

Thermal Desorption Applications Guide:

Environmental monitoring

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







Introduction

Environmental monitoring

Monitoring organic chemicals in the air – whether they arise from anthropogenic or natural sources – is vital for assessing everything from their impact on human health to their role in global climate.

In this Applications Guide, we describe how thermal desorption (TD) can be used to monitor compounds in a wide range of scenarios across the field of environmental monitoring.

The main sampling techniques covered include:

- Passive (diffusive) sampling of air on to sorbent tubes.
- Pumped (active) sampling of air on to sorbent tubes.
- On-line monitoring of air/gas streams.
- Pre-concentration of air samples collected in canisters.

For more information on any of the applications described, or to discuss how TD could benefit you, please contact our helpful and knowledgeable applications specialists at enquiries@markes.com, or by telephoning any of our regional offices (see back cover for details).

Throughout this Guide, this icon is used to indicate where you will find more details of the applications discussed (please note you will need to register with us to download our Application Notes, and may need to pay to download scientific journal papers).





What is thermal desorption?

Thermal desorption (TD) is a versatile pre-concentration technique for gas chromatography (GC) that is used to analyse volatile and semi-volatile organic compounds (VOCs and SVOCs) in a wide range of sample types.

By extracting organic vapours from a sample and concentrating them into a very small volume of carrier gas, TD maximises sensitivity for trace-level target compounds, helps to minimise interferences, and routinely allows analyte detection at the ppb level or below. It also greatly improves sample throughput, by allowing full automation of sample preparation, desorption/extraction, pre-concentration and GC injection.

TD can be used:

- **On its own** for example, for analysis of sorbent tubes or traps, or for direct desorption of materials.
- In combination with other GC sampling techniques, such as headspace or sorptive extraction, to enhance their performance.

TD is applied to a wide range of situations, comprehensively covered by our set of Applications Guides. The analyses described within have all been carried out on Markes' single-tube and 100-tube thermal desorbers (and related accessories) – as indicated in the "Typical analytical conditions" sections.

Launched in May 2016, Markes' new 'xr' series of instruments offer performance at least equal to earlier models, with the additional benefits of extended re-collection capability, wider analyte range, and improved reliability. See page 60 and our website for more details.



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



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

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Regulations and standard methods

SIGNATURE



The regulatory environment

A number of national and international regulations relating to volatile organics in the environment have been developed, mainly in response to concern over hazardous anthropogenic compounds in the air. Four groups are particularly important:









- Halocarbons: Some low-boiling compounds containing fluorine, chlorine and bromine are greenhouse gases or stratospheric ozone depletants, and are the subject of international agreements to limit their use.
- 'Ozone precursors' are highly volatile hydrocarbons that contribute to the formation of low-level ozone in urban areas.
- 'Air toxics' (also known as 'hazardous air pollutants') are a major contributor to poor air quality. Benzene, toluene, ethylbenzene and the xylenes (collectively known as BTEX) are often the focus of these monitoring efforts.
- Semi-volatile organic compounds (SVOCs) long been the subject of soil/water regulations. There is now growing realisation that one group, the polycyclic aromatic hydrocarbons (PAHs), can have negative health effects even at the low levels present in ambient air.

Key national regulations relating to VOCs

International:

The Montreal Protocol operates to reduce levels of ozone-depleting chlorofluorocarbons (CFCs), and it is now due to be extended to include the phase-out of hydrofluorocarbon (HFC) greenhouse gases.

USA:

- The 1990 Clean Air Act and subsequent regulations require states to set up Photochemical Assessment Monitoring Stations (PAMS) in places where ozone levels are high.
- Amended Federal Regulation CFR 40 lays down a requirement for monitoring of benzene at refinery fencelines.

EU:

- The Air Quality Framework Directive (96/62/EC) and its 'daughter directives' describe how air quality should be assessed, and define limit levels and monitoring requirements relating to certain groups of compounds, including ozone precursors and PAHs.
- The 'Clean Air Programme for Europe', currently under consideration, includes stricter national emissions ceilings for VOCs, amongst a wide range of other measures.

China:

The 13th Five-Year Plan specifies the need for greater control of VOC emissions into the atmosphere from industry, and a 10% reduction of target VOCs has been proposed.



Overview of methodologies

The various standard methods developed to monitor VOCs in the environment are all compatible with TD, and fall into two broad categories (1 and 2), with five commonly used sampling approaches (A-E). These are described in more detail on the following pages.







1 Air monitoring



Pumped (active) sampling is a versatile option for air monitoring. Up to three sorbents can be used within a single tube, allowing compounds from C_2 to C_{44} (and reactive species) to be monitored. Sample volumes typically range from 1–100 L for VOCs, and up to 500 L for SVOCs.



See pages 12, 13, 22, 30, 33, 34, 38, 40, 42, 44, 48 and 56 for examples of pumped sampling.

Key standard methods applicable to pumped sampling:

- ISO 16017-1
- ASTM 6196
- US EPA Method TO-17
- Chinese EPA Method HJ 644
- Chinese EPA Method HJ 734

- EN 14662-1
- CEN/TS 13649
- NIOSH Method 2549
- UK Environment Agency Method LFTGN 04
- For a full listing of all standard methods for speciated monitoring of vapour-phase organic chemicals in air, see Application Note 003.

Passive sampling onto sorbent tubes

Passive (diffusive) sampling is a convenient, quantitative and low-cost method for monitoring compounds from C_2 to C_{44} (including reactive species).

Tubes for passive sampling are packed with a single sorbent, and although uptake of analytes is relatively low, this makes it applicable to a variety of air monitoring applications.

For example, passive tubes can be used in environments with a wide range of air turnover rates, or when a longer-term average concentration is needed. They are particularly well-suited to both short-term (0.5–12-hour) personal exposure monitoring and longer-term (1–4-week) monitoring of ambient air.

See pages 24, 37, 42, 49, 51, 52 and 57 for examples of passive sampling.

Key standard methods applicable to passive sampling:

- US EPA Method 325
- ASTM 6196

EN 14662-4

US EPA Method TO-17

ISO 16017-2



1 Air monitoring (continued)

C Ca

Canisters and bags

Canister sampling remains popular for monitoring C_2 to C_{14} , including a small number of non-polar compounds that are too volatile to be quantitatively retained by sorbent tubes at ambient temperatures – such as some very-low-boiling hydrocarbons and freons.



Canister-sampled VOCs are transferred directly onto a sorbent-packed focusing trap,

which is then rapidly heated to transfer the analytes to the GC column.

Canisters or sampling bags are a useful alternative to sorbent tubes, although adsorption on the interior surfaces of the canister (or partitioning into any water present) can compromise release of less-volatile compounds.

See pages 14, 18 and 26 for examples of canister sampling.

Key standard method applicable to canister/bag sampling:

US EPA Method TO-15 (which supersedes TO-14a)



On-line monitoring

Like canisters, on-line monitoring is applicable to the analysis of C_2 to C_{14} , in situations where sorbent tubes cannot quantitatively retain the compounds of interest. In addition, it is a valuable approach where round-the-clock monitoring is desired.



Samples are introduced directly onto a sorbent-packed focusing trap, which is then heated to transfer the analytes to the GC column.

On-line monitoring is often used for volatile hydrocarbons known as 'ozone precursors' – as carried out by the US network of Photochemical Assessment Monitoring Stations (PAMS) – or for sulfur compounds. This approach is now attracting significant interest in China, not just for the most volatile analytes but also for semi-volatile PAHs.



See pages 15, 16, 18, 25, 28 and 50 for examples of on-line monitoring.

Key standard method applicable to on-line monitoring:

US EPA PAMS Method



2 Water monitoring

E Sorptive extraction

Headspace and immersive sorptive extraction using probes are powerful approaches to sampling VOCs and SVOCs from water, because the large volume of PDMS sorbent means that sample capacity is much higher than for solid-phase micro-extraction (SPME).

These techniques also eliminate the labourintensive sample preparation associated with liquid-extraction methods, and are easily interfaced with thermal desorption, allowing the analyst to benefit from their high sensitivity, analyte range and ability to re-collect split samples.

See page 58 for an example of sorptive extraction.







Ambient air monitoring



E END

'Air toxics' – Sorbent tubes

Pumped-tube sampling in accordance with US EPA Method TO-17

Volatile organic 'air toxics' or 'hazardous air pollutants' (HAPs) are monitored in industrial and urban environments as a measure of air quality. These compounds are most effectively monitored using pumped sampling onto sorbent tubes, and US EPA Method TO-17 is the most widely-used protocol.

Markes' cryogen-free TD technology meets all the requirements of Method TO-17. The use of multi-bed sorbent tubes ensures reliable monitoring of compounds over a wide range of polarities and volatilities, while leak-checking and internal standard addition further enhance the reliability of results.

Typical analytical conditions:

- Sample: 1 mL of a vapour-phase 'air toxics' standard in nitrogen (1 ppm per component), loaded onto a sorbent tube.
- *Equivalent to...* Pumped (active) sampling: 1 L air containing 1 ppb per component, at 50 mL/min for 20 min.
- TD (UNITY or TD100): Tube (Universal): Desorbed at 280°C (5 min). Trap (Air toxics): Analytes trapped at 25°C, desorbed at 320°C (3 min). Split ratio: Splitless. Analysis: GC-MS.



Excellent chromatographic separation and peak shape is obtained for all 62 components of this 'air toxics' mix. Minimum detection limits were found to be below 0.1 ppb for all components. For the peak listing see Application Note 086.

Application Note 086

'Air toxics' – Sorbent tubes

Pumped sampling using Chinese EPA Method HJ 644



Method HJ 644 aims to protect human health and the environment by stipulating a procedure for the monitoring of hazardous air pollutants. The method closely mirrors US EPA Method TO-17 (see page 12) – the 34 analytes listed are all included in TO-17, and the suggested column and run conditions only differ slightly.

As a result of these similarities, the sampling and analytical equipment and protocols used for TO-17 can also be applied to HJ 644. As for TO-17, Markes' TD equipment also meets certain specific requirements of HJ 644 – namely, two-stage desorption, fast focusing-trap heating rate, and a uniformly-heated inert flow path. The use of optimised sampling tubes and focusing traps, splitting & re-collection capabilities and dry-purging further enhance the ability of Markes' systems to efficiently analyse samples using this method.

Typical analytical conditions:

Sample: 20 mL of a vapour-phase 'air toxics' standard in nitrogen (100 ppb per component), loaded onto a sorbent tube.

Equivalent to... Pumped (active) sampling: 1 L air at 2 ppb per component.

TD (UNITY or TD100): Tube (Universal): Desorbed at 325°C (3 min). Trap (Air toxics): Analytes trapped at 35°C, desorbed at 325°C (5 min). Split ratio: Outlet: 5:1.

Analysis: GC-MS.

Application Note 116 (available in Chinese only)

 1,1-Dichloroethene 1,1,2-Trichloro-1,2,2- trifluoromethane Allyl chloride Dichloromethane 1,1-Dichloroethane cis-1,2-Dichloroethane 1,1,1-Trichloroethane 2arbon tetrachloride 1,2-Dichloroethane 	 12 Trichloroethene 1,2-Dichloropropane 14 <i>cis</i>-1,3-Dichloropropene 15 Toluene 16 <i>trans</i>-1,3-Dichloropropene 1,1,2-Trichloroethane 18 Tetrachloroethene 19,2-Dibromoethane 20 Chlorobenzene 21 Ethylbenzene 22 <i>m</i>-/<i>p</i>-Xylene 23 <i>o</i>-Xylene 	 24 Styrene 25 1,1,2,2-Tetrachloroethane 26 4-Ethyltoluene 27 1,3,5-Trimethylbenzene 28 1,2,4-Trimethylbenzene 30 1,4-Dichlorobenzene 31 Benzyl chloride 32 1,2-Dichlorobenzene 33 1,2,4-Trichlorobenzene 34 Hexachlorobutadiene
(store of the second s	22 18 20 16 7 9 10 12 14 19 6 8 Time (min)	$\begin{array}{c} 34 \\ 29^{30} \\ 32 \\ 24 \\ 2627 \\ 25 \\ 31 \\ 10 \\ 12 \end{array}$

TD-GC-MS allows analysis of all 34 compounds listed in Chinese **EPA Method HJ 644**, with excellent RSDs of 4.6–7.8% (n = 7). Using this method, limits of detection varied from 0.056 ppb for tetrachloromethane to 0.150 ppb for *m-/p*-xylene.

'Air toxics' - Canisters

'Grab'-sampling compliant with Method TO-15

Canister sampling of volatile air pollutants in accordance with US EPA Method TO-15 is popular with many analysts as an alternative to pumped-tube sampling. However, pre-concentration is still required to focus analytes and selectively eliminate bulk constituents such as oxygen, nitrogen and water, which would otherwise negatively affect analytical performance.

Markes' CIA Advantage has been designed to comply with Method TO-15 for canister analysis, while overcoming the limitations of traditional cryogen-cooled technology. In addition, electronic splitting capability and the option of small-volume gas-loop sampling enhance compatibility with high-concentration samples, eliminating the need for time-consuming sample preparation steps such as canister dilution.

Typical analytical conditions:

- Sample: 1 ppm 62-component vapour-phase TO-15 standard.
- Canister sampling (CIA Advantage): 1 mL.
- *Equivalent to...* 1 L of air containing 1 ppb per component.
- TD (CIA Advantage): Trap (Air toxics): Analytes trapped at 25°C, desorbed at 280°C (3 min). Split ratio: Splitless.

Analysis: GC-MS.



Application Note 081





The effectiveness of simple 'grab' sampling using canisters is illustrated by this analysis of an 'air toxics' mix. This level of performance can now be achieved with highly humid canister samples, using the Kori-xr system (see page 18).

Ozone precursors – On-line



Monitoring urban air pollutants

Volatile hydrocarbons known as 'ozone precursors' contribute to the formation of ground-level ozone, a major constituent of smog. Laboratories in the USA monitor these compounds using on-line analysis (see page 16), and this approach is now attracting attention in China too. In such studies, automated systems that can operate remotely are needed in order to carry out pollutant mapping, and monitor the effects of industrial emissions, traffic density and weather conditions.

Markes' TD instruments overcome the challenge of remote operation by using a modern software interface, and an electrically-cooled focusing trap that dispenses with the need for cryogen. They also allow a wide range of compounds to be analysed in a single run, including sulfur species and oxygenates as well as ozone precursors, while providing a number of options for effective water management.

Typical analytical conditions:

Sample: Calibration standard.

- *Equivalent to...* On-line sampling (Air Server): 500 mL air containing ~4 ppb per component, at 50 mL/min for 10 min.
- TD (UNITY): Trap (Ozone precursors): Analytes trapped at $-30\,^\circ\text{C},$ desorbed at $325\,^\circ\text{C}$ (5 min). Split ratio: Splitless.
- Analysis: GC–MS, or GC–dual FID using a two-column Deans switch system, as shown here.



Application Note 016



The efficient operation of Markes' thermal desorbers provides limits of detection (LODs) well below the 0.5 ppb required, for ozone precursors ranging in volatility from acetylene to trimethylbenzene. A dual-column setup was used here to provide the high degree of separation needed for FID detection – but single-column systems are now appearing with the rising use of GC-MS in mobile laboratories.

Ozone precursors – On-line

Monitoring volatile hydrocarbons in humid ambient air using GC-MS

Analysis of 'ozone precursors' by the US network of Photochemical Assessment Monitoring Stations (PAMS) has long been carried out using on-line thermal desorption and GC-dual FID using a two-column Deans switch system (see page 15). The addition of further compounds of interest to the list of suggested analytes, as well as the desire to identify unknown compounds, has led to the need to use MS detection. However, the high humidity of the environments sampled causes concern, and traditional approaches to water management compromise the analysis of certain compound classes.

The Kori-xr water management device (see page 63) automatically removes water vapour before it reaches the GC column without the need for Nafion[™] dryers or cryogenic cooling, improving sample collection and optimising the analytical workflow.

Typical analytical conditions:

Sample: Ozone precursor standard blended with interferents. TD (Kori-xr–UNITY–Air Server): Trap (Ozone precursors): Analytes trapped at –30°C, desorbed at 270 °C (5 min). Split ratio: Splitless.

Analysis: GC–MS, using a TraceGOLD[™] Bond Q column (30 m × 0.32 mm × 10 μm).





Ozone precursors – On-line

Reliable unattended monitoring of pollutants over the course of a day

Monitoring low-level volatile and ultra-volatile pollutants as they change with time demands both analytical excellence for these challenging analytes, and robust automation to eliminate the need for continuous human presence.

UNITY-Air Server systems meet these needs by offering both efficient splitless analysis and sophisticated sequence programming for automated operation and calibration. The start of a monitoring sequence can be programmed for a specific date and time, and the period between each sampling cycle can be fixed. This ensures reliable round-the-clock monitoring without user intervention.

Typical analytical conditions:

Sample: Urban air.

On-line sampling (Air Server): 200-1000 mL air. at 10-25 mL/ min for 20-40 min.

TD (UNITY): Trap (Ozone precursors): Analytes trapped at -30°C, desorbed at 300°C (3 min). Split ratio: Splitless. Analysis: GC-FID.

The narrow focusing traps used in Markes' instruments allow an entire sample to be trapped and released without compromising chromatographic quality, giving increased sensitivity for low-concentration compounds.





Application Note 016

Topic continued from previous pages



Levels of key pollutants rise substantially during the evening 'rush-hour' in this set of ambient air analyses, collected and analysed using the UNITY-Air Server with GC-FID.

Monitoring humid air streams

Options for canister and on-line monitoring

The analytical interference caused by high levels of water in air streams can shift retention times, alter split ratios and damage the column and detector. However, removing moisture from canister and on-line air streams can be difficult, because at least one strong (typically hydrophilic) sorbent is usually required in the focusing trap. In addition, the need to achieve low detection limits using a single focusing step precludes the use of small sample volumes or a high split ratio.

To overcome this problem, there are three options available that can help avoid water entering the GC when carrying out canister and on-line analysis (see page 63 for more on each of these):

- Using Markes' Kori-xr module to condense-out water in an empty trap, before it reaches the focusing trap. This approach does not cause compound loss, making it a versatile approach to water management.
- Using a **Nafion[™] dryer** to extract water from the air stream but note that monoterpenes and some polar compounds can also be lost.
- Using trap dry-purging, which has the advantage of not requiring additional hardware, but the disadvantage of being incompatible with C₂ hydrocarbons.

Typical analytical conditions:

Sample: 1 ppb vapour-phase TO-15 standard with 80% RH. Canister sampling (CIA *Advantage*): 500 mL. *Equivalent to...* On-line sampling (Air Server): 500 mL air containing ~1 ppb per component, at 50 mL/min for 10 min.

TD (Kori-xr-UNITY): Trap (Air toxics): Analytes trapped at -30°C, • desorbed at 300°C (3 min). Split ratio: 2.5:1.

Analysis: GC-MS.

The efficient (and cryogen-free) removal of water by Kori-xr permits lower temperatures to be used in the focusing trap without risk of ice formation, allowing quantitative retention of even the most volatile compounds on the thermal desorber.



Using Markes' Kori-xr to remove water from a humid air stream, before TD-GC-MS analysis, allows interference-free monitoring of polar compounds (•) that would not be possible using a Nafion dryer, as illustrated for this early-eluting segment of a US EPA Method TO-15 mix.



Monitoring humid air streams

Options for tube-based sampling

Monitoring humid air using sorbent tubes can be a challenge because high levels of moisture can reduce breakthrough volumes by up to an order of magnitude, while analytical interference can shift retention times, alter split ratios and damage the analytical column and detector.

Tube-based sampling and analysis using Markes' TD systems offers several options to avoid water entering the GC. These include:

- Avoiding use of the most hydrophilic **sorbents** where possible.
- Using low sample volumes and/or high split ratios to reduce the amount of water collected/trapped.
- A room-temperature 'dry-purge' of the sample tube and/or focusing trap – see page 63 for more on this option.

All three of these approaches were employed in the accompanying example.

Typical analytical conditions:

Sample: Landfill gas.

Grab-sampling (Easy-VOC): 100 mL.

TD (UNITY or TD100): Tube (Sulfur): Desorbed at 200°C (5 min) then 300°C (5 min). Trap (Sulfur): Analytes trapped at 30°C, desorbed at 220°C (5 min). Split ratio: Inlet 9:1, Outlet 18:1. Analysis: GC-MS.



Application Notes 026 and 047

The Easy-VOC allows multiple precise 50 mL and 100 mL samples to be collected onto sorbent tubes.





Topic continued from

Time (min)

The high humidity of a landfill gas sample does not compromise the detection of a wide range of analytes (including sulfur compounds), thanks to use of a relatively small gas volume and appropriate choice of TD settings.

MARKES

Abundance (× 10⁵ counts)

Monitoring semi-volatiles

Reliable analysis of hydrocarbons up to n-C₄₄

The vast majority of aliphatic hydrocarbons encountered in environmental monitoring scenarios have chain lengths below C_{30} . However, longer-chain hydrocarbons, with their very high boiling points and tendency to 'stick' in any cold spots, are widely used as a test of analytical system performance for semi-volatile organic compounds (SVOCs) in general.

With their short, inert, uniformly-heated flow paths, Markes' thermal desorbers offer the best available performance for a wide range of SVOCs, including semi-volatile hydrocarbons up to $n-C_{44}$, PAHs (pages 21–23), phthalates (page 53) and PCBs (page 54). All Markes' TD systems (manual and automated) are unique in being equipped with quantitative sample re-collection for repeat analysis and validation of analyte recovery.

Typical analytical conditions:

Sample: Hydrocarbon standard (40 pg per component), loaded onto a sorbent tube.

TD (UNITY or TD100): Tube (SVOC air): Desorbed at 300°C (15 min). Trap (General-purpose carbon): Analytes trapped at 25°C, desorbed at 350°C (10 min). Split ratio: Outlet 18:1.

Analysis: GC-MS.



Zero system carryover for high-boiling compounds on Markes' TD systems is demonstrated by two successive desorptions of the same tube containing a long-chain n-alkane standard.



Polycyclic aromatic hydrocarbons

Optimised sorbent-tube sampling of PAHs in air



Polycyclic aromatic hydrocarbons (PAHs) are harmful compounds formed as a result of the incomplete combustion of organic materials such as coal and gasoline. The limit levels for urban and workplace air are very low, and current methods based on solvent extraction are laborious and struggle to achieve detection at these concentrations.

Addressing these issues, Markes has developed a new sorbent tube dedicated to PAH analysis. By avoiding the need for solvent dilution, and by providing high-efficiency extraction and GC injection, TD offers outstanding sensitivity for these challenging analytes. In addition, high linear gas velocities and uniform TD flow path temperatures ensure quantitative recovery across the full range of target 2–6-ring PAHs.

Typical analytical conditions:

Sample: PAH standard (10 ng per component), loaded onto a sorbent tube. *Equivalent to...* Pumped (active) sampling: 100 L air at 0.1 µg/m³ per component. For phenanthrene this would be a concentration of 14 ppt.
TD (UNITY or TD100): Tube (PAH): Desorbed at 350°C (12 min). Trap (PAH): Analytes trapped at 25°C, desorbed at 380°C (8 min). Split ratio: Outlet 11:1.
Analysis: GC-MS.

Application Note 115

http://dx.doi.org/10.1016/j.atmosenv.2013.07.059

B. Lazarov *et al.*, Optimisation steps of an innovative air sampling method for semi volatile organic compounds, *Atmospheric Environment*, 2013, 79: 780–786.





Polycyclic aromatic hydrocarbons

Simple and reliable quantitation of ppt-level PAHs in air using sorbent-tube sampling

Monitoring polycyclic aromatic hydrocarbons (PAHs) in air has traditionally been carried out using very large sampling volumes (typically 1000+ litres) and labour-intensive solvent-extraction and evaporation procedures.

TD is far more easily automated than solvent extraction, and together with its enhanced sensitivity allows smaller sampling volumes to be used. The dedicated PAH sorbent tube developed by Markes, analysed using optimised TD procedures, offers excellent performance for these challenging analytes, as illustrated by this analysis of urban air.

Typical analytical conditions:

nternatio

Sample: Urban air collected in Shanghai, P.R. China. Pumped (active) sampling: 180 L, at 250 mL/min for 12 h. TD (UNITY or TD100): Tube (PAH): Desorbed at 350°C (12 min). Trap (PAH): Analytes trapped at 25°C, desorbed at 380°C (8 min). Split ratio: Outlet 11:1. Analysis: GC-MS.



Using a sample volume far lower than that required by traditional monitoring protocols, several ppt-level PAHs were detected in this complex urban air sample.





Polycyclic aromatic hydrocarbons

Analysis of high-boiling particulatebound PAHs by direct desorption

The low volatilities of the heavier polycyclic aromatic hydrocarbons (PAHs) mean that in ambient air, they predominantly occur bound to particulate matter. However, traditional solvent-extraction protocols for analysis of particulates are labour-intensive and run the risk of introducing contaminants.



TD offers a way round this problem by allowing PAHs to be released from a filter, simply by heating it to transfer the vapours to the thermal desorber. Such particulate analyses can provide data complementing the sampling of PAHs in air using sorbent tubes (see previous pages).

Typical analytical conditions:

- Sample: 4 cm long × 4 mm wide section of quartz filter (cut from a larger piece used to collect particulates from a diesel exhaust), placed in an empty TD tube.
- TD (UNITY or TD100): Sample: Desorbed at 300°C (15 min). Trap (highboilers): Analytes trapped at 30°C, desorbed at 320°C (5 min). Split ratio: Inlet 3: 1, Outlet 134: 1. Note that this application requires scrupulous and regular routine maintenance to overcome the deposition of non-volatiles that would otherwise impact system performance over time. Analysis: GC-MS.



Application Note 097



Despite the extreme complexity of this exhaust particulate sample, TD-GC-MS analysis provides the sharp peaks needed to confidently identify PAHs spanning the full volatility range.

Mapping environmental pollutants

Simplifying data handling for large-scale diffusive monitoring campaigns

Accurate mapping of pollution levels across urban centres requires a large number of sampling points. Key considerations in such campaigns are cost, the ease of sampler deployment, and the ability to accurately capture and transcribe the data collected.

Diffusive samplers are low-cost and easy to deploy, facilitating such large-scale campaigns. In addition, Markes' unique RFID TubeTAG system eliminates transcription errors and enhances traceability – see page 64.

Typical analytical conditions:

Sample: Ambient air near Rouen, France.
Passive (diffusive) sampling: 7-14 days.
TD (UNITY or TD100): Tube (Graphitised carbon black): Desorbed at 320°C (5-10 min). Trap (EPA 325): Analytes trapped at 30°C, desorbed at 320°C (5 min). Split ratio: Outlet ~20:1.
Analysis: GC-FID or GC-MS.

All Markes' sampling tubes are etched with a unique serial number in numerical and barcode format for ease of identification.









Mapping benzene concentrations in this part of northern France over five days involved the deployment of over 90 diffusive samplers, and showed that the highest levels are associated with the more heavily built-up areas (yellow dots).

Markes' portable TAG^{SCRIBE} unit enables tube and sample information to be associated with a tagged tube in the field.





VOC and SVOC time-profiling

Continuous monitoring of hazardous air pollutants



Increasing concerns over the harmful effect of urban air pollutants on human health means there is a need to understand daily variations in VOC and SVOC levels, and to establish links between high pollution levels and possible emission sources. However, both these tasks require highly time-resolved data, and no gaps due to instrument downtime.

Markes' TT24-7 provides continuous monitoring of volatile and semi-volatile organic compounds, with its reciprocating dual traps ensuring no 'blind spots' in data collection. Furthermore, quantitative trapping and compatibility with a wide range of sampling flows offers high sensitivity with shorter cycle times than other on-line air monitoring systems.

Typical analytical conditions:

Sample: Air at a light-industrial location in the UK. On-line sampling: 1.5 L, sampled at 50 mL/min every ~30 min. TD (TT24-7): Traps (Ozone precursors): Analytes trapped at -30°C, desorbed at 325°C (5 min). Split ratio: Outlet 2.67:1. Analysis: GC-FID.

See page 17 for an example of using the UNITY-Air Server for discontinuous time-profiling of air pollutants.



Application Note 106



Complementing the results of longer-term passive sampling, near-realtime monitoring using on-line systems provides detailed data on pollutant concentrations as they vary over the course of a day. Note the ability of the TT24-7 to detect low or sub-ppb analytes, demonstrating its exceptional sensitivity even with conventional FID detection.

Low-concentration environments

Maximising sensitivity for tube or canister sampling

The very low concentrations of air pollutants present in rural environments or remote locations present a considerable challenge for the analyst, because of the difficulty in achieving good chromatography when running splitless samples.

Whether sampled using canisters or sorbent tubes, the efficiency of trap heating in Markes' TD instruments provides optimum desorption efficiency even under low-flow splitless conditions. This ensures excellent peak shape and the best possible detection limits for trace-level compounds.

Typical analytical conditions:

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Sample: Rural air.

Canister sampling (CIA Advantage): 1 L, at 50 mL/min for 20 min.

TD (CIA Advantage): Trap (Air toxics): Analytes trapped at 25°C, desorbed at 320°C (3 min). Split ratio: Splitless. Analysis: GC–MS.



Maximum sensitivity is achieved for this canister sample of rural air, analysed using the CIA *Advantage* and TD–GC–MS. Despite the splitless operation, there is no reduction in the quality of the peak shape – as exemplifed by the extracted-ion chromatograms for isopropanol and toluene.



Atmospheric research

On-line or canister-based monitoring of ultra-volatile greenhouse gases and ozone-depleting substances

Many halocarbons are potent greenhouse gases and/or ozone depletants, making them of considerable importance to atmospheric chemists. However, the extreme volatility of some of these compounds – especially the perfluorocarbons – makes them difficult to trap and measure at the very low levels required.

Markes' UNITY-Air Server is uniquely well-suited to monitoring these compounds on-line, because of its cryogen-free trap cooling and efficient splitless desorption. The CIA *Advantage* offers the same performance for off-line canister-based sampling of these challenging compounds.

Typical analytical conditions:

Sample: Gas standard (100 ppb per component).

On-line sampling (Air Server) or Canister/bag sampling (CIA Advantage): 25 mL, at 10 mL/min for 2.5 min.

TD (UNITY): Trap (Greenhouse gases): Analytes trapped at -30°C, desorbed at 300°C (3 min). Split ratio: Splitless. Analysis: GC-MS.



Efficient splitless desorption ensures that Markes' instruments are able to monitor ultra-volatile perfluorocarbons and tracer gases with high global warming potentials (GWPs). Detection limits are as low as 0.05 ppt for SF₆ and 0.2 ppt for C_2F_6 respectively.

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Application Notes 087 and 099

Atmospheric research

Understanding pollution events using continuous on-line monitoring

Wildfires can contributely significantly to atmospheric levels of VOCs and carbon-containing aerosols, which in turn can have major impacts upon atmospheric composition. Understanding processes such as long-range transport of these volatiles and 'washing-out' by precipitation is vital to improve representation of wildfires in atmospheric models.

On-line TD eliminates the inconvenience of canister storage for airborne sampling of atmospheric pollutants. In this example a Markes TT24-7 configured with GC–MS was installed in an aircraft and used to repeatedly sample volatiles from a wildfire plume, with the short cycle times allowing detailed profiles to be plotted.



Typical analytical conditions:

Sample: Air within a wildfire plume.

On-line sampling: 750 mL, at 300 mL/ min over 2.5 min, at intervals of ~6 min. TD (TT24-7): Traps (Tenax TA): Analytes trapped at 20°C. Analysis: GC–MS.



Clear enhancements in benzene, toluene and other air pollutants are demonstrated by near-real-time analysis of air collected during 'straight-and-level' runs in and out of a smoke plume from a major fire in Ontario, Canada, in July 2011.

Data reproduced courtesy of Professor Alastair Lewis, University of York, UK.



Biogenic emissions

Dynamic headspace for detecting VOCs released from plants

Biologically-derived VOCs (BVOCs) are primarily emitted by plants, fungi and microorganisms, and are studied by atmospheric chemists dealing with their impact on air quality and atmospheric processes in general. BVOCs primarily comprise isoprene, monoterpenoids and sesquiterpenoids, with many of these being highly reactive and prone to decomposition within the analytical system.

The inertness and adjustable flow-path temperature of Markes' TD systems ensures reliable analysis of a wide range of analytes, including reactive species such as monoterpenes. Validating recovery of these reactive species is made possible by Markes' splitting and re-collection technologies – see page 53.

Typical analytical conditions:

Sample: 5 g fresh basil leaves.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 50 mL/min for 20 min. Chamber temperature: 40°C.

> TD (UNITY or TD100): Tube (Tenax TA): Desorbed at 280°C (10 min). Trap (Tenax TA): Analytes trapped at 20°C, desorbed at 290°C (3 min). Split ratio: Inlet 2:1, Outlet: 16:1.

Analysis: GC-MS.



The fully passivated flow path of Markes' TD instruments, in conjunction with inert TD tubes and sorbents, enables detection of a large number of terpenoids in this analysis of leaf headspace.

Biogenic emissions

Assessing the effect of climate change on VOC emissions using pumped sampling

Many biologically-derived VOCs (BVOCs) are very reactive, and are oxidised in the upper atmosphere to heavier molecules. These condense to form secondary organic aerosols (SOAs), which can act as cloud condensation nuclei. Understanding how BVOC emissions from plants may change with rising temperature is therefore necessary to shed light on global climate feedback mechanisms.

A team at the University of Copenhagen has used *in situ* pumped sampling onto sorbent tubes, followed by TD–GC–MS analysis, to study the effect of different conditions upon BVOC emissions of Arctic heathland. For this application, the short growing season and the remote location demand large numbers of samplers, making sorbent tubes an ideal choice because of the long-term stability of analytes and the ease of tube transport.

Typical analytical conditions:

Sample: A polycarbonate container 20 cm high was placed over a 22 \times 22 cm plot of subarctic heath in Abisko, Sweden, with a temperature of 21–25°C.

Pumped sampling: 200 mL/min for 30 min (total volume 6 L).

TD (UNITY or TD100): Tube (Tenax TA-Carbograph 1TD): Desorbed at 250°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at -10°C, desorbed at 300°C (3 min). Split ratio: Outlet 10:1.

Analysis: GC-MS.

http://dx.doi.org/10.1111/gcb.12953

H. Valolahti, M. Kivimäenpää, P. Faubert, A. Michelsen and R. Rinnan, Climate change-induced vegetation change as a driver of increased subarctic biogenic volatile organic compound emissions, *Global Change Biology*, 2015, 21: 3478–3488.



emission rates of certain mono- and sesquiterpenes. Data and photograph reproduced courtesy of Professor Rikka Rinnan, University of Copenhagen, Denmark.

ucally tol depinence

3.Thulene

net 10

Monoterpenes

net 201

Comparison of four different treatments, sustained over a

period of 12 years, shows that warming, and to a lesser extent the addition of leaf litter, causes significant alterations in the

d.Selinene

Sesauiterpenes

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Emission rate (µg m⁻² h⁻¹)

4

3

2

Biogenic emissions

Secure, straightforward sampling of reactive VOCs

Simple and reliable VOC sampling procedures are paramount when monitoring in remote locations, as is the need to minimise the risk of sample integrity being accidentally compromised.



Researchers in the Amazon rainforest have addressed both these issues by using Markes' Easy-VOC with SafeLok tubes. This allowed convenient, rapid sampling of air from a 50-metre 'walk-up' tower (pictured), while eliminating risk of analyte loss or sample contamination during transport of tubes to the TD–GC–MS laboratory. The result of their studies was valuable information on the levels of highly-reactive ppt-level monoterpenes implicated in organic aerosol formation and as plant antioxidants.

Typical analytical conditions:

Sample: Air in the rainforest canopy, 60 km NNW of Manaus, Brazil. Grab-sampling (Easy-VOC): 1000 mL.

TD (UNITY or TD-100): Tube (SafeLok, Universal): Desorbed at 290°C (5 min) then 300°C (5 min). Trap (Air toxics): Analytes trapped at 0°C, desorbed at 290°C (3 min). Split ratio: Outlet 3:1.

Analysis: GC-MS.

http://dx.doi.org/10.1002/2014GL062573

A.B. Jardine et al., Highly reactive light-dependent monoterpenes in the Amazon, Geophysical Research Letters, 2015, 42: 1576–1583.



Speciation of monoterpenes in rainforest air by simple grab-sampling and TD–GC–MS analysis (SIM m/z 93) showed clear variation with canopy height, assisting the elucidation of environmental effects on VOC emissions. Data and photo reproduced courtesy of Dr Angela Jardine and Dr Kolby Jardine, Instituto Nacional de Pesquisas da Amazônia, Manaus, Brazil.



Industrial air monitoring and occupational health



Stack emissions

Pumped-tube analysis of high-concentration samples

Pollutants in stack gases need to be monitored for a variety of reasons, including compliance with environmental legislation. While most measurements of bulk organic vapours in stack gases are made using sensors, lower-level toxic organics require much greater sensitivity.

Grab-sampling or low-flow pumped sampling with TD analysis offers a quick, highly sensitive alternative to solvent extraction for the analysis of VOCs in stack gases (see page 34). A valuable feature of Markes' TD systems for this application is their ability to split high-concentration samples (>1000 ppm) during tube and trap desorption – allowing overall split ratios up to 125,000:1.



Typical analytical conditions:

Sample: Stack gas.

Pumped (active) sampling: 50–1000 mL, at ~15 mL/min for a few min to 1 h. Grab-sampling: 50–100 mL.

TD (UNITY or TD100): Tube (General-purpose hydrophobic or Graphitised carbon black): Desorbed at 280°C (5 min) for General-purpose hydrophobic, or 330°C (5 min) for Graphitised carbon black. Trap (as for tube): Analytes trapped at -30°C, desorbed at 300°C (3 min). Split ratio: Inlet: 10:1, Outlet 300:1. Analysis: GC-MS or GC-FID.



Application Note 077



Stack emissions

Key standard methods for monitoring industrial emissions

Since its publication in 2001, the key standard method for monitoring stack gases, EN 13649, had specified the collection of airborne vapours onto glass tubes packed with activated carbon, followed by extraction of analytes with carbon disulfide (CS₂) and analysis by GC–MS.

However, TD has now become far more popular than solvent extraction for analysis of airborne VOCs, because of its much greater sensitivity and avoidance of laborious sample preparation. As a result, in 2014 a revised edition of the method (CEN/TS 13649) was released that cites TD as an alternative to solvent extraction. A TD-based method is also cited in the new Chinese EPA Method HJ 734-2014.

Typical analytical conditions:

Sample: Air from the exhaust of a restaurant. Pumped (active) sampling: 300 mL. TD (UNITY or TD100): Tube (Universal):

Desorbed at 300°C (5 min). Trap (Air toxics): Analytes trapped at 25°C, desorbed at 250°C (3 min). Split ratio: Outlet 7.7:1. Use of an ambienttemperature trap-low reduces the risk of water interference that can occur in traps cooled to <5°C, as well as avoiding operational problems that may be caused by ice formation. Topic continued from previous page



Sampling onto TD tubes has numerous benefits over solvent extraction, and Markes' low-flow ACTI-VOC pump is specifically optimised for this purpose.





As well as improving sensitivity and facilitating automation, use of TD-based methods offers options for handling humid air streams, as illustrated by this analysis of air from a restaurant vent during a busy lunchtime period. A three-bed sorbent tube offered low water retention, while allowing quantitative analysis of compounds specified in CEN/TS 13649 (relevant compounds are listed).

Analysis: GC-MS.



Application Note 117 (available in Chinese only)



Application Note 119

MARKES international

Odorous industrial emissions

On-line monitoring of thermally labile thiols and sulfides

Sulfur compounds generated by industrial processes, being typically highly odorous, must be controlled to sub- or low-ppb levels. However, these compounds are difficult to analyse because they are thermally labile, particularly when in contact with metals. In addition, a number of compounds are very volatile – such as hydrogen sulfide and methanethiol.

On-line sampling with analysis by TD–GC and a sulfur-specific detector is the method of choice for light sulfur species. Markes' TD systems are well-suited to analysing these compounds, because low flow path temperatures (typically 80°C) can be selected without installation of special valving. In addition, the reliability of Markes' TD systems makes them ideally suited to unattended field operation.

Typical analytical conditions:

Sample: Sulfur gas standards (10 or 20 ppb) and a typical QA/QC check-sample. *Equivalent to...* On-line sampling (Air Server): 100–500 mL air (containing 10 or 20 ppb per component) at 50 mL/min for 2–10 min, respectively.

TD (UNITY): Trap (Hydrogen sulfide): Analytes trapped at -30°C, desorbed at 250°C (5 min). Split ratio: Outlet 12:1. Note that a reduced trap heating rate of 40°C/s gives optimum results for these analytes.

Analysis: GC-PFPD (pulsed flame photometric detection).



	Hydrogen sulfide	Methane thiol	Dimethyl sulfide	Dimethyl disulfide
Detection limit (ppb)	0.15	0.15	0.15	0.10
R ² (at ppb levels)	0.9973	0.9983	0.9999	0.9993
RSD (%) at 20 ppb	4.1	1.8	0.8	0.8
Recovery (%) at 80% RH	93	108	107	108



Exceptional analytical performance and reliability for thermally labile species is demonstrated in this analysis of sulfur standards using Markes' on-line UNITY-Air Server system, in accordance with the 2005 Korean standard method for off-odour analysis.





Detecting compounds at high and low concentrations

Identification of odorous compounds can be challenging because of their low or sub-ppb odour thresholds – a particular issue when they are present in highly complex polluted air samples containing compounds at much higher concentrations.

Markes' sample splitting and re-collection technology solves such problems by allowing a highly concentrated sample to be subjected to a high split to quantitate the most abundant species. The re-collected sample is then split with a low ratio to quantitate the trace-level compounds. An additional benefit of re-collection using TD is that different detection methods can be used. For example, carrying out olfactometry on exactly the same sample would enable the results to be validated against the GC data, which is useful because olfactory responses can vary substantially between individuals.

Typical analytical conditions:

Sample: A 3:1 mix of nitrogen and air from the outlet of a biological waste processing plant.

Pumped (active) sampling: 1 L.

TD (UNITY or TD100): Tube (Sulfur): Desorbed at 120°C (5 min) then 260°C (8 min). Trap (Sulfur): Analytes trapped at 25°C, desorbed at 300°C (3 min). Split ratio: Outlet 30:1 (high split), 4:1 (low split). Analysis: GC-MS.



Back-to-back GC analyses of a single sample split at different ratios allow both high- and low-concentration components to be accurately quantitated.

MARKES internationa

Fenceline monitoring

Passive monitoring of benzene emissions in accordance with US FPA Method 325

US EPA Method 325 was issued in September 2015, and requires two-week diffusive monitoring of benzene at refinery fencelines. Key challenges are handling the large number of samples required and ensuring consistently high analytical performance.

Markes' automated thermal desorbers help address the challenge of Method 325, by allowing up to 100 samples to be analysed in sequence, reducing running costs and allowing unattended operation over entire weekends. Stringent leak-testing, automatic addition of internal standards and quantitative re-collection (for repeat analysis) further enhance analytical rigour.



Typical analytical conditions: Sample: Fenceline air. Passive (diffusive) sampling: 14 davs. TD (TD100): Tube (EPA 325): Desorbed at 320°C (5 min). Trap (EPA 325): Analytes

trapped at 25°C, desorbed at 320°C (3 min). Split ratio: Outlet low split.

Analysis: GC-MS or GC-FID.



As well as monitoring levels of benzene, the passive tubes stipulated by Method 325 are also perfect for capturing other analytes contributing to poor air quality, such as the hydrocarbons identified in this refinery air sample.

Application Note 114



Fenceline monitoring

Extending analyte range by use of pumped-tube sampling



In situations where a wide range of airborne chemicals need to be monitored, it is desirable to save time by avoiding the use of multiple sampling techniques for different classes of analytes.

In a single run, a wide range of VOCs and SVOCs can be sampled onto TD tubes packed with multiple sorbents, using a low-flow pump such as Markes' ACTI-VOC, or the MTS-32 multi-tube sampler. Analysis of these tubes on Markes' TD instruments ensures that all these compounds are efficiently released and focused, for optimum chromatography and maximum sensitivity.

Typical analytical conditions:

Sample: Air at the fenceline of a factory producing synthetic rubber. Pumped (active) sampling (ACTI-VOC): 12 L, at 50 mL/min for 4 h. TD (UNITY or TD100): Tube (Universal): Desorbed at 300°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at 20°C, desorbed at 300°C (3 min). Split ratio: Outlet 20:1.

Analysis: GC-MS.

See page 44 for an example of the same method being used to monitor air inside a factory.



Application Note 037



- 2 Dichloromethane
- 3 2-Chlorobutadiene 4 Chloroform
- 5 Butan-2-one
- 6 Benzene
- 7 Toluene



- 9 2-Ethvlhexan-1-ol
- 10 Decamethylcyclo-
- pentasiloxane
- 11 Dodecamethylcyclohexasiloxane
- 12 Butylated hydroxy toluene

The backflush operation of Markes' thermal desorbers ensures there is no risk of higher-boiling or 'sticky' analytes becoming bound to the strongest sorbents in multi-bed tubes and traps.



A number of industrial air pollutants at low-ppb levels are detected in this sample of fenceline air, sampled onto sorbent tubes using Markes' lightweight, compact, low-flow ACTI-VOC pump specifically optimised for TD tubes.

Landfill gas

An optimised grab-sampling method for odorous sulfur species

Landfill sites containing domestic and commercial waste produce a variety of volatile organic compounds (VOCs), depending on both the materials they contain and the decomposition processes they undergo. Many of these compounds can be toxic and/or odorous, with sulfur species in particular a focus of attention because of their ability to have negative impacts on local communities at very low levels.

Markes' TD instruments are fully compatible with environment agency protocols for landfill gas analysis. Importantly, the inertcoated stainless steel tubes that are recommended for this application eliminate the risk of reactive species such as sulfur compounds decomposing on the metal surface during desorption.

Typical analytical conditions:

Sample: Landfill gas.

Grab-sampling (Easy-VOC): 100 mL.

TD (UNITY or TD100): Tube (Sulfur): Desorbed at 200°C (5 min) then 300°C (5 min). Trap (Sulfur): Analytes trapped at 30°C, desorbed at 220°C (5 min). Split ratio: Inlet: 4:1, Outlet 25:1.

Analysis: GC-MS.

See page 19 for approaches to dealing with the high humidity of landfill gas.

Application Note 047



Three key sulfur species – as well as a large number of other VOCs and SVOCs – are detected using convenient grab-sampling and TD analysis in accordance with a UK Environment Agency protocol.

Odours from abbatoirs

Identifying labile compounds arising during meat processing using pumped sampling



GC is used extensively to monitor odours associated with meat processing, but the chemicals of interest often decompose at high temperatures, making optimisation of the analytical conditions challenging.

Markes' TD systems make the analysis of reactive species straightforward, thanks to their short, inert and uniformly heated flow paths. In addition, the ability to trap at temperatures above 0°C using electrical cooling avoids the risk of ice blockage during the analysis of humid samples, while retaining the ability to use low-split or splitless conditions for maximum sensitivity.

Typical analytical conditions:

Sample: Air from a swine facility.

Pumped (active) sampling: 0.5-2 L.

TD (UNITY or TD100): Tube (Tenax TA-strong graphitised carbon black): Desorbed at 280°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at 20°C, desorbed at 300°C (3 min). Split ratio: Outlet <5:1.

Analysis: GC-MS.



Amines and fatty acids – which can be prone to decomposition at high temperatures – are handled without problems in this analysis of meat vapour. Data reproduced courtesy of APS Adamsen, LugTek, Denmark – experts in odours from livestock production.

Biogas

Monitoring siloxanes using sorbent tubes



Biogas used for power generation commonly contains siloxanes, which derive from consumer products and from the silicones used in wastewater treatment. This is a problem because during biogas combustion the siloxanes are oxidised to silicon dioxide particles, which can damage turbines. Monitoring of siloxanes in biogas is therefore necessary, and this has historically been carried out by laborious solvent-based methods.

To speed up the analysis of siloxanes in biogas, either sorbent tubes or canisters can be used. However, unlike canisters, sorbent tubes are suitable for sampling compounds boiling higher than $n-C_{14}$, and allow analyses to be validated by sample splitting, re-collection and repeat analysis. Sorbent tubes also offer operational advantages, such as being easier to clean and less bulky to transport.

Typical analytical conditions:

- Sample: 1 μL of a siloxane standard (1000 ng/ μL per component) in methanol, loaded onto a sorbent tube.
- *Equivalent to...* Pumped (active) sampling: 1 L air containing 100 μ g/m³ per component. For decamethyltetrasiloxane this would be a concentration of 8 ppb.
- TD (UNITY or TD100): Tube (Air toxics): Desorbed at 320°C (10 min). Trap (Air toxics): Analytes trapped at 25°C, desorbed at 320°C (3 min). Split ratio: Outlet 56:1.

Analysis: GC-MS.



- 2 Hexamethylcyclotrisiloxane
- 3 Octamethyltrisiloxane
- 4 Octamethylcyclotetrasiloxane
- 5 Decamethyltetrasiloxane
- 6 Decamethylcyclopentasiloxane D₅







L₂

D₂

L2

D₄

L

Ls

Excellent peak shape and separation is observed for all the siloxanes in this standard mix, including the heaviest – confirming the TD conditions as optimum for this challenging set of analytes.

Monitoring personal exposure to chemicals by sorbent tube sampling

By their very nature, many industrial and manufacturing processes involve the use of hazardous volatile chemicals. Increased knowledge of the long-term effects of exposure to these airborne VOCs at work has resulted in occupational exposure limit levels being reduced. This has in turn increased demand for more sensitive monitoring methodology.

Diffusive or pumped sampling of workplace air onto sorbent tubes followed by TD-GC, because of its ease of use and sensitivity, is one of the most popular methods for obtaining the time-weighted-average values needed to check compliance with threshold limit values (TLVs).

Typical analytical conditions: Sample: Workplace air. Passive (diffusive) sampling: 8 h. Pumped sampling: 4.8 L, at 20 mL/min for 8 h. TD (UNITY or TD100): Tube (Tenax TA): Desorbed at 300°C (5 min). Trap (General-purpose hydrophobic): Analytes trapped at 20°C, desorbed at 300°C (5 min). Split ratio: Outlet 20:1. Analysis: GC-MS.



Unobtrusive, low-cost diffusive samplers for personal exposure monitoring can be worn close to the breathing zone without affecting worker behaviour.





Airborne nitrogen-containing compounds and solvents are readily monitored by diffusive or pumped-tube sampling onto sorbent tubes, as demonstrated by these two analyses of workplace air.



Application Note 037

MARKES nternational

Easy grab-sampling for convenient industrial hygiene monitoring

Grab-sampling is a useful technique for monitoring air in industrial settings, because it allows samples to be collected quickly and easily. Originally, grab-sampling was only possible using canisters, but these are inconveniently large, expensive, and limited to compounds boiling below n-tetradecane.

Addressing this problem, Easy-VOC allows factory air to be grabsampled directly onto low-cost, compact sorbent tubes. The use of these tubes inherently ensures compatibility with $C_{3/4}-C_{44}$ compounds and reactive species. At the same time, performance for the most volatile components is aided by sub-litre sampling volumes, accurately collected using the Easy-VOC. This is because using relatively small volumes avoids the risk of light compounds escaping from the non-sampling end of the tube (breakthrough).

Typical analytical conditions:

Sample: Factory air.

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Grab-sampling (Easy-VOC): 5 × 100 mL, collected successively.

TD (UNITY or TD100): Tube (Graphitised carbon black): Desorbed at 350°C (8 min). Trap (General-purpose carbon): Analytes trapped at 10°C, desorbed at 350°C (5 min). Split ratio: Outlet 40:1.

Analysis: GC-MS.





Hydrocarbons from industrial solvents predominate in this analysis of factory air, sampled in a matter of minutes using the Easy-VOC. The concentrating power of TD allows sub-ppb or ppt sample concentrations to be detected, even with these relatively small sample volumes.

Industrial hygiene monitoring using pumped sampling

Pumped sampling onto sorbent tubes is a highly versatile method for monitoring VOCs in factory air, because it allows analytes over a wide range of volatilities (and at high and low concentrations) to be monitored in a short space of time. However, not all pumps are optimised for sorbent tubes.

ACTI-VOC is a compact pump that provides outstandingly consistent performance across the range of air flows used for TD applications. It is also lightweight, making it suitable for on-the-spot sampling in industrial settings.

Typical analytical conditions:

Sample: Air close to an emission source in a synthetic rubber factory. Pumped (active) sampling (ACTI-VOC): 100 mL, at 50 mL/min for 2 min.

TD (UNITY or TD100): Tube (Universal): Desorbed at 300°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at -10°C, desorbed at 300°C (3 min). Split ratio: Outlet 20:1. Analysis: GC-MS.

See page 38 for an example of

the same method being used to monitor air at a factory fenceline.







Rapid sampling using ACTI-VOC allows ppb-level VOCs in factory air to be sampled easily (use of splitless desorption could even allow detection at the sub-ppb level). Repeat desorption of the analysed sorbent tube shows none analyte retention, illustrating the efficiency of backflush desorption using Markes' TD instruments.



Pumped-tube monitoring of pesticide vapours

Agricultural workers involved in pesticide application must be monitored to ensure that their exposure to these highly toxic chemicals does not exceed safe levels. However, pesticides are typically high-boiling, and can also be prone to decomposition on hot surfaces within analytical instruments.

The use of suitably inert sorbent tubes for pumped sampling, together with the fully inert flow path and wide analyte compatibility of Markes' thermal desorbers, provides a reliable and highly sensitive monitoring method for these difficult compounds.

Typical analytical conditions:

Sample: Pesticide standard (240–250 ng per component), loaded onto a sorbent tube.

Equivalent to... Pumped (active) sampling: 1 L air containing 250 μ g/m³ per component. For chlorpyrifos this would be a concentration of 17 ppb.

TD (UNITY or TD100): Tube (Tenax TA): Desorbed at 280°C (10 min). Trap (Tenax TA): Analytes trapped at 20°C, desorbed at 300°C (3 min). Split ratio: Outlet ~10:1. Analysis: GC-MS.





Quantitative recovery of pesticides through the analytical system is shown by splitting, re-collection and re-analysis of a pesticide standard. This capability also benefits occupational hygiene applications by allowing samples to be archived for repeat analysis under different conditions.

Breath monitoring

Assessing personal exposure by sampling VOCs in breath



As well as being studied by analysis of ambient air (see pages 42–44), personal exposure can also be assessed by biological monitoring. This involves measuring chemical concentrations in the blood, urine or breath, to provide a more accurate idea of the actual bodily burden of chemicals – whether ingested, absorbed through the skin, or inhaled.

Sampling breath is less invasive than blood and urine monitoring, and doesn't require trained medical personnel. This makes it particularly well-suited to large-scale studies of workers – for example, to make sure exposure levels don't increase over time, or to assess the effectiveness of personal protective equipment (PPE).

Typical analytical conditions:

- Sample: 411 mL breath, collected onto a sorbent tube using a Bio-VOC breath sampler.
- TD (UNITY or TD100): Tube (Bio-monitoring): Desorbed at 270°C (8 min). Trap (Material emissions): Analytes trapped at 10°C, desorbed at 290°C (3 min). Split ratio: Outlet 3:1.

Analysis: GC-MS.

The Bio-VOC body, with a volume of 129 mL, collects just the last part of an exhaled breath. The VOC profile of this end-exhaled air is known to correlate closely with the concentrations in the blood – making breath sampling a viable alternative to more invasive methods.



Exhaled breath is quickly and easily sampled using the Bio-VOC, with analysis by TD–GC–MS identifying a range of compounds including endogenous compounds such as isoprene, acetone and acetic acid, and likely exogenous pollutants including benzene, toluene and styrene.





Indoor air monitoring



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Indoor air

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

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

Pumped or passive sampling on to sorbent tubes using Markes' TD instruments provides the flexibility to monitor indoor air pollution over different VOC volatility ranges and time periods, in compliance with key methods such as ISO 16017 (parts 1 & 2), ASTM D6196, EN 13528 and US EPA Method TO-17.

Typical analytical conditions:

Sample: Indoor air.

Pumped (active) sampling (ACTI-VOC): 2–20 L, for a period of minutes to hours. TD (UNITY or TD100): Tube (Universal or Air toxics): Desorbed at 280°C (5 min). Trap (Universal or Air toxics): Analytes trapped at –30°C, desorbed at 300°C (3 min). Split ratio: Outlet ~15:1.

Analysis: GC-MS.





A wide range of potentially harmful chemicals at ppt and ppb levels are identified in this indoor air sample, collected by pumped sampling onto sorbent tubes over relatively short time periods.

Indoor air

Passive sampling for convenient and unobtrusive personal monitoring

Valuable insights into indoor air quality are easily obtained by pumped or passive monitoring at stationary locations, but to achieve a full understanding of personal exposure it is useful to sample the air in the breathing zone as people move around a building.

Low-cost, unobtrusive, and with no need for a pump, passive samplers are ideal for large-scale personal exposure monitoring. The use of TubeTAG technology (see page 64) aids such studies, by allowing tube and sample information to be recorded without the risk of transcription errors associated with written records.

Typical analytical conditions:

Sample: Ambient air.

Passive (diffusive) sampling: Typically 24 h.

TD (UNITY or TD100): Tube (Single-bed, sorbent depending on target analyte range): Desorbed at 320°C (5 min). Trap (to match tube sorbent): Analytes trapped at 20°C, desorbed at 320°C (3–5 min). Split ratio: Outlet ~10:1. Analysis: GC–MS.

See pages 42–44 for examples of using pumped-tube monitoring to assess personal exposure.



Diffusion caps replace the storage cap at the sampling end of the TD tube for the duration of the exposure period, and stop dust or other materials entering.



The poor indoor air quality in this home is clearly mirrored in the personal exposure of the residents, assessed using passive samplers. In this case a diesel car parked in a garage under the living space was found to be the source of the problem.



Fragrance profiling

Monitoring changing levels of airborne volatiles in near-real-time

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

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

Typical analytical conditions:

- Sample: Air from a room containing a plug-in air freshener.
- On-line sampling: 3 L, sampled at 158 mL/min every ~19 min. Air freshener switched on at t = 0.
- TD (TT24-7): Traps (Tenax TA): Analytes trapped at 25°C, desorbed at 300°C (3 min). Split ratio: Outlet 29:1. Analysis: GC-MS.



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

freshener using the TT24-7 shows how the concentrations rise and fall over a period of 6 hours. The potential allergen linalool generated by far the largest response, and although concentrations decreased fairly rapidly after the air freshener was turned off. it nevertheless remained detectable in the air until the end of the experiment, 4.75 hours later.





Δ

3

2

1

Abundance (× 10⁷ counts)

Vapour intrusion

Passive sampling of indoor air using sorbent tubes

Vapour intrusion – when chemicals migrate into a building from contaminated soil – is commonly monitored using canisters or by pumped sampling onto sorbent tubes, but with these methods it is difficult to assess the longer-term average concentrations relevant to assessments of health risk.

Passive (diffusive) samplers have long been used for industrial hygiene assessment (see page 42), and with their low cost, ease of use, and applicability to longer-term sampling, are now attracting attention for vapour intrusion applications too. Of the various designs available, axial-type samplers offer the advantages of having well-validated uptake rates, being compatible with standard methods, and providing a small area of exposed sorbent that avoids 'starvation' in confined-volume sampling setups.

Typical analytical conditions:

Sample: Indoor air.

Passive (diffusive) sampling: Hours to days.

TD (UNITY or TD100): Tube (Tenax TA): Desorbed at 265°C (10 min). Trap (Tenax TA): Analytes trapped at 25°C, desorbed at 300°C (3 min). Split ratio: Splitless.

Analysis: GC-MS.

Application Note 010

http://dx.doi.org/10.1039/C4EM00560K

T. McAlary *et al.*, Passive sampling for volatile organic compounds in indoor air – Controlled laboratory comparison of four sampler types, *Environmental Science: Processes & Impacts*, 2015, 17: 896–905.





Ventilation studies

Using on-line monitoring or sorbent tube sampling of tracer gases to understand air exchange

Sulfur hexafluoride (SF₆) and perfluorocarbons (PFCs), as well as being used in industry, find application as tracer gases for determining ventilation rates in buildings, and to aid detection of coolant leaks from underground electrical lines.

The rise and fall of tracer gas concentrations is easily monitored using TD. On-line sampling is preferred for monitoring SF_6 or when high time-resolution is needed, whereas tube-based monitoring (pumped or diffusive) is effective and convenient for PFCs.

Typical analytical conditions (for diffusive monitoring of PFCs):

Sample: Indoor air.

Passive (diffusive) sampling: 24 h.

TD (UNITY or TD100): Tube (Tenax TA): Desorbed at 300°C (5 min). Trap (Generalpurpose hydrophobic): Analytes trapped at 20°C, desorbed at 300°C (5 min). Split ratio: Splitless or low split.

Analysis: GC-MS or GC-ECD.

Conditions for on-line monitoring of SF₆ are described on page 27. Note that SF₆ can also be monitored using low-volume (100–500 mL) sampling onto tubes packed with relatively strong sorbents (e.g. 'Sulfur' tubes).



On-line monitoring is the optimum approach for sulfur hexafluoride (here detected at 0.1 ppb), while perfluorocarbons are easily monitored by tube-based sampling.

Topic continued on next page

Monitoring semi-volatiles

Efficient re-collection of phthalate esters

Phthalates (diesters of phthalic acid) have been widely used since the 1950s as plasticisers, but many are now suspected of being endocrine disruptors, and some are listed as 'substances of very high concern' under the European REACH regulation. However, the polarity of PAHs and the fact that many are normally supplied as multi-component fractions ('technical mixes') makes it particularly important to validate the analytical method.

Markes' quantitative splitting and re-collection technology allows split portions to be quantitatively re-collected onto a clean sorbent tube. As illustrated here for a range of phthalates, this provides a convenient means of demonstrating quantitative recovery of analytes through the entire TD system.

Typical analytical conditions:

- Sample: Phthalate standard (100 $ng/\mu L$ per component), loaded onto a sorbent tube.
- *Equivalent to...* Pumped (active) sampling: 1 L air at 100 μ g/m³ per component. For bis(2-ethylhexyl) phthalate this would be a concentration of ~6 ppb.

TD (UNITY or TD100): Tube (quartz wool-graphitised carbon blacks): Desorbed at 350°C (10 min). Trap (High-boilers): Analytes trapped at 0°C, desorbed at 370°C (5 min). Split ratio: Outlet 7.7:1.

Analysis: GC-MS.

Application Note 053

http://dx.doi.org/10.1016/j.atmosenv.2013.07.059

B. Lazarov et al., Optimisation steps of an innovative air sampling method for semi volatile organic compounds, Atmospheric Environment, 2013, 79: 780–786.



Phthalates across the boiling range, from dimethyl phthalate (b.p. 283°C) to di-n-decyl phthalate (b.p. ~450°C), are efficiently transferred through the flow path of Markes' thermal desorbers, as shown by splitting and re-collection of this standard sample.



Monitoring semi-volatiles

Efficient re-collection of PCBs

Polychlorinated biphenyls (PCBs) enter the environment *via* contaminated dielectric liquids in capacitors and transformers, various thermal processes and from the disposal of some electronic components. Their persistence in the environment has led to concern about such practices, and has in turn highlighted the need for reliable detection methods.

As for high-boiling alkanes (page 20), PAHs (pages 21–23) and phthalates (page 53), the short, inert, uniformly heated flow path and heated valve of Markes' TD systems ensures quantitative recovery of PCBs.

Typical analytical conditions:

Sample: PCB standard (10 ng per component), loaded onto a sorbent tube. *Equivalent to...* Pumped (active) sampling: 100 L air containing 0.1 μ g/m³ per component. For PCB 189 this would be a concentration of 6 ppt.

TD (UNITY or TD100): Tube (quartz wool-graphitised carbon blacks): Desorbed at 350°C (10 min). Trap (High-boilers): Analytes trapped at 0°C, desorbed at 370°C (5 min).

Split ratio: Outlet 7.25:1.

Analysis: GC-MS.







Repeat analysis of the PCB standard Aroclor 1260 shows quantitative recovery of these high-boiling compounds. The splitting and re-collection technology used here provides a convenient means of demonstrating quantitative recovery of analytes through the entire TD system.

Soil gas and water monitoring



TAKU

Underground contamination

Sub-slab monitoring of soil contaminants using pumped sorbent tubes

Redevelopment of old industrial sites requires assessment and removal of any residual contamination – including, for example, organic pollutants such as petroleum hydrocarbons, pesticides and solvents. However, the popular approach of canister sampling is limited to compounds boiling below $n-C_{14}H_{30}$, which excludes many heavier organic pollutants.

Pumped sampling onto sorbent tubes with analysis by TD addresses this by being compatible with a much wider volatility range than canisters. The petrochemical-contaminated samples shown here illustrate just one aspect of this – for details of the applicability of TD to a range of semi-volatiles, see pages 20–23, 53 and 54.

Typical analytical conditions:

Sample: Soil gas.

Pumped (active) sampling: 50 mL, at 25 mL/min for 2 min. TD (UNITY or TD100): Tube (Soil gas): Desorbed at 300°C (5 min). Trap (Soil gas): Analytes trapped at 25°C, desorbed at 330°C (5 min). Split ratio: Low-level contamination – Splitless. High-level contamination – Inlet 20:1, Outlet 250:1. Analysis: GC-MS.

See page 51 for information on the application of TD to assessing vapour intrusion.





20

22

California, USA.

ARKES

14

16

18

Time (min)

Underground contamination

In situ passive monitoring of contaminated land and chemical pipelines

Underground leaks of fuel or chemicals present a serious risk to the environment, but assessing the nature and extent of any contamination can be difficult.

Markes' VOC-Mole soil probes – especially when used with passive samplers for analysis by TD – allow cost-effective, *in situ* screening of large areas of land. Amongst the other benefits of Markes' TD equipment such as analyte volatility range, the ability to accurately split samples at high ratios is useful here, because it helps avoid contamination of the analytical system when soil pollution is at high levels.

Typical analytical conditions:

Sample: Soil gas at an industrial site.

Passive (diffusive) sampling: 15 min to 48 h.

TD (UNITY or TD100): Tube (Tenax TA): Desorbed at 280°C (5 min). Trap (Tenax TA): Analytes trapped at 25°C, desorbed at 320°C (3 min). Split ratio: Low contamination – Splitless. High contamination – Inlet 20:1, Outlet 250:1.

Analysis: GC–MS or GC–FID.



VOC-Mole soil probes can be left *in situ* if regular monitoring is required.

Image credit: Joe Roberts, Harper Adams University, UK.



Drinking water

Rapid, versatile sorptive extraction of VOCs and SVOCs

Drinking water can become contaminated by volatile compounds with low odour thresholds, and by semi-volatile environmental pollutants that may pose health concerns. Monitoring such chemicals has historically required timeconsuming liquid-liquid extraction, or solid-phase extraction with solvent elution.

Markes' HiSorb sorptive extraction technology, as well as avoiding the inconvenience of solvent extraction, offers higher sensitivity than solid-phase micro-extraction (SPME)

> for contaminants in drinking water, assisted by the efficient trapping and release of analytes within the thermal desorber.

Typical analytical conditions:

Sample: 20 mL of drinking water, spiked with a mix of common odorants.

Sorptive extraction (HiSorb probe): Agitated for 2 h at 300 rpm and 40°C (HiSorb Agitator). Probe then placed in an empty TD tube.

TD (UNITY or TD100): Tube: Desorbed at 280°C (12 min). Trap (General-purpose carbon): Analytes trapped at 20°C, desorbed at 310°C (8 min). Split ratio: Outlet 5:1.

Analysis: GC-MS (SIM m/z: 95 + 108 + 110 for methyl isoborneol; 210 + 212 for trichloroanisole; 112 + 125 for geosmin; 344 + 346 for tribromoanisole).

HiSorb probes are pushed through the vial caps into the sample, agitated to ensure equilibration, and then desorbed in a standard TD tube. The large volume of PDMS on the HiSorb probe results in high sensitivity for trace-level analytes.



Four commonly-encountered odorants are easily detected in drinking water using the ability of sorptive extraction with TD to enhance the concentration of semi-volatiles.



Relevant sampling and analytical techniques

markes.com



122

ENA

markes.com

IKes.com

es.con

23456

Thermal desorption

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

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

- Analyte range Compounds ranging in volatility from acetylene to n-C₄₄H₉₀ and reactive species can all be analysed on a single TD platform.
- Quantitative re-collection of split flows enables repeat analysis and simple method validation, overcoming the historical 'one-shot' limitation of TD.
- High sensitivity Two-stage desorption using sorbent tubes allows concentration enhancements of up to 10⁶.
- Wide dynamic range Two-stage desorption and sample splitting means that Markes' thermal desorbers can handle analyte concentrations ranging from part-per-trillion up to low-percent levels.
- Sample compatibility As world leaders in TD technology, Markes offers an unmatched range of innovative and labour-saving sampling accessories for liquids, solids and gases.
- Analytical quality The narrow-bore design of the focusing trap ensures that a highly concentrated band of vapour is introduced to the GC, allowing true splitless operation and optimising both resolution and sensitivity.
- **Reduced running costs** Electrical cooling eliminates the cost of cryogen, and also avoids problems with ice formation.
- Cleaner chromatography By circumventing the need for sample preparation, solvent artefacts are eliminated, while unwanted high-abundance components such as water can also be selectively removed.



 $\begin{array}{l} \mbox{Markes' patented} \\ \mbox{inert valving} \\ \mbox{enables } C_2 \mbox{-} C_{44} \\ \mbox{and reactive} \\ \mbox{species to be} \\ \mbox{analysed on a} \\ \mbox{single thermal} \\ \mbox{desorption system.} \end{array}$

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



- For more on the principles, benefits and applications of TD, download Application Note 012.
- For more on the the single-tube UNITY-xr™ thermal desorber and the multi-tube automated TD100-xr™ instrument, visit www.markes.com.



Sorbent tube sampling - Pumped

Active (pumped) sampling onto sorbent tubes is a versatile option for simultaneous monitoring of multiple compounds.

Markes' backflush technology allows tubes to be packed with multiple sorbent beds, widening the analyte range detectable from a single sample.

Three accessories are available from Markes for pumped sampling onto TD tubes:

- ACTI-VOC[™] is a lightweight, compact low-flow pump specifically optimised for TD tubes, which can operate in constant-flow or constant-pressure modes.
- Easy-VOC[™] is a manually-operated grab-sampler that allows precise volumes of air or gas to be sampled directly onto sorbent tubes. By avoiding the need for batteries or electrical power, it is ideal for field sampling.
- The MTS-32[™] is a compact, portable sampler for the unattended sequential sampling of air onto a series of sorbent tubes. Constant-flow pump technology ensures that the same volume of air is collected onto each tube.
 - See pages 38, 44 and 48 for applications using ACTI-VOC, and pages 19, 31, 33, 39 and 43 for applications using Easy-VOC.

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

Sorbent tube sampling - Passive

Passive (diffusive) sampling using sorbent tubes provides a convenient, quantitative and low-cost method for a range of air monitoring applications.

Analytes compatible with passive sampling range from the very volatile such as nitrous oxide to semi-volatiles such as naphthalene. The nature of passive sampling means that only single-bed sorbent tubes can be accommodated – so if a wider analyte range is desired, then pumped sampling onto multi-bed tubes is recommended.



A wide range of sorbentpacked TD tubes are available from Markes for passive sampling.



- See pages 24, 37, 42, 49, 51, 52 and 57 for applications using passive sampling.
- For more on passive sampling, see Application Notes 008 and 010.



Canister/bag sampling

Canisters are most useful for sampling very volatile, non-polar compounds such as C_2 hydrocarbons and the most volatile freons, which can be difficult to retain on sorbent tubes at ambient temperature.

However, canisters are not normally suitable for time-weightedaverage monitoring, personal exposure assessment,

higher-boiling compounds (above $n-C_{14}$), or higher-concentration atmospheres. Careful attention also needs to be paid to cleaning procedures.

Markes' **CIA Advantage™** is an advanced autosampler for analysing air samples in up to 27 canisters or bags (as well as tubes). Operating cryogen-free and incorporating Markes' patented heated valve, it maximises productivity, flexibility and analyte scope available to canister users.



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

- See pages 14, 18 and 26 for applications using the CIA Advantage.
- For more on the CIA Advantage and to download the brochure, visit www.markes.com.
- For a full comparison on the benefits of tubes and canisters, see Application Note 079.

On-line sampling

On-line sampling – the collection of vapours directly into the focusing trap of the thermal desorber – is a useful approach to monitoring ultra-volatile compounds that are too volatile to be retained on sorbent tubes at ambient temperature. On-line TD systems are also valuable for continuous sampling and for near-real-time monitoring.

Two on-line monitoring systems are available from Markes:

- The **Air Server-xr**[™] samples air for a defined period of time and delivers it to the focusing trap of the UNITY thermal desorber.
- The **TT24-7**[™] uses two focusing traps, working alternately, to sample air continuously, without interruption.



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

- See pages 15, 16, 17 and 18 for applications using the Air Server, and pages 25, 28 and 50 for applications using the TT24-7.
- For more on these products and to download the brochures, visit www.markes.com.



Water management

Air streams monitored using tubes, canisters or by on-line methods often contain high levels of water. This moisture can lower sensitivity, cause poor peak shape and repeatability, and reduce column and detector lifetime. Three main approaches are available for eliminating water from air streams, each with differing abilities to quantitatively analyse certain polar species and ultra-volatiles. These methods are summarised below.

Water management method Sampling compatibility		Analyte compatibility					
	Tubes	Canisters	On-line	C ₂	Non-polar C ₃	Polar VOCs	Mono- terpenes
 Markes' Kori-xr[™] module removes water using a cryogen-free trap, which is placed upstream of the sorbent- packed focusing trap. This high- performance system is ideal for GC- MS analysis of complex air samples. 	×	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
■ Nafion [™] dryers contain a hydrophilic co-polymer that selectively removes water from the air stream.	×	\checkmark	\checkmark	\checkmark	\checkmark	×	×
• Trap dry-purging , assisted by appropriate choice of sorbent materials and trap temperature, eliminates most of the water in an air stream.	\checkmark	\checkmark	\checkmark	×	\checkmark	\checkmark	\checkmark
See pages 18 and 19 for examples of these water management approaches.	To d	ownload th t www.mark	e brochure (es.com.	on these	water mana	gement	t options,

Electronic tube tagging

Markes' **TubeTAG**[™] system uses read/write radio-frequency identification tags that allow information to be electronically associated with a sorbent tube, so providing ultimate tube traceability, and helping to reduce transcription errors.



Using TubeTAG, a simple stepwise process enables electronic logging of tube- and sample-related information in the field and lab.

For more on TubeTAG and to download the brochure, visit www.markes.com.

Sorptive extraction

Extending the capability of thermal desorption (TD), probe-based sorptive extraction using **HiSorb™** is a versatile, easy-to-use approach to the sampling of VOCs and SVOCs from liquids and solids.

The large volume of PDMS on each probe means that HiSorb has higher sensitivity for trace-level analytes than solid-phase micro-extraction (SPME), while being much less labour-intensive than solvent extraction.

HiSorb probes are simply lowered into a standard headspace vial containing the sample under investigation, agitated using a **HiSorb Agitator**, rinsed and dried, and then inserted into a 3½" TD tube for direct desorption and TD-GC-MS analysis.

See page 58 for an example of an application using HiSorb.



Stainless steel and inert-coated HiSorb probes are available in two lengths, for sorptive extraction from liquids or solids in ordinary 20 mL or 10 mL headspace vials.

For more on HiSorb and to download the brochure, visit www.markes.com.

Compound identification software

TargetView[™] is an easy-to-learn GC–MS software package that complements TD by making it easier to spot trace-level components in complex samples.

TargetView features:

- Automated screening of chromatograms for identification of targets and 'unknowns'.
- Dynamic baseline compensation (DBC) to remove column bleed and unwanted background interference.
- Advanced spectral deconvolution for cleaner spectra of co-eluting or masked compounds.
- Rapid creation of spectral libraries from various sources.
- Automated calculation of retention index values to assist compound confirmation.
- Compatibility with GC-MS file types from most major vendors.

For more on TargetView, visit www.markes.com.



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



About Markes International

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

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

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

As well as environmental monitoring, Markes' products are used extensively in multiple routine and research applications – everything from food aroma profiling to chemical ecology.

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







ACTI-VOC[™], Air Server,[™] Air Server,[™], Bio-VOC[™], CIA Advantage[™], Easy-VOC[™], 325 Field Station[™], HiSorb[™], Kori-xr[™], Micro-Chamber/Thermal Extractor[™], JI-CTE[™], MTS-32[™], TAG^{SCRBE™}, TargetView[™], TD100[™], TD100-xr[™], TT24-7[™], TubeTA6[™], UNTY[™], UNITY-xr[™] and VOC-Mole[™] are trademarks of Markes International.

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Analytical conditions presented in this document are intended as a guide only, and Markes International makes no guarantee that the performance indicated can be achieved under different circumstances.



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