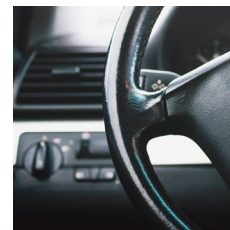
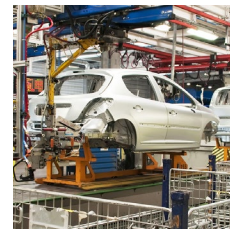


Thermal Desorption Applications Guide: Automotive studies

A comprehensive guide to using
thermal desorption in the
vehicle-manufacturing industry



Introduction

Automotive studies

Concern over passenger health and safety because of poor vehicle interior air quality (VIAQ) has led to regulations on the materials used in vehicles, and the development of associated sampling and analytical methods. The aim of these methods is to aid understanding of the VOC and SVOC content of car trim, emission profiles, and the overall quality of in-vehicle air.

In this Applications Guide, we describe the role of thermal desorption (TD) within these methods, and show how it can be applied to a range of applications in the automotive industry. Examples covered include whole air testing of car cabins, direct desorption of small samples, and chamber/bag methods for certification and screening.

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 22 and our website for more details.



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

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

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Regulations and standard methods

SIGNATURE

The VIAQ regulatory framework

Vehicle interior air quality (VIAQ) has been a topic of interest since the late 1970s, when concern over the effect of VOCs on the indoor environment began to be replicated in the automotive industry. This concern is in two main areas – the effect of VOCs on health, and concerns of consumers regarding vehicle odour.

As a result, guidelines have been developed on acceptable levels of VOCs in vehicle air, although many manufacturers are adhering to the most stringent rule – the Chinese regulation GB/T 27630-2011. Like its less rigorous counterpart guidelines in Japan and Korea, this is government-led – in contrast to the EU and US, where limit levels have largely been defined by manufacturers.

Responsibility for demonstrating conformance with specified limits for VIAQ rests with the car manufacturer. However, in general a failure to meet these requirements is passed successively down the manufacturing chain to:



- Tier 1 suppliers (who manufacture entire components such as car seats).
- Tier 2 suppliers (who manufacture the individual materials such as plastics, carpet or leather).
- Raw material suppliers.

This process places considerable pressure for suppliers of Tier 2 components and raw materials to understand the regulatory framework, and to check emissions from the materials they produce.

Global VIAQ working groups

International Organization for Standardization (ISO):

- Technical committees 22 and 146/SC 6 WG 13 – Interior air of road vehicles.

Organisation Internationale des Constructeurs d'Automobiles (OICA):

- Informal Working Group on VIAQ.
- Technical Working Group/Task Force on VIAQ.

European Automobile Manufacturers' Association (ACEA):

- Task Force on VIAQ.

United Nations Economic Commission for Europe (UNECE):

- World Forum for Harmonization of Vehicle Regulations (WP.29).

SAE International (Society of Automotive Engineers):

- VOC committee (for USA).

Verband der Automobilindustrie (VDA):

- Indoor Air workgroup (for Germany).

United States Council for Automotive Research (USCAR):

- U.S. Automotive Materials Partnership (USAMP) – VIAQ committee.

Overview of methodologies

To assess whether or not VIAQ complies with the required levels, a large number of standard methods for sampling and analysis of VOCs and SVOCs have been developed by national standards agencies, automotive societies and manufacturers. These standard methods are all compatible with TD, and fall into three broad categories (1–3), with five sampling approaches (A–E). These are described in more detail on the following pages.

1 In-vehicle air sampling



A Pumped air sampling

2 Screening of emissions from assembly parts



B Small chambers



C Sampling bags

3 Screening of emissions from components



D Microchambers

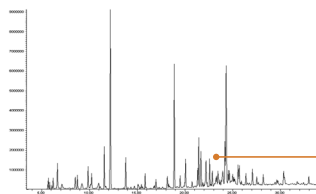


E Direct desorption

The five main sampling approaches for assessing VIAQ and emissions from automotive components are all compatible with TD.



Thermal desorption – see page 22 for more detail



Analysis by gas chromatography

TD-based approaches can detect:

- VOCs (boiling up to $n\text{-C}_{16}$).
- SVOCs or FOG compounds (boiling above $n\text{-C}_{16}$).
- Odorous or reactive species.



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 16 for more information.

1 In-vehicle air sampling

A Pumped air 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 the criteria defined in national regulations.

For more information on pumped sampling, see page 24.



Manufacturer- or country-led regulations/methods

- China – Regulation GB/T 27630-2011 is now mandatory in China; the associated method is HJ 400.
- Japan – New models of passenger cars must satisfy the indoor concentration guidelines established for 13 VOCs by the Ministry of Health, Labour and Welfare.
- South Korea – An Automobile Management Act (Article 33-3) on VIAQ in newly manufactured vehicles came into force in 2012.

Harmonised methods

- ISO 12219-1 describes the pumped sampling of cabin air under three different conditions, onto sorbent-packed TD tubes, with analysis of the tubes by GC-MS.

What are harmonised methods?

In the automobile industry, there are literally hundreds of methods for VOC and SVOC sampling and analysis that have been developed by various organisations and companies, but in general it is not possible to correlate the results of these methods. This means that manufacturers typically have to carry out multiple (often similar) analyses before being able to export their vehicles.

Addressing this problem are the ISO 12219 series of standards, developed by the ISO Indoor air committee (ISO/TC 146/SC 6). These harmonised methods describe consensus on current best practice for a number of sampling methodologies, and provide a single set of universally-applicable protocols, so streamlining product R&D and approval.

2 Screening of emissions from assembly parts

B Small chambers

'Small' chambers (typically 1 m³) are used to assess emissions from complete components, with vapours being collected onto sorbent tubes. Standard reference tests for final product certification typically require that this is done over periods of days.



Manufacturer- or country-led regulations/methods

- VDA 276 is a long-standing German method that has been adopted by many manufacturers.
- Other methods include JIS A1901, BMW GS 97014-3 ("Summer test"), and generic chamber methods such as ASTM D5116-97 and ISO 16000-9.

Harmonised methods

- ISO 12219-4 (for VOCs) is carried out using a 1 m³ chamber at 65°C, and is run for 3 hours (not including pre-heating or cleaning).
- ISO 12219-6 (for SVOCs) is similar to ISO 12219-4, but is run at 100°C.

C Sampling bags

Sampling bags are employed by Tier 1 suppliers (primarily in Asia) as an alternative to small chambers for assessing emissions from large components. Bags of various sizes are used, with vapours being pumped directly into the focusing trap of the thermal desorber.



Manufacturer- or country-led regulations/methods

- JASO M902 has been developed by the Society of Automotive Engineers of Japan.
- Other methods include MS300-55 (Hyundai-Kia), NES M0402 (Nissan), TSM 0508G (Toyota) and DWG 0094Z SNA 0000 (Honda).

Harmonised methods

- ISO 12219-2 involves pumping headspace from a 10 L bag in which the sample material is placed, following a suitable incubation period.
- ISO 12219-9 is analogous to ISO 12219-2, but uses a 2000 L bag.

3 Screening of emissions from components

D Microchambers

Microchambers (44 cm³ or 114 cm³) are a quick and convenient approach for Tier 2 suppliers to sample emissions onto sorbent tubes. Importantly, the results of microchambers can be correlated to the outcome of small-chamber studies.

For more information on Markes' Micro-Chamber/Thermal Extractor, see page 23.



Manufacturer- or country-led regulations/methods

- Jaguar Landrover.
- General Motors GMW17082.

Harmonised methods

- ISO 12219-3 is a microchamber-based method for rapid qualitative and semi-quantitative screening of vapour-phase organic compounds under simulated real-use conditions.

See page 17 for an example.

E 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.

For more information on direct desorption, see page 23.



Manufacturer- or country-led regulations/methods

- VDA 278 has long been used for screening of materials.

See page 18 for an example.

Harmonised methods

- Because it is generally applicable to small, homogeneous samples, direct desorption has not been translated into a harmonised ISO method.

A close-up photograph of a car's interior, focusing on the steering wheel and dashboard. The steering wheel is black with a textured leather-like surface and a silver-colored rim. The dashboard features a circular air vent and various control buttons. A semi-transparent purple rectangular box is overlaid on the left side of the image, containing the text "Automotive studies" in white.

Automotive studies

Monitoring in-vehicle air quality

Using pumped sampling to assess levels of VOCs and SVOCs in car cabins

Vapour-phase levels of VOCs and SVOCs emitted from car trim can easily build up at elevated temperatures – for example, if the car is left parked on a sunny day. The result can be a negative effect on in-vehicle air quality, which has given rise to health concerns and the development of regulations worldwide.

Markes' TD systems are ideally suited to monitoring of IVAQ by pumping air from the cabin onto sorbent tubes, for analysis by TD-GC-MS. The use of multi-bed tubes allows a wide range of analytes (C_3 – C_{44}) to be sampled simultaneously, while the short, inert, uniformly-heated flow path of the thermal desorber aids recovery of labile analytes.

Typical analytical conditions:

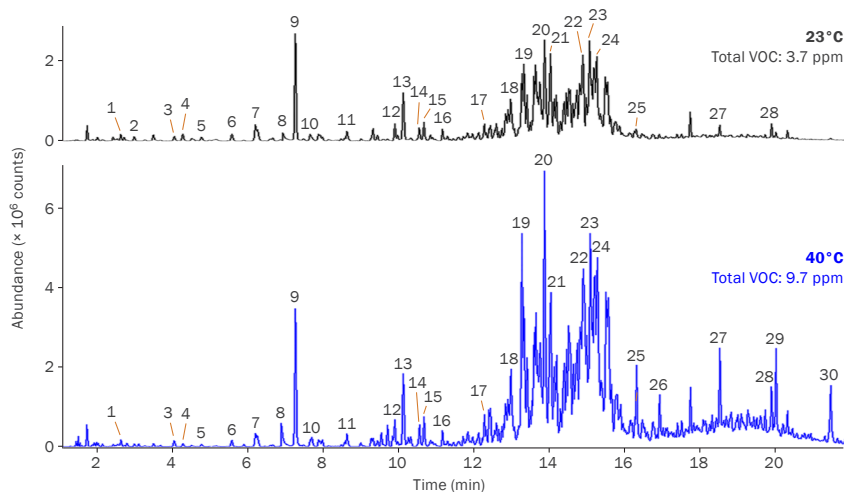
Sample: Car cabin air.

Pumped sampling (ACTI-VOC): 2–10 L, sampled onto a sorbent tube.

TD (UNITY or TD100): Tube (Material emissions): Desorbed at 280°C (6 min). Trap (Material emissions): Analytes trapped at 20°C, desorbed at 300°C (3 min). Split ratio: 50:1 to 200:1.

Analysis: GC-MS.

- | | | |
|-----------------------|---------------------------------|---------------------------------------|
| 1 Methyl ethyl ketone | 11 n-Octane | 21 $C_{11}H_{24}/C_{12}H_{26}$ isomer |
| 2 n-Hexane | 12 Ethylbenzene | 22 $C_{11}H_{24}/C_{12}H_{26}$ isomer |
| 3 Benzene | 13 <i>m</i> -/ <i>p</i> -Xylene | 23 $C_{12}H_{26}$ isomer |
| 4 Cyclohexane | 14 Styrene | 24 $C_{13}H_{28}$ isomer |
| 5 Isoheptane | 15 o-Xylene | 25 2-(2-Butoxyethoxy)ethanol |
| 6 n-Heptane | 16 n-Nonane | 26 n- $C_{12}H_{26}$ |
| 7 Methylcyclohexane | 17 Ethyltoluene | 27 n- $C_{13}H_{28}$ |
| 8 <i>N,N</i> -DMF | 18 Trimethylbenzene | 28 Cubebene/Copaene |
| 9 Toluene | 19 n-Decane | 29 n- $C_{14}H_{30}$ |
| 10 Isooctane | 20 Dimethylbenzylamine | 30 Butylated hydroxy toluene |



A complex range of VOCs are identified in these analyses of car cabin air, with a 3-fold increase in total VOC levels being found at 40°C compared to ambient temperature.



Application Note 033

Quick component screening

Microchambers for routine sampling of VOCs and SVOCs

Manufacturers of materials used in car-part assemblies need to understand the emission profiles of their materials for compliance and for researching new formulations. This demands rapid, reproducible sampling and analysis, as well as reliable comparison against control samples. Such quick turn-around is difficult or impossible using the small-chamber techniques required for long-term reference tests.

The Micro-Chamber/Thermal Extractor (μ -CTE) is a valuable tool for routine sampling, because it allows vapour profiles to be taken from multiple samples side-by-side under identical conditions. The combined sensitivity enhancement offered by dynamic headspace and TD makes it a powerful approach for generating representative, detailed VOC profiles. Moreover, the data can be used to predict the results of reference tests – see page 14.

Typical analytical conditions:

Sample: Foam used in automotive components.

Dynamic headspace (Micro-Chamber/Thermal Extractor):

Flow rate 50 mL/min. Chamber temperature: 65°C.

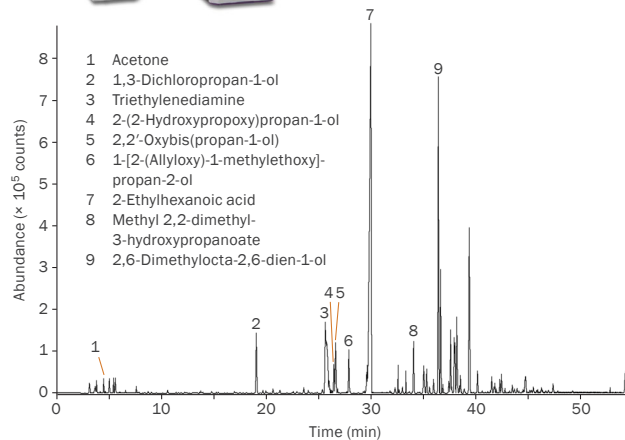
Equilibration: 15 min. Sampling: 15 min.

TD (UNITY or TD100): Tube (Material emissions), desorbed at 300°C (10 min). Trap (Material emissions): Analytes trapped at 5°C, desorbed at 320°C (5 min). Split: Outlet 26:1.

Analysis: GC–MS.



The μ -CTE is available in two models: one with six chambers and a maximum temperature of 120°C (left), and the other with four chambers and a maximum temperature of 250°C (right).



Rapid sampling of volatiles on to multi-bed sorbent tubes using the μ -CTE (in accordance with ISO 12219-3), with analysis on Markes' thermal desorbers, allows comprehensive profiles to be generated, as shown here for a sample of automotive foam.

Small chamber–microchamber correlation

Using quick dynamic headspace sampling to predict the results of long-term reference tests

The reference tests needed for certification testing of car-trim materials, 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 car trim components, and gives results that are a reliable indicator of the outcome of longer-term reference tests.

Typical analytical conditions:

Sample: Carpet.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate 50 mL/min.

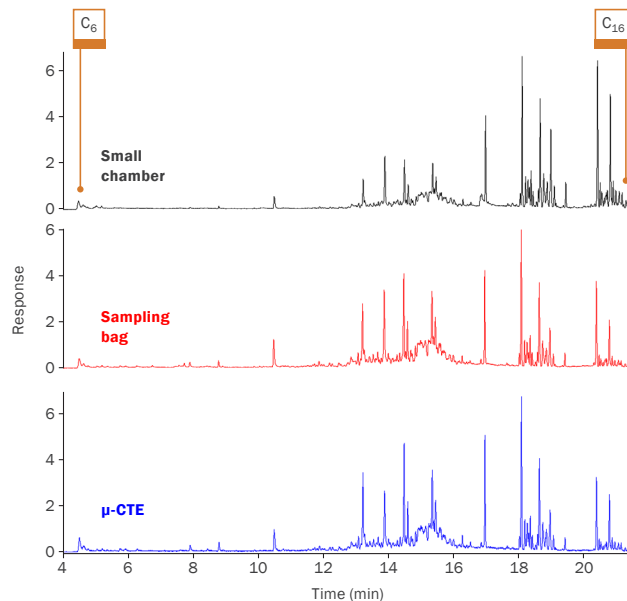
Chamber temperature: 65°C. Equilibration: <30 min. Sampling: 15 min.

TD (UNITY or TD100): Tube (Material emissions), desorbed at 300°C (10 min). Trap (Material emissions): Analytes trapped at 5°C, desorbed at 320°C (5 min).

Analysis: GC–MS.



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



In a matter of minutes, car trim emissions data (in this case carpet) can be obtained using Markes' μ -CTE in accordance with ISO 12219-3, and then correlated to data obtained by longer-term small-chamber and bag methods.

Data reproduced courtesy of Professor Mangoo Kim, Kangwon National University, South Korea.

Emissions from flat samples

Avoiding edge effects from planar materials

Assessment of 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.

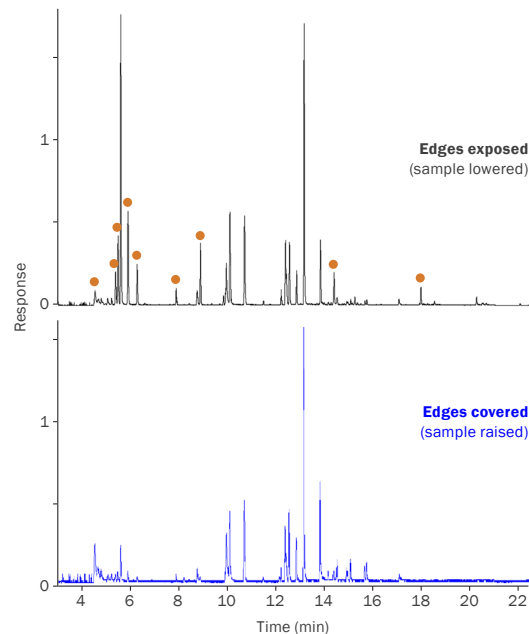
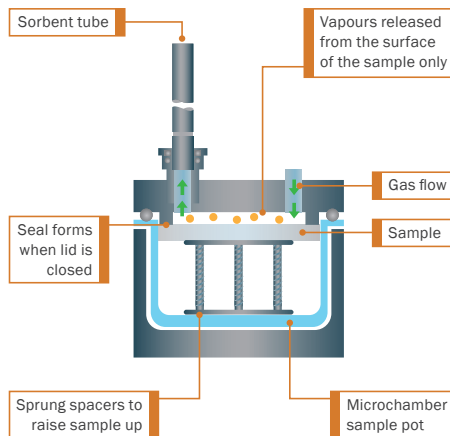
Typical analytical conditions:

Sample: Injection-moulded plastic car body part, coated with an oil-based paint.

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.



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

Formaldehyde emissions

Detecting volatile carbonyl compounds using a microchamber method

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):

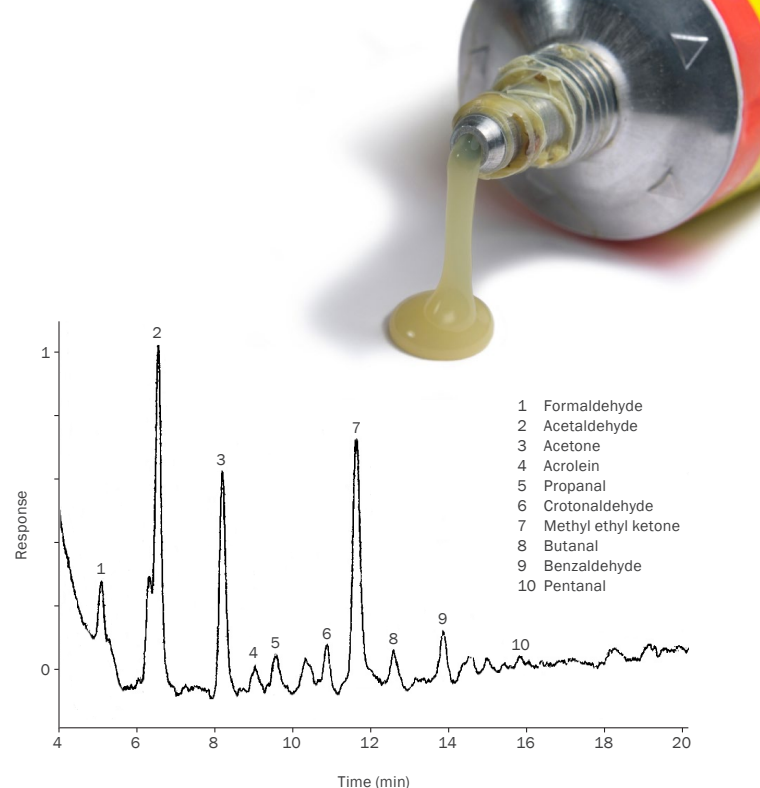
Sample: Wood veneer.

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.



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.



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.

Improving reproducibility

Lowering RSDs for testing emissions from car trim

Emissions testing with conventional small chambers and emission cells is a complex, multi-step process with many opportunities for error to creep in. As a result of this, 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.

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.



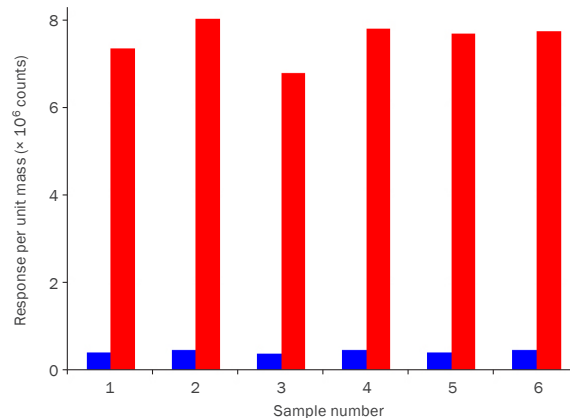
MARKES
international

The sampling pots of the μ -CTE are available with diameters of 4.5 or 6.4 cm.



Butadiene – RSD 7.6%

Styrene – RSD 5.4%



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.



Application Note 093

Quick screening of small samples

Direct desorption of vehicle trim to assess emission levels

VDA 278 is widely used within the automotive industry for assessing car trim, and involves the direct desorption of a small sample of material, to give an estimate of the emissions of VOCs and SVOCs (fogging compounds).

Markes' TD systems are ideal for carrying out analysis by VDA 278, with automation options allowing efficient running of multiple samples. Because of their short, inert, heated flow paths, they are also able to reliably recover semi-volatiles boiling up to $n\text{-C}_{44}$.

Typical analytical conditions:

Sample: Polypropylene car trim, placed in an empty TD tube.

TD (UNITY or TD100): Sample: Desorbed at 90°C (30 min) for VOCs, then at 120°C (60 min) for SVOCs. Trap (General-purpose hydrophobic or Tenax® TA): Analytes trapped at -30°C , desorbed at 300°C (3 min for 'VOC' analysis, 5 min for 'FOG' analysis).

Split ratio: Inlet: 2:1. Outlet 16.4:1.

Analysis: GC-MS (note that different column conditions are used for the two runs).

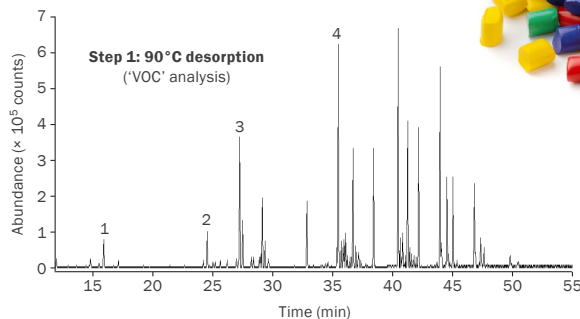


Sample tubes in Markes' TD instruments are held horizontally, eliminating any risk of the sample blocking the tube during analysis.

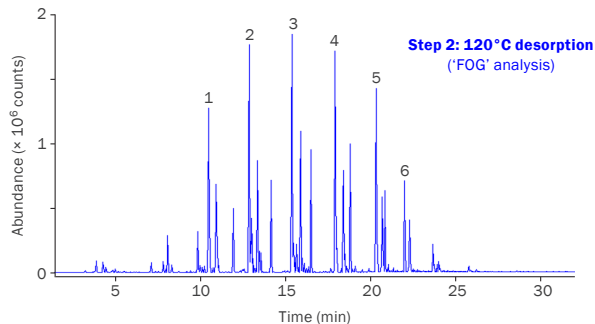


Application Note 059

Topic continued on
next page



- 1 2,4-Dimethylhept-1-ene
- 2 Decane
- 3 $\text{C}_{12}\text{H}_{26}$
- 4 $\text{C}_{16}\text{H}_{34}$



- 1 $\text{C}_{12}\text{H}_{26}$
- 2 $\text{C}_{16}\text{H}_{34}$
- 3 $\text{C}_{18}\text{H}_{38}$
- 4 $\text{C}_{20}\text{H}_{42}$
- 5 $\text{C}_{22}\text{H}_{46}$
- 6 $\text{C}_{24}\text{H}_{50}$

Successive direct desorption of a single sample of plastic car trim at two temperatures – as stipulated in VDA 278 and some company-specific protocols – is used to assess levels of VOCs and SVOCs.

Quick screening of small samples

Topic continued from previous page

Troubleshooting quality issues using direct desorption

Problems affecting textile or leather car-trim components can be challenging for analytical techniques using conventional liquid extraction, because this method is laborious and has limited sensitivity. It also risks introducing artefacts from the solvent, or causing skewed profiles due to loss of the more volatile species during sample handling.



Thermal desorption is an efficient and effective alternative to solvent-based approaches, because of the ease of automation and the sensitivity-enhancing nature of the extraction/focusing process. In this example, direct desorption was used, which being quick and operationally simple, is a convenient way of investigating issues such as discolouration or odour from small, relatively homogeneous samples.

Typical analytical conditions:

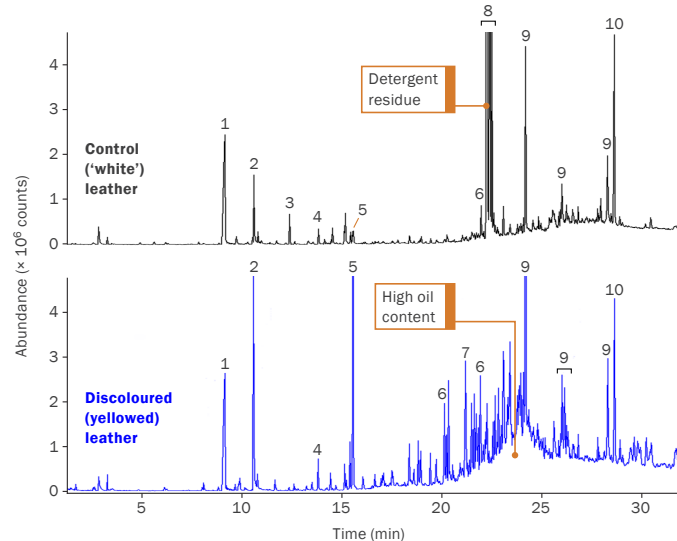
Sample: Leather (~30 mg), placed in an empty TD tube.

TD (UNITY or TD100): Sample: Desorbed at 150°C (5 min). Trap (General-purpose hydrophobic): Analytes trapped at 25°C, desorbed at 300°C (3 min). Split ratio: Outlet 14:1.

Analysis: GC-MS.

Application Note 040

- | | | |
|-----------------------------|--------------------------------|--|
| 1 Diethylene glycol | 5 <i>tert</i> -Butylphenol | 9 C ₁₆ -C ₁₈ fatty acids |
| 2 1-Methylpyrrolid-2-one | 6 Octylphenol isomers | 10 Dioctyl adipate |
| 3 Nonanal | 7 Chlorotriazine derivative | |
| 4 2-(2-Butoxyethoxy)ethanol | 8 Tris(chloropropyl)phosphates | |



High levels of natural oils were found to be the cause of a patchy yellow discolouration on white leather upholstery, as assessed by comparison of a sample of the affected material with a control. Note the detection of long-chain fatty acids at the same time as lower-boiling compounds.

Exhaust particulates

Efficient analysis of PAHs

Vehicle exhaust is a major source of carcinogenic polycyclic aromatic hydrocarbons (PAHs), which, being low volatility, tend to occur bound to airborne particulate matter. Monitoring PAHs in such particulate matter is therefore important to understand the health impact of air pollution, but they can be difficult to analyse by TD-GC.



Markes' TD systems efficiently transfer a wide range of semi-volatile species through the analytical system, thanks to the high linear velocities in the flow path and the absence of cold spots. Capable of analysing SVOCs boiling up to n-C₄₄, they can also handle the range of PAHs encountered in vehicle exhaust, with efficient focusing within the TD instrument providing the well-resolved chromatography needed to assist identification.

Typical analytical conditions:

Sample: 4 cm long × 4 mm wide section of quartz filter (cut from a larger piece used to collect particulates from a diesel exhaust), placed in an empty TD tube.

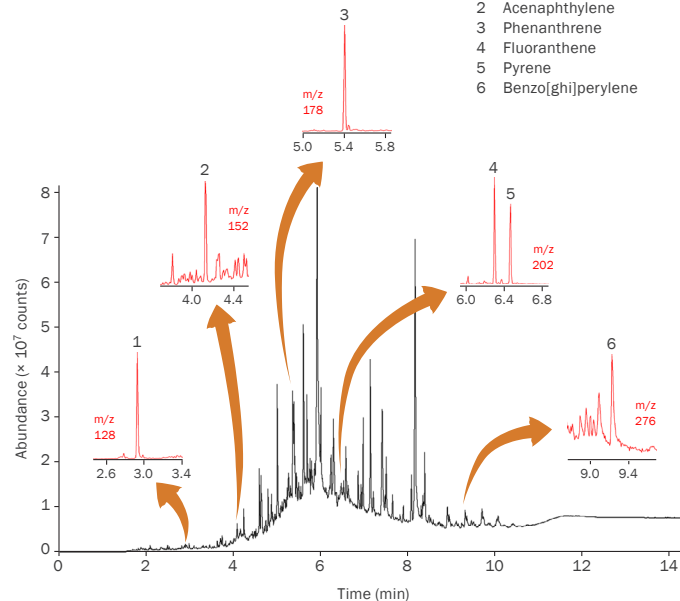
TD (UNITY or TD100): Sample: Desorbed at 300°C (15 min). Trap (high-boilers): Analytes trapped at 30°C, desorbed at 320°C (5 min). Split ratio: Inlet 3:1, Outlet 134:1.

Analysis: GC-MS.

Application Note 097

Insets show EICs for:

- 1 Naphthalene
- 2 Acenaphthylene
- 3 Phenanthrene
- 4 Fluoranthene
- 5 Pyrene
- 6 Benzo[ghi]perylene



A range of PAHs are found in this profile of particulate matter from diesel exhaust. The detection of benzo[ghi]perylene (b.p. 500°C) is an excellent example of the power of TD-GC-MS to analyse trace-level high-boiling components.



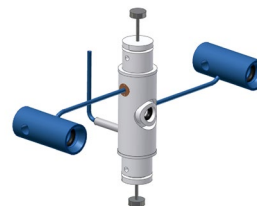
Relevant sampling and analytical techniques

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 $n\text{-C}_{44}\text{H}_{90}$ 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 $\text{C}_2\text{--C}_{44}$ 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.

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 cm³, depending on the model chosen.

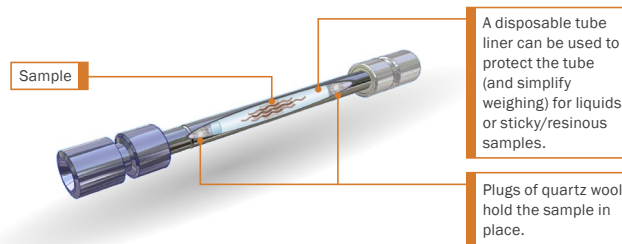
➔ See pages 13–17 for applications using the μ-CTE.

📄 ➔ 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 18–20 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 page 12 for an application 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 in the automotive industry. 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.

- **The CIA Advantage™** 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.
- **Air Server-xr™** systems allow sampling of air from up to eight channels.



The CIA Advantage uses UNITY-xr trapping technology for optimum performance.



The Air Server-xr (right) integrates with UNITY-xr.

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

Also suitable for continuous on-line monitoring of car-cabin air

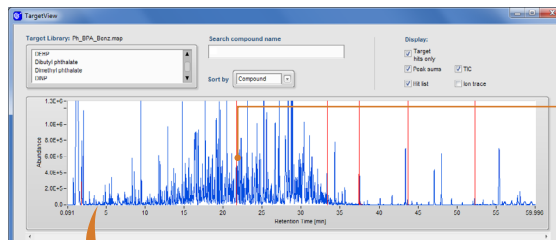
Compound identification software

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.

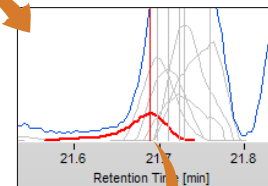
TargetView features:

- 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.



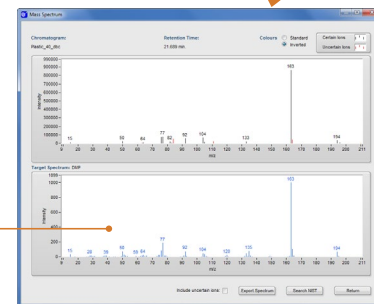
Clicking on a peak pulls up the deconvoluted profile of the target (dimethyl phthalate in this case) and any nearby peaks.



Target compound	CAS no.	Retention time (min)	Expected retention time (min)	delta RT (seconds)	Retention index library	Match score	Peak score (100 = 100%)	Extracted MS
Acetone	64662-88-6	1.8224	-	-	0.776	281209	-	-
Dimethyl phthalate	133-11-3	21.0294	-	-	0.945	1462026	-	-
Diethyl phthalate	84-74-2	33.3524	-	-	0.795	6121053	-	-
Phthalic acid	85-85-7	37.4079	-	-	0.900	7364037	-	-
Diethyl isophthalate	117-81-7	43.8884	-	-	0.605	1468114	-	-
Dimethyl isophthalate	26551-12-0	52.2770	-	-	0.763	1289055	-	-

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 a plastic sample, 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.

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 automotive applications, Markes' products are used extensively in multiple routine and research applications – everything from food aroma profiling to disease diagnosis.

Markes is headquartered near Cardiff, UK, and also has laboratory and demonstration facilities in Cincinnati and Sacramento, USA, and near Frankfurt, Germany. Markes is a company of the Schauenburg International Group.



ACTI-VOC™, Air Server-xr™, CIA Advantage™, Easy-VOC™, Micro-Chamber/Thermal Extractor™, µ-CTE™, MTS-32™, TargetView™, TD100™, TD100-xr™, UNITY™ and UNITY-xr™ are trademarks of Markes International.
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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.

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