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Thermal Desorption Applications Guide:

Consumer environmental health

A comprehensive guide to the use of thermal desorption to assess chemical emissions from construction materials and consumer products

Introduction

Consumer environmental health

Rising awareness of the potential health risks associated with poor indoor air quality has led to increasing calls for the regulation and labelling of products and materials used indoors – including everything from plasterboard and carpet to furniture, scented candles and toys.

In this Applications Guide, we describe how thermal desorption (TD) and related sampling techniques can be used to rapidly produce meaningful information on chemical emissions from a variety of materials. In many scenarios, such analyses are carried out in accordance with national and international standard methods.

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 27 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

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

Regulations and standard methods

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The regulatory environment

Construction materials

Increased awareness of the potential health risks associated with poor indoor air quality has led to increasing calls for the regulation and labelling of construction materials used indoors.

These regulations and labels include:

- The European **Construction Products Regulation** (CPR), which came into force in 2013.

- Those developed by various European national agencies – such as the **AgBB scheme** and the **'Ü' mark** (Germany), the **'Émissions dans l'air intérieur'** regulation and a rule on selling products containing **CMR substances** (France). Some or all of these will likely be superseded by the CPR, in due course.

- The European **REACH** regulation on the Registration, Evaluation, Authorisation and Restriction of CHemical substances, which came into force in 2007 and is being phased-in over 11 years.

- **'Chinese REACH'**, which makes similar requirements to the European regulation, and came into force in 2010.

- A range of US-led initiatives, including **LEED** and the **Green Label** program.

Each of these regulations typically demand product testing in accordance with standard methods (see the next page).

Consumer products

Consumer products are now starting to be regulated for their potential impact on human health:

- **EU Directive 2011/8/EU** prohibits the use of bisphenol A (BPA) for the manufacture of polycarbonate infant feeding bottles.

- **Substances of very high concern** (SVHCs) – including some phthalates – are covered under REACH.

- Consumer product labelling is now required in some countries – such as stipulations made under the **Clean Air Act** in the US, and the **Paint Varnish Directive 2004/42/CE** in the UK.

Other projects concerned with emissions from fragranced products, combustible air fresheners and other household goods are also in progress. It is anticipated that standard methods in this area will use very similar methodologies to those used to assess construction materials.

Overview of methodologies

The various standard methods developed to assess emissions from construction materials and consumer products are all compatible with TD, and fall into three broad categories (1–3), with four commonly used sampling approaches (A–D). These are described in more detail on the following pages.

1 Indoor air monitoring

2 Final product certification

3 Screening of emissions from components

A Pumped sampling

B Small chambers

C Microchambers

D Direct desorption

Formaldehyde monitoring

Note that formaldehyde and other aldehydes, unlike other VOCs/SVOCs, are analysed by HPLC rather than GC–MS, and require special sampling and analysis equipment such as DNPH cartridges. See page 20 for more information.
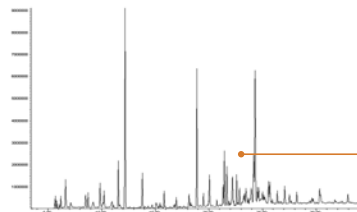
The four main sampling approaches for assessing emissions from products and materials are all compatible with TD.

Thermal desorption – see page 27 for more detail

Analysis by gas chromatography

TD-based approaches can detect:

- **VOCs** (boiling up to n-C_{16}).
- **SVOCs** or FOG compounds (boiling above n-C_{16}).
- **Odorous** or **reactive** species.

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1 Indoor air monitoring

A Pumped sampling

Whole-air sampling is carried out by pumped sampling of air onto sorbent tubes, to assess whether or not the overall VOC profile meets defined criteria.

Indoor air monitoring is discussed on page 11 of this Guide, but for application-specific advice, please contact Markes' specialists.

For more information on pumped sampling, see page 29.

Key standard methods applicable to analysis of indoor air:

- ISO 16000-6.
- US EPA Method TO-17.
- EN ISO 16017-1.
- ASTM D6196.

2 Final product certification

B Small chambers

'Small' chambers (typically 1 m^3) are used to assess emissions from final products under simulated real-world conditions, with vapours being collected onto sorbent tubes at specific times (typically 3, 10 or 28 days).

See pages 16 and 17 for examples of the use of sorbent tubes with small chambers.

Image credit:
SP Technical
Research Institute
of Sweden

Key standard methods applicable to small chambers:

- ISO 16000-9.
- ASTM D5116.
- California Specification 01350.
- EN 13999 (adhesives).
- CEN/TS 16516 also stipulates TD–GC–MS parameters, and will likely be required to comply with the European CPR (the proposal is under approval at the time of writing (July 2016)).

3 Screening of emissions from components

C Microchambers

Microchambers are a quick and convenient approach for manufacturers to sample emissions onto sorbent tubes. Importantly, the results obtained with microchambers can be correlated to the outcome of small-chamber studies.

For more information on Markes' Micro-Chamber/Thermal Extractor, see page 28.

Key standard methods applicable to microchambers:

- ASTM D7706, relating to materials and products.

- ISO 16000-25 applies to SVOCs from building products.

- VDI 2083-17A for the classification of cleanroom-suitable materials, and two related methods, MF1982-1110 and SEMI E108-0307.

- ISO 12219-3 on materials used in vehicle interiors – see our *Automotive studies* TD Applications Guide.

D Direct desorption

Direct desorption involves heating small samples of a material in a TD tube, to give an estimate of the VOC and SVOC emissions.

Widely used in the automotive industry (for example using the standard method VDA 278), direct desorption is also relevant to a range of other materials-testing applications.

For more information on direct desorption, see page 29.

Consumer environmental health

Assessing air quality

Identifying the cause of poor-quality indoor air with pumped-tube monitoring

Regulators are increasingly concerned about the impact of poor indoor air quality (or 'sick building syndrome') on human health. Indoor pollutants primarily arise from sources such as construction materials, furnishings, cleaning products and consumer goods, and activities such as cooking and smoking.

Pumped or passive sampling on to sorbent tubes using Markes' TD instruments provides the flexibility to monitor indoor air pollution over different volatility ranges of VOCs and time periods.

Typical analytical conditions:

Sample: Indoor air.

Pumped (active) sampling (ACTI-VOC): 2–20 L, for a period of minutes to hours.

TD (UNITY or TD100): Tube (Universal or Air toxics): Desorbed at 280°C (5 min). Trap (General-purpose carbon): Analytes trapped at –30°C, desorbed at 300°C (3 min). Split ratio: Outlet ~15 : 1.

Analysis: GC–MS.

Application Note 028

1	1,1-Difluoroethane	14	Tetrachloromethane	27	Limonene
2	1,1,1,2-Tetrafluoroethane	15	Benzene	28	Undecane
3	Dichlorodifluoroethane	16	Methylcyclohexane	29	Benzyl alcohol
4	1,1-Difluoro-1-chloroethane	17	Toluene	30	Nonanal
5	Isopentane	18	Hexanal	31	Dodecane
6	Ethanol	19	Tetrachloroethane	32	Tridecane
7	Trichlorofluoromethane	20	Ethylcyclohexane	33	Tetradecane
8	Propanol	21	Ethylbenzene		
9	Freon® 113	22	o-/p-Xylene		
10	Acetone	23	Styrene		
11	Dichloromethane	24	α-Pinene		
12	Hexane	25	Decane		
13	Ethyl acetate	26	Trimethylbenzene		

Pumped sampling can capitalise on Markes' backflush technology, by enabling tubes and traps to be packed with multiple beds of sorbent with different strengths. This allows analytes over a wide volatility range to be collected in a single run.
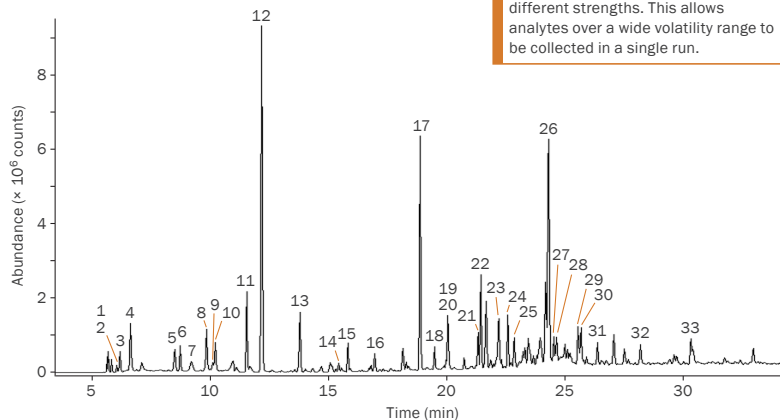
A wide range of potentially harmful chemicals at ppt and ppb levels are identified in this indoor air sample, collected by pumped sampling onto sorbent tubes over relatively short time periods.

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Assessing air quality

Identifying chemicals emitted from museum display cases

The display cases used in museums have very low air exchange rates to protect the artefacts within from environmental pollutants and moisture. However, if the materials used to construct the display case emit chemicals themselves, damage to the artefacts can still result. There is therefore a need to check the levels of VOCs within display-case air, and to assess the materials used in the manufacture of the cases.

Markes' TD technologies can help to address both the above challenges, through the use of pumped sampling of air (as shown by the example opposite), by dynamic headspace analysis of materials (see page 28), or by direct desorption of small samples (see page 29).

Typical analytical conditions:

Sample: Air in a museum display case.

Pumped (active) sampling (ACTI-VOC): 25 mL/min for 10 min (total volume 250 mL).

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 300°C (5 min). Trap (Tenax TA): Analytes trapped at 20°C, desorbed at 300°C (10 min).
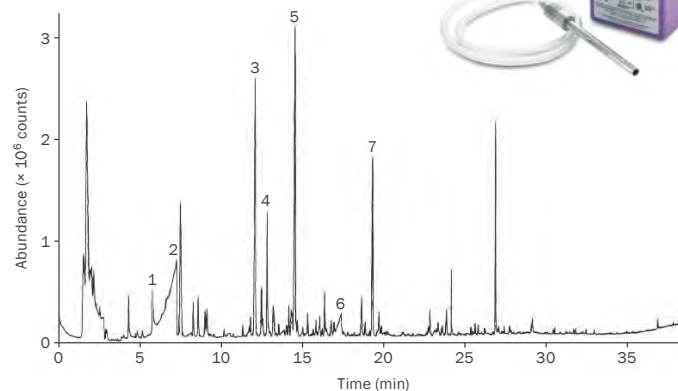
Analysis: GC–MS.

Application Note 110

1 Butanol
2 Acetic acid
3 α-Pinene
4 Hexanal
5 Carene
6 Hexanoic acid
7 Benzaldehyde

ACTI-VOC low-flow pump ready for air sampling.

Using guidelines developed under the BEMMA scheme for assessing chemicals in museum display cases, pumped sampling was able to identify acetic acid as the likely cause of decay in an enamel artefact. The same method can also be applied to detect chemicals posing a health hazard – for example, highly volatile solvents remaining from cabinet manufacture, and semi-volatile pesticides formerly used for insect control.

Near-real-time air monitoring

Monitoring changing levels of airborne volatiles

Fragranced products such as air fresheners emit numerous VOCs, and understanding how certain suspected allergens may impact indoor air quality is a topic of current interest.

Time-profiling indoor air is a powerful approach to this, but three factors are key to obtain good results – high sensitivity, 100% data-capture, and short cycle times. All these points are addressed by Markes' on-line twin-trap TT24-7 system for continuous near-real-time monitoring.

1	β-Myrcene
2	Linalool
3	Fructone
4	Benzyl acetate
5	Bergamol
6	Vertenex
7	Verdyl acetate

Typical analytical conditions:

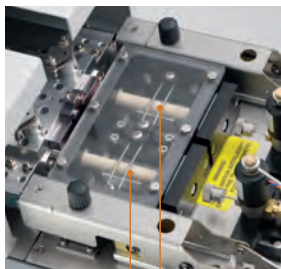Sample: Air from a room containing a plug-in air freshener.

On-line sampling: 3 L, sampled at 158 mL/min every ~19 min. Air freshener switched on at t = 0.
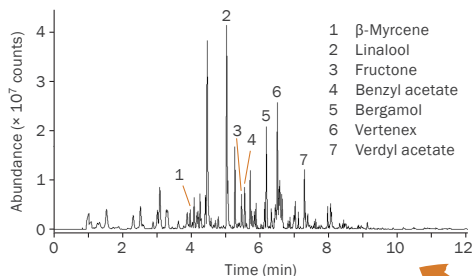
TD (TT24-7): Trap (Tenax® TA): Analytes trapped at 25°C, desorbed at 300°C (3 min). Split ratio: Outlet 29:1.

Analysis: GC–MS.

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

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.

Air freshener turned off

- Linalool
- Vertenex
- Bergamol
- Verdyl acetate
- β-Myrcene
- Benzyl acetate
- Fructone
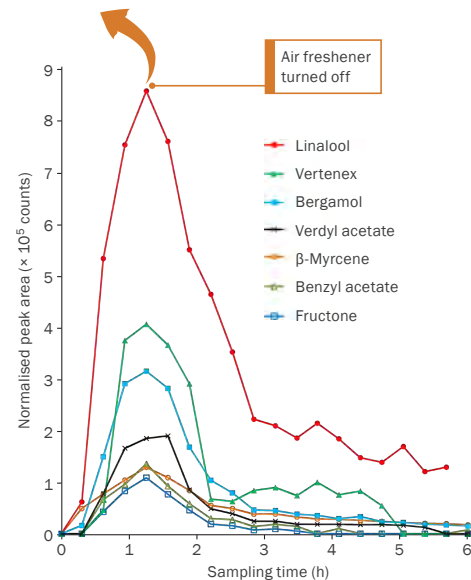
Application Note 105

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Extending analyte range

Using TD for comprehensive odour profiling

A wide range of materials are used in indoor furnishings, and can release a correspondingly large number of chemicals into the indoor environment, especially when new. GC-based techniques are widely used to assess levels of these chemicals, but conventional sampling techniques can limit the range of chemicals detectable in a single run.

Sorbent-tube sampling with TD analysis is widely used in this area to generate comprehensive vapour profiles, with the inert flow-paths and backflush capabilities of Markes' TD instruments ensuring reliable recovery of a wide range of analytes. 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. Chamber temperature: 60°C. Equilibration: 10 min. Sampling: 15 min.

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.
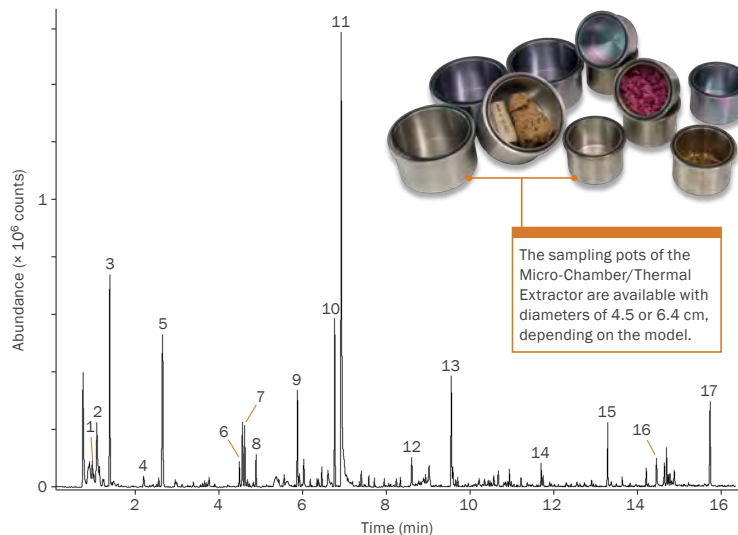
Analysis: GC–MS.

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

1	Butane	8	Octanal
2	Acetic acid	9	Nonanal
3	Benzene	10	Decanal
4	Toluene	11	2-Phenoxyethanol
5	Hexamethylcyclotrisiloxane	12	Geranyl acetone
6	Benzaldehyde	13	2,2,4-Trimethyl-1,3-pentanediol diisobutanoate
7	Phenol	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.
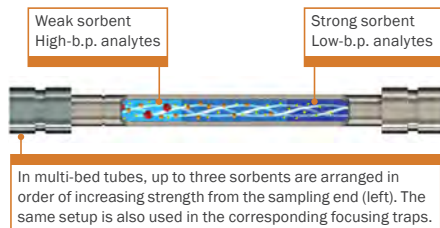
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Extending analyte range

Multi-bed TD tubes for single-run VOC and SVOC analysis

Growing demand to measure both VVOCs and SVOCs in indoor air has led to increased use of sampling tubes packed with additional sorbents, which are able to capture and release a wider range of chemicals than single-bed tubes. This is reflected in their citation in ISO 16000-6 – the key international standard method for material emissions testing and indoor air monitoring.

Markes' TD systems are fully compatible with multi-bed tubes, because they employ 'backflush' operation, whereby the gas flow during sampling is reversed during desorption. This means that the analytes enter and leave the tube at the end with the weakest sorbent, ensuring that the less volatile components cannot become irreversibly bound to the stronger sorbents.

Weak sorbent
High-b.p. analytes

Strong sorbent
Low-b.p. analytes

In multi-bed tubes, up to three sorbents are arranged in order of increasing strength from the sampling end (left). The same setup is also used in the corresponding focusing traps.

Application Note 113

http://dx.doi.org/10.1039/c3ay40224j

V.M. Brown and D.R. Crump, An investigation into the performance of a multi-sorbent sampling tube for the measurement of VVOC and VOC emissions from products used indoors, *Analytical Methods*, 2013, 5: 2746–2756.
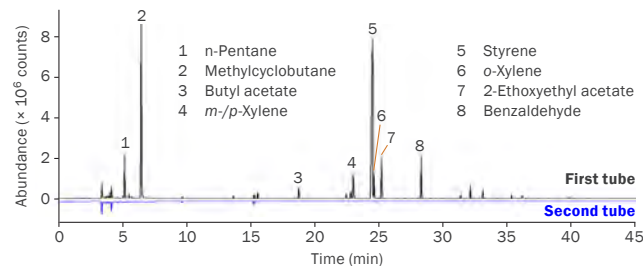
Typical analytical conditions:

Sample: Polyurethane (PU) foam cut from a composite door.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 50 mL/min. Chamber temperature: 23°C. Sampling: 15 min.

TD (UNITY or TD100): Tube (Material emissions): Desorbed at 280°C (8 min). Trap (Material emissions): Analytes trapped at –10°C, desorbed at 300°C (3 min). Split ratio: Outlet 8.7 : 1.

Analysis: GC–MS.

1	n-Pentane	5	Styrene
2	Methylcyclobutane	6	o-Xylene
3	Butyl acetate	7	2-Ethoxyethyl acetate
4	m-/p-Xylene	8	Benzaldehyde

Compared to multi-bed tubes, some loss of the more volatile analytes (n-pentane and methyl-cyclobutane) occurred when single-bed Tenax® TA sorbent tubes were used.

* = Response ÷ 10
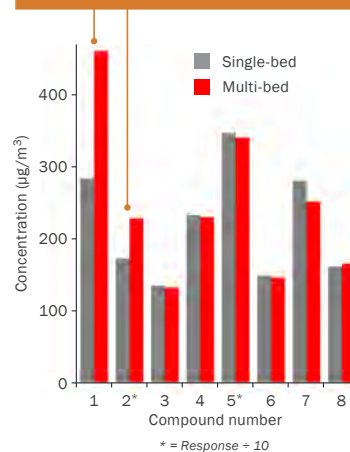
Multi-bed sorbent tubes efficiently sampled and released analytes emitted from PU foam, as assessed by the use of a second tube in series to measure break-through (above). *Data courtesy of Dr Veronica Brown and Dr Derrick Crump, Cranfield University, UK, and adapted from* Analytical Methods *with permission from the RSC.*

Testing using small chambers

Pumped-tube monitoring for reference tests

Many standard methods for material emissions testing require the use of small test chambers, which aim to simulate real-world emissions by exposing a sample to typical ambient conditions for an extended period. Protocols for sample preparation and experimental conditions are tightly defined, to help ensure that the results can be related directly to maximum permissible vapour concentrations in a reference ('model') room.

Markes' thermal desorption systems are used for final certification testing of materials (such as the adhesive shown here), using small chambers in accordance with standard methods such as the ISO 16000 series. An added benefit of Markes' systems is the capability for sample splitting and re-collection, which allows repeat analysis and so overcomes the need for lengthy sampling procedures to be repeated.

Typical analytical conditions:

Sample: Tile adhesive.

Chamber conditions: Temperature: 23°C (25°C in Korea, 28°C in Japan). Relative humidity: 50%. Air velocity: 0.1–0.3 m/s. Air exchange rate: 0.5–1 h^{-1}.

Pumped sampling: 50–100 mL/min for ~10 min (total volume 1–2 L*), after 3, 14 or 28 days.

TD (UNITY or TD100): Tube (Tenax® TA or Material emissions): Desorbed at 280°C (10 min). Trap (Tenax TA or Material emissions): Analytes trapped at 25°C, desorbed at 290°C (3 min). Split ratio: Outlet 5 : 1.

Analysis: GC–MS or GC–FID.

* Maximum volume dependent upon safe sampling volume (SSV) – see ISO 16000-6 for advice.

Small chambers vary in size from 20 L to ~5 m^3, but are typically 1 m^3. Sample emissions are collected directly onto sorbent-packed TD tubes.

Image credit: SP Technical Research Institute of Sweden

1   Acetone
2   Acetic acid
3   Tetrahydrofuran
4   1,2-Ethanediol
5   Toluene
6   n-Decane
7   Indene
8   Naphthalene
9   Butylated hydroxy toluene
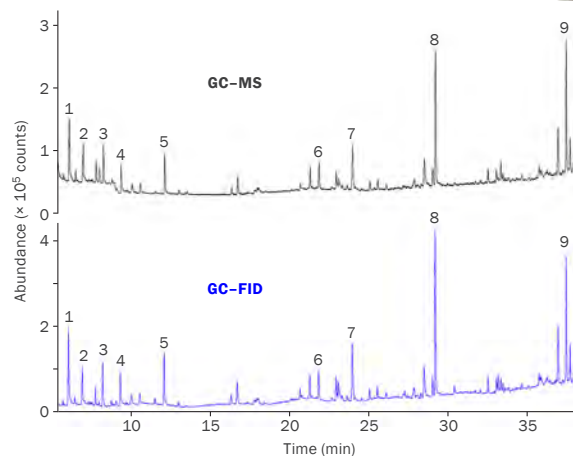
Small-chamber sampling onto sorbent tubes is used to assess levels of volatiles from a low-emission tile adhesive. *Data reproduced courtesy of Dr Mikaela Decio and colleagues, Mapei, Milan, Italy.*

Predicting results of reference tests

Correlating the results of quick dynamic headspace sampling to longer-term methods

The reference tests needed for certification testing of final products, although providing comprehensive information about emissions under real-world conditions, take 3–28 days to complete, making them impractical for routine use.

Addressing this problem, Markes' Micro-Chamber/Thermal Extractor (μ-CTE) provides a fast way of screening emissions from a wide range of products and materials (including liquids, resins and emulsions). Importantly, it gives results that can be correlated with those from longer-term reference tests, making it valuable for product R&D.
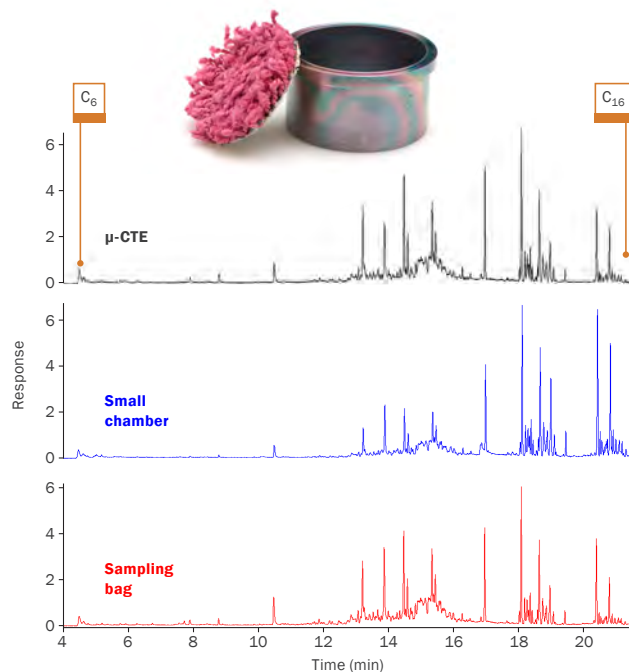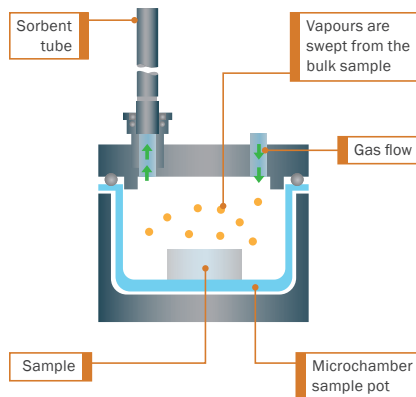
Typical analytical conditions:

Sample: Carpet.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate 50 mL/min. Chamber temperature: 65°C. Equilibration: <30 min. Sampling: 15 min.

TD (UNITY or TD100): Tube (Tenax TA), desorbed at 280°C (10 min). Trap (Material emissions): Analytes trapped at 25°C, desorbed at 290°C (3 min). Split: Outlet 5:1.

Analysis: GC–MS.

Application Note 069

C_6 C_{16}

μ-CTE

Small chamber

Sampling bag

Response

Time (min)

Sorbent tube

Vapours are swept from the bulk sample

Gas flow

Sample

Microchamber sample pot

In a matter of minutes, emissions data (in this case from carpet) can be obtained using Markes' μ-CTE, and then correlated to data obtained by longer-term methods employing small-chamber or bag sampling.
Data reproduced courtesy of Professor Mangoo Kim, Kangwon National University, South Korea.

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Improving reproducibility

Lowering RSDs for testing emissions from materials

Emissions testing with conventional small chambers and emission cells is a complex, multi-step process with many opportunities for error to creep in. Consequently, even the best results carried out between and within laboratories give relative standard deviations (RSDs) of 15–30%.

Markes' Micro-Chamber/Thermal Extractor (µ-CTE) offers an alternative approach, with tightly controlled sampling parameters that lead to minimal variation between runs. This leads to exceptional reproducibility within the context of material emissions testing, and makes it ideal for quantitative emissions screening. The work shown here was carried out in accordance with ISO 12219-3 for car-trim testing.

Typical analytical conditions:
Sample: Plastic used in car dashboards.
Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate 50 mL/min. Chamber temperature: 65°C. Equilibration: 5 min. Sampling: 15 min.
TD (UNITY or TD100): Tube (Material emissions), desorbed at 280°C (20 min). Trap (Material emissions): Analytes trapped at 20°C, desorbed at 300°C (3 min). Split: Splitless.
Analysis: GC–MS.

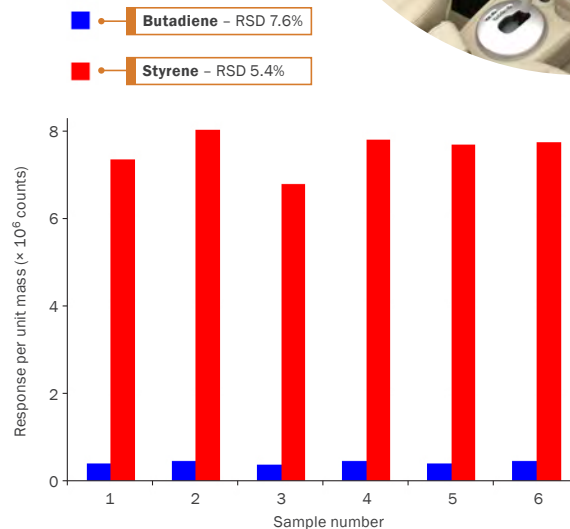The µ-CTE allows up to six different samples to be taken simultaneously.

📄 **Application Note 073** (independent assessment of the µ-CTE)

📄 **Application Note 093** (application to car trim)

■ **Butadiene** – RSD 7.6%

■ **Styrene** – RSD 5.4%

Response per unit mass (× 10^6 counts) vs Sample number (1–6)

Reproducibilities of just 5–8% RSD were obtained when Markes' µ-CTE was used to test six identical samples of plastic material used in car dashboards.

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Speeding up product screening

Microchamber sampling for faster product formulation

Understanding the effect of manufacturing processes on emissions of volatiles is a key issue for manufacturers needing to comply with regulations such as the European CPR and REACH.

Markes' Micro-Chamber/Thermal Extractor (µ-CTE) is a versatile device for sampling of emissions from materials. Sampling typically takes just 20–40 minutes, and as a result the µ-CTE is a valuable approach to assessing vapour-phase emissions during the process of product formulation. Examples are the quick screening of materials in development (as shown here), the comparison of products with those of competitors, and identifying the root cause of high VOC levels in the final product.

Typical analytical conditions:

Sample: Circular section of flooring tile.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate 50 mL/min. Chamber temperature: 40°C. Equilibration: 30 min. Sampling: 30 min.
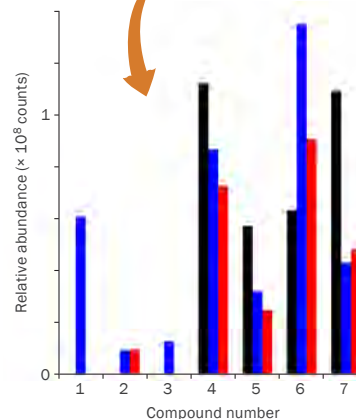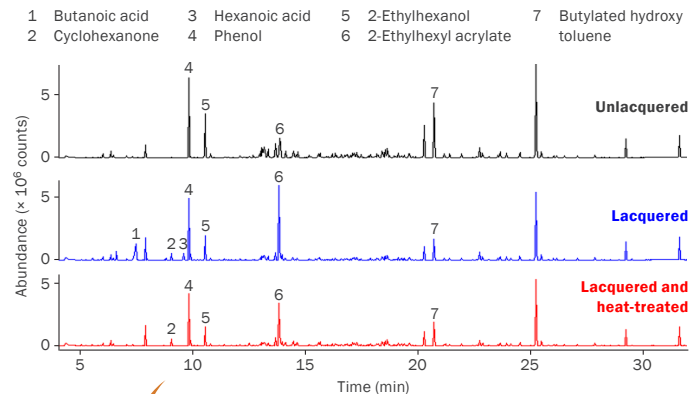
TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 320°C (10 min). Trap (Material emissions): Analytes trapped at 5°C, desorbed at 320°C (5 min). Split ratio: Outlet 26 : 1.

Analysis: GC–MS.

The sampling pots of the µ-CTE are available with diameters of 4.5 or 6.4 cm – large enough to allow vapour-phase emissions testing from representative sections of material or entire products such as small plastic toys.

Application Note 103

1	Butanoic acid	3	Hexanoic acid	5	2-Ethylhexanol	7	Butylated hydroxy toluene
2	Cyclohexanone	4	Phenol	6	2-Ethylhexyl acrylate		

The effect of lacquering on emissions from a floor tile was studied using the µ-CTE. Levels of phenol (#4) and BHT (#7) were high in the unlacquered tile (■), and although these reduced upon lacquering (■), the amount of odorous butanoic acid (#1) rose. Heat treatment (■) resolved this problem, and also reduced emissions of phenol further.

Formaldehyde emissions

Detecting volatile carbonyl compounds in solid samples

Wood veneer manufacturers frequently use formaldehyde-based adhesives in the production process. However, the carcinogenicity of formaldehyde has made emission levels from wood veneers a concern.

Markes' Micro-Chamber/Thermal Extractor (µ-CTE) can be used to sample formaldehyde and other carbonyl compounds that are not compatible with TD (as well as a wide range of VOCs and SVOCs). The example illustrated here follows the ISO 16000-3 standard method.

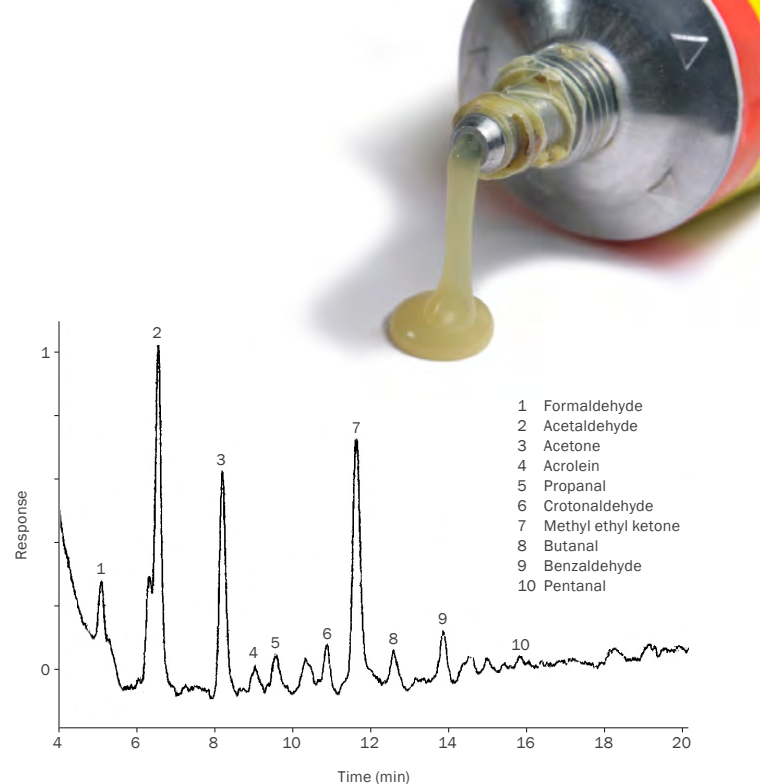**Typical analytical conditions (for formaldehyde):**
Sample: Wood veneer.
Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 250 mL/min. Chamber temperature: 65°C. Equilibration: 20–30 min. Sampling: 2–4 h.
Analysis: HPLC with UV detection.

Formaldehyde is too reactive to monitor by TD–GC–MS, but the µ-CTE can nevertheless be used for sampling. Vapours are simply swept onto a cartridge containing 2,4-dinitrophenylhydrazine (DNPH), which reacts with the formaldehyde to generate a stable derivative. The cartridge is then analysed by high-performance liquid chromatography (HPLC). The air volume for these analyses is typically 30–60 L, with up to six samples being processed every 2–4 hours.

Image credit: Waters

1	Formaldehyde
2	Acetaldehyde
3	Acetone
4	Acrolein
5	Propanal
6	Crotonaldehyde
7	Methyl ethyl ketone
8	Butanal
9	Benzaldehyde
10	Pentanal

High levels of volatile aldehydes are apparent in this emission profile of a wood veneer collected onto a DNPH cartridge using the µ-CTE (by ISO 12219-3), and analysed by HPLC (by ISO 16000-3). *Data reproduced courtesy of the International Automotive Research Centre, University of Warwick, UK.*

Emissions from flat samples

Avoiding edge effects from planar materials

Assessing emissions from flat samples involves taking account of 'edge effects' (the emissions from the edges of the sample), which due to treatment or ageing processes may be substantially different from the surface.

Markes' Micro-Chamber/Thermal Extractor (µ-CTE) allows such effects to be eliminated, by raising samples up within each microchamber, so that the surface presses gently against a collar projecting down from the lid. This prevents edge emissions from contributing to the vapours sampled, ensuring that a representative surface emission profile is obtained.

Typical analytical conditions:

Sample: Coated polymer.

Dynamic headspace (Micro-Chamber/Thermal Extractor):
  Flow rate 50 mL/min.
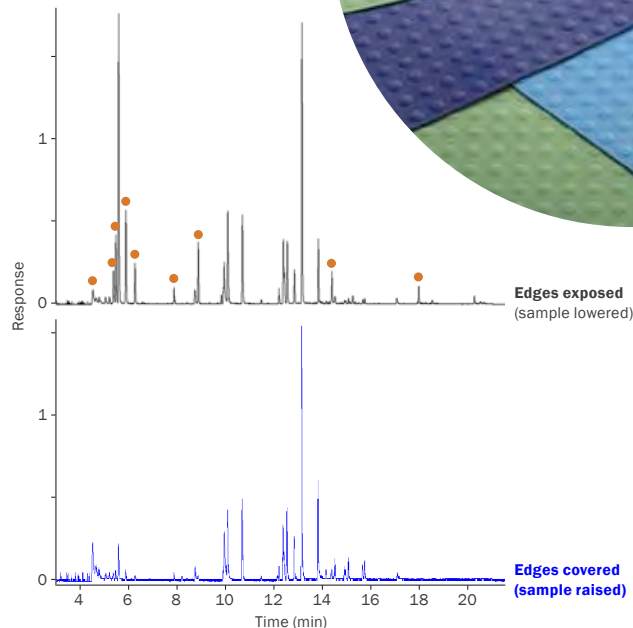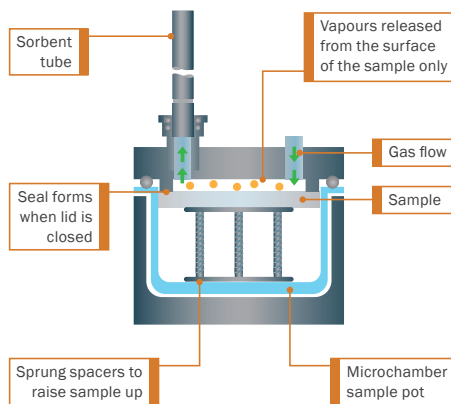 Chamber temperature: 65°C.
  Equilibration: <30 min.
  Sampling: 15 min.

TD (UNITY or TD100): Tube (Material emissions), desorbed at 280°C (10 min).
  Trap (Material emissions): Analytes trapped at 20°C, desorbed at 300°C (3 min).

Analysis: GC–MS.

Sorbent tube

Vapours released from the surface of the sample only

Gas flow

Sample

Seal forms when lid is closed

Sprung spacers to raise sample up

Microchamber sample pot

Edges exposed (sample lowered)

Edges covered (sample raised)

Response

Time (min)

Raising a sample up within the µ-CTE eliminates a number of volatile components mainly released by the edge of this coated polymer sample (●).
Data reproduced courtesy of Professor Mangoo Kim, Kangwon National University, South Korea.

MARKES international

Permeation studies

Examining migration of chemicals through materials

Understanding the migration of VOCs through materials is an important field of study, with relevance to efficacy of food packaging and personal protective equipment. Although the transfer of gases and volatile chemicals through thin films is well-understood theoretically, the structural complexity of polymers makes all but the simplest systems very difficult to model.

The need for reliable experimental data in this area is met by permeation accessories for Markes' Micro-Chamber/Thermal Extractor (µ-CTE). These allow the movement of vapours through a material to be assessed in a controlled fashion.
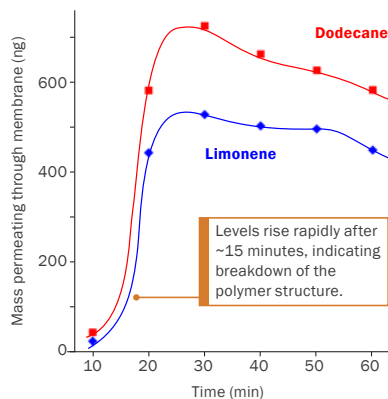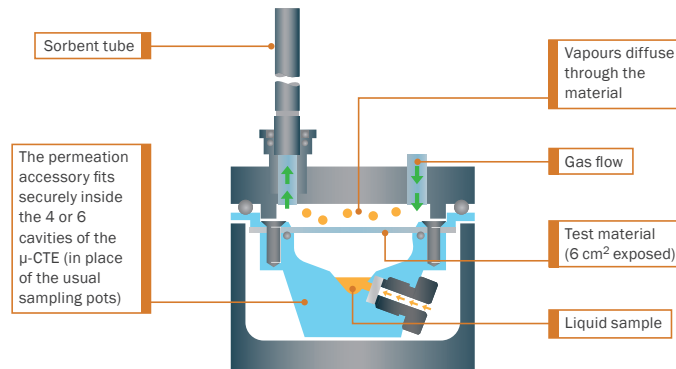
Typical analytical conditions:

Sample: 10 µL each of limonene and dodecane migrating through polypropylene (PP) with 70 µm thickness.

Dynamic headspace (Micro-Chamber/Thermal Extractor with permeation accessory): Flow rate: 50 mL/min. Chamber temperature: 30°C. Sorbent tube changed approximately every 10 min.

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 280°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at 10°C, desorbed at 350°C (3 min). Split ratio: Inlet 2:1, Outlet 21:1.

Analysis: GC–MS.

📝 **Application Note 121**

Sorbent tube

Vapours diffuse through the material

The permeation accessory fits securely inside the 4 or 6 cavities of the µ-CTE (in place of the usual sampling pots)

Gas flow

Test material (6 cm² exposed)

Liquid sample

Dodecane

Limonene

Mass permeating through membrane (ng)

Levels rise rapidly after ~15 minutes, indicating breakdown of the polymer structure.

Time (min)

Using the permeation accessory for the µ-CTE (above) allowed assessment of the migration rate of two chemicals through a polymer sheet.

Rapid analysis of small samples

Readily automated sampling of homogeneous materials

Analytical protocols used for routine quality control or to determine the root cause of high VOC levels depend critically on the robustness of the the sample preparation protocol. For example, volatile residues in polymers are typically determined by static headspace analysis of a suspension of the polymer in solvent – a process that itself risks the introduction of contaminants.

Thermal desorption is an efficient and effective alternative to solvent-based approaches, as well as being easily automated and offering high sensitivity due to the optimised extraction/focusing process. Sampling of larger samples is best carried out using Markes' Micro-Chamber/Thermal Extractor (μ-CTE), while an alternative method for small, relatively homogeneous samples is direct desorption, as illustrated here.

Typical analytical conditions:

Sample: 200 mg of ground PET, placed in an empty TD tube.

TD (UNITY or TD100): Sample: Desorbed at 160°C (10 min). Trap (Odour): Analytes trapped at –10°C, desorbed at 300°C (3 min). Split ratio: Outlet 21:1.

Analysis: GC–MS.

Samples for direct desorption are simply weighed directly into empty TD tubes. Tube liners can be used to avoid contamination of the tube, and if the sample is finely divided, it can be prevented from moving by supporting it with inert plugs of quartz wool.
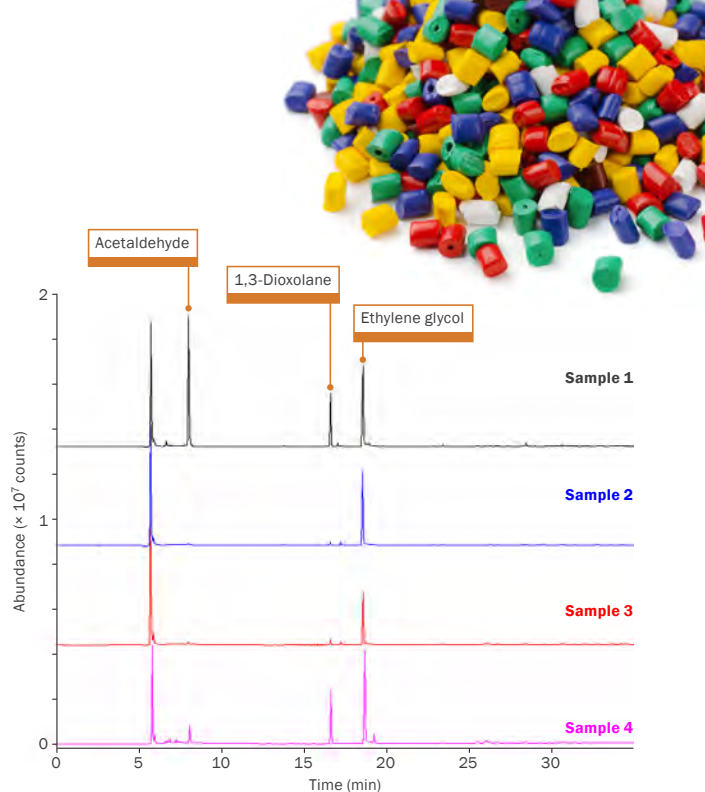
Direct desorption is a quick, operationally simple way of comparing similar samples in order to troubleshoot taint. 1,3-Dioxolane and acetaldehyde are clear issues in two of these samples of polyethylene terephthalate (PET), a polymer widely used in plastic drinks bottles.

Sampling from liquids and resins

Using direct desorption for challenging samples

GC analysis of volatile content is sometimes used as an indicator of emission potential, particularly for liquid products such as paint. However, direct injection of samples into the GC inlet can result in contamination, especially if solid content is high.

Direct desorption of liquids, resins, emulsions and gels using TD tubes overcomes this risk of system contamination, as well as being more readily automated than direct injection. An additional valuable feature of Markes' TD systems for such highly-concentrated samples is their ability to split the sample during tube *and* trap desorption – allowing overall split ratios up to 125,000 : 1.

Typical analytical conditions:

Sample: Water-based emulsion paint (3.3 mg), applied to a small piece of glass wool, and placed within a PTFE liner in an empty TD tube.
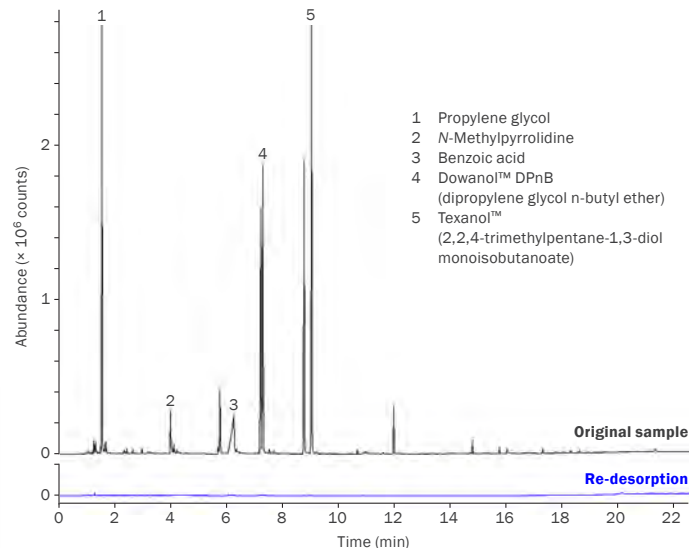
TD (UNITY or TD100): Sample: Desorbed at 200°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at –10°C, desorbed at 300°C (3 min). Split ratio: Outlet 51 : 1, or higher depending on analyte concentration.
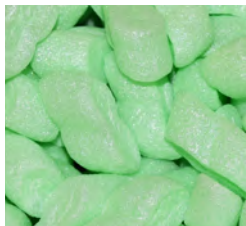
Analysis: GC–MS.

📝 **Application Note 057**

1 Propylene glycol
2 *N*-Methylpyrrolidine
3 Benzoic acid
4 Dowanol™ DPnB (dipropylene glycol n-butyl ether)
5 Texanol™ (2,2,4-trimethylpentane-1,3-diol monoisobutanoate)

Original sample

Re-desorption

Direct desorption from a TD tube releases all the volatiles from a sample of liquid paint, as illustrated by subsequent re-desorption of the same tube. Paint solids remain in the TD tube-liner, while analytical interference from water is avoided by the use of a hydrophobic sorbent in the focusing trap, a pre-desorption dry-purge, and a high outlet split. Note that liquids and semi-solids can also be sampled using Markes' Micro-Chamber/Thermal Extractor – see page 28.

Evolved gas analysis

Assisting material identification by thermogravimetry

Thermogravimetric analysis (TGA) measures changes in the mass of a sample as it is heated, and is widely used to characterise polymeric and pharmaceutical materials. TGA can be coupled with GC–MS to analyse the gases evolved, and so identify unknown materials, but the large mass of vapour eluted can cause saturation of the GC–MS signal.

The double-split capability of Markes' TD technology makes it ideally suited to accommodate such concentrated samples. In addition, separate samples can be collected at different points in the TGA analysis, corresponding to different temperature ranges or weight loss steps in the TGA profile.

Typical analytical conditions:

Sample: Polystyrene or Nylon-4,6.

TGA: 20°C to 600°C at 10°C/min, with nitrogen purge.

TD (UNITY or TD100): Tube (Hydrophobic): Desorbed at 50°C (3 min) then 250°C (5 min). Trap (General-purpose carbon): Analytes trapped at 20°C, desorbed at 350°C (10 min). Split: Inlet 2:1. Outlet 10:1.
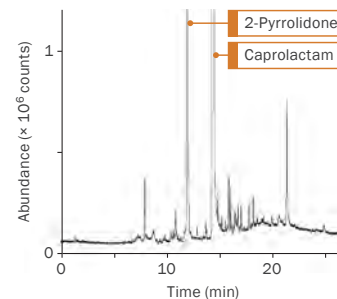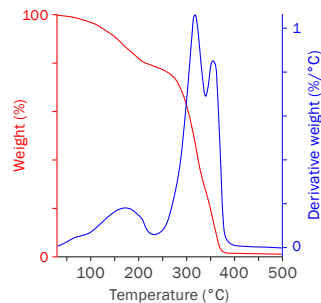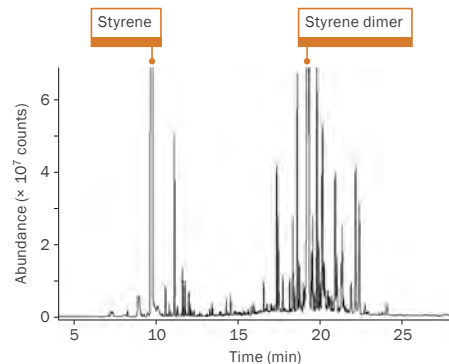
Analysis: GC–MS.

📝 **www.sump4.com/publications/conf012.pdf**

T.J. Lever, D.M. Price and S.B. Warrington, Evolved gas collection from a thermogravimetric analyzer and identification by gas chromatography-mass spectrometry, *Proceedings of the 28th Conference of the North American Thermal Analysis Society*, Orlando, FL, USA, October 2000, pp. 720–725.

A detailed profile of decomposition products is obtained by carrying out TD–GC–MS analysis of polystyrene as it is heated, aiding interpretation of the TGA data.

An unknown material is identified as nylon-4,6 from its two-step TGA profile and the ratio of 2-pyrrolidone and caprolactam in the TD–GC–MS analysis.

Relevant sampling and analytical techniques

Thermal desorption

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

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

- **Analyte range** – Compounds ranging in volatility from acetylene to n-$C_{44}H_{90}$ *and* reactive species can all be analysed on a single TD platform.

- **Quantitative re-collection of split flows** enables repeat analysis and simple method validation, overcoming the historical 'one-shot' limitation of TD.

- **High sensitivity** – Two-stage desorption using sorbent tubes allows concentration enhancements of up to 10^6.

- **Wide dynamic range** – Two-stage desorption and sample splitting means that Markes' thermal desorbers can handle analyte concentrations ranging from part-per-trillion up to low-percent levels.

- **Sample compatibility** – As world leaders in TD technology, Markes offers an unmatched range of innovative and labour-saving sampling accessories for liquids, solids and gases.

- **Analytical quality** – The narrow-bore design of the focusing trap ensures that a highly concentrated band of vapour is introduced to the GC, allowing true splitless operation and optimising both resolution and sensitivity.

- **Reduced running costs** – Electrical cooling eliminates the cost of cryogen, and also avoids problems with ice formation.

- **Cleaner chromatography** – By circumventing the need for sample preparation, solvent artefacts are eliminated, while unwanted high-abundance components such as water can also be selectively removed.

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

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

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

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

Microchamber sampling

Markes' **Micro-Chamber/Thermal Extractor™ (µ-CTE™)** is a stand-alone sampling accessory for dynamic headspace sampling of organic vapours from a wide variety of materials.

Operation is simple, with short sampling times (typically <60 minutes) and the capability to analyse up to four or six samples at once, depending on the model chosen.

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.

➜ **See pages 14, 15, 17, 18, 19, 20, 21 and 22 for applications using the µ-CTE.**

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

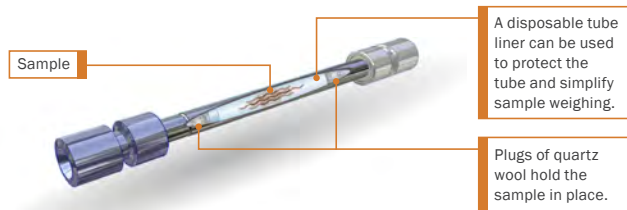**Now available with humidifier accessory**

Two models of the µ-CTE are available – one with six 44 cm^3 sampling pots and a maximum temperature of 120°C (left), and the other with four 114 cm^3 sampling pots and a maximum temperature of 250°C (right).

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.

Sample

A disposable tube liner can be used to protect the tube and simplify sample weighing.

Plugs of quartz wool hold the sample in place.

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 23 and 24 for applications using direct desorption.

For more on direct desorption, see Application Note 009.

Pumped sampling onto sorbent tubes

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 11, 12 and 16 for applications using pumped sampling.

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

Bag sampling

Sampling bags are widely used for collecting organic vapours from large samples or whole products. Markes offers two systems suitable for bag analysis, both of which pre-concentrate vapours on an electrically-cooled focusing trap before injecting them into the GC.

- **Air Server-xr™** systems allow sampling of air from up to eight channels. As well as bags (and canisters), it can also be applied to on-line monitoring (see opposite).

- **The CIA *Advantage-xr*™** automates the analysis of air from up to 27 channels. Gas-loop and MFC-controlled sampling options combined with quantitative sample splitting allow compatibility with a wide range of sample concentrations.

Both the **Air Server-xr** (left) and the **CIA *Advantage-xr*** (right) couple with the UNITY-xr thermal desorber, and use electrical trap cooling for optimum performance.

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

On-line sampling

On-line sampling involves the collection of vapours directly into the focusing trap of the thermal desorber. It is particularly valuable for continuous sampling of air/gas over a period of time, as well for monitoring ultra-volatile compounds that are not quantitatively retained on sorbent tubes at ambient temperature.

Two systems for on-line monitoring are available from Markes:

- The **Air Server-xr** (pictured opposite), samples air for a defined period of time and delivers it to the focusing trap of the UNITY-xr thermal desorber.

- The **TT24-7™** uses two focusing traps, working alternately, to sample and analyse air continuously, making it ideal for time-profiling.

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

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

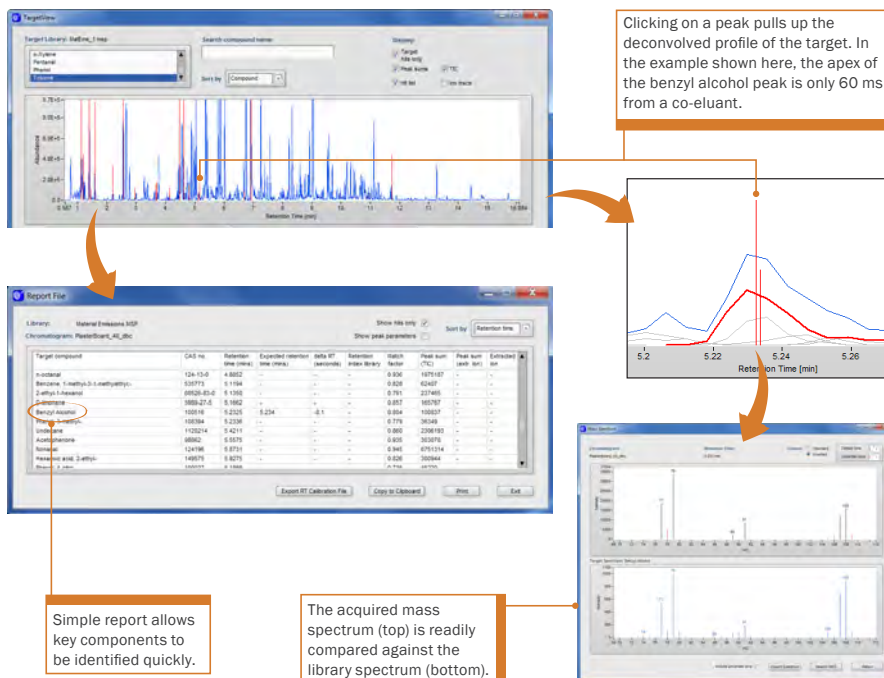For more on these products and to download the brochures, visit www.markes.com.

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. In the example shown here, the apex of the benzyl alcohol peak is only 60 ms from a co-eluant.

Simple report allows key components to be identified quickly.

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

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

MARKES
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About Markes International

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

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

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

As well as studies into consumer environmental health, Markes' products are used extensively in multiple routine and research scenarios – everything from forensic analysis to chemical ecology.

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.

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