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THE QUEEN'S AWARDS FOR ENTERPRISE: 2015

What is thermal desorption?

A guide to the history, principles and applications of thermal desorption for gas chromatography

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> Thermal desorption is a versatile pre-concentration technique for gas chromatography that is used to analyse volatile and semi-volatile organic compounds.



In this e-book, we'll explain:

01 The basics of TD

How it evolved, how it works, why it's so versatile, and aspects of sorbent choice

02 Sampling options

Pumped and passive, canisters and on-line, headspace and more

03 Applications

Why do analysts use TD, and what do they use it for?

We hope that, by the end of this document, you'll have an understanding of how TD benefits GC analysts across a wide range of scenarios – and how it might be able to help you.

For more about TD, visit our website at
www.markes.com

01

THE BASICS

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Why use TD?

> Thermal desorption arose out of the need to improve upon conventional sample preparation techniques for gas chromatography (GC).

GC is very popular for analysing mixtures of organic compounds, but getting the analytes from the sample and into the vapour phase can be difficult.

Thermal desorption overcomes the drawbacks of conventional sample preparation techniques such as solvent extraction, solid-phase micro-extraction, purge-and-trap, and static headspace.

Specifically, it:

- Gives greater sensitivity than these techniques.
- Can be used for a wider range of compound classes.
- Is applicable to a wide range of sample types.
- Is safer and more environmentally-friendly than solvent extraction.
- Is easily automated.
- Is easy to validate.
- Complies with key standard methods.

How does TD work?

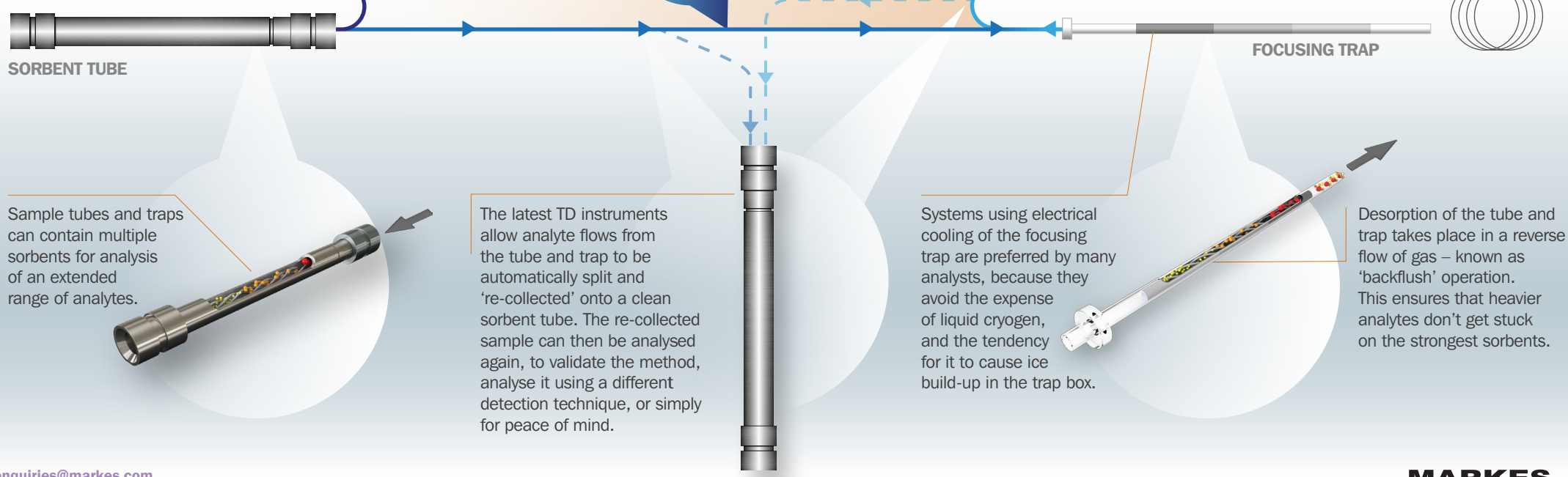
The majority of TD applications use sorbent tubes and a two-stage desorption process to focus the analytes into a narrow band of gas, and so achieve the maximum sensitivity enhancement.

Sample collection
Up to **100 L** of vapour is sampled off-line onto a sorbent tube.

Tube desorption
The sorbent tube is heated and the analytes are swept onto a focusing trap in **100–200 mL** of carrier gas.

Trap desorption
The focusing trap is heated rapidly and the analytes transferred to the GC column in **100–200 µL** of carrier gas.

Volume of gas transferred



Sample tubes and traps can contain multiple sorbents for analysis of an extended range of analytes.

The latest TD instruments allow analyte flows from the tube and trap to be automatically split and ‘re-collected’ onto a clean sorbent tube. The re-collected sample can then be analysed again, to validate the method, analyse it using a different detection technique, or simply for peace of mind.

Systems using electrical cooling of the focusing trap are preferred by many analysts, because they avoid the expense of liquid cryogen, and the tendency for it to cause ice build-up in the trap box.

Desorption of the tube and trap takes place in a reverse flow of gas – known as ‘backflush’ operation. This ensures that heavier analytes don’t get stuck on the strongest sorbents.

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The versatility of TD

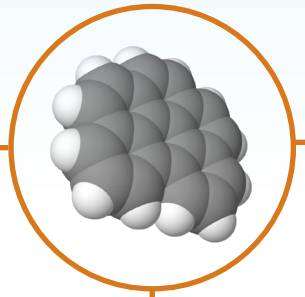
A major advantage of thermal desorption is that it can be applied to such a wide range of analytes and samples.

RANGE OF **ANALYTES**

Organic compounds boiling down to –100 °C...

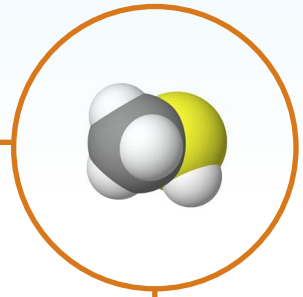
C_2 hydrocarbons

...to compounds boiling up to 500 °C...



Polycyclic aromatic hydrocarbons

...including reactive species



Sulfur compounds

RANGE OF **SAMPLE TYPES**

From

Gases

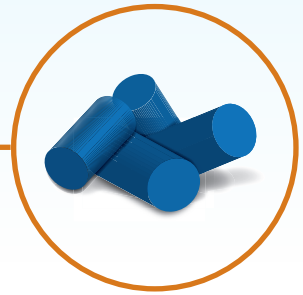
- Pumped sampling
- Passive sampling
- On-line
- Canisters

...to...

Liquids

- Immersive sorptive extraction

...to...



Solids

- Dynamic headspace
- Headspace sorptive extraction
- Direct desorption

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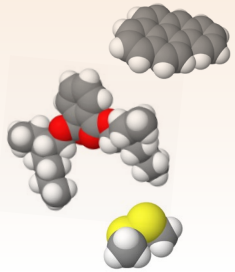
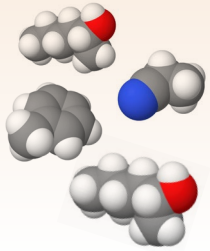
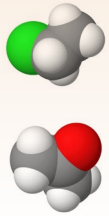
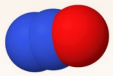
Choosing TD sorbents

Sorbents lie at the heart of why thermal desorption works. Packing tubes and traps with the appropriate sorbent(s) is therefore crucial for the success of all TD methods.

Sorbent type:	Porous polymers	Graphitised carbon blacks	Carbonised molecular sieves	Zeolite molecular sieves
The porous polymer sorbent Tenax® TA is the most popular sorbent for TD				
Sorbent strength: The weaker the sorbent, the better it is at analysing heavier and reactive molecules.				 Strong sorbents are usually used for monitoring small, volatile analytes.
Water retention: Weaker sorbents are generally more hydrophobic, making them a better choice for sampling humid environments.				 Conversely, strong sorbents tend to be highly hydrophobic.

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The evolution of TD

Over the course of nearly five decades, the capability of thermal desorption has advanced greatly, aided by advances in equipment.

Early 1970s: Scientists begin to experiment with thermal desorption by packing standard GC injector liners with sorbent material.

Mid-1970s: Environmental Monitoring Systems introduces the first commercial thermal desorber.

1981: PerkinElmer introduces the first commercial automated thermal desorber.

Early 1990s: Technical improvements made to improve performance.

1998: Markes introduces the UNITY™ thermal desorber.

2001: Markes introduces ULTRA™ and Air Server™ modules to extend the sampling options.

2005: Markes introduces the TT24-7™ thermal desorber for continuous monitoring.

2008: Markes launches series 2 thermal desorbers.

Late 2000s: Markes introduces range of accessories to expand the application range of TD.

2016: Markes introduces the 'xr' series of thermal desorbers.

1970

- 3½-inch × ¼-inch TD tubes made standard

1980

- Two-stage TD
- Electrical cooling
- Pre-desorption checks
- 50-tube automation

1990

- Efficient focusing trap
- Low-volume valving
- Tube sealing for automation

2000

- Quantitative re-collection of split flows
- Backflush desorption
- Analysis of tubes, canisters and on-line air streams
- Internal standard addition
- 100-tube automation
- Twin-trap operation for continuous sampling
- Analysis of ultra-volatiles, high-boilers and reactive compounds
- Automation for tube, canister and on-line monitoring
- RFID sample tracking

2010

- TD interfaces for dynamic headspace, sorptive extraction, breath sampling, and more

2020

- Fully automated re-collection of inlet and outlet split flows
- Quantitative analysis of C_2 to C_{44}

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02

SAMPLING OPTIONS

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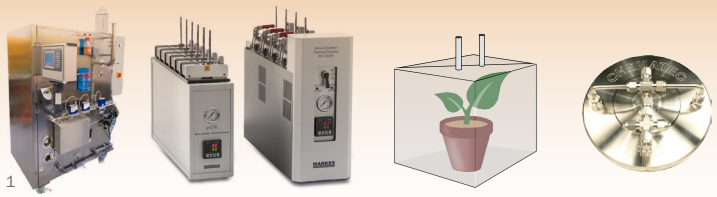
Sampling options for TD

Thermal desorption can be used with a range of sample introduction methods. Each of those mentioned below is described on the following pages.

Sorbent tubes

Pumped (electric or manual) | Passive (axial or radial)

Dynamic headspace

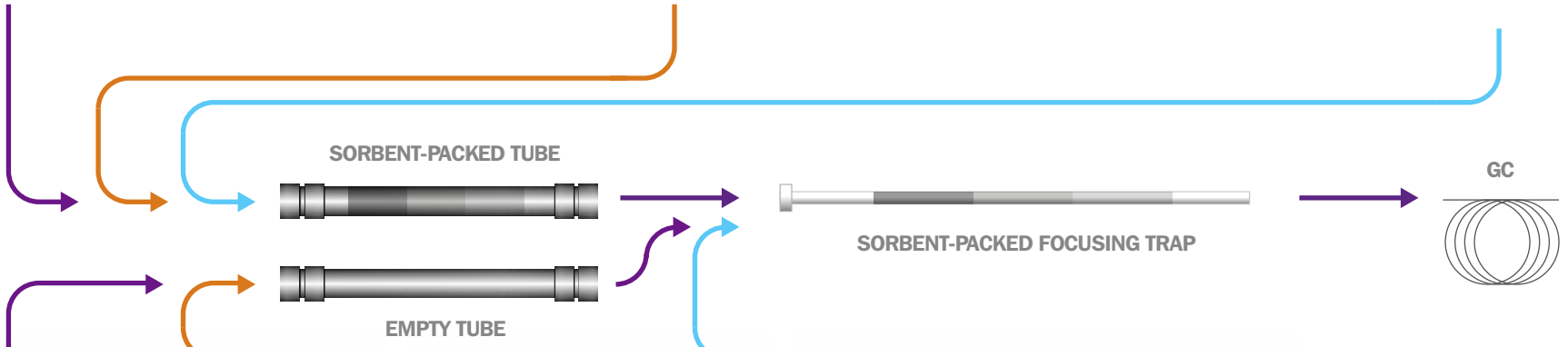


Small chambers | Microchambers | Headspace containers | Emission cells

Breath

Breath samplers

These methods use two stages of sorbent trapping, and so are ideal for trace-level analysis.



Solids | Semi-solids

Direct desorption

Probes | Bars / Cartridges

Sorptive extraction

Canisters | Bags | On-line

'Whole air'

These methods use a single stage of sorbent trapping, and so tend to be used when analyte concentrations are higher.

Image credits: 1 SP Technical Research Institute of Sweden. 2 Owlstone Medical. 3 Equipco.

Pumped sampling

BASIC OPERATION

- Air is pulled through a sorbent tube using a pump
- Single-bed or multi-bed tubes can be used
- A constant flow of gas into the vessel aids release of analytes onto a sorbent tube

TYPICAL ANALYTES MONITORED

- C_3 to C_{44}

PROS AND CONS

+ Sampling is quick (minutes to hours)
+ A wide range can be monitored in one run
– Sampling conditions need to be optimised so that the most volatile compounds don't 'break through' the sorbent bed

COMMONLY USED FOR

- All types of ambient air monitoring

TOP TIP

A range of tubes are available ready-optimised for key applications

Return to Sampling Options

Passive sampling

BASIC OPERATION

- Analytes migrate across an air gap onto a bed of sorbent
- Only single-bed tubes can be used

PROS AND CONS

+ Easy to deploy
– A limited range can be monitored in one run
– Relatively slow sampling

TYPICAL ANALYTES MONITORED

- C_3 to C_{44}

COMMONLY USED FOR

- Factory fenceline monitoring
- Personal monitoring

TOP TIP

Quantitation is easy if you know the uptake rate – and these are available for sampling of a large number of compounds onto common sorbents using industry-standard 3½" × ¼" tubes

Return to Sampling Options

Canister sampling

BASIC OPERATION

- Air is allowed to flow at a controlled rate into an evacuated canister
- The air sample is then transferred to a sorbent-packed focusing trap

PROS AND CONS

+ Ideal for ultra-volatiles
– Not suitable for SVOCs
– Single-stage desorption restricts detection limits
– Bulky to transport

TYPICAL ANALYTES MONITORED

- Freons
- C_2 hydrocarbons up to C_{10}

COMMONLY USED FOR

- Ambient air monitoring for volatile ‘air toxics’
- Atmospheric research

TOP TIP

In-line water removal devices greatly improve analytical performance

Return to Sampling Options

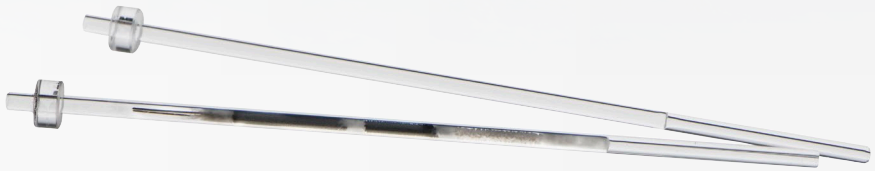
On-line monitoring

BASIC OPERATION

- Air is pulled directly into a sorbent-packed focusing trap

PROS AND CONS

+ Ideal for ultra-volatiles
– Not suitable for SVOCs
– Single-stage desorption restricts detection limits



TYPICAL ANALYTES MONITORED

- Freons
- C_2 hydrocarbons up to C_{14}

COMMONLY USED FOR

- Continuous monitoring for source apportionment
- Rapid detection of hazardous compounds
- Atmospheric research

TOP TIP

Some systems allow continuous monitoring (using two traps working alternately)

Return to Sampling Options

Dynamic headspace sampling

BASIC OPERATION

- The sample is placed in a headspace vessel – options include environmental chambers (~1 m^3), microchambers (44 or 114 cm^3), sampling bags and cuvettes
- A constant flow of gas into the vessel aids release of analytes onto a sorbent tube

PROS AND CONS

+ Highly sensitive
+ Easily adapted to the requirements of the application
– Standard methods for environmental chambers are often time-consuming

TYPICAL ANALYTES MONITORED

- Generally C_3 to C_{20}

COMMONLY USED FOR

- Product certification/compliance
- Quality control
- Rapid product profiling for R&D

TOP TIP

Microchambers can be fitted with accessories for surface and permeation testing

Return to Sampling Options

Sorptive extraction

BASIC OPERATION

A polymer-based sorbent is:

- Placed in a liquid sample *(immersive sorptive extraction)*
- *Suspended above it (headspace sorptive extraction)*
- The sorbent is then placed in an empty TD tube and desorbed

TYPICAL ANALYTES MONITORED

- Generally C_3 to C_{30}

PROS AND CONS

+ Suitable solids and liquids
+ Considerably easier than solvent extraction
– Analytes need to be relatively concentrated

COMMONLY USED FOR

- Aroma profiling of foods and beverages

TOP TIP

Immersive sampling is better than headspace sampling for less volatile compounds

Return to Sampling Options

Direct desorption

BASIC OPERATION

- A small sample is heated in an empty TD tube

PROS AND CONS

+ Quick and easy
+ Suitable for solids and semi-solids
– Only applicable to relatively homogeneous samples

TYPICAL ANALYTES MONITORED

- Generally C_3 to C_{30}

COMMONLY USED FOR

- Analysis of solids, pastes and resins
- Rapid profiling of polymers
- Analysis of car trim

TOP TIP

Glass tubes make it easy to assess the state of the sample

Return to Sampling Options

Breath sampling

BASIC OPERATION

- Breath is captured onto a sorbent tube

PROS AND CONS

+ Less invasive than sampling bodily fluid
+ Sampling doesn't require medical professionals
– Natural variability in breath makes analysis challenging

TYPICAL ANALYTES MONITORED

- Generally C_4 to C_{20}

COMMONLY USED FOR

- Occupational health monitoring
- Research into disease diagnosis

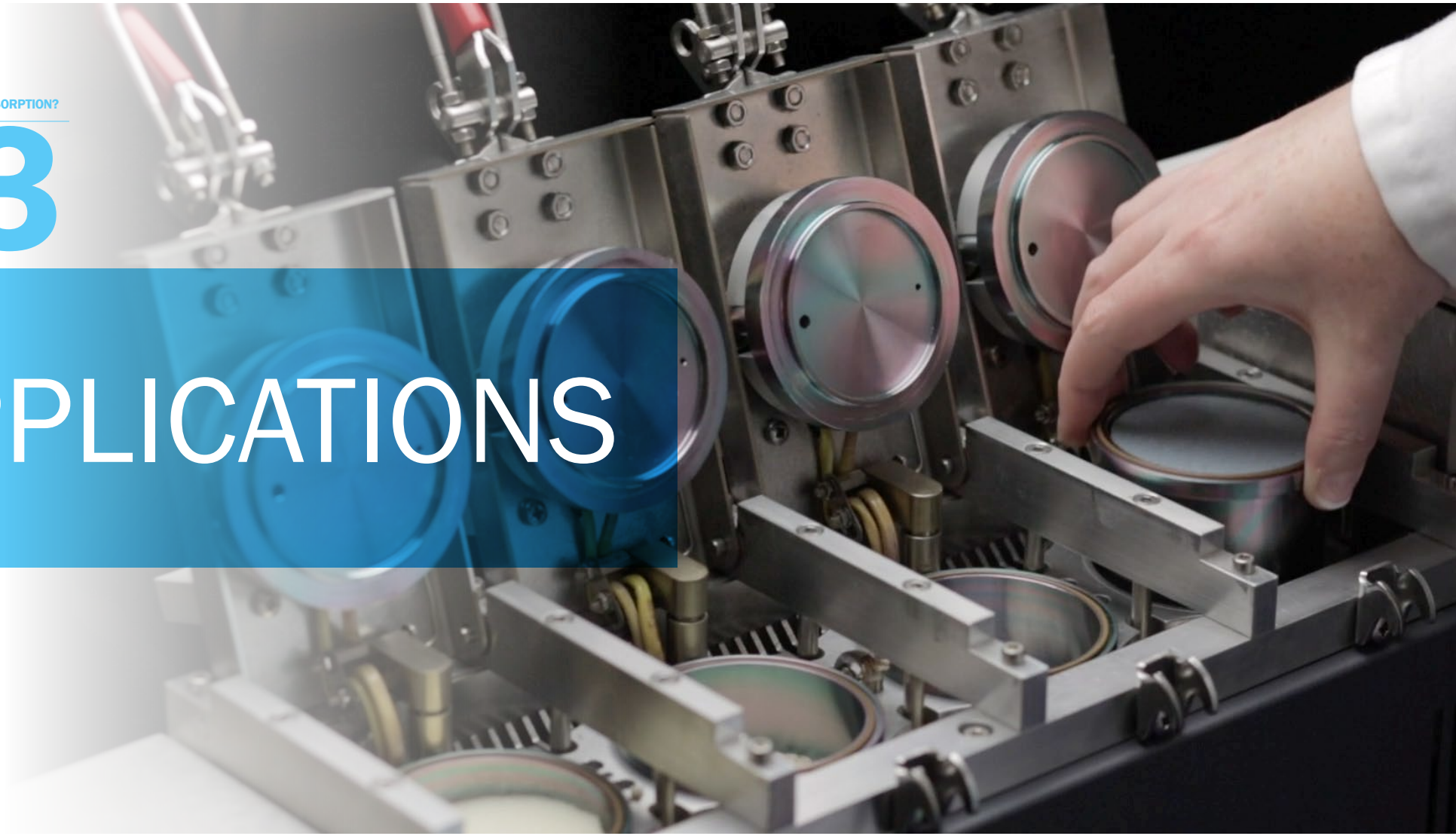
TOP TIP

Devices that capture the last portion of air from the lungs provide the most useful results

Return to Sampling Options

03

APPLICATIONS



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Why do analysts use TD?

> The need for advanced analytical techniques like thermal desorption is driven by a number of factors.

Regulations:

Many national and international regulations cite standard methods that rely on TD to achieve the necessary analytical performance.

Emerging products:

Public concern over the health impacts of everyday products – such as fragranced goods – demands rigorous, reliable information on the chemicals they contain. TD is a valuable item in the analyst's toolkit for investigating such products.

Lowering limit levels:

Our understanding of the long-term impacts of chemicals on our health and the environment is constantly improving. Acceptable levels of these chemicals are falling as a result, increasing the need for highly sensitive analytical techniques like TD.

Quality control:

Manufacturers are continually looking for ways to improve their products... for example, by improving consistency, or understanding the causes of off-odours that give rise to customer complaints.

Brand comparison:

The repeatability of thermal desorption and associated sampling techniques make it valuable for carrying out rigorous product comparisons.

The versatility of thermal desorption makes it applicable to a wide range of areas.

For examples of TD in action, download one of our Application Guides.



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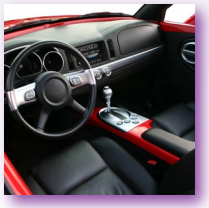
Thermal Desorption Applications Guide:
Environmental monitoring

A comprehensive guide to monitoring chemicals in the environment and the workplace using thermal desorption

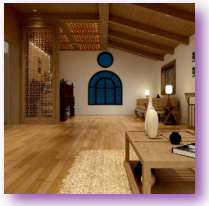
Ambient air monitoring



Automotive studies

Soil gas and water monitoring

Human health



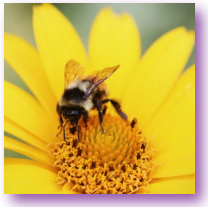
Consumer environmental health

Food and drink

Forensics

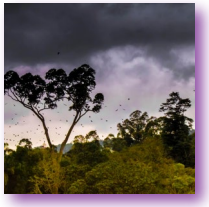
Fragrance and odour profiling

Industrial air monitoring and occupational health



Chemical ecology

Defence and homeland security



Ecosystems and the environment

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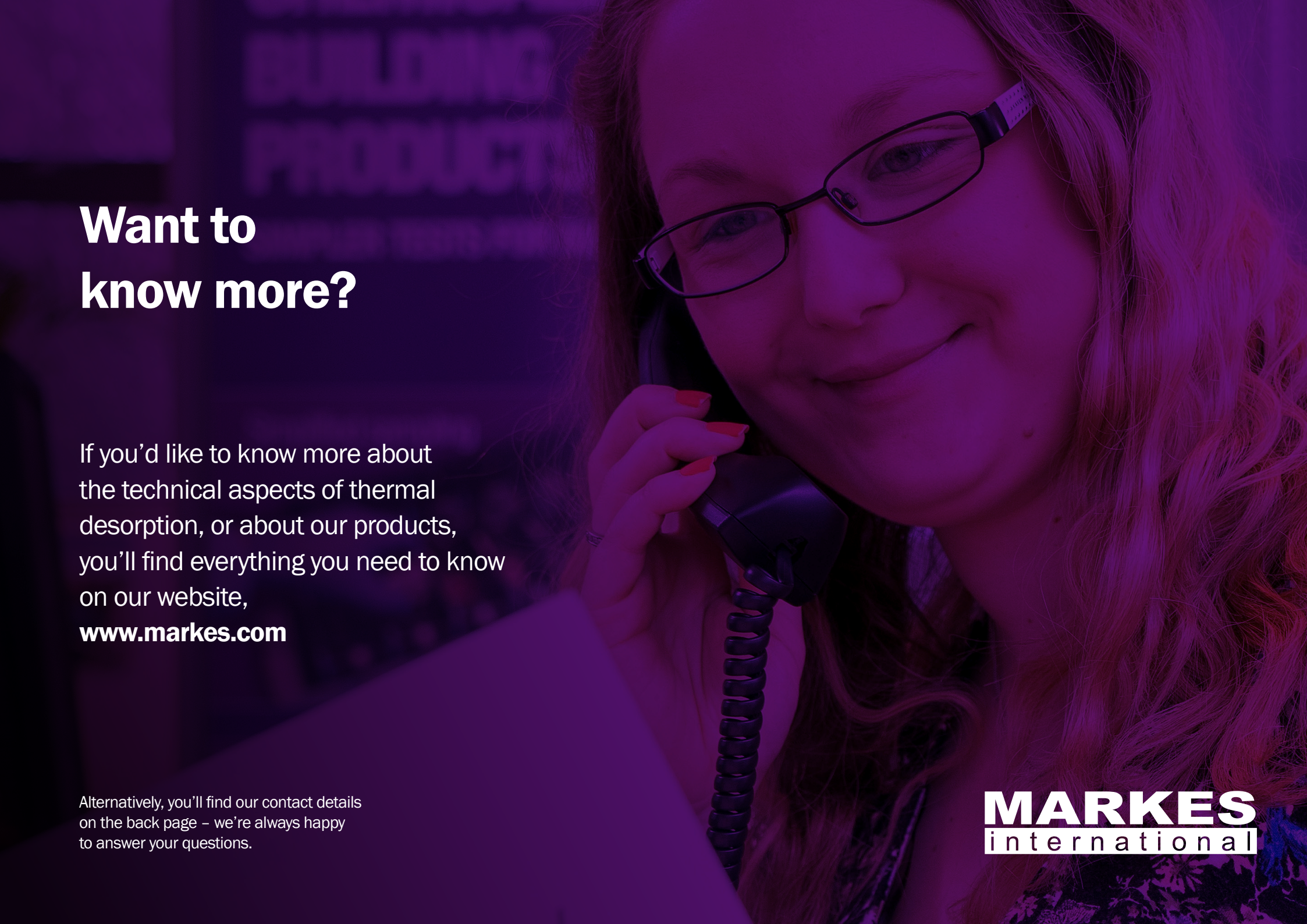
Our customers

Companies and organisations around the world use Markes' equipment for product quality control and research.

We'd better point out that although we supply all the companies listed on this page, we're not indicating that they've provided an actual endorsement or recommendation. We like to think they might though!



Want to know more?

If you'd like to know more about the technical aspects of thermal desorption, or about our products, you'll find everything you need to know on our website,
www.markes.com

Alternatively, you'll find our contact details on the back page – we're always happy to answer your questions.

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Since 1997 20 YEARS ANNIVERSARY

Markes International

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

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

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

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

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