used to link individual cartridges or weapons to specific crimes (see TDTS 58).

Experimental conditions

System: UNITY™ 2 TD–GC/FPD.
Tube: Silcosteel, packed with quartz wool and Tenax® TA.
Tube desorption: 3 min at 180°C, followed by 2 min at 210°C
Trap: Multi-sorbent quartz–Tenax at +20°C.
Trap desorption: 300°C at 20°C/s with 50 mL/min split flow and 3 mL/min column flow.
Flow path: 180°C.
Column: 30 m × 0.25 mm × 0.5 µm.
GC oven: 60°C to 250°C at 20°C/min.
Scan range: 35–300 amu.

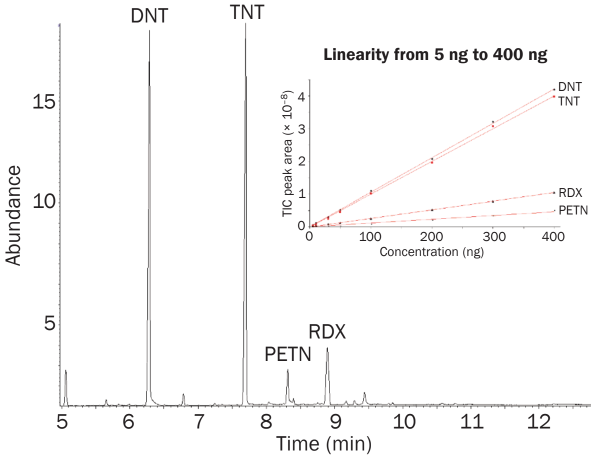


Figure 31: Using TD–GC/MS for detection of trace explosive vapours in air.

13.4 Characterisation of materials

Many materials can be reliably characterised from their VOC profile. Key examples include paper, ink and natural materials such as plants and their fossilised derivatives[122,133].

Figure 32 shows direct desorption of organic volatiles/semi-volatiles from paper with and without writing. Investigations like this may be used to link documents to a particular paper source and/or specific ink/pen ('forensication'). The extent of selective losses of the most volatile constituents in the ink can also be useful in estimating the age of a document.

For more information on forensic applications of thermal desorption, see Markes' Applications Guide III.

Experimental conditions

System: Direct TD–GC/MS using a UNITY™ system.
Sample: ~2 mm × 20 mm sections of paper (with and without ink).
Desorption: 100°C for 5 min.
Flow: 30 mL/min carrier gas.
Trap: Tenax®/Carbograph™ 1 at +25°C.
Trap desorption: 300°C with 20 mL/min split flow.
Flow path: 200°C.
Column: 30 m × 0.32 mm × 1.0 µm.
GC oven: 60°C (5 min hold) to 280°C at 10°C/min.
Scan range: 45–350 amu.

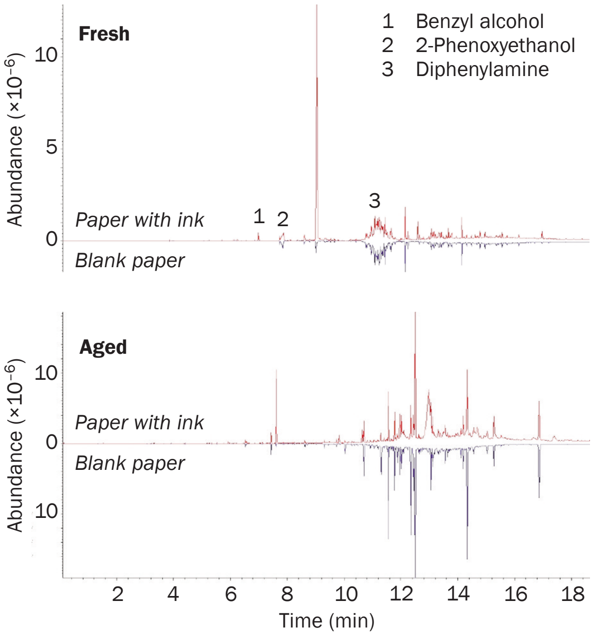


Figure 32: Direct desorption of documents for forensic characterisation of paper and inks.

14 Monitoring chemical processes

The concentrating power of thermal desorption makes it invaluable for detecting leaks in dangerous industrial chemical processes. Key examples include chemical agent destruction facilities and monitoring chemical syntheses that generate lethal by-products such as bis(chloromethyl) ether[134]. In these cases, continuous or very regular monitoring is necessary to ensure the safety of plant personnel.

TD–GC/MS systems are also increasingly used for routine product quality control and development of low-emission materials. Relevant industries include construction products, electronic components, manufacturers of car interior trim, carpeting, furniture, decorative materials and consumer products (air fresheners, domestic cleaning agents, *etc.*) – see Section 9.

Other examples of TD implementation for industrial/process applications include:

- Monitoring trace impurities in CO_2 supplying the food and beverage industries
- Monitoring tracer gases for leak detection in critical fuel pipes or lines
- Control of monoethylene glycol (MEG) and other additives to domestic fuel gas supplies – see TDTS 43.

When used to monitor trace organic impurities in process gas streams such as CO_2, thermal desorption may sometimes be coupled directly to real-time detectors such as sensors (‘e-nose’ technology) or process mass spectrometry. The GC can sometimes be eliminated in these cases, provided the process gas stream is well-characterised, and as long as the range of failure modes and potential contaminants are well known – see Section 15.2. Excluding the GC allows cycle times to be minimised and facilitates rapid detection/notification of any contaminants exceeding control levels.

15 GC-related technologies complementing TD

The concentration power and application range of thermal desorption is enhanced by a number of recent developments in other GC-related fields. Some of the most important examples are discussed below.

15.1 Mass spectrometry

Many of the recent developments in GC/MS are directly relevant to thermal desorption. Triple-quadrupole mass spectrometers, for example, are well suited to TD applications that require detection of specific target compounds at ultra-low levels[77,86,89]. However, given that TD is predominantly used for uncharacterised samples and/or for screening large numbers of compounds, the development of GC-compatible time-of-flight (TOF) mass spectrometers, which offer both high sensitivity AND full spectral information, is particularly exciting.

Sensitivity: As TOF technology does not involve scanning, it should theoretically offer 2 or 3 orders of magnitude better sensitivity than conventional quadrupole MS systems operating in scan mode (depending on mass range). Actual GC/TOF sensitivity varies significantly from instrument to instrument, but modern systems like ALMSCO’s BenchTOF-dx™ are able to provide full spectral information at levels approaching single-ion detection limits on a regular quadrupoles – see Figure 23. This aids quantitative and qualitative analysis of toxic or odorous analytes at the lowest possible levels, and it is thus a perfect detector for many thermal desorption applications.

Using high-sensitivity MS detectors can also benefit routine work by allowing collection of smaller samples without compromising method detection limits. For example, 100 mL of air analysed by TD–GC/TOF may provide as much qualitative and quantitative information as 10 L of air analysed using a conventional quad-MS-based system. Quick/easy low-volume ‘grab’ sampling options[135] and short-term diffusive monitoring can both significantly simplify air monitoring.

Another advantage of the high-sensitivity of BenchTOF-dx as a complement to TD is that it facilitates implementation of more robust and VOC-relevant configurations of comprehensive GC (GC×GC). While the immense resolving power of GC×GC has already been usefully applied to particularly complex thermal desorption applications such as breath and atmospheric research[88,136], most system configurations have, until recently, been based on thermally-modulated GC×GC technology. This uses intermittent cooling and heating to achieve a two-dimensional separation, and works best in expert hands[137]. More robust flow-modulated GC×GC technology is a better option for thermal desorption because it can accommodate volatile compounds[138]. However, as it requires flows in the order of 20 mL/min, implementation with MS has been limited by sample splitting. Given that BenchTOF-dx offers roughly 100 times better sensitivity than regular quad-MS systems operating in scan mode, the necessity to split is no longer so much of an issue – flow-modulated TD–GC×GC systems linked to BenchTOF-dx can still readily exceed standard TD–GC/MS method performance requirements without compromising the collection of full spectral information.

Speed: TOF is the preferred MS technology for fast GC and GC×GC operation because it generates in the order of 10,000 full spectra per second (typically from 10 to 1500 amu and above) without scanning. This eliminates the spectral skew that can sometimes be observed when using conventional quadrupole MS systems to scan fast peaks, and improves signal-to-noise ratios. The high data-collection rate of TOF also allows more efficient application of ‘data-mining’ algorithms such as spectral deconvolution, which are increasingly important for TD applications – see Section 15.2.

Mass resolution and stability: Some of the most recently introduced GC/TOF technologies offer high mass resolution (*e.g.* to 5 ppm), enabling individual compounds to be identified from their accurate mass. These systems are typically at the high end of the cost scale and may not offer the best available sensitivity, but they do provide an invaluable tool for some important environmental applications such as distinguishing the most toxic PCBs or dioxins within complex mixtures of congeners.

However, while accurate mass is rarely a critical issue for the primarily (semi-)volatile-related applications of thermal desorption, mass resolution below 1 amu (*e.g.* 0.1 or 0.01 amu) can be a real advantage, provided it is combined with long-term mass stability. ALMSCO’s BenchTOF-dx offers this important combination of sub-

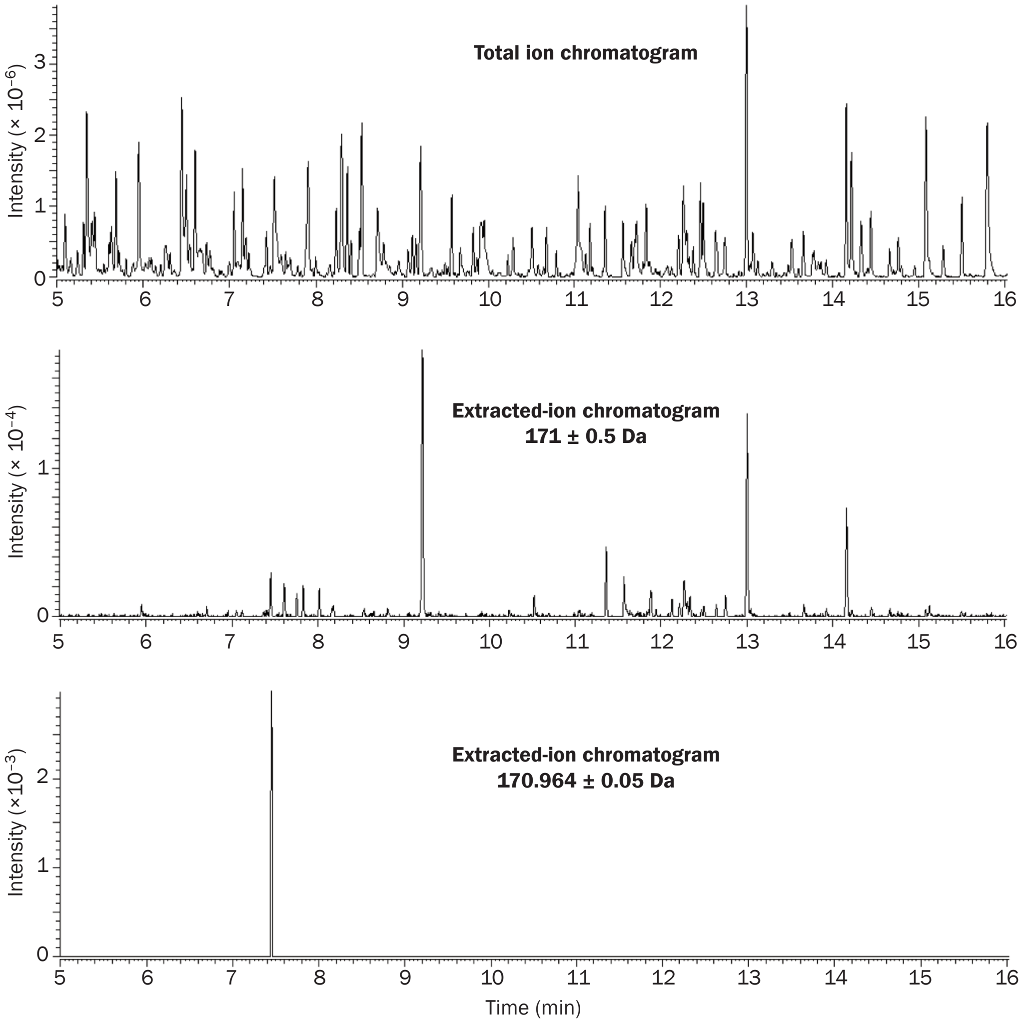


Figure 33: Applying sub-unit mass resolution to minimise chromatographic background and enhance the signal-to-noise ratio in TD–GC/TOF MS analysis of trace components: detection of 1 pg dichlobenil in unprocessed apple extract using an Agilent 7890 GC in conjunction with ALMSCO's BenchTOF-dx™.

unit mass resolution and long-term stability. This means it offers selective and reliable elimination of bulk interferences (Figure 33), thus enhancing identification of trace toxic or odorous compounds. Relevant TD applications include environmental research, chemical agent detection and odour profiling.

15.2 Real-time organic vapour monitors such as sensors or process mass spectrometry

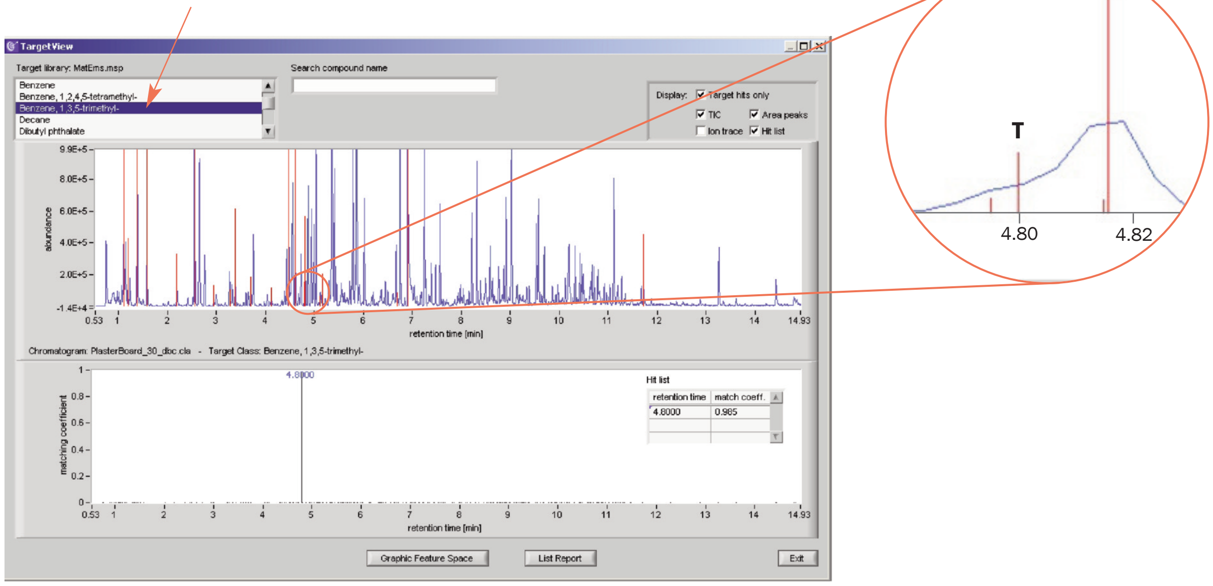
On-line TD configurations are occasionally coupled directly to technology for direct measurement of organic vapours – *i.e.* without a GC interface. Key examples include process mass spectrometry or organic vapour sensors (sometimes called 'e-noses'). In both cases TD improves detection limits (typically by three orders of magnitude) and allows selective elimination of bulk interferences such as air, water and ethanol which could otherwise swamp (mask) the detector response to the compounds of interest.

Near-real-time TD configurations involving direct read-out detectors work best for monitoring stable, well-characterised samples such as industrial gas streams or processes. They are well suited for ensuring vapour composition is within control limits and for detecting significant variations. However, when a deviation is detected, conventional TD–GC/MS invariably offers the most flexible and powerful analytical option for investigating the cause.

15.3 GC/MS data-mining software

Many TD applications generate complex organic profiles (Figure 24), with the odorous or toxic compounds of interest frequently comprising the smallest components in a chromatogram. New MS technologies such as BenchTOF-dx can help by generating accurate (classical) spectra at increased data acquisition rates and with sub-unit mass resolution to eliminate interferences. However, without the benefit of advanced/automated processing functionality such as spectral deconvolution; data analysis remains a skilled and time-consuming task.

Many powerful and automated data-mining software packages are now available commercially, and can be applied to enhance TD–GC/MS data analysis post-run. Some of these compensate for variable background



Target compound –
1,3,5-Trimethylbenzene (**T**)

TargetView

Target library: MatEms.msp

Search compound name

- Benzene
- Benzene, 1,2,4,5-tetramethyl-
- Benzene, 1,3,5-trimethyl-
- Decane
- Dibutyl phthalate

Display: ☑ Target hits only
☑ TIC ☑ Area peaks
☐ Ion trace ☑ Hit list

Chromatogram: PlasterBoard_30_dbc.cla - Target Class: Benzene, 1,3,5-trimethyl-

Hit list

retention time	match coeff.
4.8000	0.985

Figure 34: Application of TargetView™ to detect trace levels of 1,3,5-trimethylbenzene in a composite peak within the complex TD–GC/MS emission profile of a plasterboard sample (see Figure 24).

signals (see TDTS 83 and 85), while others comprise spectral deconvolution algorithms that ‘separate’ (deconvolute) co-eluting compounds by evaluating the rate of change of individual mass ions (see TDTS 66 and 90). Spectral deconvolution identifies the numbers of components present in a single chromatographic peak and assigns individual mass ions and peak profiles to respective constituents.

One of the original and most widely used spectral deconvolution packages for GC/MS was originally developed by NIST in the US and is now available free of charge under the tradename AMDIS (Automated Mass spectral Deconvolution and Identification System). However, applying AMDIS is a complex manual process, and other more automated options such as TargetView™ (ALMSCO) have since become available. TargetView offers a unique and powerful combination of spectral deconvolution algorithms and principal components analysis. It can be applied to screen complex TD–GC/MS total ion data sets (such as that shown in Figure 24) for multiple trace target analytes – see Figure 34. Results are produced automatically within minutes, and are at least as reliable as those that can be generated manually by a GC/MS expert over several hours.

16 Final observations

Thermal desorption is unequalled among GC front-end technologies, and adoption of TD–GC(MS) methods is accelerating, both generally and in key areas such as material emissions testing. The question remains, however, as to why it has taken almost 30 years for serious expansion to begin. While you might expect at least one in ten GC(MS) systems to benefit significantly from interfacing to TD given the application range (considerably more if you consider all the TD-associated procedures such as purge-and-trap, headspace trap and sorptive extraction) why is it that actual take-up is still only a fraction of this?

Probably the most significant limiting factor historically has been availability. Modern, high-performance TD technology was not offered by many of the mainstream GC(MS) manufacturers until very recently. Now that good TD technology is more widely available, this is beginning to lead to a better general understanding of how to get the most out of the technique and a much broader appreciation of its versatility and application potential – gone are the days when thermal desorption was pigeon-holed into a narrow range of VOC air-monitoring applications.

Recent technical advances such as addressing the one-shot limitation and implementing robust automation (cryogen-free operation, reliable tube sealing, *etc.*) have also made it possible for regulators to rely more heavily on TD–GC-based methods, both for service laboratories and for quality control of manufacturing. Going forward, it is possible to see that growth in TD–GC/MS applications will accelerate even faster, both in the area of pre-packaged ‘ruggedized’ systems for regulated industrial applications and, in combination with some of the new GC/MS technologies, for advanced research.

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