

The background of the cover features several rolls of colorful, patterned fabrics in shades of red, yellow, and blue, standing upright. In the foreground, a white, textured cloth is draped across the bottom. The overall lighting is bright and slightly hazy.

Thermal Desorption: A Practical Applications Guide

II. Residual Volatiles & Material Emissions Testing

2nd Edition

MARKES
international

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Introduction to Markes International Ltd

Formed in 1997, Markes International is world leader in the development and manufacture of analytical thermal desorption (TD) instrumentation and associated sampling equipment for measuring VOCs and semi-volatiles in air & materials.

Markes has pioneered major TD innovations such as quantitative re-collection for repeat analysis (**SecureTD-Q™**), **TubeTAG™** RFID tube labels, **DiffLok™** enabling technology for robust tube automation and cryogen-free analysis of multiple canister air samples. All these innovations feature in Markes' well known modular range of TD instruments: **UNITY™**, **ULTRA™**, **Air Server™** and the most recent addition, the **TD-100™**. Other ground-breaking TD products from Markes International include the twin-trap **TT24-7™** for continuous, online air monitoring, and unique sampling accessories such as the **Micro-Chamber/Thermal Extractor™** and **HS5-TD™** for liquid and solid samples.

Markes' TD units can be seamlessly combined with all major brands of GC and GC/MS to provide trace or high level monitoring solutions.

What is analytical TD?

Analytical thermal desorption is a sample introduction technique for GC and GC/MS, which uses heat and a flow of inert gas, rather than an organic solvent, to extract/desorb analytes from the sample media, delivering them directly to the gas chromatograph. Since the early 1980s, TD has provided the ultimate versatile sample introduction technology for GC, by combining selective concentration enhancement with direct extraction into the carrier gas and efficient transfer/injection, all in one fully automated and labour-saving package.



Markes International Ltd, UK headquarters

Overview

Thermal desorption is now recognised as the technique of choice for environmental air monitoring and occupational health & safety. Relevant standard methods include: ISO/EN 16017, EN 14662 (parts 1 & 4), ASTM D6196, US EPA TO-17 and NIOSH 2549.

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

This publication presents several real-world applications of TD for measuring residual solvents and for materials emissions testing. Accompanying publications cover the application areas of:

- Food, flavour, fragrance & odour profiling
- Defence & forensic
- Environmental monitoring and occupational health & safety

Residual solvents & material emissions testing

Residual solvents (volatile compounds) present in a product, raw ingredient or packaging can be toxic. For measuring residual volatile content, TD provides a convenient and fully automated alternative to conventional solvent extraction.

Vapour-phase organic chemicals are also emitted (released) from a variety of materials and everyday products. Under new regulations, manufacturers are responsible for knowing what chemicals are coming out of their products and making sure they are safe for consumers. Relevant test methods include CEN TC351 standards, the ISO 16000 series, the ISO 12219 series, ASTM 5116, ASTM D6196 and ASTM D7143.



Chemical content testing

Residual volatiles can cause taint/off-odour problems in a wide range of consumer goods. In rare cases, they may also present a health risk to consumers. Therefore there is a need to assess the volatile content of raw materials, products and packaging.

TD provides a convenient, fully automated alternative to conventional solvent extraction techniques for measuring volatile content.

Products ranging from ointments to drug powders and from packaging films to polymer beads may be weighed directly into empty sample tubes for desorption/extraction and transfer of target analytes to the GC(MS) analyser or E-Nose.

Markes' headspace-TD sampling solutions also comply with regulatory methods, e.g. the analysis of residual solvents from drugs *per* USP method 467, and provide improved levels of sensitivity over traditional headspace techniques.



Example applications include:

- Solvents in food packaging film
- Active ingredients and essential oils in ointments and pastes
- Residual solvents in pharmaceuticals/drug powders
- Residual monomer in polymer



Analysis by direct thermal desorption/extraction



The horizontal orientation of sample tubes in Markes Series 2 UNITY & TD-100 systems minimises the risk of material shifting within the tube or falling out.

Background:

In comparison to traditionally used solvent extraction techniques, direct thermal desorption (TD) provides a labour-saving way to extract volatiles from solids, resins, pastes, emulsions and liquids.

To an analyst, this technique simply involves placing a small amount of sample directly into an empty thermal desorption tube and positioning it on the thermal desorber.

Once the tube is in position, the sample is heated in a stream of inert gas. The volatiles are swept out and pre-concentrated on the focusing trap. This trap is subsequently desorbed and vapours are transferred (injected) into the GC(MS) analytical system.

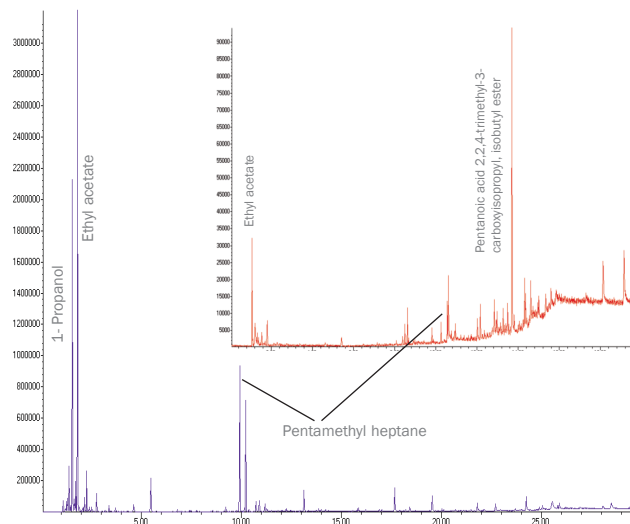
Direct TD allows selective concentration of extracted compounds, whilst water or other solvents may be purged to vent, thus minimising interference, meaning only components of interest are transferred.

Direct desorption is used for both:

- Complete (exhaustive) extraction
- Characterisation of materials using a representative vapour profile



Headspace & direct desorption of residual solvents in food packaging



Direct desorption of 'energy food bar' wrapper (red) and concentrated headspace vapours from the same material (blue)

Background:

Organic chemicals in food packaging can cause taint. Markes' versatile TD systems offer three simple methods for packaging analysis on a single platform:

- Direct thermal desorption
- Headspace (HS)-TD with conventional HS vials
- Desorption of sorbent tubes onto which headspace vapours from larger bulk samples have been concentrated

In this example, TD was used to analyse residual solvents in printed 'energy food bar' wrappers by direct thermal desorption & concentrated headspace. Direct TD allows simultaneous analysis of both volatiles and semi-volatiles, whereas volatiles and ultra-volatiles are preferentially concentrated in the HS sample.

Typical analytical conditions:

Sample: 50 cm³ film rolled and inserted into empty glass tube for direct TD, or 250 mL headspace vapours drawn from the sample container and into a Tenax® TA sorbent tube

TD system: UNITY 2 with HS5 module (HS and direct TD) or TD-100 (automated direct TD)

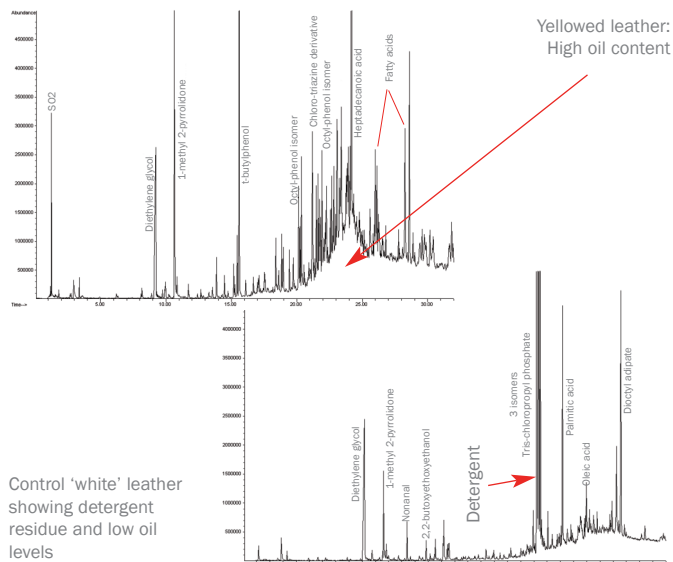
Primary desorption: 10 mins at 60°C (direct TD) and 10 mins at 300°C (HS sample on Tenax tube)

Trap: U-T2GPH-2S (General purpose [hydrophobic])

Split: 30:1

Analysis: GC/MS

Direct desorption of leather to identify the cause of discoloration



(S)VOC profile for discoloured leather upholstery (top) and control sample (bottom)

Reference: TDTS 40 (Direct desorption of volatile and semi-volatile organic compounds from furnishings such as leather or textiles)

Background:

Problems affecting textile or leather furnishings, e.g. discolouration or odour, can present a challenging analytical application for conventional liquid extraction. However, they can be readily investigated by directly desorbing a small section of the offending material and comparing the VOC profile with that from a control sample. In this case, direct TD was used to determine the cause of patchy yellow discolouration on white leather upholstery. The problem was found to be high levels of natural oils in the yellow patches.

Many off-odour and discolouration problems are caused by reactive compounds (e.g. those containing nitrogen or sulphur). Markes' patented heated valve accommodates reactive compounds without compromising the recovery of high boilers. VOCs, SVOCs (to n-C₄₀) and reactive compounds can all be analysed using Markes' universal TD platform; series 2 UNITY (single-tube) or TD-100 (100-tube automation).

Typical analytical conditions:

Sample: ~30 mg

TD system: UNITY 2 or TD-100

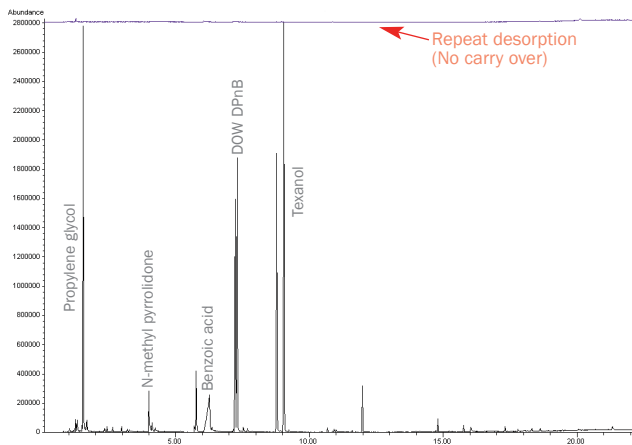
Primary desorption: 5 mins at 150°C

Trap: U-T2GPH-2S (General purpose [hydrophobic])

Split: 14:1

Analysis: GC/MS

Wet paint: Direct, exhaustive extraction for content testing



Direct desorption of 3.3 mg of wet emulsion paint. Water selectively eliminated

Direct TD at ~200°C allows complete extraction of volatiles and water, while solids remain in the liner. Water is selectively purged from the focusing trap, allowing interference-free TD-GC/MS analysis of target organics.

Reference: TDTS 57 (Characterisation of paint samples by direct desorption TD-GC/MS)

Background:

GC analysis of volatile content is sometimes used as an indicator of emission potential, particularly for liquid construction products such as paint. However, GC injectors are prone to contamination during paint analysis, especially if the sample has high solid content. Direct desorption using sorbent tubes provides a readily automated alternative which overcomes risk of system contamination.

High sample capacity coupled with innovative DiffLok caps make the Markes TD-100 system a simple, reliable autosampler for routine analysis of solvents in paint. DiffLok caps facilitate robust automation as they seal a tube whilst it is not being sampled, but allow a flow of gas through when pressure is applied. They remain in place and no capping or uncapping is necessary.

The split flow versatility of Markes TD also means that quantitative analysis of solvent content levels from sub-ppm to high percent can be accommodated.

Typical analytical conditions:

Sample: Low μL samples applied to glass wool in PTFE liner

TD system: UNITY 2 or TD-100

Primary desorption: 10 mins at 200°C

Trap: U-T9TNX-2S (Tenax TA)

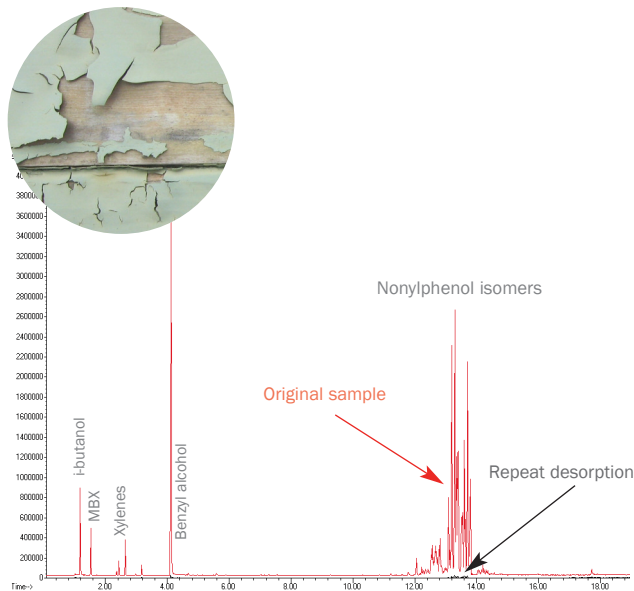
Split: To suit analyte concentration

Analysis: GC/MS

For other conditions see 'Paint flakes' below



Paint flakes: Direct exhaustive extraction for content testing



Direct desorption of dry paint flakes. Repeat desorption shows complete extraction

Background:

In accordance with indoor air quality regulations, paint manufacturers regularly measure VOC emissions from wet-applied products after they have dried/cured using standard emissions tests. However, direct thermal desorption/extraction can also be used as a quick, complementary check on the (S)VOC content of small samples of dried paint flakes.

Similar methodology can also be used for forensic characterisation of paint. Markes TD technology accommodates simultaneous analysis of SVOC and VOC with very low carryover, making it ideally suited to forensic analysis. (For more information, see the 'Defence and Forensic' TD application guide in this series.)

Typical analytical conditions:

Sample mass: ~2 mg

TD system: UNITY 2 or TD-100

Primary desorption: 10 mins at 220°C

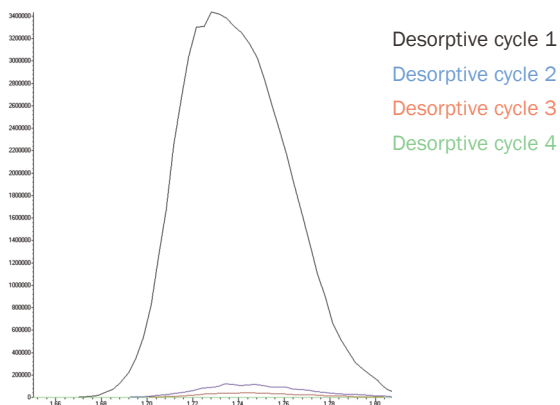
Trap: U-T9TNX-2S (Tenax TA)

Double split: 300:1

Analysis: GC/MS

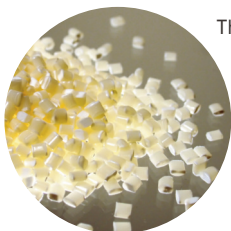
Reference: TDTS 57 (Characterisation of paint samples by direct desorption TD-GC/MS)

Direct desorption of residual monomer in polymer



Overlaid extracted ion (54) chromatograms showing the release of 1,3-butadiene over 4 successive desorptions

Descriptive cycle number	1	2	3	4
Percentage of 1,3-butadiene released	96.8	1.6	1.0	0.7



The table shows the relative proportion of the 1,3-butadiene released in each TD cycle; the first 20 minute desorption releases >95% of the 1,3-butadiene present.

Background:

Acrylonitrile-butadiene-styrene (ABS) is a thermoplastic resin widely used in the automobile industry, e.g. for instrument panels, consoles, radiator grills, headlight housings and interior trim. The determination of residual monomer is generally carried out using conventional static HS on dissolved (or slurried) samples of polymer. The success of this approach depends on finding a solvent which will dissolve the polymer adequately and reproducibly.

Direct thermal desorption (dynamic headspace) of ground samples of polymers, eliminates the dissolution step, simplifying automation and reducing uncertainty (risk of error).

HS methods are associated with incomplete dissolution and recovery. Data shown here demonstrate >95% release of 1,3-butadiene from ABS terpolymers in the first thermal desorption/extraction cycle, allowing straightforward quantification.

Typical analytical conditions:

Sample mass: 50 mg

TD system: UNITY 2 or TD-100

Primary desorption: 20 mins at 180°C

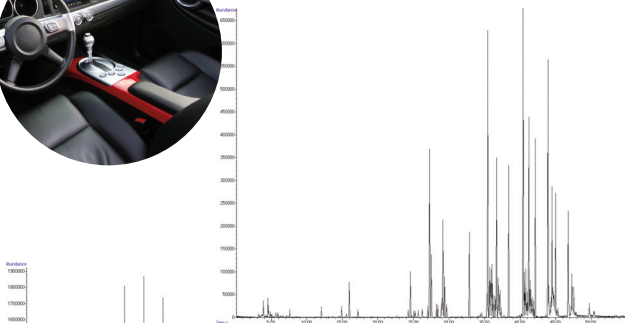
Trap: U-T12ME-2S (Material emissions)

Split: Splitless

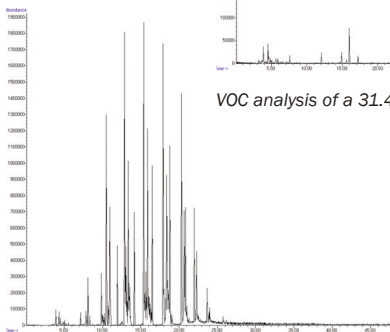
Analysis: GC/MS

Reference: TDTS 92 (Fast quantitative analysis of residual monomer in polymer by automated direct thermal desorption)

Direct desorption of plastic vehicle trim as a guide to emission levels (VDA 278)



VOC analysis of a 31.4 mg sample of polypropylene



FOG (SVOC fogging compound) analysis of polypropylene sample

Background:

Emissions from vehicle trim components (PVC, polyurethane foam, adhesives, etc.) can adversely affect car cabin air quality and are therefore subject to regulation. Direct desorption of a small sample of car trim at low temperatures can be used to obtain an estimate of the VOC and SVOC (fogging compound) emissions.

Standard methods include VDA 278 and other automotive company-specific protocols.

Markes' TD systems offer splitless, single split or double split operation for compatibility with the widest possible concentration range. They also allow simultaneous analysis of volatile and semi-volatile compounds.

Typical analytical conditions:

Sample mass: ~30 mg

TD system: UNITY 2 or TD-100

Primary desorption: 30 mins at 90°C (VOC) or 60 mins at 120°C (SVOC)

Trap: U-T2GPH-2S (General purpose [hydrophobic]) or U-T9TNX-25 (Tenax TA)

Analysis: GC/MS

Reference: TDTS 59 (Direct desorption of car trim materials for VOC and SVOC analysis, in accordance with method VDA 278)

Analysis by headspace–thermal desorption (HS-TD)

Combining headspace with thermal desorption (HS-TD) provides a high sensitivity alternative to conventional static (equilibrium) headspace methods.

Using HS-TD, the headspace vial is repeatedly pressurised and discharged through a sorbent focusing trap in a multi-step process. The trap then desorbs rapidly to transfer/inject trapped HS vapours into the GC(MS) analytical system.

HS-TD allows significantly larger volumes of headspace vapour to be sampled, thus increasing sensitivity by as much as one or two orders of magnitude relative to conventional static HS methods. The compatible analyte volatility range is also extended by this dynamic process.

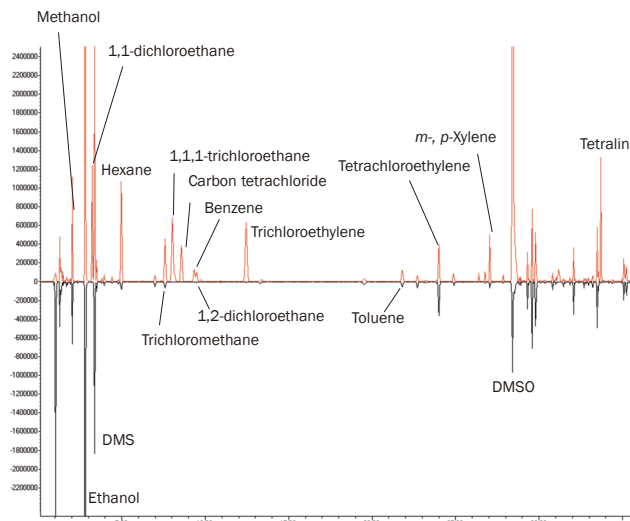


HS5-TD

Markes' HS5-TD has been designed as a dedicated headspace sampler for thermal desorption. This simple-to-use instrument can accommodate up to five sample vials, from which vapours can be repeatedly extracted and desorbed in a 'dynamic' approach to headspace sampling.



Enhancing the sensitivity of USP headspace procedures for residual solvents in drugs



Analysis of a drug (omeprazole) by HS-TD showing a 'typical' sample (black) and spiked sample (red)

Reference: TDTS 91 (Using a simple headspace-thermal desorption (HS-TD) method to enhance the measurement of residual solvents in drugs via USP 467)

Background:

Standard method 467 (USP 467) specifies headspace-GC/MS analysis of residual solvents. These solvents are categorised by class, according to their toxicity:

- Class 1: Carcinogenic, toxic or environmentally harmful
- Class 2: Non-genotoxic carcinogens or have suspected toxicity

It is the responsibility of the manufacturer to ensure that such solvents are not present above levels which could impact the quality or safety of their products.

Samples of a real-world pharmaceutical preparation (omeprazole) were dissolved in DMSO and water in HS vials. Some of the vials were spiked with a mix of solvents. The samples were then analysed using Markes' HS5-TD system with GC/MS. The powerful concentration capability of Markes HS-TD comfortably facilitates detection of residual solvents at the lowest required levels.

Typical analytical conditions:

TD System: UNITY 2 with HS5 module

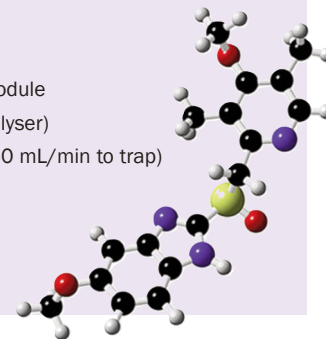
Trap: U-T15ATA-2S (Air toxics analyser)

Sampling (flow rate): 1.5 mins (30 mL/min to trap)

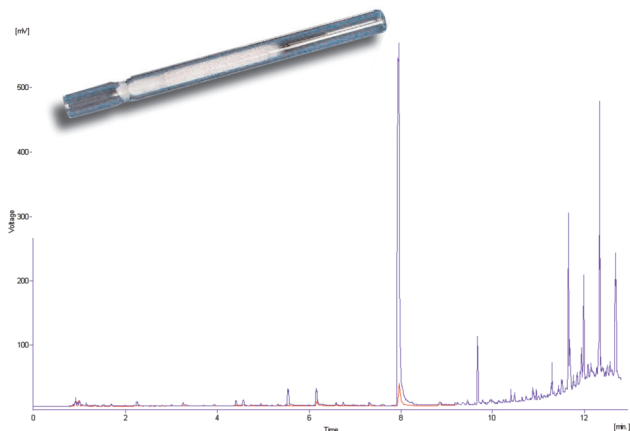
Split: 10 mL/min

Vial temperature: 85°C

Analysis: GC/MS



Direct desorption (dynamic headspace analysis) of volatiles from pharmaceutical powders



Approx. 3 mg of development drug powder weighed into a PTFE tube liner and directly desorbed. Repeat desorption shows >95% recovery in the first run.

Reference: TDTS 41 (Analysis of residual solvent (dimethyl sulphoxide [DMSO]) in a drug precursor)

Background:

Residual solvents in pure drugs and pharmaceutical preparations are often by-products of manufacturing or may be introduced during packaging and storage.

Standard method USP 467 specifies static headspace plus GC/MS analysis of residual solvents. However, direct TD can eliminate manual sample preparation and typically offers >95% extraction efficiency, thus simplifying calibration relative to conventional headspace methods. Moreover, only 2-10 mg of sample is required, allowing the method to be used for research compounds as well as drugs in production.

Markes' leading edge TD-100 system offers 100-tube capacity for maximum throughput and round-the-clock operation.

For information on the wide range of sample tubes and tube liners available to facilitate direct TD of difficult samples such as drugs, please consult the Markes Accessories & Consumables catalogue.

Typical analytical conditions:

Sample: ~3 mg powder weighed into glass tube

TD system: UNITY 2 or TD-100

Primary desorption: 10 mins at 225°C

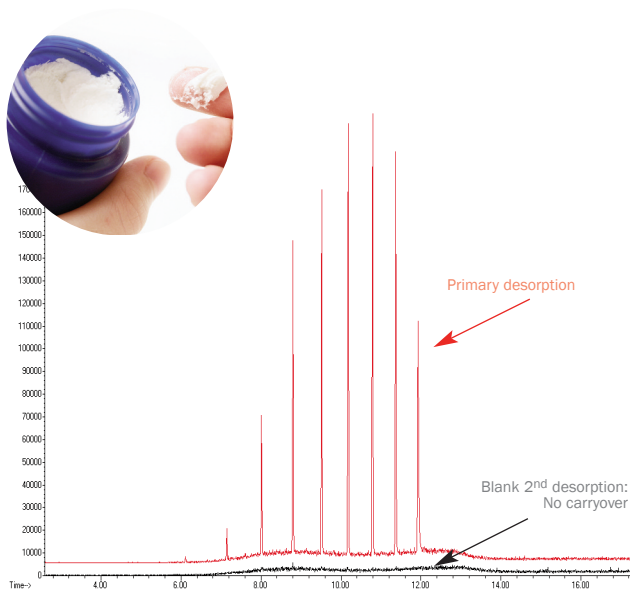
Trap: U-T9TNX-2S Tenax TA

Split: To suit analyte concentration

Analysis: GC-FID or GC/MS



Direct desorption of active ingredients from ointment



Direct desorption of high molecular weight polysiloxanes from white ointment

Other typical ointment analytes include essential oils and fragrance ingredients such as methylsalicylate, camphor and menthol.

Background:

Ointments present a very challenging matrix for GC, historically requiring labour intensive, multi-step preparation. Even after lengthy liquid extraction, steam distillation, etc., residue from the ointment base (e.g. petroleum jelly) can still contaminate the extract and cause analytical interference.

However, direct desorption of a small amount of ointment smeared around the inside of a PTFE liner and inserted into a TD tube behind a short bed of Tenax TA/quartz wool can overcome these issues, allowing fast, interference-free analysis with minimal sample preparation.

Markes thermal desorbers are uniquely compatible with both high-boiling and thermally labile compounds, providing the application versatility required for ointment analysis.

Typical analytical conditions:

Vary depending on target analytes but typically include:

TD system: UNITY 2 or TD-100

Primary desorption: 100–200°C for 5-10 mins

Trap: U-T9TNX-2S Tenax TA

Split: Typically double split 100 to 1000:1

Analysis: GC/MS

NB: A fresh plug of quartz wool should be used for each sample. If a Tenax TA bed is used, this will usually need replacing after ~10 uses.

Reference: TDTS 9 (Monitoring materials and processes for trace level VOCs)

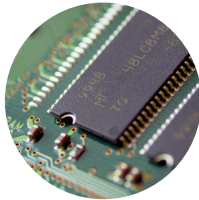
Testing chemical emissions from everyday products

Vapour-phase organic chemicals are emitted from a variety of materials such as construction products, car trim components, electronics and consumer goods during normal use. This causes elevated concentrations of VOCs indoors and in vehicle cabin air, which may have adverse health effects.

With the advent of new legislation requiring the measurement and reporting of VOC emissions as part of product certification (e.g. CE marking), there is increasing pressure on manufacturers to test their products for chemicals which may be released during use. Standard methods for testing (S)VOC emissions specify chambers, micro-chambers or cells in combination with thermal desorption and GC-MS/FID. Examples include: EN/ISO 16000(-6, -9, -10, -11 & -25), CEN TC351 standards, ISO 12219 parts 1-4, ASTM D7143, ASTM D5116 and ASTM D6196.

Relevant applications include:

- Construction products e.g. paints, plasterboard, flooring
- Car trim components e.g. wood veneers, moulded PVC, adhesives
- Carpets and textiles
- Electronics
- Plastic toys
- Detecting banned substances
- Composite wood products
- Structural plastics and insulation materials
- Cleaning products and other consumer goods



Equipment for chemical emissions testing

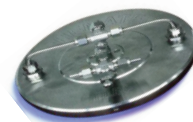
Testing chemical emissions from products and materials under simulated real-world conditions is a multi-step procedure as follows:

- Representative samples are first selected from the manufacturing batch or retail store.
- The samples are prepared to ensure they simulate normal use. In the case of small chambers this may involve masking the edges and rear surfaces of flooring and ceiling products.
- The prepared samples are then placed in small test chambers, cells or micro-chambers under controlled conditions of temperature, % relative humidity and air flow/exchange rate. *(Note: The amount and orientation of the sample placed in a small chamber is often specified by the relevant method.)*
 - Emitted vapours are sampled from the exhaust at prescribed times – typically 3, 10 or 28 days for chamber/cell-based reference tests, or less than 1 hour for micro-chamber screening methods.



- Vapours are sampled onto sorbent tubes ([S]VOC) or DNPH cartridges (formaldehyde).
- Subsequent analysis:
 - Thermal desorption (TD) plus gas chromatography–mass spectrometry (GC/MS) analysis for VOCs and SVOCs.
 - Liquid chromatography (HPLC) analysis for formaldehyde.
- Data are typically reported as area (or mass) specific emission rate ($\mu\text{g}/\text{m}^2$), or in terms of vapour concentration in a specified 'reference (model) room'.

Markes International prides itself on providing in-depth technical expertise to all of its customers. Markes' specialists will be happy to advise you on any aspect of material emissions testing.



Micro-Chamber/Thermal Extractor (μ -CTE) for fast emissions screening (various draft standards)

Markes' compact Micro-Chamber/Thermal Extractor (μ -CTE) units are designed to meet the growing demand for fast emissions screening in manufacturing industry and third party test labs.

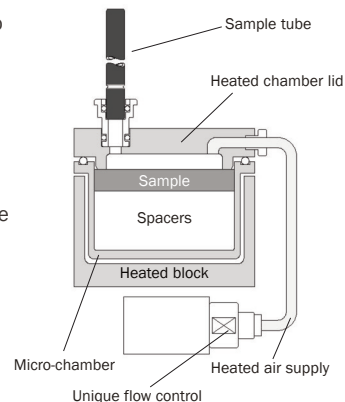


Applications include routine industrial quality control and evaluation of new, low-emission products under development. μ -CTE data have been shown to correlate with results from longer-term chamber tests for many common materials and products.

Markes supplies two variants of the μ -CTE which comprise either four or six individual micro-chambers (volumes of 114 mL & 44 mL, respectively). These chambers allow multiple sample emissions (surface-only or bulk) to be tested simultaneously at temperatures from ambient to 250°C or 120°C, depending on the unit used. The design of each micro-chamber lid assembly ensures edge effects are excluded during surface emissions testing.

A controlled flow of pure air/gas (10–500 mL/min) is passed through all micro-chambers simultaneously to sweep emitted vapours onto attached sorbent tubes or DNPH cartridges for analysis by TD-GC/MS or HPLC. Proprietary flow technology is used to maintain a constant flow of air/gas through each individual micro-chamber, whether or not vapour sampling tubes are attached. No pumps are required.

Typical μ -CTE tests for VOC emissions take 35–45 minutes, allowing four or six samples to be processed every hour.



FLEC® emission test cell **EN ISO 16000-10, ASTM D7143**

The Field and Laboratory Emission Cell (FLEC) is an easy-to-use device for the certification of indoor products/materials according to their VOC emission levels (EN ISO 16000-10, ASTM D7143). FLEC differs from conventional chambers because it is open on one side. This open side is placed onto planar materials such that the sample surface effectively becomes one wall of the emission cell (sample holders are available for compressible materials).



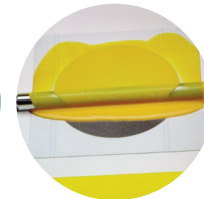
Pure humidified air enters around the perimeter of the cell and emitted vapours are pumped onto one or two sorbent tubes, or DNPH cartridges, attached to the FLEC exhaust.

FLEC accessories

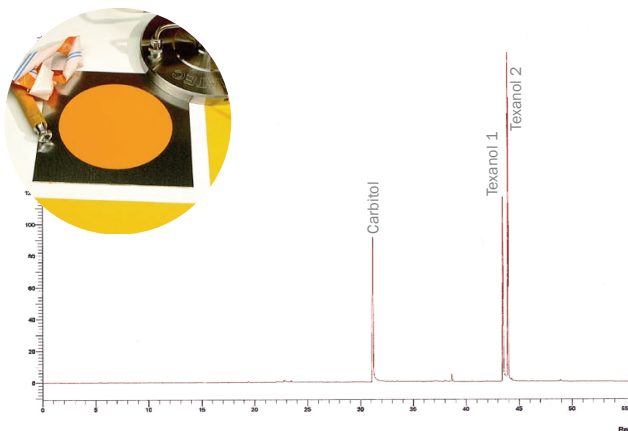
Fully adjustable FLEC base units and test plate accessories extend FLEC applications beyond emissions from planar surfaces. Carpets with varying depth and uniformity of pile, polymer beads, textiles and irregular objects can all be evaluated using the dedicated accessories. Test plates and application rollers are also available for testing paints and coatings.

Advantages of FLEC

- Ease-of-use compared to small chambers
- No edge effects or sample orientation issues
- Compatible with non-destructive field testing of construction products



FLEC: Paint



FLEC-TD-GC/MS analysis of emissions from water-based emulsion paint



* Note: Pk10 Tenax TA sorbent tubes (packed, conditioned & capped), part number C1-AAXX-5003

Pk 10 Quartz/Tenax TA/Carbopack X sorbent tubes (as described opposite), part number C2-AAXX-5256

Cost-effective uncapped, unconditioned versions are also available

Background:

FLEC provides an easy-to-use device for the certification of emissions from the surface of planar materials including dried/cured paints and coatings. Emissions from paints and coatings are typically evaluated by applying an even film of the product to an inert substrate using a steel roller. FLEC is then applied on top of the painted substrate at 3, 10 or 28 days as required. Note: Emissions tests are not usually started until after the product has dried or cured.

Standard Methods: EN/ISO 16000-10, ASTM D7143.

Markes is proud to offer FLEC globally to complement its comprehensive portfolio of material emissions test equipment.

Typical analytical conditions:

Sample area: 177 cm²

Vapour sampling: 15-30 mins using a Tenax TA or a Quartz/Tenax TA/Carbopack X tube*

Test time: As dictated by prescribed test

TD system: UNITY 2 or TD-100

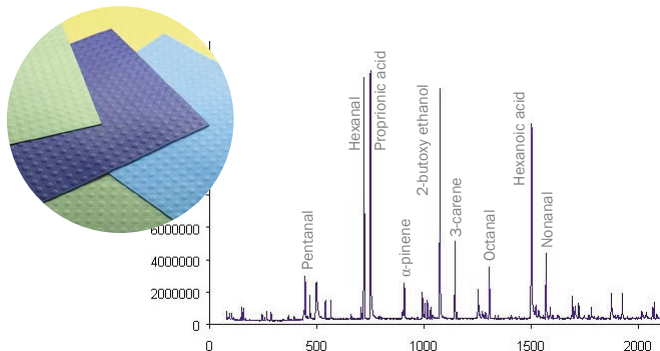
Trap: U-T9TNX-2S (Tenax) or U-T12ME-2S (Material emissions)

Analysis: GC/MS

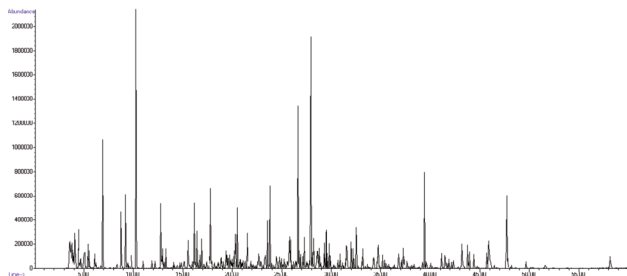
References: TDTS 70, 71 & 72 (Using the FLEC cell for emissions testing), TDTS 55 (Material emissions testing using FLEC), TDTS 56 (TD-GC/MS analysis of material emissions)

Data courtesy of BRE, UK

FLEC: Emissions from flooring materials



FLEC-TD-GC/MS analysis of emissions from rubber flooring.
Data courtesy of Prof. Dr Peder Wolkoff, DK



Testing VOC emissions from carpet using FLEC with Tenax TA tubes & TD-GC/MS analysis. Reproduced with the kind permission of VITO, Belgium.

Background:

FLEC is portable and may be used for non-destructive testing of chemical emissions from products already installed in a building. Testing emissions from resilient flooring is a common FLEC application. Round robin evaluation of emissions from flooring and other products using both FLEC and small chambers have shown good correlation between the two^{1,2}. For field work, FLEC may be used with only 1–2 hour equilibration.

Typical analytical conditions:

Sample area: 177 cm²

Test time: Equilibration 24 hrs (certification), 1–2 hrs (routine)

Vapour sampling: 15–30 mins using a Tenax TA or Quartz/Tenax TA/Carbopack X tube

TD System: UNITY 2 or TD-100

Trap: U-T9TNX-2S (Tenax) or U-T12ME-2S (Material emissions)

Analysis: GC/MS

References:

(1) **Investigations for the improvement of the measurement of VOCs from floor coverings within the health-related evaluation of construction products**, W. Horn *et al.*, (2009), BAM Federal Institute for Materials Research and Testing, Research-number: ZP 52-5-20.49.1-1251/07

(2) P. Wolkoff *et al.*, (2005) **Emission cells & comparison to small chambers for materials emissions testing**. *Gefahrstoffe - Reinhaltung der Luft* 65 (3): 93

Conventional small test chambers EN ISO 16000-9, ASTM D5116

Many of the standard methods for material emissions testing require the use of small test chambers, which vary in size from 20 L to approx. 5 m³. They are usually made from polished stainless steel or glass to minimize background artefacts and sink effects.



1 m³ chamber



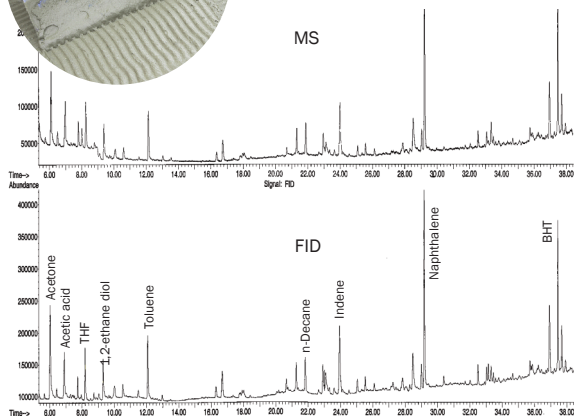
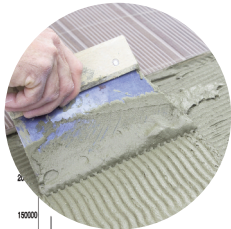
20 L Adpac™ chamber

The exposed area (amount) and orientation of a sample placed in a small chamber is intended to simulate real-world use. The ratio of the area of product/material exposed within the chamber and the volume of the chamber itself is called the product loading factor. The required loading factor will vary depending on the product type (flooring, wall covering, ceiling tile, insulation, sealant, etc.) and will be dictated by the method used. Typical test chamber parameters are detailed in the table opposite.

Time	3 & 28 days or 10-14 days
Temperature	23 ± 1°C (25°C Korea, 28°C Japan)
Relative humidity (RH)	50 ± 5 %
Air velocity	0.1–0.3 m.s ⁻¹
Air exchange rate	0.5–1 h ⁻¹
Product loading factor:	
Walls	1 m ² .m ⁻³
Floor, ceiling	0.4 m ² .m ⁻³
Small surfaces (e.g. doors)	0.05 m ² .m ⁻³
Sealants	0.007 m ² .m ⁻³

Product emission limits are often specified in terms of vapour concentrations in a reference (model) room. If appropriate loading factors and other chamber parameters are applied, vapour concentrations in the test chamber can be related directly to vapour concentrations in the reference (model) room and can therefore be used for direct comparison with limit values.

Small chamber: Tile adhesive



New, very low-emission adhesives (shown above) release less than 500 $\mu\text{g}/\text{m}^3$ after 10 days. Vapours collected on Tenax TA tubes.

Reproduced with kind permission from Dr ssa Decio, Dr Cerulli, Dr Leoni and colleagues at MAPEI S.p.A., Milan, Italy.

Background:

Indoor air contaminants emitted by adhesives and sealants may be odorous and, in rare cases, can cause throat and airway irritation. Manufacturers are now developing water-based, low-emission products to minimise emission levels and eliminate potential health effects.

Markes thermal desorption systems are used with Tenax TA tubes and GC/MS/FID analysis for formal testing of emissions from adhesives using conventional small test chambers. Relevant standard methods include EN 13999, CEN TC351 and the ISO 16000 series.

The flexible SecureTD-Q feature of Markes' thermal desorbers allows sample re-collection and repeat analysis, thus overcoming the need to ever repeat lengthy emission chamber procedures.

Typical analytical conditions:

Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack X

TD system: UNITY 2 or TD-100

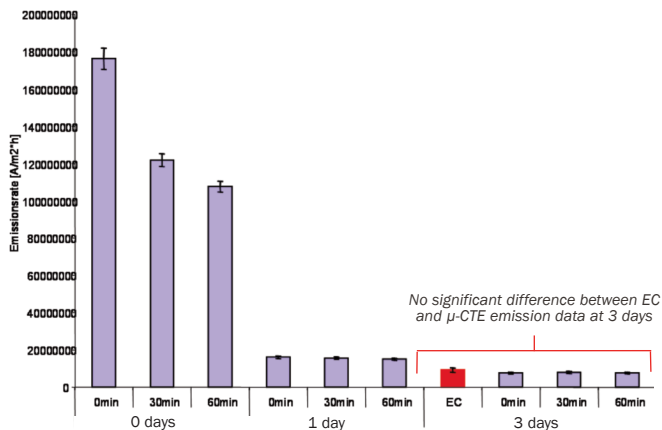
Primary desorption: 10 mins at 280°C

Trap: U-T12ME-2S (Material emissions)

Split: 5:1 on outlet only

Analysis: GC/MS or GC/FID

Absolute correlation between the μ -CTE and conventional small emission test chambers



Area-specific emission rates determined for the μ -CTE (blue) and an emission chamber (red) up to 3 days for a building product. Agreement is observed between the 2 methods.

Background:

The Markes Micro-Chamber/Thermal Extractor (μ -CTE) was developed for fast emissions screening (*i.e.* for industrial quality control) but it can also be used for longer-term emissions tests of homogeneous materials if required.

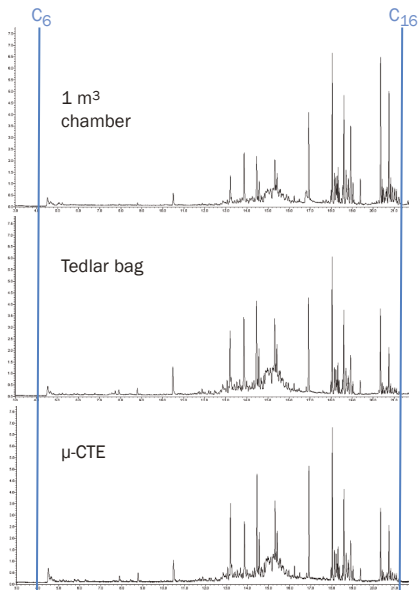
Emissions were evaluated using both the μ -CTE and a 1 m³ emission (EC) chamber over three days. Comparison of the area-specific emission rate data ($\mu\text{g}/\text{m}^3$) obtained at three days showed excellent correlation in absolute terms (quantitative and qualitative).

Analytical conditions:

Parameter	μ -CTE	EC
Sample area (m ²)	1.282×10^{-3}	1
Chamber volume (m ³)	3.2×10^{-6}	1
Load Factor (m ² /m ³)	400	1
Exchange rate (h ⁻¹)	1875	1
Gas Supply (L/min)	0.1	16.7
Chamber Temp. (°C)	23	23

Reproduced with kind permission from Fraunhofer Wilhelm-Klauditz Institute, Germany

Relative Micro-Chamber/Thermal Extractor correlation for fast emission screening



Data reproduced with the kind permission of Prof. Mangoo Kim, Kangwon National University, Korea.

Background:

Reference methods for testing chemical emissions from products require small chambers or test cells and typically specify 3 to 28 day tests. The Markes Micro-Chamber/Thermal Extractor provides a complementary tool for rapid emissions screening for up to four or six samples simultaneously.

Emissions screening data obtained within minutes using the μ -CTE can be used as a reliable indicator of longer term results from reference tests (e.g. at 3, 10 or 28 days). This makes it suitable for factory production control of chemical emissions in a routine industrial QC environment. μ -CTE units can also be used by industry to screen raw materials, compare competitive products and evaluate low-emission prototype products under development.

Typical analytical conditions:

μ -CTE gas flow: 50 mL/min

μ -CTE temperature: 65°C

Sample quantity: 1–6 simultaneously

Test time: <30 mins equilibration, 15 mins vapour sampling

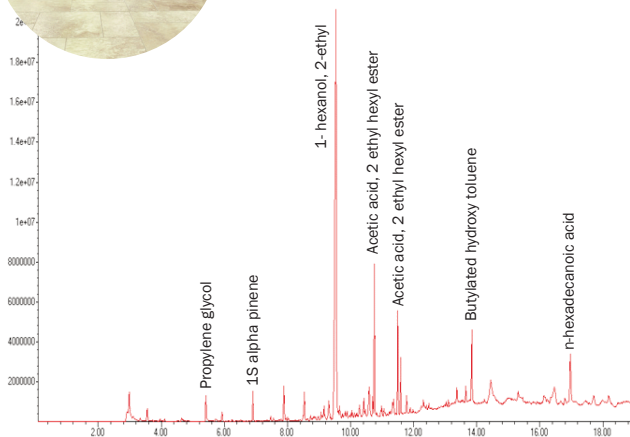
Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack X

TD system: UNITY 2 or TD-100

Trap: U-T12ME-2S (Material emissions)

Reference: TDTS 67 (Introducing the Micro-Chamber/Thermal Extractor™ (μ -CTE™) for rapid screening of chemicals released (emitted) by products and materials)

Micro-Chamber/Thermal Extractor: Screening emissions from resilient flooring



Surface emissions from a sample of vinyl flooring and adhesive tested using the μ -CTE at 40°C with 50 mL/min air flow for 20 mins

Background:

To simulate real-world use of flooring products, only surface emissions need to be measured. Therefore, Markes' μ -CTE incorporates a collar (or baffle) projecting down from the micro-chamber lid to eliminate edge effects without extensive sample preparation.

Testing requires a 4.5 cm or 6.4 cm (120°C and 250°C μ -CTE, respectively) diameter circular test specimen to be cut or punched from the sample material. Spacers, including some compressible devices, are placed underneath to raise the sample until the emitting surface just touches the collar, whatever its original thickness. The collar also defines the exposed surface area and the volume of air above the sample, optimising reproducibility.

Typical analytical conditions:

μ -CTE gas flow: 50 mL/min

μ -CTE temperature: 40°C

Sample quantity: 1–6 simultaneously

Test time: 30 mins equilibration, 15 mins vapour sampling

Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack X

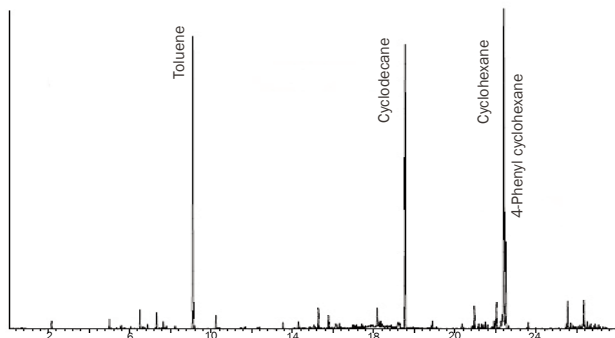
TD system: UNITY 2 or TD-100

Trap: U-T12ME-2S (Material emissions)

Analysis: GC/MS (FID)



Micro-Chamber/Thermal Extractor: Screening emissions from carpet



Emissions from textile floor covering analysed using μ -CTE

Typical analytical conditions:

Gas flow: 50 mL/min (VOC) or 250 mL/min (formaldehyde)

Temperature: 30–60°C

Sample quantity: 1–6 simultaneously

Equilibration time: <30 mins

Vapour collection: Tenax TA tubes for 15 mins (VOC), DNPH cartridges for 2 hrs (formaldehyde)

TD system: UNITY 2 or TD-100 (VOCs)

Trap: U-T12ME-2S (Material emissions)

Analysis: GC/MS(FID) for VOCs or HPLC for DNPH derivative of formaldehyde

Background:

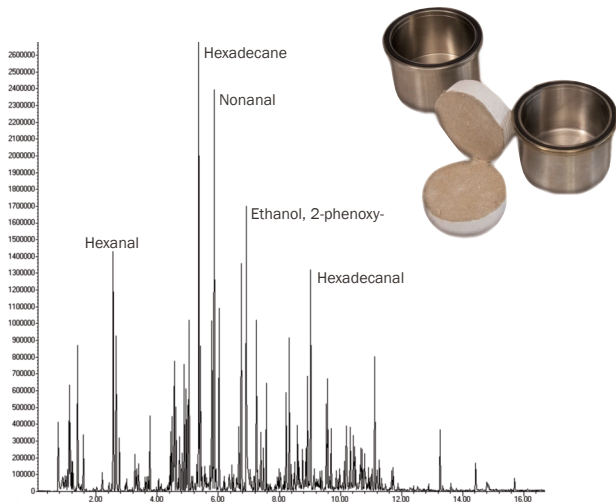
Carpets and textile flooring fall under the EC Construction Products Directive/Regulation and are similarly impacted by various national laws and “green chemistry” initiatives around the world. Many of these regulations require chemical emissions to be evaluated as part of product certification.

While long-term (3–28 day) reference tests will continue to be required for labelling, Markes' μ -CTE provides a quick, low-cost tool for pre-screening emissions (e.g. prior to certification testing) to confirm the uniformity of emission profiles across a product range, and to monitor continued product conformity with prescribed emission limits.

Despite the small sample size and relative complexity (*i.e.* the inhomogeneity of many textile floorings), data from quick micro-chamber tests at 40°C correlate well with those from standard small chambers, allowing the μ -CTE to be used for rapid and reliable quality control by manufacturers and accredited test labs.



Micro-Chamber/Thermal Extractor: Screening emissions from plasterboard (drywall)



Reference: US consumer product safety commission (2009), Summary of contractors indoor air quality assessment of homes containing Chinese drywall

Background:

Plasterboard or 'drywall' is used extensively to create smooth walls and ceilings indoors. Although it invariably ends up being covered by paint or wallpaper, the relatively complex range of chemicals emitted by some plasterboard (drywall) products migrate through most coverings and into the indoor environment. Covering construction products may delay the onset of high emission levels, but rarely eliminates emissions completely.

Markes' μ -CTE can be used for rapid qualitative and quantitative screening of chemical emissions from construction products like plasterboard. The inert, uniformly heated flow path of Markes' thermal desorbers also ensures compatibility with a wide analyte range. Compatible compounds include volatiles, semi-volatiles and reactive sulphur compounds which have all been reported to be present in drywall products.

Typical analytical conditions:

μ -CTE gas flow: 100 mL/min

μ -CTE temperature: 50°C

Test time: 20 mins equilibration, 15 mins vapour sampling

Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack X

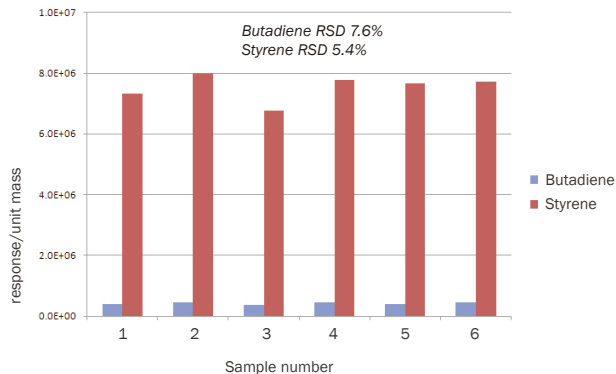
TD system: UNITY 2 or TD-100

Trap: U-T12ME-2S (Material emissions)

Analysis: GC/MS (FID)



Reproducibility of Micro-Chamber/Thermal Extractor assessments



Background:

Emissions testing with conventional small chambers and emission cells is a complex, multi-step process with many opportunities for error to creep in. Intra- and inter-lab studies have shown the best results to be in the order of 15–30% RSD.

Markes' μ -CTE was used to test six replicate samples of plastic material used in car dashboards. RSD results of 7.6% for 1,3-butadiene and 5.4% for styrene were obtained. This represents exceptional reproducibility within the context of material emission testing and confirms the suitability of the μ -CTE for quantitative emissions screening.

Typical analytical conditions:

μ -CTE gas flow: 50 mL/min

μ -CTE temperature: 65°C

Test time: 5 mins equilibration, 15 mins vapour sampling

Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack™ X

TD system: UNITY 2 or TD-100

Primary desorption: 20 mins at 180°C

Split: Splitless

Trap: U-T12ME-2S (Material emissions)

Analysis: GC/MS

References: TDTS 92 (Fast quantitative analysis of residual monomer in polymer by automated direct thermal desorption)

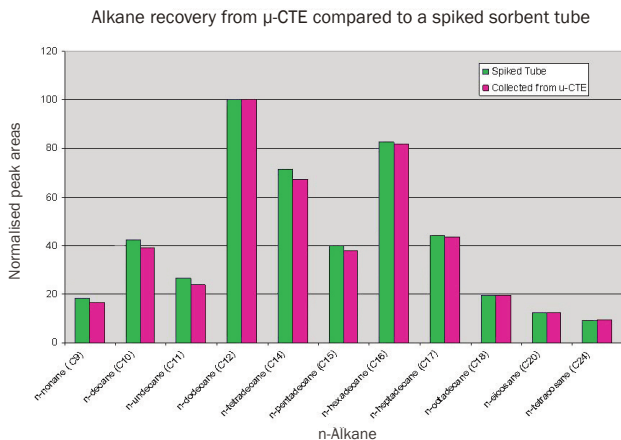
Markes International Ltd

T: +44 (0)1443 230935 F: +44 (0)1443 231531

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

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Quantitative SVOC analysis using the Micro-Chamber/Thermal Extractor



Data for 1 μ L solutions of semi-volatile alkanes (C₉-C₂₄) thermally extracted from a sorbent tube (green) and a Micro-Chamber/Thermal Extractor (pink)

Background:

Vapour-phase semi-volatile emissions are prone to condensation and present a challenge to quantitative analysis. Markes' μ -CTE units incorporate independent heating of micro-chamber pots, lids and gas lines to ensure quantitative recovery of SVOCs. This is demonstrated by comparing TD-GC/MS chromatograms from an alkane test mix (C₉-C₂₄) spiked onto a sorbent tube and the same volume of the alkane test mix introduced into empty micro-chambers.

Markes offers a comprehensive selection of TD tubes to complement the μ -CTE. These include standard Tenax TA tubes and special quartz/Tenax TA/Carbopack X tubes, optimised for evaluating emission profiles over a wide volatility range. Both are available in stainless steel, glass or Silicosteel®. Customised multi-sorbent tubes are also available; consult your Markes catalogue for details. (See informative Annex D of ISO 16000-6).

Typical analytical conditions:

μ -CTE gas flow: 50 mL/min (no pumps required)

μ -CTE sampling: 10 mins at 120°C; no equilibration

Sample: 1 μ L of C₉-C₂₄ test mix

Sorbent tube: Quartz/Tenax TA/Carbopack X

TD system: UNITY 2 or TD-100

Primary desorption: 10 mins at 300°C

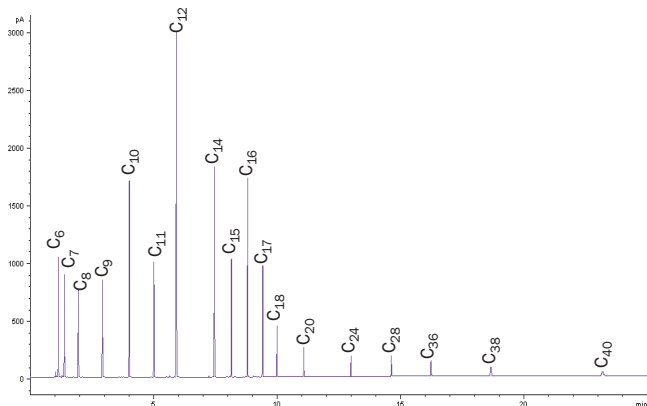
Trap: U-T12ME-2S (Material emissions)

Split: ~30:1

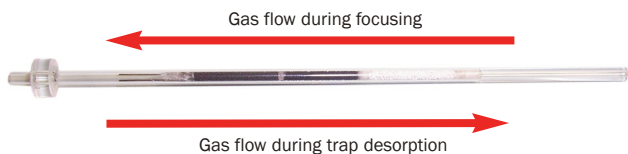
Analysis: GC/MS



Multi-sorbent focusing trap for simultaneous VOC & SVOC analysis



C₆ to C₄₀ in one analysis



Multi-sorbent focusing trap

Background:

Markes has developed a proprietary multi-sorbent focusing trap for simultaneous TD-GC/MS analysis of VOC and SVOC emissions. Vapours enter the trap through weak sorbents at the inlet/outlet, where semi-volatiles are retained, and more volatile compounds are retained by the stronger sorbents at the rear of the trap.

During secondary (trap) desorption, Markes' patented thermal desorption valve reverses the carrier gas flow. This allows the volatile and semi-volatile analytes to be 'backflushed' from the trap simultaneously. High-boiling compounds never come into contact with the stronger sorbents at the back of the trap and are therefore quantitatively recovered.

Typical analytical conditions:

TD system: UNITY 2 or TD-100

Sample: Standard loaded onto Quartz/Tenax TA/Carbopack X tubes

Primary desorption: 10 mins at 320°C

Trap: U-T12ME-2S (Material emissions)

Outlet split only: 20:1

Analysis: GC/MS

Reference: TDTS 64 (Simultaneous TD-GC(MS) analysis of VOCs and semi-VOCs)

ISO 16000-25: Testing semi-volatile emissions using micro-chambers



Background:

Markes' four-chamber version of the μ -CTE can be operated at temperatures up to 250°C. This makes it compatible with standard method ISO 16000-25 (Determination of the emission of semi-volatile organic compounds by building products - Micro-chamber method).

An overview of the ISO 16000-25 procedure is as follows:

- The rear surface and edges of the sample are enclosed in clean foil so that only the top surface is exposed.
- Prepared samples are then placed in the μ -CTE set at 23°C (28°C in Japan).
- A 50–100 mL/min flow of gas is applied to each micro-chamber and the emitted vapours collected on sorbent tubes for 24 hours.
 - At the end of this time, the samples are removed and the sampled sorbent tubes replaced with fresh, conditioned sorbent tubes.
 - The empty micro-chambers are then heated to 200–220°C for 40 mins under a 50–100 mL/min flow of gas to thermally desorb semi-volatiles from the micro-chamber walls and transfer them to the replacement sorbent tubes.
- SVOC emission data are determined by summing the results from both parts of the test for each sample.

Micro-Chamber/Thermal Extractor: SVOC emissions from laminate flooring by ISO 16000-25

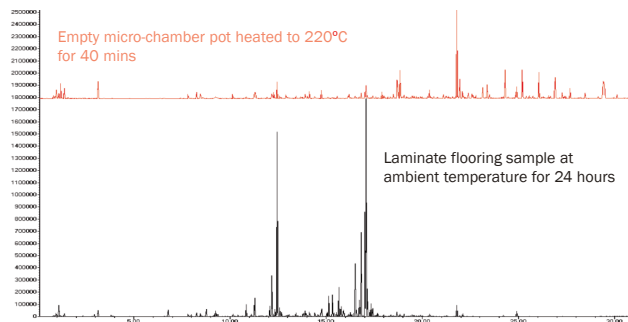


Figure 1: Sample of laminate flooring analysed in 2 steps according to ISO 16000-25

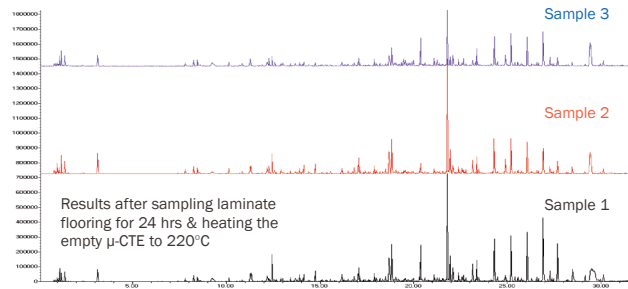


Figure 2: Data from step 2 of the ISO 16000-25 test carried out on 3 replicate samples of the same laminate flooring (area 4 x 3 x 0.8 cm)

Background:

The operation of Markes' μ -CTE for testing laminate flooring by ISO 16000-25 is shown opposite.

Figure 1 shows the results from both step 1 (24 hrs at 23°C) and step 2 (thermal desorption of the empty microchamber at 220°C) for a single sample.

Figure 2 shows reproducibility for three samples of the same laminate flooring during step 2 of the test.

Typical analytical conditions:

μ -CTE gas flow: 50–100 mL/min

Vapour sampling: 24 hrs at 23°C then 40 mins at 200–220°C

Sorbent tube: Quartz/Tenax TA

TD system: UNITY 2 or TD-100

Primary desorption: 10 mins at 320°C

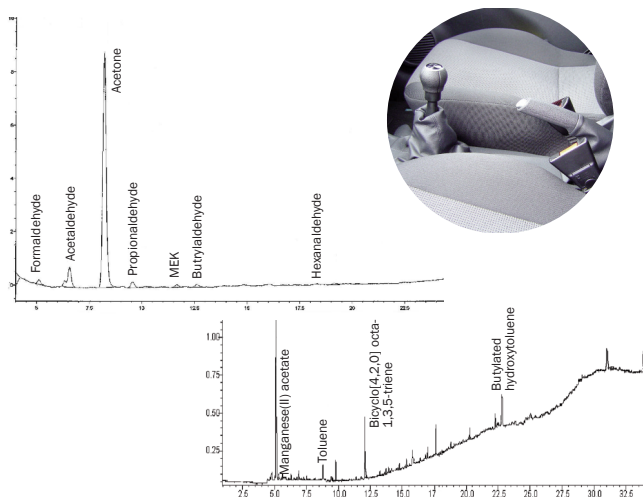
Trap: U-T2GPH-2S (General purpose [hydrophobic])

Split: 30:1

Analysis: GC/MS



Micro-Chamber/Thermal Extractor: VOC emissions from vehicle interior trim (ISO 12219-3)



Emissions from polyurethane foam car trim component. Formaldehyde (HPLC) chromatogram (top) & VOC (TD-GC/MS) chromatogram (bottom)

Reproduced with kind permission from the International Automotive Research Centre, UK

Reference: G.J. Williams, M. Pharaoh, (2009), PARD Report: Correlation between the VDA 276 test and micro-chamber testing, Issued by WMG, University of Warwick, UK.

Background:

The potential effect of a given vehicle interior trim component (plastic, foam, textile, wood, etc.) on car cabin air quality can be assessed by materials emissions testing using a 1 m³ chamber at elevated temperatures (65°C) (ISO 12219-4, VDA 276, etc). However, such tests take several hours *per sample*.

Markes' μ -CTE provides a solution for rapid screening of emissions from car trim components at 65°C for correlation with VDA 276. The μ -CTE allows up to six different materials to be evaluated every few minutes, with sample collection onto either DNPH cartridges (formaldehyde) or sorbent tubes ([S]VOCs). Car trim emissions data obtained in minutes using Markes' μ -CTE have been shown to correlate quantitatively and qualitatively with longer-term small chamber and bag methods (see also p. 24)

Standard method: ISO 12219-3

Typical analytical conditions for VOC:

μ -CTE gas flow: 50mL/min

μ -CTE temperature: 65°C

Trim material: Polyurethane foam

Test time: 20–30 mins equilibration, 15 mins vapour sampling

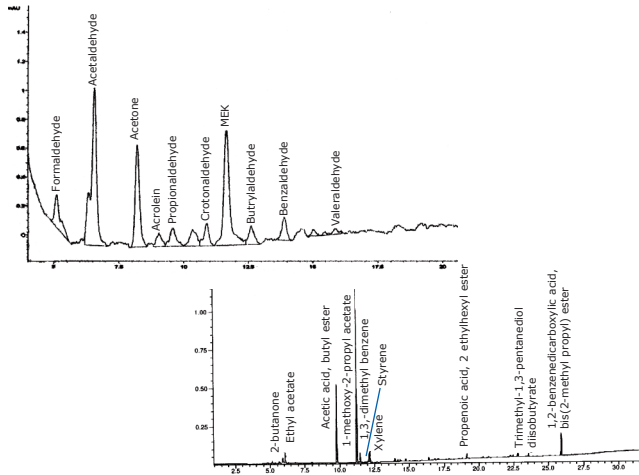
Sorbent tube: Tenax TA or Qtz/Tenax TA/Carbopack X

TD system: UNITY 2 or TD-100

Trap: U-T12ME-2S (Material emissions)

Analysis: GC/MS

Micro-Chamber/Thermal Extractor: Emissions from timber and wood-based vehicle trim



Emissions from wood veneer; formaldehyde (HPLC) top and VOC (TD-GC/MS) bottom

Background:

Wood veneer manufacturers frequently use formaldehyde-based adhesives in the production process. However, the carcinogenicity of formaldehyde has made emission levels from wood veneers used indoors a concern. Markes' μ -CTE was used to test emissions from wood veneers used in cars. Samples were tested using DNPH cartridges to sample formaldehyde and other carbonyls with subsequent analysis by HPLC.

μ -CTE tests for formaldehyde using DNPH cartridges are typically carried out using 250 mL/min flow rate and total 30-60 L air sample volumes. Up to six samples can therefore be processed every 2-4 hours.

Typical analytical conditions for formaldehyde:

μ -CTE gas flow: 250mL/min

μ -CTE temperature: 65°C

Trim material: Wood veneer

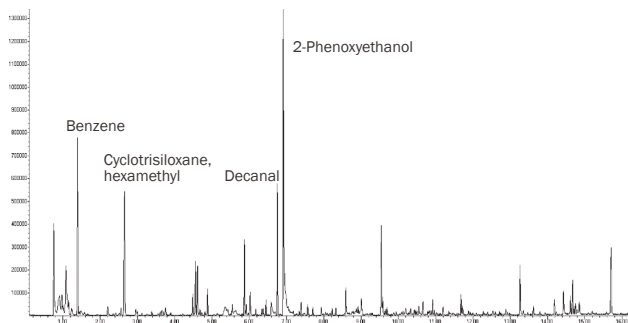
Test time: 20-30 mins equilibration, 2-4 hours vapour sampling

Analysis: HPLC/UV detection

Reproduced with kind permission from the International Automotive Research Centre, UK.



Micro-Chamber/Thermal Extractor: Evaluating VOC emissions from wood



Emissions from natural timber: Mahogany



Background:

Timber and wood-based products are used extensively indoors, e.g. for building construction, interior design and domestic furniture. The wood and wood-product industries have always been at the forefront of emissions testing and control, particularly with respect to formaldehyde e.g. the CARB 'Formaldehyde rule', European standard EN 717 and relevant Japanese labelling requirements. Timber and wood-based products can also emit significant levels of VOCs.

Markes' μ -CTE can be used for fast screening of either formaldehyde or VOC emissions from wood and wood-based products. In this example, a sample of mahogany was evaluated at 80°C and was found to emit a wide range of volatile and semi volatile organics

Typical analytical conditions:

μ -CTE gas flow: 100 mL/min

μ -CTE temperature: 80°C

Test time: 20–30 mins equilibration, 15 mins vapour sampling

Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack X

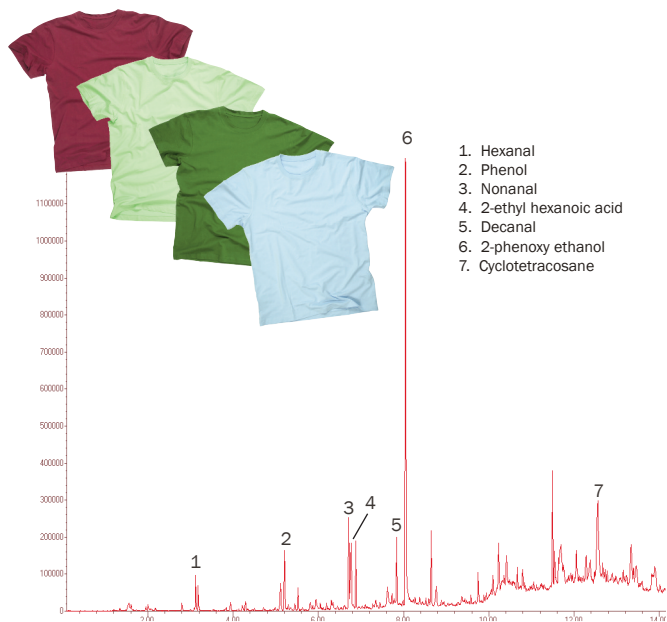
TD system: UNITY 2 or TD-100

Trap: U-T12ME-2S (Material emissions)

Analysis: GC/MS



Micro-Chamber/Thermal Extractor: Emissions from textiles



Low temperature emissions from nylon sampled using the μ -CTE and analysed using TD-GC/MS

Background:

With reports of childhood asthma and allergies on the rise, chemical emissions from children's clothing and other textiles are of increasing interest. In this case, routes of exposure can include both inhalation and dermal absorption.

Chemicals emitted from a 100 x 50 mm section of nylon were collected onto a Tenax TA sorbent tube using the μ -CTE. Key compounds of interest in this case are phenol and 2-phenoxy ethanol. Phenol is used in the production of caprolactam, which is an intermediate in the manufacture of nylon. 2-phenoxy ethanol is a solvent used in textile dyeing.

Markes' μ -CTE is a versatile tool which allows chemical emission testing at body temperature, recreating normal use.

Typical analytical conditions:

μ -CTE gas flow: 100 mL/min

μ -CTE temperature: 40°C

Test time: 20 mins equilibration, 15 mins vapour sampling

Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack X

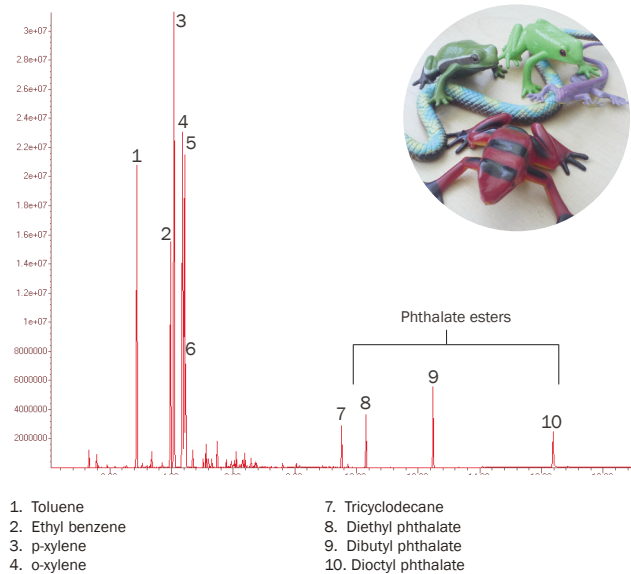
TD system: UNITY 2 or TD-100

Trap: U-T12ME-2S (Material emissions)

Analysis: GC/MS

Further information: Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Phenol. U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. (1989)

Micro-Chamber/Thermal Extractor: Testing chemicals released by children's plastic toys



A typical chromatogram for plastic toy animals; compounds ranging in volatility from C₇-C₂₄ were identified

Background:

With the growing concern surrounding the potential health impact of chemical exposure on young children, the demand for emissions testing of toys has increased dramatically.

VOCs from toys may be evaluated using the μ -CTE in accordance with method prEN 71-11. The chemical emission profile shown here was obtained from a plastic toy animal using the μ -CTE at 40°C. The chromatographic data includes volatiles such as toluene, plus some higher boiling phthalates, which are classified as 'Substances of Very High Concern' (SVHC) under REACH (Registration, Evaluation, Authorisation and restriction of Chemicals legislation) in EC & P.R. China.

Markes' micro-chambers are large enough to allow vapour-phase bulk emissions testing from whole toys or large sections of toys.

Standard Method: prEN 71-11

Typical analytical conditions:

μ -CTE gas flow: 100 mL/min

μ -CTE temperature: 40°C

Test time: 20 mins equilibration, 15 mins vapour sampling

Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack X

TD system: UNITY 2 or TD-100

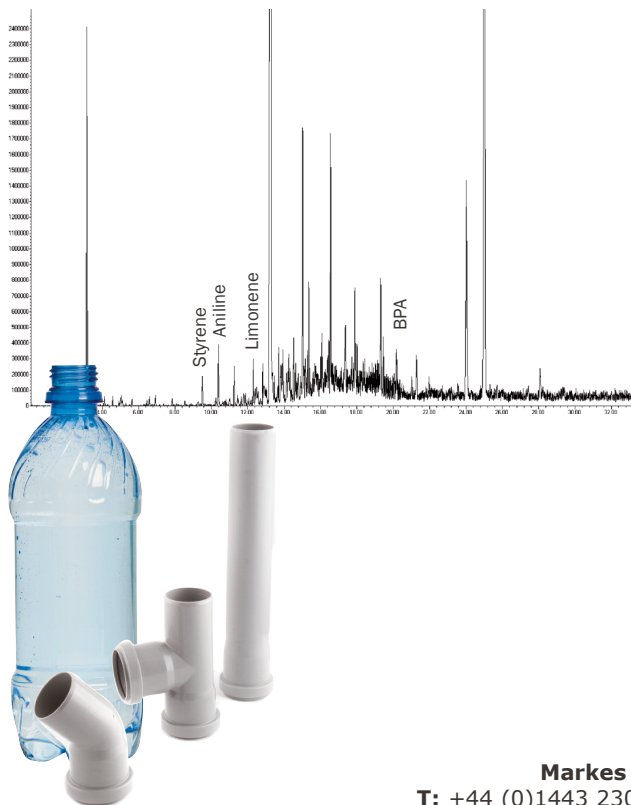
Trap: U-T12ME-2S (Material emissions)

Analysis: GC/MS



Plastic toy placed in micro-chamber

Micro-Chamber/Thermal Extractor: Screening for bisphenol A (BPA) release



Background:

Bisphenol A (BPA) is a common additive to the type of rigid polycarbonate plastics often used to make drink bottles or toys. It is also used as an additive to the inner coating of food cans and water supply pipes. However, BPA is a known endocrine disrupter *i.e.* it interferes with the actions of hormones. A recent US study has also found that BPA may be linked with behavioural issues in children, prostate cancer and even autism.

A toy was bought from a major retailer and evaluated using the μ -CTE at 90°C. Significant levels of BPA were detected in conjunction with styrene, aniline & limonene.

Markes thermal desorption equipment facilitates studies of toys by allowing simultaneous analysis of VOC & SVOC, as well as reactive species such as amines.

Typical analytical conditions:

μ -CTE gas flow: 50 mL/min

μ -CTE temperature: 90°C

Test time: 20 mins equilibration, 15 mins vapour sampling

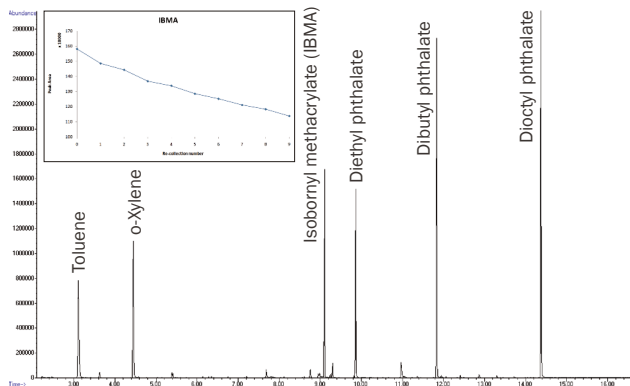
Sorbent tube: Quartz/Tenax TA/Carbopack X

TD system: UNITY 2 or TD-100

Trap: U-T12ME-2S (Material emissions)

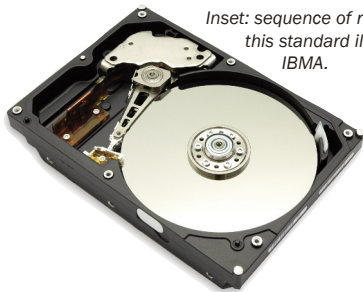
Analysis: GC/MS

Out-gassing from PC components (e.g. hard disk drives)



Standard of toluene, o-xylene, IBMA, diethyl phthalate, dibutyl phthalate & dioctyl phthalate in methanol (300 ng/ μ L); sorbent tube containing 1 μ L analysed by TD-GC/MS.

Inset: sequence of re-collection & repeat analyses of this standard illustrating quantitative recovery of IBMA.



Background:

The performance of data storage devices such as hard drives can be adversely affected by sources of Airborne Molecular Contamination (AMC) such as chemical out-gassing from clean room construction products or PC components.

Hard disk drive manufacturers were therefore one of the first industries to implement emissions testing (dynamic headspace) as part of routine factory production control.

The hard drive assemblies are placed in micro-chambers such as Markes' larger, 4-chamber μ -CTE unit at 85°C. Emitted vapours are trapped on a combination of carbon sorbents & analysed by TD-GC/MS (analytical conditions are listed below).

Components of interest include sticky & reactive species, e.g. isobornyl methacrylate (IBMA). The inert, uniformly heated flow path of Markes' TD technology ensures quantitative recovery & analysis of these challenging compounds (as shown opposite)

Typical analytical conditions:

Test time: 20 mins equilibration, 15 mins vapour sampling

TD system: UNITY 2 or TD-100

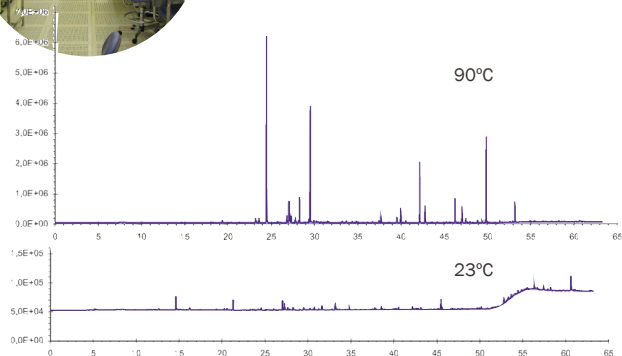
Desorption: 10 min at 320°C

Trap: U-T13DHS-2S (DHS application)

Analysis: GC/MS

Reference: TDTS 14, TDTS 53 & TDTS 62 (Materials emissions of high boiling species in the semiconductor industry)

Micro-Chamber/Thermal Extractor: Construction materials for cleanroom fabrication facilities



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Background:

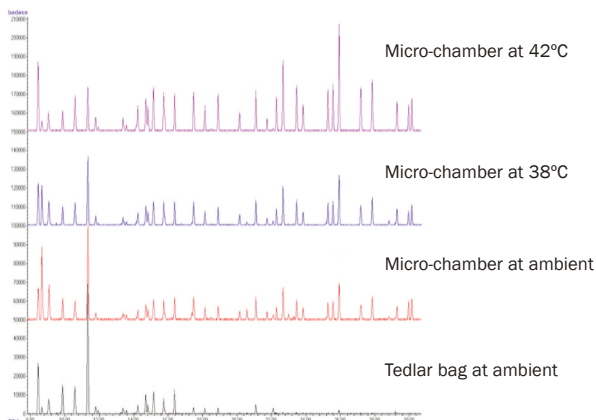
The presence of volatile and semi-volatile organic vapours in cleanroom air can adversely affect the growth of silicon wafer crystals, the performance of microprocessors and data storage devices. Construction materials and fittings used in cleanroom fabrication facilities must therefore have negligible chemical emission levels.

Micro-Chamber/Thermal Extractor units combined with Markes' high sensitivity TD technology are ideal for screening chemical emissions from cleanroom components and materials according to VDI 2083. Similar methodology is under development in ISO.

Analytical conditions recommended in VDI 2083

Parameter		
Temperature	23°C	90°C
Sampling time	1-60 mins	
Flow	100 mL/min	
Chamber volume	44 mL or 114 mL	
Equilibration time	0-15 mins	

Micro-Chamber/Thermal Extractor: Measuring solvents from printed circuit boards (PCBs)



Recovery of standard from the Tedlar bag compared with the micro-chamber

List of solvents:

- Freon 113
- Methylene chloride
- 1,1-dichloroethane
- Trans-1,2-dichloroethene
- Chloroform
- TCA
- Carbon tetrachloride
- TCE
- 1,3 DCP
- 1,1,2-trichloroethane

Background:

Conventional methods for testing banned halogenated solvents in PCBs involve incubating the samples in Tedlar® bags in an inert atmosphere. However, Tedlar bags are known to have relatively high artefact levels and can absorb some organic compounds. They are also limited to one use only.

Markes' μ -CTE technology presents a simpler, re-usable alternative which also offers better recovery of a wider volatility range of target compounds.

Typical analytical conditions:

μ -CTE gas flow: 20 mL/min

Sampling: 20 mins with the μ -CTE at ambient temp, 38°C & 42°C; no equilibration

Sorbent tube: Carbograph 1TD/Carboxen 1003

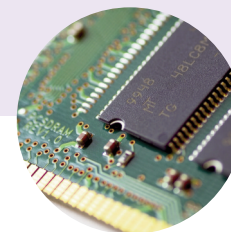
TD system: UNITY 2 or TD-100

Primary desorption: 10 mins at 320°C

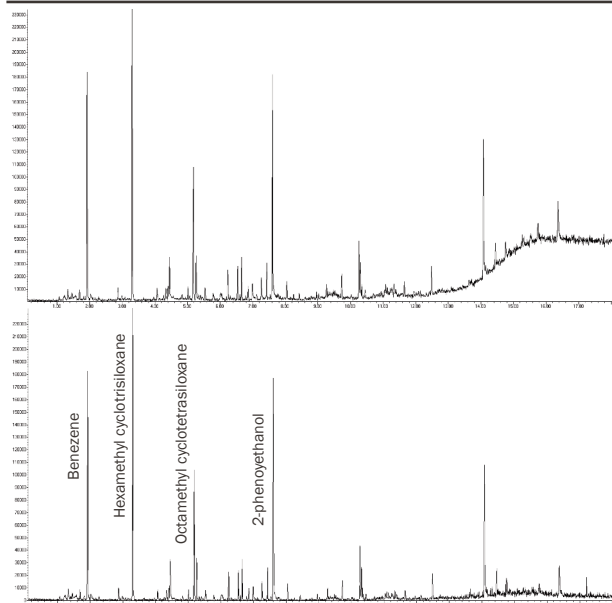
Trap: U-T15ATA-2S (Air toxics analyser)

Split: 15:1

Analysis: GC/MS



Removing background interference with ClearView™



Emission profile of a plastic toy; original data (top) and ClearView reprocessed data (bottom)

References: TDTS 83 & 85 (Using ClearView reprocessing to enhance trace GC/MS analysis)

Background:

Complex GC/MS data can be compromised by interference/'noise' which can make interpretation difficult. New software has been developed to address this.

ClearView™ is one of a suite of state-of-the-art GC/MS data reprocessing packages from ALMSCO International, available from Markes. It uses a sophisticated algorithm to accurately and dynamically compensate for chromatographic background as it changes throughout a run. Key advantages include:

- Reduced signal to noise for improved sensitivity/detection
- Improved spectral purity which improves automatic identification of trace components

ClearView is compatible with the data files of most makes of GC/MS software.

Original data files are retained intact for TVOC analysis.

Typical analytical conditions:

µ-CTE: Gas flow at 50 mL/min, temperature at 60°C

Test time: 10 mins equilibration, 20 mins vapour sampling

Sorbent tube: Tenax TA/Carbopack X1003

TD system: UNITY 2 or TD-100

Trap: U-T12ME-2S (Material emissions)

Split: 10:1

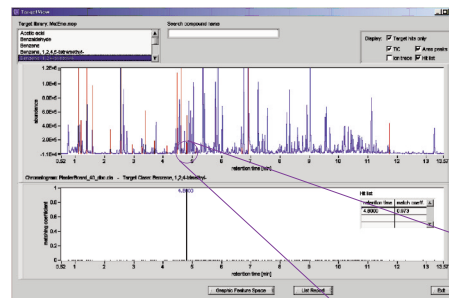
Analysis: GC/MS



Identifying trace target compounds in complex mixtures: TargetView™

TargetView builds upon the foundation of ClearView. It is a sophisticated GC/MS data-mining package, offering automatic interpretation of complex material emission profiles. TargetView facilitates the detection and measurement of target compounds even if they are at trace levels and co-eluting with other compounds. Original data files are left intact and unaffected, so operation of TargetView is risk-free. It works as follows:

1. Dynamic background compensation (ClearView) is applied to eliminate interferences such as column bleed.
2. The GC/MS data (total ion chromatogram [TIC]) of the sample is deconvoluted and 'principal component analysis' identifies targets from the selected library.
3. Any target compounds identified are assigned match coefficients, depending on the correlation between sample & library spectra.
4. A report listing all identified target compounds & associated area counts is produced.
5. A plot of the TIC with target compounds represented by red bars (the HPlot) may also be displayed.



Below: Enlarged view of section of TIC showing the target compound trimethyl benzene (*) co-eluting with multiple compounds in one small peak

Above: TargetView interface. Upper pane shows plasterboard emission profile with automatic detection of target peaks (HPlot: red bars). Lower pane shows highlighted detection of trimethyl benzene and corresponding match coefficient.

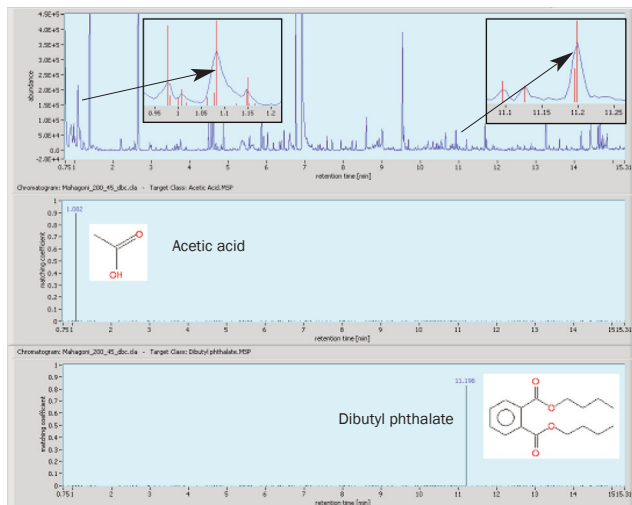
Report File
Report: MatEms_PlasterBoard_30_dbc.t1
Library: MatEms.msp
Chromatogram: PlasterBoard_30_dbc

Target compound	Retention time	Matching coefficient	Area counts
Acetic acid	1.116	0.989	1966354
Ethyl Acetate	1.197	0.984	424984
Benzene	1.393	0.980	2078610
Pentanal	1.583	0.936	986370
Toluene	2.198	0.994	330378
Hexanal	2.556	0.977	4505409
Furfural	2.952	0.996	130450
Ethylbenzene	3.280	0.977	104854
o-Xylene	3.387	0.997	613125
Nonane	3.708	0.921	181650
.alpha.-Pinene	4.130	0.964	116217
Benzaldehyde	4.484	0.992	1152047
Phenol	4.613	0.997	1321759
Benzene, 1,3,5-trimethyl-	4.800	0.965	152449
Decane	4.816	0.980	567945

Automated post-run report displaying target hits

For analytical conditions see page 27

TargetView: Target compound identification in emissions profiles



Highlighted identification of 2 target compounds in mahogany chromatogram; acetic acid at 1.082 mins and dibutyl phthalate at 11.198 mins

Background:

VOC emissions tests for product certification or routine quality control often require the detection of trace toxic or odorous target compounds in complex emission profiles.

TargetView software simplifies and enhances the process of screening complex material emission profiles for multiple trace target compounds. It allows experienced labs to improve and speed up data processing and automates data interpretation/reporting for routine industrial labs.

TargetView can be applied to GC/MS data files from most major manufacturers. It is available pre-programmed with libraries of target compounds relevant to emissions testing; AgBB/ AFSSSET 'LCIs', Cal 01350 'CRELs', etc.

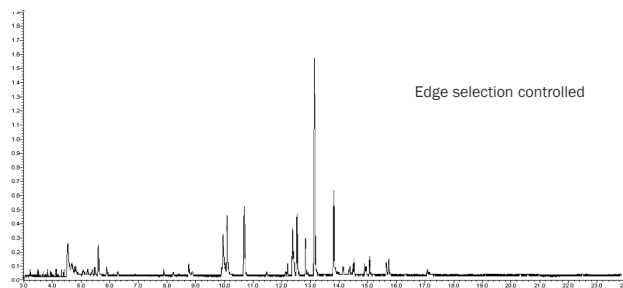
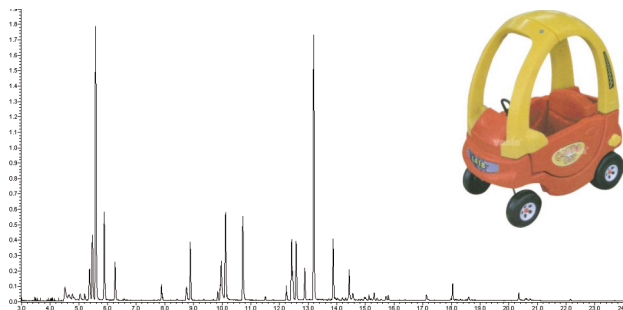
Examples of the software in action to evaluate emission profiles from mahogany and plasterboard using the AgBB library are shown.

Original data files are left intact and available, e.g. for TVOC analysis. This means no information can be lost by the TargetView process and operation is risk-free.

For analytical conditions, see page 35



Using the Micro-Chamber/Thermal Extractor to evaluate and eliminate edge effects



Reproduced with the kind permission of Prof. Mangoo Kim, Kangwon National University, Korea.

Background:

The importance of eliminating edge effects in order to obtain representative surface emission profiles can be seen in the following example. An injection moulded plastic (a car body part), coated with an oil-based paint was tested using the Micro-Chamber/Thermal Extractor.

The top chromatogram shows the results obtained by positioning the sample lower down in the micro-chamber. In this case, both the coated surface and the cut edges of the plastic contributed to the emission profile. The lower chromatogram shows the results from raising the sample up within the micro-chamber using spacers, so that the surface pressed gently against the collar (baffle) projecting down from the micro-chamber lid. In this case, only the oil-based coating emissions are seen.

Typical analytical conditions:

μ -CTE temperature: 65°C

μ -CTE gas flow: 50 mL/min

Sample quantity: 1–6 simultaneously

Test time: <30 mins equilibration, 15 mins vapour sampling

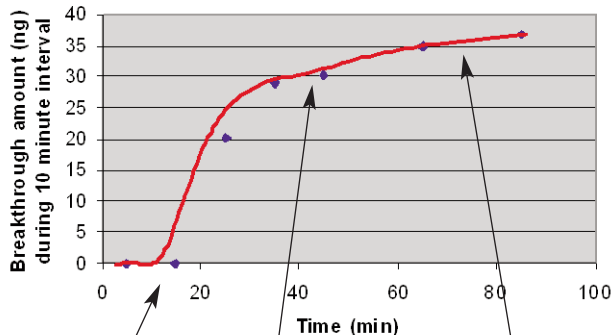
Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack X

TD system: UNITY 2 or TD-100

Trap: U-T12ME-2S (Material emissions)



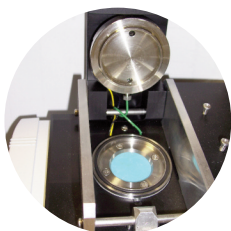
Micro-Chamber/Thermal Extractor: Permeation testing



Breakthrough time ~15 mins

Steady state permeation.
Permeation rate ~0.5 ng/cm²/min

Swelling/degradation of test material membrane.
Permeation rate ~0.6 ng/cm²/min



μ-CTE permeation accessory with test material installed

Background:

Permeation of chemicals through protective fabrics, films and membranes can be conveniently assessed using Markes micro-chamber units configured with the proprietary permeation accessory. A small droplet of test compound is placed in a well at the bottom, and a sample of the test material is stretched over the top and sealed around the perimeter. Test compound can also be injected into the well after the test material has been put in place.

The complete assembly is then placed inside one of the μ-CTE micro-chambers and incubated, typically at ambient or near-ambient temperature. Clean air is passed over the surface of the stretched material in each micro-chamber. Permeation of the test compound through the material is assessed by monitoring the air exhausting from the micro-chambers using a series of sorbent tubes and TD-GC/MS analysis in the normal way.

Typical analytical conditions:

μ-CTE temperature: 35°C

μ-CTE gas flow: 50 mL/min

Sampling: Every 10 mins onto a Tenax TA tube (no equilibration)

TD system: UNITY 2 or TD-100

Primary desorption: 5 mins at 300°C

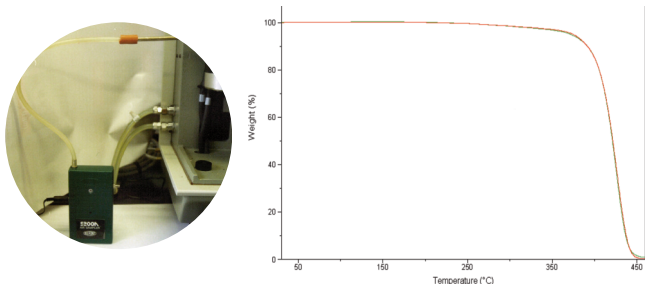
Trap: Quartz/Tenax TA/Carbopack X

Split: 5:1

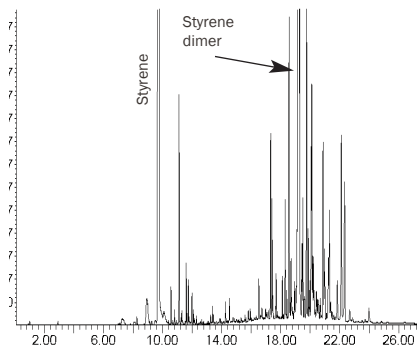
Analysis: GC/MS



Characterising evolved gases during TGA analysis with TD-GC/MS



Thermo-gravimetric analysis of polystyrene with and without evolved gas collection shows that vapour collection has negligible impact on the TGA data



TD-GC/MS analysis of vapours collected during TGA tests of polystyrene show over 30 components in addition to styrene and styrene dimer. These are due to chemical decomposition of additives such as anti-oxidants and process enhancers.

Background:

Thermogravimetric analysis (TGA) measures changes in the mass of a sample as it is heated. TGA is more versatile than pyrolysis because it may be carried out under either inert or oxidative atmospheres. The technique is used extensively to characterise polymeric and pharmaceutical materials (man-made fibres/textiles, polymeric films, paints, bulk plastics, etc.).

Markes' sorbent tubes may be coupled to TGA equipment to collect gases evolved as the sample is heated. In the example opposite, TD-GC/MS analysis of gases evolved during TGA of polystyrene provided a detailed profile of chemical decomposition products and aided interpretation of the TGA data.

Typical analytical conditions:

TGA: 10°C/min, ambient to 600°C, N₂ purge

Sorbent tube: Tenax TA/Carbograph 1

Desorption: 3 mins at 50°C & 5 mins at 250°C

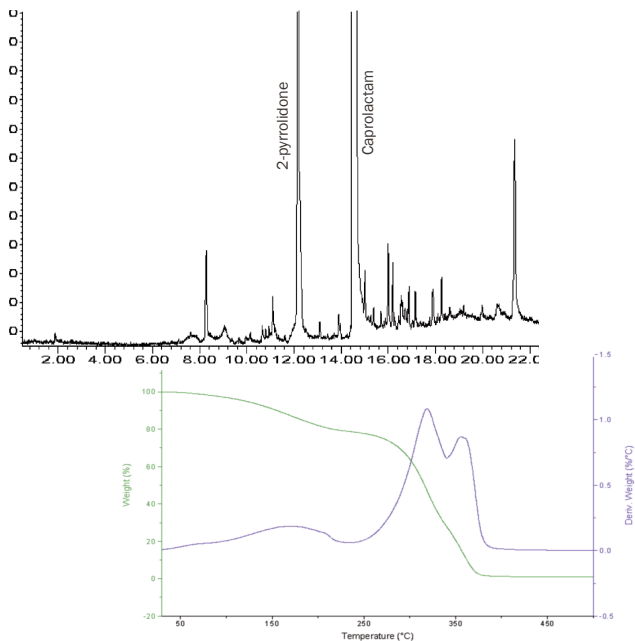
Trap: U-T2GPH-2S (General purpose [hydrophobic]) or U-T11GPC-2S (general purpose carbon)

Double split: ~500:1

Analysis: GC/MS

Reference: Lever, T. J., Price, D. M., Warrington, S. B., (2000), Evolved Gas Collection from a Thermogravimetric Analyzer and Identification by Gas Chromatography-Mass Spectrometry. Proc. 28th North American Thermal Analysis Society Conference, Orlando, Florida, USA, pp. 720-725

Characterising materials via TGA evolved gas analysis



TGA tests on an unknown sample of nylon (bottom).
TD-GC/MS analysis of vapours collected during TGA tests confirm nylon 4,6 (top)

Background:

TGA coupled with TD-GC/MS analysis of evolved gases can be used to identify unknown materials. In this example, nylon 4,6 was identified from its two-step TGA profile and ratio of 2-pyrrolidone and caprolactam in the chromatogram of evolved gases.

Two or more separate evolved gas samples can be collected from a single TGA experiment, if required, corresponding to different temperature ranges or weight loss steps in the TGA profile. This allows independent chemical analysis of the processes occurring at each stage of analysis.

The double split capability of Markes' TD technology makes it ideally suited to accommodate the large masses of vapour eluted from TGA experiments, without overloading the GC/MS analytical system.

Typical analytical conditions:

TGA: 10°C/min, ambient to 600°C, N₂ purge

Sorbent tube: Tenax TA/Carbograph 1

Desorption: 3 mins at 50°C & 5 mins at 250°C

Trap: U-T2GPH-2S (General purpose [hydrophobic]) or U-T11GPC-2S (general purpose carbon)

Double split: ~500:1

Analysis: GC/MS

References

Further detailed applications information can be found in the following Markes' TDTS Application Notes

- 9 Monitoring materials and processes for trace level volatile organic compounds (VOCs)
- 14 Analysis of labile, high-boiling organic vapours known to cause contamination issues when present in Semiconductor cleanroom fabrication facilities
- 40 Direct desorption of volatile and semi-volatile organic compounds from furnishings such as leather or textiles
- 41 Analysis of residual solvent (dimethylsulfoxide (DMSO)) in a drug precursor
- 53 Quantitative recovery of high boiling point (>450°C) semi-volatiles (SVOCs) using thermal desorption–GC/MS
- 55 Using the FLEC cell to determine volatile organic emissions from indoor materials and products
- 56 TD-GC/MS analysis of VOCs for materials emissions testing
- 57 Characterisation of paint samples by direct desorption TD-GC/MS
- 59 Direct desorption of car trim materials for volatile organic compounds (VOCs) and semi volatile organic compounds (SVOCs) analysis, in accordance with method VDA 278
- 62 Materials emissions testing in the semiconductor and associated industries
- 64 Simultaneous TD-GC(MS) analysis of VOCs and semi-VOCs
- 66 Improving the identification and measurement of trace odorous and toxic components during materials emissions testing
- 67 Using the Micro-Chamber/Thermal Extractor (μ -CTE) to automate materials emissions testing for industrial quality control
- 68 Using Markes emission screening technology to simplify compliance with the latest construction product regulations
- 70 Materials emissions testing using the FLEC cell: Testing recovery and sink effects
- 71 Summary of FLEC applications
- 72 Comparison of FLEC with conventional chambers for testing VOC emissions from materials summary of published data
- 83 Enhancing TD-GC/MS methods for trace compound analysis using ClearView™ reprocessing software
- 85 GC/MS data analysis using ClearView™ reprocessing software: Dealing with common ions
- 89 Thermal desorption technology for testing chemical emissions from construction products and consumer goods
- 90 Automatic detection of trace target compounds in complex chemical emission profiles from products and materials
- 91 Using a single headspace-thermal desorption (HS-TD) method to enhance the measurement of residual solvents in drugs via USP 467
- 92 Fast quantitative analysis of residual monomer in polymer by automated direct thermal desorption
- 93 Application of rapid microchamber tests (ISO 12219-3) for screening chemical emissions from plastic car trim components

The Markes International advantage

Markes is the world leader in analytical thermal desorption and has pioneered important technical innovations such as SecureTD-Q (quantitative sample re-collection for repeat analysis), TubeTAG electronic labels for sorbent tubes and universal (multi-application) heated valve technology.

Markes leadership in TD now extends to:

- The widest available product portfolio and application range
- Product quality and reliability
- Excellence in technical and applications support

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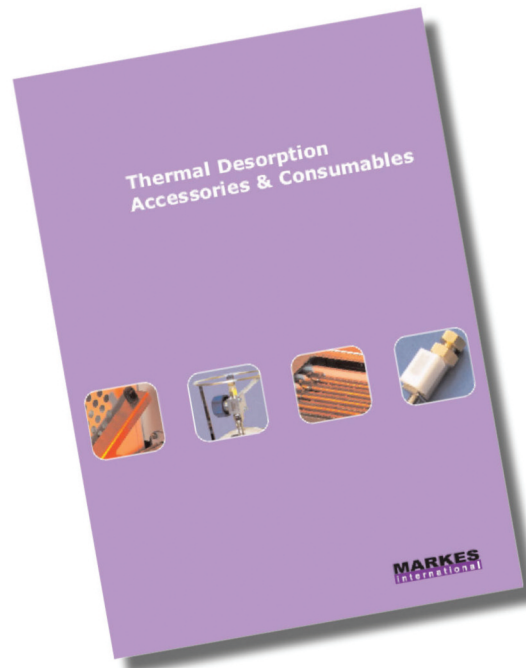
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Markes International Ltd

Gwaun Elai Medi Science Campus
Llantrisant
RCT
CF72 8XL
United Kingdom

T: +44 (0)1443 230935 **F:** +44 (0)1443 231531
E: enquiries@markes.com **W:** www.markes.com