# Thermal Desorption Technical Support

## Note 89: Thermal desorption technology for testing chemical emissions from construction products and consumer goods

**Keywords:**

REACH, construction products, consumer goods, VOC, SVOC

### Introduction

High-profile international regulatory developments and increased consumer awareness of 'green' issues are driving global demand for improved assessment and labelling of products with respect to their intentional or unintentional release (emission) of chemicals. Mandate M/366 (2005)[1] of the EC Construction Products Directive[2], its successor the EC Construction Product Regulation (CPR)[3], new chemicals legislation 'REACH' (Europe[4] and China[5]), and recent US initiatives to include mandatory emission testing within building codes[6-8], are key examples of regulatory developments that will increase the need for chemical emissions testing as part of product certification.

These new regulations impact a large proportion of the manufacturing industry, with producers of flooring, furniture, toys, domestic goods, cleaning products, wood-based products, insulation materials, coatings/adhesives/sealants and general construction products all being in the front line, together with all their suppliers.

Testing product/material emissions to indoor air is a multi-step procedure. It involves putting prepared samples into a test chamber or cell, collecting the emitted vapours onto sorbent tubes and subsequent analysis by thermal desorption (TD) with GC/MS. Relevant standard methods include:

- ISO/EN 16000 parts -6, -9, -10, -11 *etc.*
- CEN TC 351 standards
- ISO 12219 series methods
- ASTM standards such as D6196, D5116, D6330, D6670, D7143 and D7339.

Markes International Ltd provides uniquely versatile TD technology for product emissions testing. Systems combine usability with analytical performance and offer full compliance with the above standards. Both manual and automated TD configurations are available (Figure 1).

***Figure 1: Manual TD is possible on the UNITY 2™ (left), whilst the TD-100™ (right) offers automated TD***

Relevant TD applications for industry include:

- Certification of products with respect to VOC emissions using chamber/cell tests
- Routine quality control (screening) of vapour-phase organic emissions
- Industrial research and development (R&D)
- Measuring emissions of semi-volatile organic chemicals
- Detection of trace carcinogens and other toxic target compounds in complex total ion profiles
- Indoor air quality assessment and associated ventilation studies

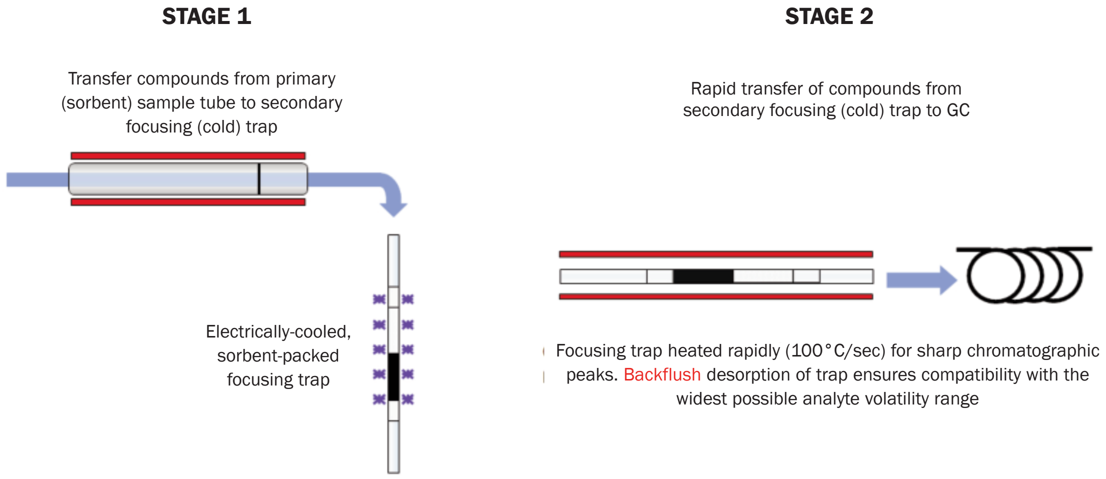


*Figure 2: The two-stage thermal desorption process*

## Thermal desorption: Technical considerations for optimising material emission testing

At its simplest level, TD involves heating up material samples or sorbent traps/tubes in a stream of inert carrier gas, and transferring (injecting) desorbed organic vapours into a GC(MS) system or alternative vapour analyser.

To optimise sensitivity and compound resolution, modern thermal desorbers include a focusing trap to selectively concentrate the compounds of interest desorbed from the primary sample tube. These are then efficiently injected into the GC(MS) in a narrow band of vapour. An overview of the two-stage TD process is illustrated in figure 2.

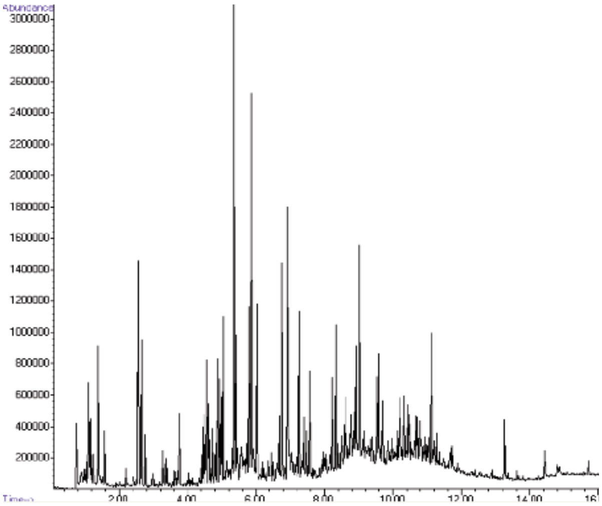


*Figure 3: Plasterboard emission profile*

A particular challenge of emissions testing is that product emission profiles are often complex (Figures 3 & 4) and may contain multiple toxic or odorous target compounds at trace levels. Target compound lists for construction product emissions may also be long and include some analytically challenging species (see examples in Appendix A).

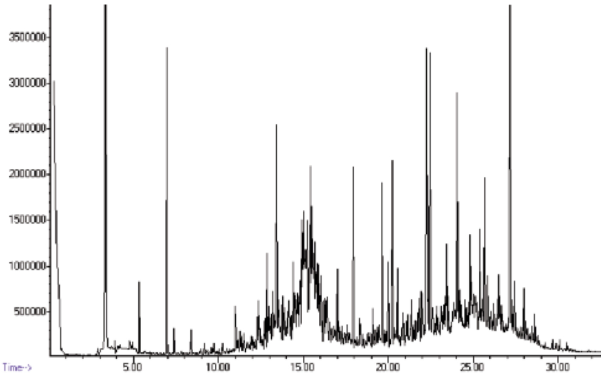


*Figure 4: Laminate flooring emission profile*

In practice, there are many factors which can influence the suitability of a thermal desorber for complex applications such as material emissions testing. A list of the most important/useful TD features is presented below.

## Reliability

Robust thermal desorption operation revolves around mechanical simplicity, electrical trap cooling and minimal installation/supply requirements (dry gas, liquid cryogen, *etc*).

*Electrical cooling* of the sorbent focusing trap is a major advantage for emissions testing. It overcomes the inconvenience and high cost of cryogenically-cooled systems. TD systems that incorporate narrow-bore (around 1 mm ID or less), cryo-cooled focusing traps are also prone to ice formation. If ice is allowed to block the sample flowpath, the process of TD stops and results are seriously compromised.

## Universality

Vapour-phase organic chemicals emitted (released) by products and materials cover a wide range of compound types[9]:

- very volatile components (VVOCs; *i.e.* more volatile than n-hexane),
- VOCs (n-$C_6$ to n-$C_{16}$),
- semi-volatiles (SVOCs; *i.e.* less volatile than n-hexadecane)
- AND reactive (odorous) species such as mercaptans & amines.

The thermal desorber must therefore be compatible with all these potential target analytes.

## Simultaneous analysis of VOCs and SVOCs

In addition to offering compatibility with the widest possible range of compounds, it is also important for the desorber to allow simultaneous analysis of volatiles and semi-volatiles, *i.e.* accommodate the entire target compound volatility range in one run, consequently minimising costs[9]. This requires backflush desorption of the focusing trap, *i.e.* compounds are introduced to the focusing trap in a stream of gas passing through the sorbents in order of increasing strength, and then desorbed with gas flowing in the opposite (backflush) direction (Figure 1). This mode of operation allows high boiling compounds to be retained and readily released from weaker sorbents at the front of the focusing trap while at the same time, light compounds are quantitatively retained and released by the strong sorbents at the rear of the trap.

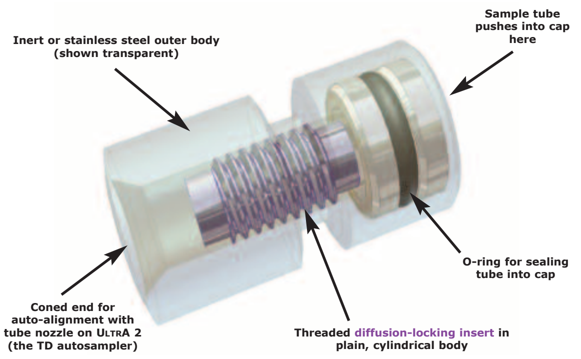
## Method compliance and data integrity

As required by standard methods, the TD system must incorporate stringent *leak testing* of each tube prior to analysis, without compromising/jeopardising the sample. Thermal desorption effectively involves breaking into the carrier gas flow path of the TD-GC(MS) system every time a new sample is introduced. Without an adequate leak test the user can never be certain of the quality or reliability of their results. This is particularly crucial for certification of emissions, where sample preparation can take days or even weeks[10].

(*NB* Leak testing must be carried out at near-ambient temperature and under stop-flow conditions such that samples which fail are not compromised.)

Another key consideration for method compliance and data integrity is *tube sealing during automated analysis*. Sorbent tubes must be adequately sealed (capped) throughout an automated TD sequence, both to prevent loss of analytes (before desorption) and to stop ingress of contaminants from laboratory air (before and after desorption). The performance of DiffLok™ analytical end caps (Figure 5) as used on Markes' automated desorption systems (TD-100 and ULTRA) is shown in figures 6 and 7.

***Figure 5: Schematic of a DiffLok cap***



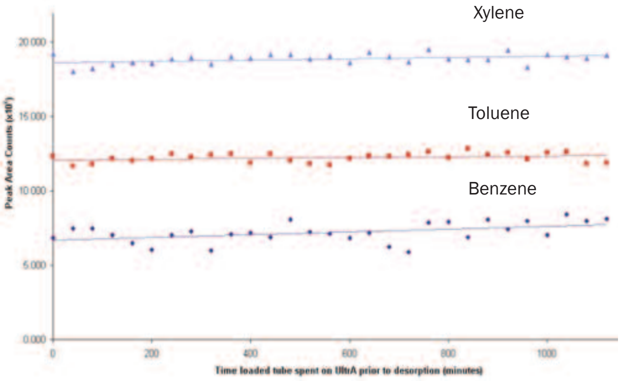


***Figure 6: Automated TD analysis of BTX on Tenax® TA tubes secured with DiffLok caps over 24 h. Data shows no loss of analytes from the capped tubes.***

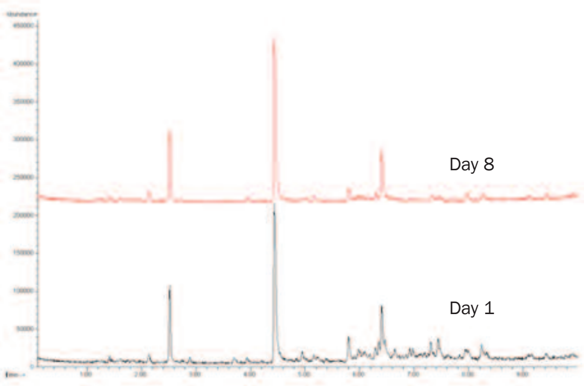


***Figure 7: Analysis of tube contents after 1 (black) and 8 (red) days storage with DiffLok caps showing no significant ingress of contaminants***

Automated thermal desorbers should also offer *internal standard addition*, at least as an option.

For compatibility with multi-sorbent tubes, gas-phase internal standard should be automatically introduced to the sampling end of the tube after leak testing and before TD analysis. Suitable internal standards include deuterated toluene.

## Quantitative sample re-collection for repeat analysis and method validation

Quantitative re-collection of the primary and secondary TD split flows onto a fresh, conditioned sorbent tube allows a significant proportion of each sample (typically >90%) to be re-trapped. This facilitates repeat analysis and data/method validation as outlined in TD standard methods[11]. This facility is useful for both manual and automated TD operation.

## Stability

Electronic control of TD carrier gas flow (column, desorption and split flows) is also important for material testing. Reliable identification of multiple trace-level target analytes in complex emission profiles benefits from stable retention times and the application of sophisticated data-processing software such as Markes' TargetView™ [12]. Electronic pneumatic control of split and desorb flows also allows the inclusion of multiple methods in one automated sequence and simplifies system resetting in a busy lab.

## Quality assurance of sorbent tubes

Electronic tube labelling (tagging) is another recent TD innovation[13,14] which can be of real benefit, particularly in a busy service or production control laboratory. RFID technology within each TubeTAG™ stores important sample- and tube-related information, such as sorbent type, packing date, number of thermal cycles, volume of air sampled, *etc*. Tags allow the history of a sorbent tube to be tracked throughout its life for improved quality assurance. Sample information can also be confidently tracked through a sequence of re-collection and repeat analyses, eliminating the risk of transcription errors.

## Concluding remarks

Modern manual and automated thermal desorbers integrate seamlessly into standard gas chromatography systems and are operated *via* software residing on the GC(MS) control PC. Leading providers of TD instrumentation, such as Markes International, also offer extensive applications expertise and a range of ancillary products to simplify and enhance system operation/application.

TD is a powerful introduction technology for GC(MS) which is widely applied for testing chemical emissions from building materials and consumer products to indoor air. Provided the technical considerations listed above are taken into account, it can be reliably deployed in both high-throughput service laboratories and in routine industrial quality control facilities.

## Trademarks

UNITY 2™, DiffLok™, TD-100™ and TubeTAG™ are trademarks of Markes International Ltd., UK

TargetView™ is a trademark of ALMSCO International, UK

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

## References

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10. CEN/TC 351/WG 2 Construction products – Assessment of release of dangerous substances – Emissions into indoor air
11. ASTM D6196 (2009) Standard practice for selection of sorbents, sampling, and thermal desorption analysis procedures for volatile organic compounds in air
12. Thermal Desorption Technical Support Note 90: Automatic detection of trace target compounds in complex chemical emission profiles from products and materials
13. Woolfenden, E. (2010) Sorbent-based air sampling methods for volatile and semi-volatile organics in air. Part 2: Sorbent selection and other aspects of optimising air monitoring methods. J. of Chrom. A. 1217: 2685–2694
14. Markes International Brochure - TubeTAG™: Sorbent Tube Informatics: Sorbent tube tagging and tracking for enhanced sample traceability

## Appendix A

### List of compounds with LCIs (lowest concentration of interest) from German AgBB scheme (2008)

Toluene

Ethyl benzene

Xylene, mix of o-, m- and p-xylene isomers

p-Xylene

m-Xylene

o-Xylene

Cumene

n-Propyl benzene

1-Propenyl benzene (ß-methyl styrene)

1.3.5-Trimethylbenzene

1.2.4-Trimethylbenzene

1.2.3-Trimethylbenzene

2-Ethyltoluene

1-Isopropyl-2-methylbenzene (o-cymene)

1-Isopropyl-3-methylbenzene (m-cymene)

1-Isopropyl-4-methylbenzene (p-cymene)

1.2.4.5-Tetramethylbenzene

n-Butylbenzene

1.3-Diisopropylbenzene

1.4-Diisopropylbenzene

Phenyloctane and isomers

1-Phenyldecane and isomers

1-Phenylundecane and isomers

4-Phenyl cyclohexene (4-PCH)

Styrene

Phenyl acetylene

Vinyl toluene (all isomers: o-,m-,p-methyl styrenes)

Naphthalene

Indene

n-Hexane

Cyclohexane

Methyl cyclohexane

n-Heptane

3-Carene

α-Pinene

ß-Pinene

Limonene

Ethanol

1-Propanol

2-Propanol

Tert-butanol, 2-methylpropanol-2

2-Methyl-1-propanol

1-Butanol

Pentanol (all isomers)

1-Hexanol

Cyclohexanol

2-Ethyl-1-hexanol

1-Octanol

4-Hydroxy-4-methyl-pentane-2-on (diacetone alcohol)

Phenol

BHT (2,6-di-tert-butyl-4-methylphenol)

Benzyl alcohol

Propylene glycol (1,2-Dihydroxypropane)

Ethanediol

Ethylene glycol-monobutylether

Diethylene glycol

Diethylene glycol –monobutylether

2-Phenoxyethanol

Ethylene carbonate

1-Methoxy propanol-2

2.2.4-Trimethyl-1,3-pentane diol, monoisobutyrate (Texanol®)

Butyl glycolate

Diethylene glycol monomethyl ether acetate

Dipropylene glycol monomethyl ether

2-Methoxyethanol

2-Ethoxyethanol

2-Propoxyethanol

2-Methylethoxyethanol

2-Hexoxyethanol

1,2-Dimethoxyethane

1,2-Diethoxyethane

2-Methoxyethyl acetate

2-Ethoxyethyl acetate

2-Butoxyethyl acetate

2-(2-Hexoxyethoxy)-ethanol

1-Methoxy-2-(2-methoxy- ethoxy) ethane

2-Methoxy-1-propanol

2-Methoxy-1-propyl acetate

Propylene glycol diacetate

Dipropylene glycol

Dipropylene glycol- monomethyl ether acetate

Dipropylene glycol- mono-n-propylether

Dipropylene glycol- mono-n-butylether

Dipropylene glycol- mono-t-butylether

1,4-Butandiol

Tripropylene glycol- monomethyl ether

Triethylene glycol-dimethyl ether

1.2.-Propylene glycol-dimethyl ether

TXIB

Ethyldiglycol

Dipropylene glycol

Dimethyl ethers

Butanal

Pentanal

Hexanal

Heptanal

2-Ethyl-hexanal

Octanal

Nonanal

Decanal

2-Butenal (crotonaldehyde, cis-trans-mix)

2-Pentenal

2-Hexenal

2-Heptenal

2-Octenal

2-Nonenal

2-Decenal

2-Undecenal

Furfural

Glutardialdehyde

Benzaldehyde

Acetaldehyde

Propanal

Ethylmethylketone

3-Methylbutanone-2

Methylisobutylketone

Cyclopentanone

Cyclohexanone

2-Methylcyclopentanone

2-Methylcyclohexanone

Acetophenone

1-Hydroxyacetone

(2 Propanone, 1-hydroxy-)

Acetone

Acetic acid

Propionic acid

Isobutyric acid
Butyric acid
Pivalic acid
n-Valeric acid
n-Caproic acid
n-Heptanoic acid
n-Octanoic acid
2-Ethylhexane acid
Methyl acetate
Ethyl acetate
Vinyl acetate
Isopropyl acetate
Propyl acetate
2-Methoxy-1-methylethyl
n-Butyl formiate
Methyl methacrylate
Other methacrylates
Isobutyl acetate
1-Butyl acetate
2-Ethylhexyl acetate
Methyl acrylate
Ethyl acrylate
n-Butyl acrylate
2-Ethylhexyl acrylate
Other acrylates (acrylic acid ester)
Dimethyl adipate
Dibutyl fumarate
Dimethyl succinate
Dimethyl glutarate
Hexamethylene diacrylate
Maleic acid dibutylester
Butyrolactone
Tetrachloroethene
1.4-Dioxan
N-methyl-2-pyrrolidon
Octamethylcyclotetra-siloxane
Hexamethylenetetramine
2-Butanonoxime
Tributyl phosphate
Triethyl phosphate
5-Chloro-2-methyl-2H-isothiazol-3-one (CIT)
2-Methyl-4-isothiazoline-3-on (MIT)
Triethylamine

### Target CREL (chronic reference exposure level) VOCs from CA/DHS/EHLB/R-174 (California Specification 01350, 2010)

Acetaldehyde
Benzene
Carbon disulfide
Carbon tetrachloride
Chlorobenzene
Chloroform
Dichlorobenzene (1,4-)
Dichloroethylene (1,1)
Dimethylformamide (N,N-)
Dioxane (1,4-)
Epichlorohydrin
Ethylbenzene
Ethylene glycol
Ethylene glycol monoethyl ether
Ethylene glycol monoethyl ether acetate
Ethylene glycol monomethyl ether
Ethylene glycol monomethyl ether acetate
Formaldehyde
Hexane (n-)
Isophorone
Isopropanol
Methyl chloroform
Methylene chloride
Methyl t-butyl ether
Naphthalene
Phenol
Propylene glycol monomethyl ether
Styrene
Tetrachloroethylene
Toluene
Trichloroethylene
Vinyl acetate
Xylenes, technical mixture (m-, o-, p-xylene combined)