MARKES
international

Thermal Desorption Applications Guide:

Fragrance and odour profiling

A comprehensive guide to assessing the odour profiles of products and materials using thermal desorption

Introduction

Fragrance and odour profiling

Analysis of fragranced products such as perfumes, tobacco, toiletries, cleaning products and air fresheners is of great importance for manufacturers, who rely on their products consistently meeting customer expectations.

In this Applications Guide, we describe how thermal desorption (TD) can be used for key applications in the field of fragrance and odour profiling – covering everything from its use for rapid quality control in the tobacco industry, to monitoring how the chemicals released from air fresheners change over time.

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

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

What is thermal desorption?

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

By extracting organic vapours from a sample and concentrating them into a very small volume of carrier gas, TD maximises sensitivity for trace-level target compounds, helps to minimise interferences, and routinely allows analyte detection at the ppb level or below. It also greatly improves sample throughput, by allowing full automation of sample preparation, desorption/extraction, pre-concentration and GC injection.

TD can be used:

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

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

Launched in May 2016, Markes' new 'xr' series of instruments offer performance at least equal to earlier models, with the additional benefits of extended re-collection capability, wider analyte range, and improved reliability. See page 23 and our website for more details.

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

Contents

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

Fragrance and odour profiling

Tobacco

Topic continued on next page

Speeding up tobacco quality control with direct desorption

Quality control of the raw materials used in cigarettes is a significant concern for cigarette manufacturers. Not only may the unprocessed tobacco vary considerably from batch to batch, but the source of any taint in the tobacco needs to be identified quickly.

Direct desorption is a simple, effective, and easy-to-automate way of assessing small quantities of relatively homogeneous materials such as tobacco. It is particularly well-suited for rapidly measuring flavour additives such as menthol or vanillin, for screening the total vapour profile, and for quickly comparing samples against controls or competitors' products.

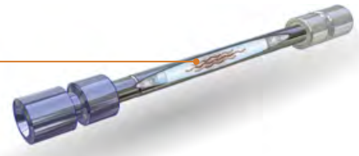
Typical analytical conditions:

Sample: Tobacco (~30 mg), placed in an empty TD tube.

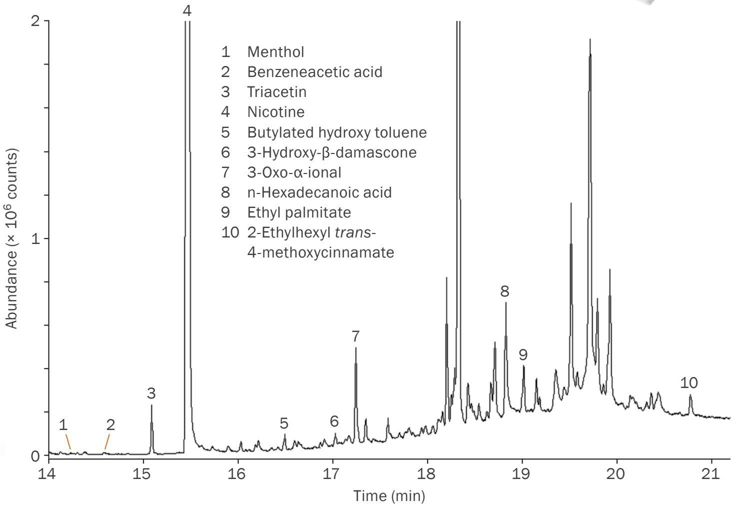
TD (UNITY or TD100): Sample: Desorbed at 120°C (8 min). Trap (General-purpose hydrophobic): Analytes trapped at –10°C, desorbed at 300°C (3 min). Split ratio: Inlet 2.7 : 1, Outlet: 50 : 1 to 100 : 1.

Analysis: GC–MS.

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



Application Note 084



Direct desorption is simple to carry out and correspondingly easy to automate. Here it was used to detect a range of aroma-active components in a tobacco sample.

Tobacco

Topic continued from previous page

Optimising tobacco headspace methods

Samples derived from natural sources, such as tobacco, are often prone to inherent batch-to-batch variability. This makes it important to optimise analytical robustness in order to generate meaningful conclusions, with sensitivity and repeatability being particularly crucial.

As well as direct desorption of small samples (see page 6), TD can be used to enhance the performance of headspace techniques for larger, more representative, samples. Coupling headspace with efficient TD trapping typically improves headspace sensitivity by one or two orders of magnitude, and extends the analyte volatility range while ensuring complete transfer of analytes through the TD flow path (low carryover).

Typical analytical conditions:

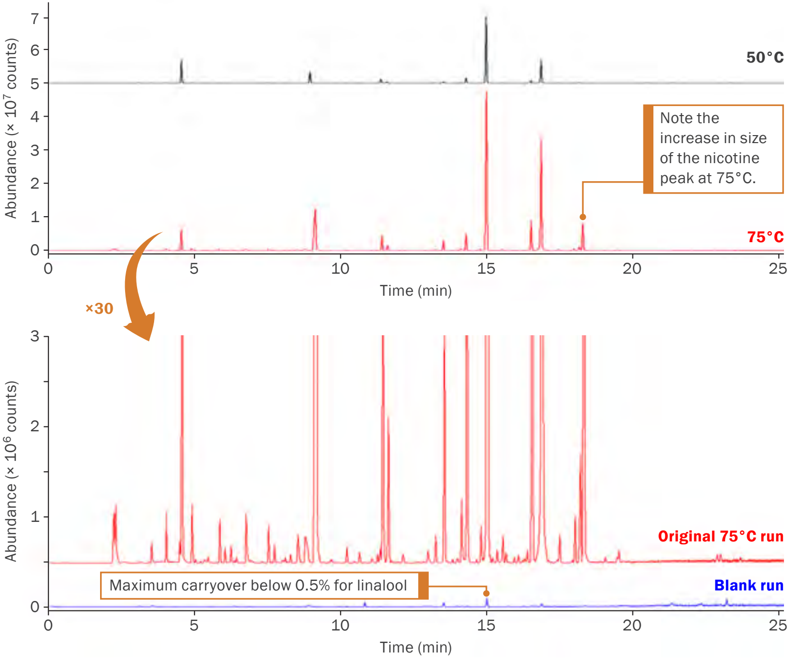
Sample: 0.5 g Indian tobacco.

Headspace (HS5-TD): Equilibration: 0.5 min at 50°C or 75°C. Sample volume: 75 mL. Sample cycles: 3.

TD (UNITY): Trap (General-purpose hydrophobic): Analytes trapped at –10°C, desorbed at 320°C (5 min). Split ratio: Outlet 13.5 : 1.

Analysis: GC–MS.

Application Note 096



Note the increase in size of the nicotine peak at 75°C.

Maximum carryover below 0.5% for linalool

Headspace analysis of tobacco at two vial temperatures shows that significantly higher concentrations and more compounds are extracted at 75°C than at 50°C. A subsequent blank run shows less than 0.5% carryover across all analytes.

Topic continued from previous page

Easy comparison of odour profiles using headspace–TD

Due to different regulations regarding acceptable tobacco additives, cigarette brands from different countries can have very different odour profiles – some of which can be extremely complex. Accurately capturing this diversity in a single analysis can be a challenge.

Headspace–TD methods enhance sensitivity by combining the larger sample sizes of headspace with the concentrating power of TD. As illustrated here, this becomes very useful when trace-level aroma-active compounds are under scrutiny.

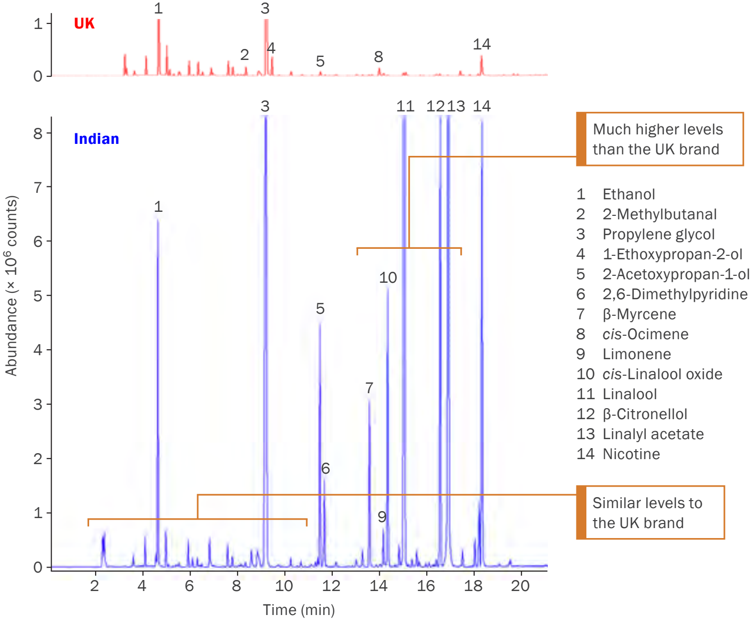
Typical analytical conditions:

Sample: 0.5 g tobacco.

Headspace (HS5-TD): Equilibration: 0.5 min at 50°C or 75°C. Sample volume: 75 mL. Sample cycles: 3.

TD (UNITY): Trap (General-purpose hydrophobic): Analytes trapped at –10°C, desorbed at 320°C (5 min). Split ratio: Outlet 13.5:1.

Analysis: GC–MS.



Drawing on the sensitivity of headspace-trap methods, and the ability of TD to handle a wide range of components, a comparative headspace analysis clearly shows the presence of some high-abundance additives in an Indian tobacco. Interestingly, though, it shows a similar degree of complexity to a milder UK brand for the lower-abundance components.

Application Note 096

E-Cigarette vapours

Rapid profiling of VOCs and SVOCs for regulatory compliance and quality control

E-Cigarettes have seen a massive growth in popularity in recent years, which has focused attention on potentially hazardous components released when the ‘e-liquids’ are vaporised. This is reflected in EU and US regulations that require manufacturers to submit information about key components of e-liquids and their vapours.

Sampling e-cigarette vapours using Markes’ Easy-VOC pump, followed by TD–GC–MS analysis, is a simple, inexpensive approach to VOC-profiling. As well as assisting regulatory compliance, this method is also valuable for quality control and product improvement – for example, by monitoring the consistency of levels of nicotine and flavour chemicals, or checking for the presence of contaminants.

Typical analytical conditions:

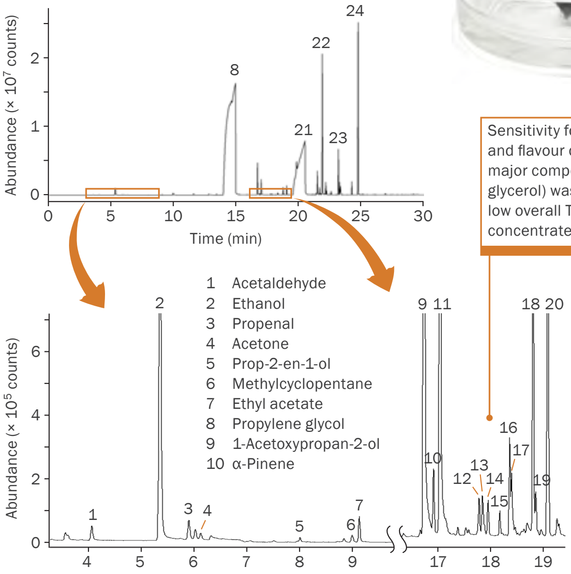
Sample: E-Cigarette filled with a ‘menthol and blueberry’ e-liquid.

Pumped sampling (Easy-VOC): 50 mL of vapour, sampled over 4 min directly into a sorbent tube.

TD (UNITY or TD-100): Tube (Odour/Sulfur): Desorbed at 320°C (10 min). Trap (Odour/Sulfur): Analytes trapped at 25°C, desorbed at 320°C (3 min). Split ratio: Inlet 6:1, Outlet 6:1.

Analysis: GC–MS.

Application Note 118



1	Acetaldehyde
2	Ethanol
3	Propenal
4	Acetone
5	Prop-2-en-1-ol
6	Methylcyclopentane
7	Ethyl acetate
8	Propylene glycol
9	1-Acetoxypropan-2-ol
10	α-Pinene
11	2-Acetoxypropan-1-ol
12	Sabinene
13	*p*-Menth-2-ene
14	β-Pinene
15	Ethyl hexanoate
16	Benzaldehyde
17	*cis*-1-Acetoxyhex-3-ene
18	Limonene
19	*m*-Cymene
20	Eucalyptol
21	Glycerol
22	Menthol
23	Carvone
24	Nicotine

Sensitivity for low-level regulated VOCs and flavour components (amongst the major compounds propylene glycol and glycerol) was enhanced by the relatively low overall TD split of 36:1 for this highly concentrated vapour.

A wide range of VOCs and SVOCs were identified in e-cigarette vapour, using a simple and rapid Easy-VOC grab-sampling method that completely avoids the need for sample preparation.

The manually-operated Easy-VOC allows precise 50 mL and 100 mL samples (or multiples thereof) to be collected onto sorbent tubes.

Betel-nut stimulants

Validating analyte recovery by sample splitting and re-collection

‘Betel nut’ or ‘paan’ is the name given to a number of chewed stimulants popular in south-east Asia. These products have recently attracted attention because of the presence of potential carcinogens, making it particularly important that the analysis is both rigorous and verifiable.

Markes’ thermal desorbers address this challenge by allowing samples to be ‘split’ at a precisely defined ratio, both at the tube and trap desorption stages. The portion of each sample not sent to the GC can be re-collected onto a clean sorbent tube, which can be analysed again to verify that there have been no losses of components within the TD system.

Typical analytical conditions:

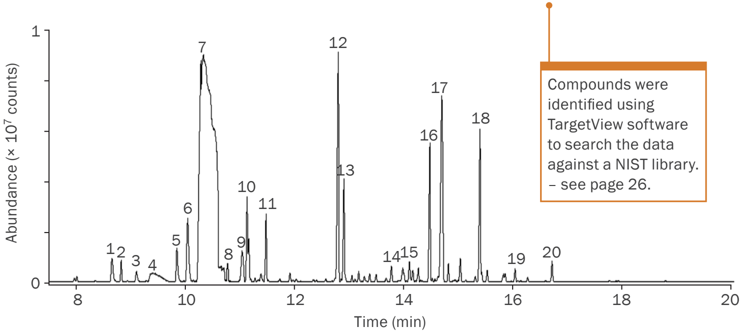
Sample: 70.5 mg of crushed areca fruit, placed in an empty TD tube.

TD (UNITY or TD100): Sample: Desorbed at 50°C (10 min). Trap (General-purpose carbon): Analytes trapped at –20°C, desorbed at 300°C (5 min). Split ratio: Outlet 10:1.

Analysis: GC–MS.

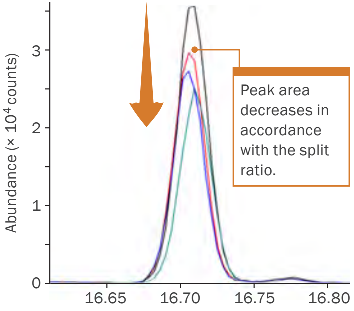
Application Note 098

1	Dihydromyrcenol	8	α-Terpineol	14	Caryophyllene
2	Phenylethyl methyl ether	9	2-Methylcyclohexyl propanoate	15	γ-Patchoulene
3	Linalool	10	β-Citronellol	16	Dihydro-β-ionone
4	Phenethyl alcohol	11	Nerol	17	A diterpene
5	Camphor	12	Terpinyl acetate	18	Sandranol
6	Isoborneol	13	Eugenol	19	Cedrol
7	Menthol			20	Patchouli alcohol



Compounds were identified using TargetView software to search the data against a NIST library. – see page 26.

Repeat desorption with a constant split is useful for validating analyte recovery, as illustrated by this example of a common ‘betel nut’ component. The response from patchouli alcohol decreases as expected from the 10:1 split ratio used during trap desorption, in a sequence of repeat runs.



Peak area decreases in accordance with the split ratio.

Mosquito coils

Quick and comprehensive screening for improved quality control

Insecticide-containing coils are widely used to repel mosquitoes, but the smoke generated when they are burnt can contain carcinogens. Some of these are subject to regulations, so testing these coils is important for protecting the public.

A versatile approach to dynamic headspace–TD is to use the Micro-Chamber/Thermal Extractor (µ-CTE). Accommodating sample volumes up to 100 cm^3, the µ-CTE enables robust and representative sampling of the wide range of compounds emitted by challenging samples such as mosquito coils. It also allows an inert-gas or air purge, allowing combustible samples to be tested while burning.

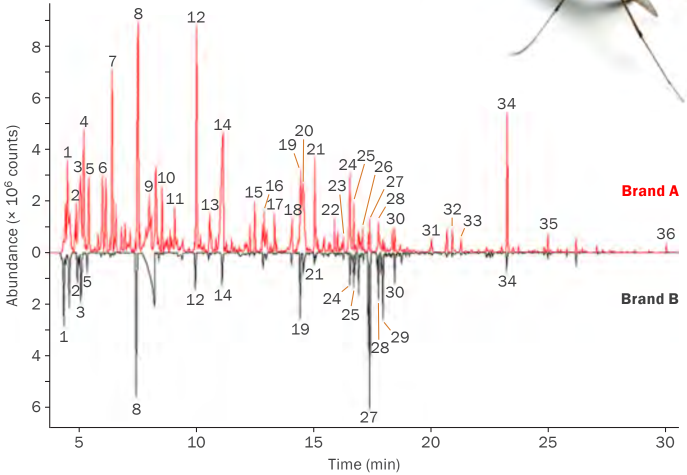
Typical analytical conditions:

Sample: Lit mosquito coil sections.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 150 mL/min for 3 min. Chamber temperature: 40°C.

TD (UNITY or TD100): Tube (Odour): Desorbed at 300°C (10 min). Trap (Sulfur): Analytes trapped at –10°C, desorbed at 300°C (3 min). Split ratio: Outlet 13.5 : 1.

Analysis: GC–MS.



1	Propene
2	Chloromethane
3	Propanol
4	Furan
5	Methyl acetate
6	2,3-Butanedione
7	3-Methylfuran
8	Benzene
9	Pentadione
10	2,5-Dimethylfuran
11	1-Methylpyrrole
12	Toluene
13	Hexanal
14	Furfural
15	Xylene
16	Styrene
17	Methoxybenzene
18	Benzaldehyde
19	Benzonitrile
20	Phenol
21	Benzofuran
22	Limonene
23	Butylbenzene
24	2-Methoxyphenol
25	Methyl benzoate
26	2-Methylbenzofuran
27	Tetramethylbenzene
28	Phenylmethyl acetate
29	2-Methoxy-4-methylphenol
30	Naphthalene
31	2-Ethyl-5-methoxyphenol
32	Tridecane
33	Dimethoxyphenol
34	Tetradecane
35	Pentadecane
36	Allethrin

The complexity of the volatile profile from two brands of mosquito coils is clear from this headspace–TD analysis. Note the presence of a number of potentially hazardous benzene derivatives.

Incense sticks

Topic continued on next page

Understanding the consequences of burning fragranced materials

Incense sticks (agarbatti), which contain a diversity of ingredients from fragrant essential oils to binding agents, have received increasing attention because of the potential for harmful components to be released when they are burnt. Manufacturers are also keen to understand the fate of the various components of a formulation.

Comprehensive analysis of such samples is provided by the Micro-Chamber/Thermal Extractor, which enables rapid collection of the entire vapour profile. This is valuable, for example, when needing to compare samples collected before and during use.

Typical analytical conditions:

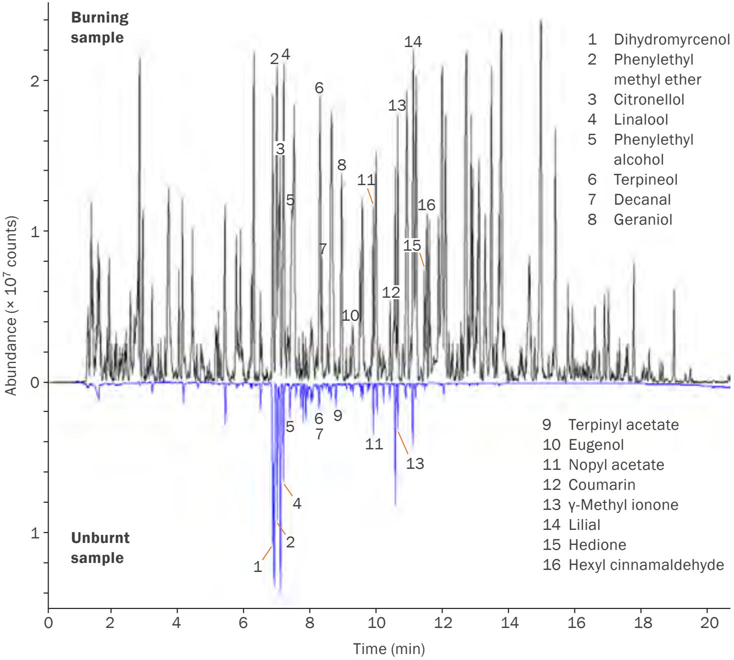
Sample: Burning and unburnt 40 mm sections of incense stick.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 50 mL/min for 30 min. Chamber temperature: 40°C.

TD (UNITY or TD100): Tube (Odour): Desorbed at 300°C (10 min). Trap (Sulfur): Analytes trapped at –10°C, desorbed at 300°C (5 min). Split ratio: Outlet 13.5 : 1.

Analysis: GC–MS.

Application Note 100



Burning an incense stick causes a dramatic expansion in the number, abundance and volatility range of compounds released, as immediately apparent from this headspace–TD analysis. The key fragrance compounds highlighted were identified by a TargetView search – see page 26.

Incense sticks

Topic continued from previous page

Identifying the causes of poor indoor air quality

The overall constituents of incense sticks are easily studied in the laboratory, but to fully understand the impact of burning them on indoor air quality, studies on real-world environments are also needed.

One problem encountered when carrying out pumped sampling of airborne volatiles in the field is that using electrically-powered pumps may not always be feasible – for example, where power supplies are not reliable. In such cases, grab-sampling onto sorbent tubes is a simple, quick, and very convenient alternative.

Typical analytical conditions:

Sample: Two burning incense sticks, 4 m away from the sampling point in a 21 m^3 room.

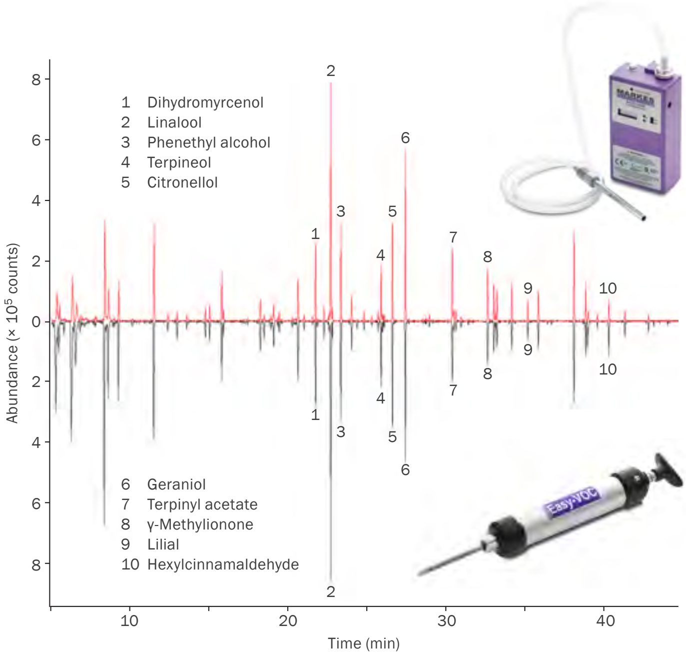
Pumped sampling (ACTI-VOC): Flow rate: 40 mL/min for 45 min. Total volume: 1800 mL.

Grab-sampling (Easy-VOC): 10 × 100 mL samples, collected successively.

TD (UNITY or TD100): Tube (Odour): Desorbed at 300°C (10 min). Trap (Sulfur): Analytes trapped at 5°C, desorbed at 320°C (5 min). Split ratio: Outlet 10 : 1.

Analysis: GC–MS.

Application Note 100



The similarity of the air profiles obtained using a constant-flow ACTI-VOC pump (top) and an Easy-VOC grab-sampler (bottom) is demonstrated here for the case of burning incense sticks. The only difference is a slight bias towards early-eluting components for Easy-VOC, reflecting the shorter sampling time used in this case.

Mahogany

Fast screening of odour profiles

Wood-based products are used extensively indoors, and can contribute significantly to VOC levels especially when new. The chemicals used in varnishes, lacquers and other treatments, as well as aromatic chemicals occurring naturally in wood resin, are generally of greatest concern.

Sorbent-tube sampling with TD analysis is widely used in this area to generate comprehensive vapour profiles. Key applications are governed by a number of standard methods, and include monitoring malodorous indoor air, rapid product screening using microchamber or headspace–TD methods, and full-scale material emissions testing.

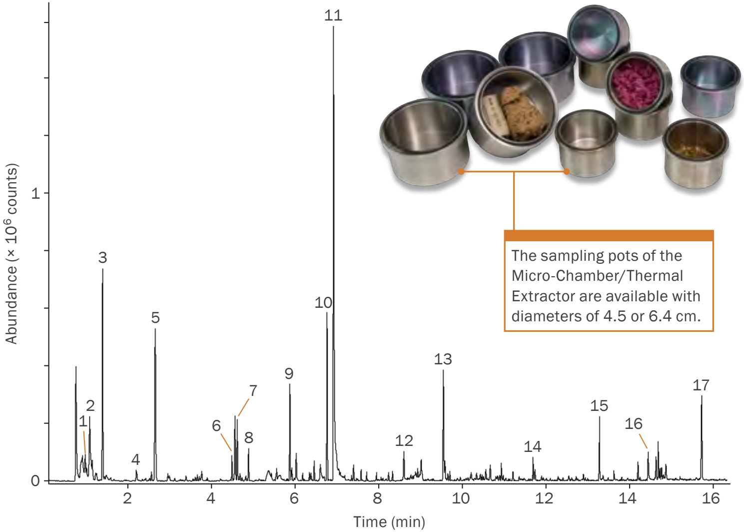
Typical analytical conditions:

Sample: Mahogany.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 100 mL/min for 15 min. Chamber temperature: 60°C.

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 300°C (5 min). Trap (Material emissions): Analytes trapped at 0°C, desorbed at 300°C (3 min). Split ratio: Outlet 25 : 1.

Analysis: GC–MS.



The sampling pots of the Micro-Chamber/Thermal Extractor are available with diameters of 4.5 or 6.4 cm.

1 Butane
2 Acetic acid
3 Benzene
4 Toluene
5 Hexamethylcyclotrisiloxane
6 Benzaldehyde
7 Phenol
8 Octanal
9 Nonanal
10 Decanal
11 2-Phenoxyethanol
12 Geranyl acetone
13 2,2,4-Trimethyl-1,3-pentanediol diisobutanoate
14 n-Hexadecanoic acid
15 2,6-Diphenylphenol
16 Diisooctyl phthalate
17 Squalene

Reflecting the versatility of TD, a range of VOCs and SVOCs – from butane (C_4H_{10}) to squalene ($C_{30}H_{50}$) – are identified in this headspace–TD analysis of mahogany using the Micro-Chamber/Thermal Extractor.

Aromatic leaves

Checking the quality of raw materials

Plants are the source of a vast array of fragrances, with many uses in consumer goods, from hand-creams to pot-pourri. Although 'botanicals' such as leaves, stems and seeds are usually processed before incorporation into the final product, rapid screening of raw materials is of considerable value for quality control.

The Micro-Chamber/Thermal Extractor allows rapid collection of the entire vapour profile from botanical samples, making it ideal for assessment of quality. In addition, the inertness and adjustable flow-path temperature of Markes' TD systems ensure reliable recovery of a wide range of analytes, including reactive compounds such as sulfur species and some monoterpenes.

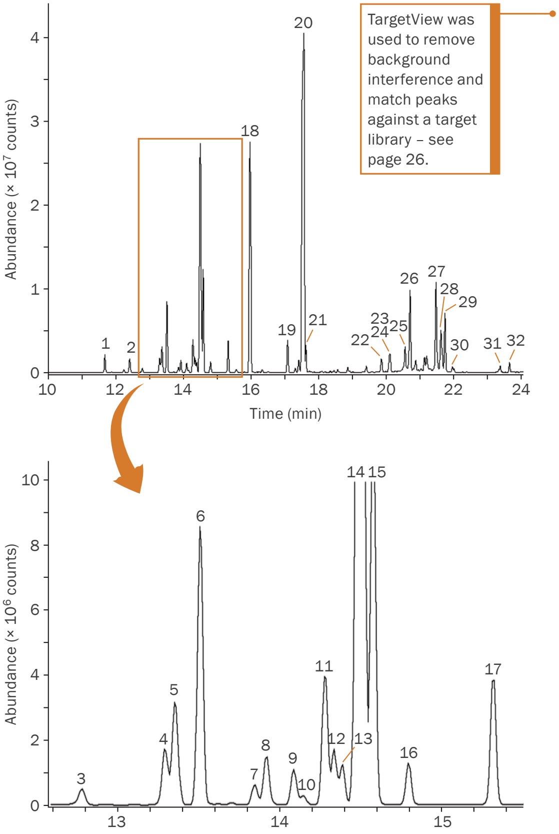
Typical analytical conditions:

Sample: 5 g pre-packaged fresh basil leaves.

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

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 280°C (10 min). Trap (Tenax TA): Analytes trapped at 20°C, desorbed at 290°C (3 min). Split ratio: Inlet 2 : 1, Outlet: 16 : 1.

Analysis: GC–MS.



TargetView was used to remove background interference and match peaks against a target library – see page 26.

1	*cis*-Hex-3-en-1-ol
2	3,6,6-Trimethyl-2-norpinene
3	Camphene
4	Sabinene
5	β-Pinene
6	β-Myrcene
7	α-Phellandrene
8	Oct-1-en-3-ol
9	α-Terpinene
10	Octan-3-ol
11	Limonene
12	α-Pinene
13	β-Phellandrene
14	1,8-Cineole
15	β-Ocimene
16	τ-Terpinene
17	α-Terpinolene
18	Linalool
19	Camphor
20	Estragole
21	α-Terpineol
22	Copaene
23	Bicyclosesquiphellandrene
24	β-Elemene
25	*trans*-α-Bergamotene
26	α-Guaiene
27	Germacrene D
28	δ-Guaiene
29	γ-Muurolene
30	*trans*-Calamenene
31	4-Methoxycinnamaldehyde
32	τ-Cadinol

A large number of mono- and sesquiterpenes were identified in this headspace analysis of basil.

Curry powder

Quick and convenient comparison of samples

Aromatic materials – from essential oils to dried botanicals – are widely employed in the fragrance and food industries. Identifying the differences between samples is of particular interest to manufacturers, both for ongoing quality control and to compare their products against those of competitors. A challenge often encountered when analysing such samples is that the VOC profiles often differ in the relative abundance of key components – differences that can be difficult to assess by traditional methods such as solvent extraction, static headspace, or SPME.

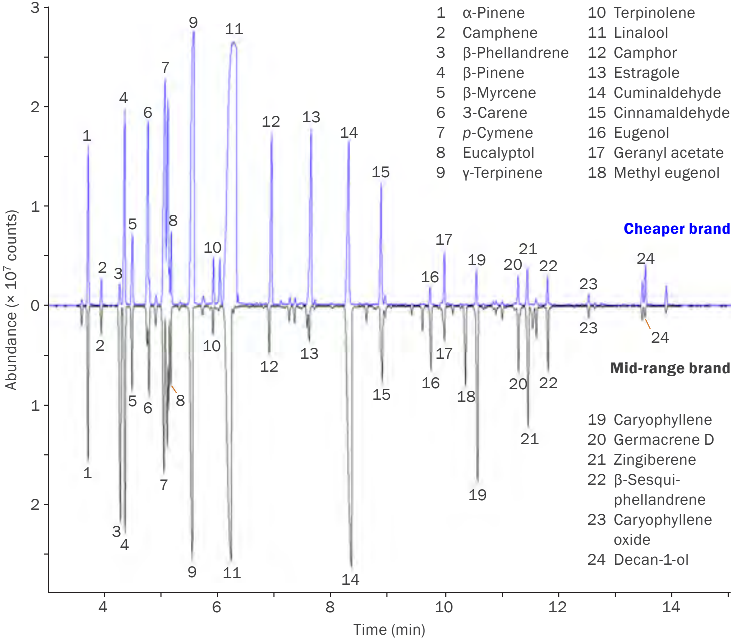
Direct desorption is ideal for relatively homogeneous, finely-divided samples, and offers rapid, simple comparison of everything from powdered spice blends to edible oils.

Typical analytical conditions:

Sample: ~50 mg curry powder, placed in an empty TD tube.

TD (UNITY or TD100): Sample: Desorbed at 50°C (3 min). Traps (Material emissions): Analytes trapped at 10°C, desorbed at 280°C (5 min). Split ratio: Outlet 25:1.

Analysis: GC–MS.



Direct desorption of two brands of curry powder shows a very similar range of analytes, but with substantial differences in relative abundance. The cheaper brand shows much higher quantities of linalool (#11), camphor (#12) and estragole (#13) compared to a mid-range brand, but lower concentrations of cuminaldehyde (#14) and caryophyllene (#19).

Air freshener

Monitoring changes in airborne volatiles over time

Air fresheners emit numerous VOCs including fragrance compounds. Monitoring their build-up and decay in indoor air is of interest to manufacturers for product formulation, and increasingly for those investigating the effect of certain suspected allergens on indoor air quality.

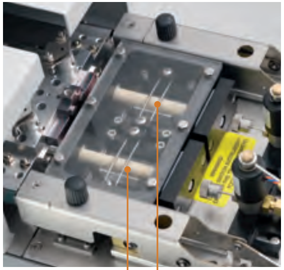
Three factors are key for robust studies in this area – high sensitivity, 100% data-capture, and short cycle times. All these points are addressed by Markes' twin-trap TT24-7 system for continuous near-real-time monitoring.

Typical analytical conditions:

Sample: Plug-in air freshener switched on at t = 0. Samples collected every 19 min thereafter (the t = 0 sample is a laboratory blank).

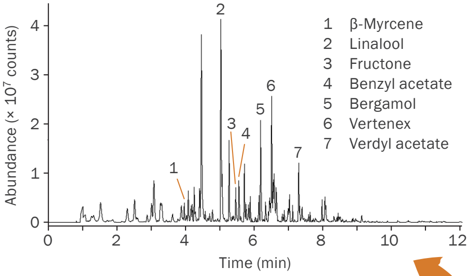
TD (TT24-7): Traps (Tenax® TA): Analytes trapped at 25°C, desorbed at 300°C (3 min). Split ratio: Outlet 29 : 1.

Analysis: GC–MS.

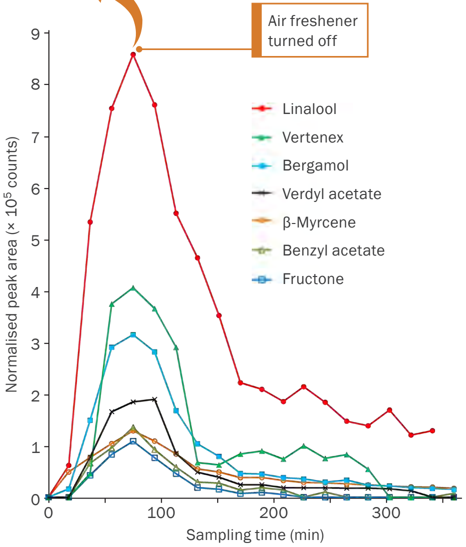


The twin traps of the TT24-7 allow 100% data capture.

Application Note 105



Time-profiling of the air in a room with a plug-in air freshener using the TT24-7 shows how the concentrations rise and fall over a period of 6 hours. The potential allergen linalool generated by far the largest response, and although concentrations decreased fairly rapidly after the air freshener was turned off, it nevertheless remained detectable in the air until the end of the experiment, 4.75 hours later.



Shampoo

Avoiding interference from water when analysing aqueous solutions

Fragranced goods often contain large quantities of water that can interfere with gas chromatography. Obtaining reliable results therefore depends upon selectively removing this water from the sample before analysis commences. However, achieving this using traditional sample preparation protocols can be time-consuming and may introduce contaminants (or cause analyte loss).

Markes' Micro-Chamber/Thermal Extractor circumvents such problems by being compatible with viscous liquids, while the choice of sorbent tube and TD focusing conditions can efficiently eliminate water before the start of the GC run.

Typical analytical conditions:

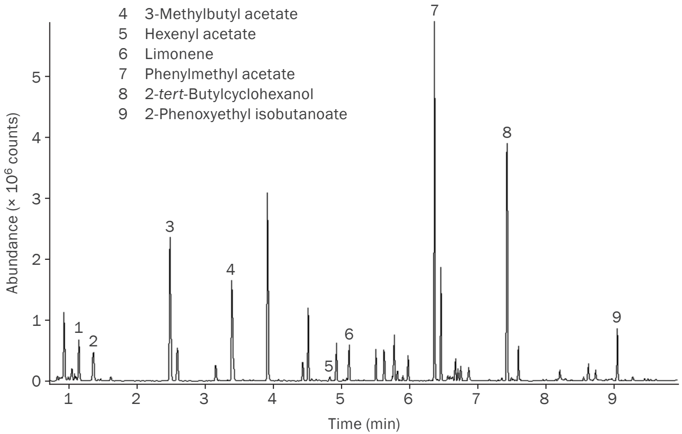
Sample: 5 mL shampoo.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 70 mL/min for 5 min. Chamber temperature: 30°C.

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 280°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at 30°C, desorbed at 300°C (3 min). Split ratio: Outlet 16 : 1.

Analysis: GC–MS.

Using strongly hydrophobic sorbents such as Tenax TA in the sorbent tube and focusing trap helps to avoid interference from water.



The volatile components of a shampoo are selectively retained and analysed without water interference, courtesy of a sorbent tube packed with hydrophobic sorbents, and a dry-purge of the sorbent tube before analysis to remove residual water.

Ointment

Identifying active ingredients

Ointments are very challenging for the analyst, typically needing lengthy liquid extraction or steam distillation to separate the active ingredients or fragrances from the matrix. Even with such multi-step procedures, residues from the matrix can still contaminate the extract and cause analytical interference.

Direct desorption overcomes these problems by minimising sample preparation and allowing the release and selective focusing of only the volatile components from the sample. In addition, Markes' thermal desorbers are compatible both with volatile fragrance compounds, and with some high-boiling ointment constituents such as siloxanes, providing the versatility needed for ointment analysis.

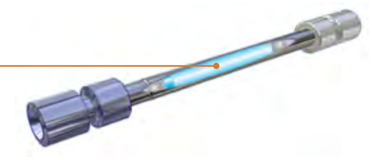
Typical analytical conditions:

Sample: Ointment (~10 mg), placed in an empty TD tube.

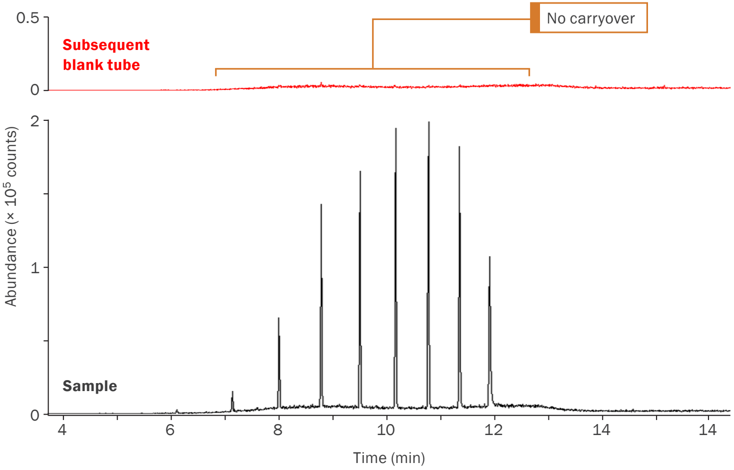
TD (UNITY or TD100): Sample: Desorbed at 100–200°C (5–10 min). Trap (Tenax® TA): Analytes trapped at 10°C, desorbed at 300°C (10 min). Split ratio: Inlet ~5:1, Outlet ~100:1.

Analysis: GC–MS.

Application Note 009



When analysing ointments by direct desorption, using a PTFE or glass liner simplifies weighing and avoids contaminating the inside of the TD tube.



Even 'sticky' high-molecular-weight polysiloxanes can be desorbed and efficiently transferred through the TD instrument, as shown by this direct desorption analysis of an ointment followed by a blank run.

Fabric conditioner

Reliable fragrance profiling

Fragrance plays a major part in market acceptance and consumer satisfaction for products such as toiletries, air fresheners and domestic cleaning materials. Accurately monitoring fragrance profiles of raw materials and finished products is therefore crucial, both for ongoing quality control and for investigating customer complaints.

TD improves the robustness and simplicity of headspace methods by greatly enhancing sensitivity and extending the analyte volatility range.

Typical analytical conditions:

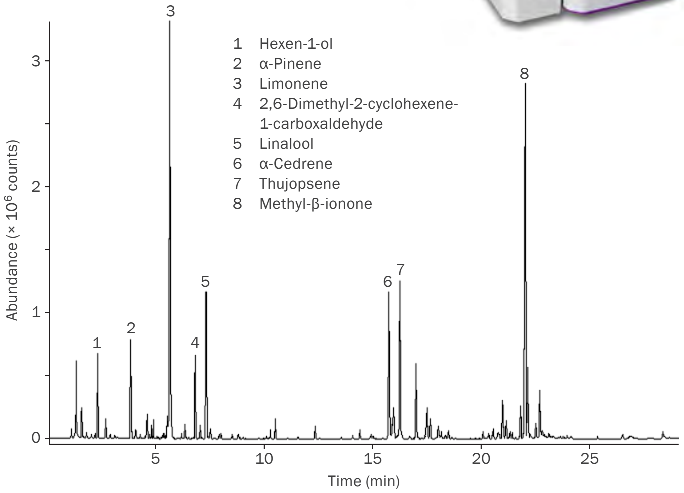
Sample: Fabric conditioner.

Headspace (HS5-TD): Equilibration: 1 min at 40°C. Sample cycles: 2.

TD (UNITY): Tube (Tenax® TA): Desorbed at 280°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at 20°C, desorbed at 290°C (3 min). Split ratio: Outlet 16:1.

Analysis: GC–MS.

The HS5-TD unit accommodates five standard 20 mL headspace vials and integrates with Markes' UNITY thermal desorber.



This headspace–TD analysis of a fabric conditioner shows the presence of a wide range of compounds commonly used in fragranced products, including α-pinene, limonene and linalool.

Laundered fabric

Checking the persistence of fragrance profiles

The characteristic ‘freshly washed’ smell of newly-laundered fabrics is of interest to manufacturers because of its appeal to consumers. It is particularly important to check that the fragrance added to the conditioner remains on the fabric after washing.

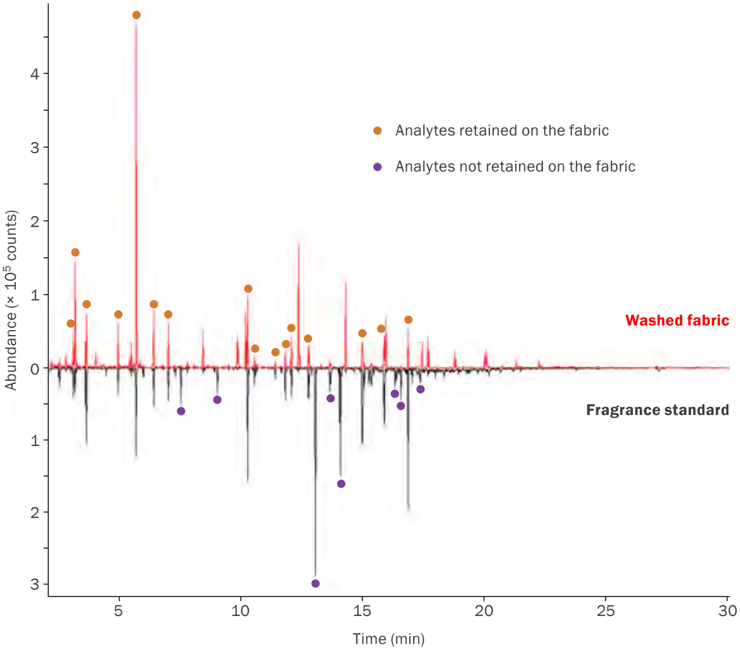
Both direct desorption and the Micro-Chamber/Thermal Extractor are convenient approaches to releasing fragrances from fabric, and generating comprehensive VOC profiles in a single run.

Typical analytical conditions:

Sample: ~50 mg of freshly-laundered fabric, placed in an empty TD tube. The liquid fragrance standard was injected onto a Tenax® TA tube.

TD (UNITY or TD100): Sample: Desorbed at 70°C (5 min) (fabric) or 280°C (5 min) (standard). Trap (General-purpose hydrophobic): Analytes trapped at 25°C, desorbed at 300°C (3 min). Split ratio: Outlet ~2:1.

Analysis: GC–MS.



Direct desorption of a small piece of washed fabric was compared with that of the original fragrance used in the fabric conditioner – showing that a significant portion of the fragrance has migrated to the clothing, and that this survives the rinse cycle.

Relevant sampling and analytical techniques

Thermal desorption

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

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

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

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

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

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

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

Micro-Chamber/Thermal Extractor

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

Now available with humidifier accessory

The µ-CTE can be used for:

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

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

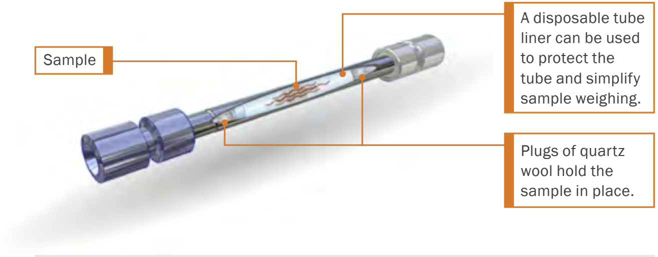
See pages 11, 12, 14, 15 and 18 for applications using the µ-CTE.

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

Direct desorption

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

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



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

See pages 6, 10, 16, 19 and 21 for applications using direct desorption.

For more on direct desorption, see Application Note 009.

Sorbent tube sampling

Active (pumped) sampling onto sorbent tubes is a versatile option for simultaneous monitoring of multiple compounds.

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

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

- **ACTI-VOC™** is a lightweight, compact low-flow pump specifically optimised for TD tubes, which can operate in constant-flow or constant-pressure modes.

- **Easy-VOC™** is a manually-operated grab-sampler that allows precise volumes of air or gas to be sampled directly onto sorbent tubes. By avoiding the need for batteries or electrical power, it is ideal for field sampling.

- **The MTS-32™** is a compact, portable sampler for the unattended sequential sampling of air onto a series of sorbent tubes. Constant-flow pump technology ensures that the same volume of air is collected onto each tube.

See pages 9 and 13 for applications using sorbent tube sampling.

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

Continuous on-line sampling

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

The **TT24-7™** is an advanced thermal desorption (TD) system for continuous near-real-time (NRT) monitoring of volatile and semi-volatile organic compounds in air or gas. Its two reciprocating focusing traps and cryogen-free operation make it ideal for continuous unattended monitoring, either in static or mobile laboratories.

The TT24-7 is an ideal choice for a wide range of challenging applications, including:

- Advanced kinetic studies.
- Routine monitoring of air pollution and odour.
- Controlling the purity of piped air/gas supplies.
- Monitoring fragrance profiles as they change over time.
- Continuous monitoring of extremely hazardous materials such as chemical agents.

See page 17 for an application using the TT24-7.

For more on the TT24-7 and to download the brochure, visit www.markes.com.

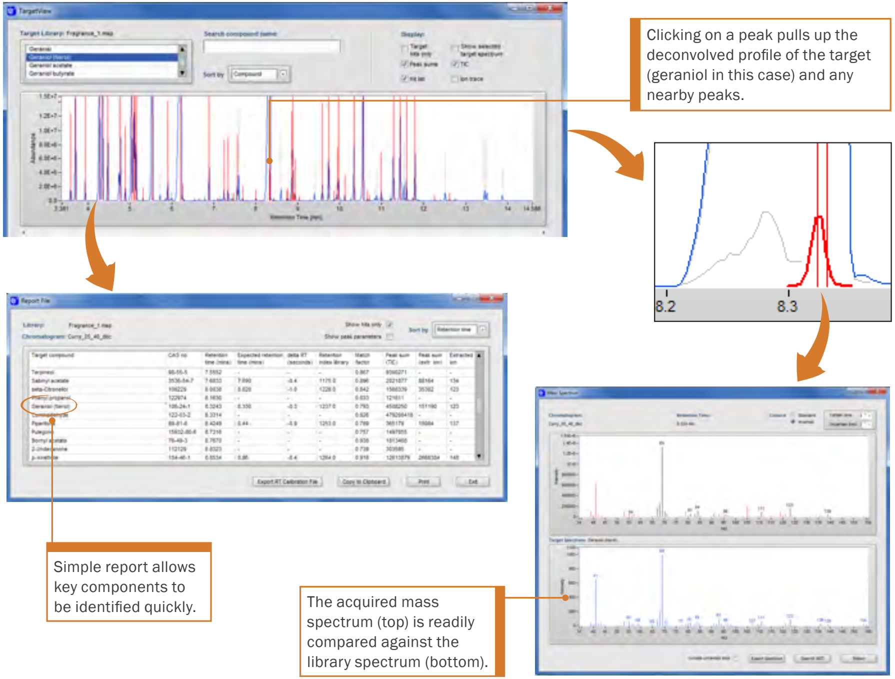
Compound identification software

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

TargetView features:

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

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



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

Simple report allows key components to be identified quickly.

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

TargetView's report easily identifies geraniol in this analysis of a curry powder, despite it being hidden under a cuminaldehyde component that is over 100 times as large.

About Markes International

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

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

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

As well as fragrance profiling, Markes' products are used extensively in multiple routine and research applications – everything from environmental analysis to metabolomic studies.

Markes is headquartered in Bridgend, UK, and also has laboratory and demonstration facilities in the USA, Germany and China. Markes is a company of the Schauenburg International Group.

ACTI-VOC™, Easy-VOC™, HS5-TD™, Micro-Chamber/Thermal Extractor™, μ-CTE™, MTS-32™, TargetView™, TD100™, TD100-xr™, TT24-7™, UNITY™ and UNITY-xr™ are trademarks of Markes International.

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

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

MARKES
international

L-0024 (090321-5)

MarkMarkes International

UK: 1000B Central Park, Western Avenue, Bridgend, CF31 3RT **T:** +44 (0)1443 230935

US: 2355 Gold Meadow Way, Gold River, Sacramento, California 95670 **T:** +1 866-483-5684 (toll-free)

Germany: Bieberer Straße 1-7, 63065 Offenbach am Main **T:** +49 (0)69 6681089-10

China: Unit 1002, Building 1, No. 418, Guilin Road, Shanghai 200233 **T:** +86 21 5465 1216

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

A company of the **SCHAUENBURG** International Group