Thermal Desorption Applications Guide: Food and drink

A comprehensive guide to the use of thermal desorption for quality and content testing in the food and beverage industries
Introduction

Profiling of food and drink

Aroma-profiling foods and beverages is vital because it allows manufacturers to identify the volatile components that provide their products with desirable (or undesirable) characters, enabling them to maintain and improve product quality.

In this Applications Guide, we describe how thermal desorption (TD) can be used for key applications in the field of food and drink VOC profiling – covering everything from comparing brands of cheese, to improving the shelf-life of ready-to-eat fresh-cut fruit.

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 39 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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### About Markes International

Markes International gratefully acknowledges all customers who have provided experimental data for this Applications Guide.
Food
Quantitating high- and low-concentration components

A range of compounds are responsible for the wide variation of cheese odours, presenting analysts with a substantial challenge when wishing to quantify key aroma-active components, which may be present at high or low concentrations.

Markes’ TD instruments can easily handle such wide concentration ranges, by virtue of their splitting and re-collection capabilities. A high split ratio is initially used during tube desorption to investigate abundant components, followed by collection of the split portion onto a clean sorbent tube for re-analysis under lower-split conditions to accurately quantify the low-level compounds. This capability, which is not possible with SPME, is also useful for validating analyte recovery.

**Typical analytical conditions:**
Sample: 3 g of grated mature Cheddar.
Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 50 mL/min for 20 min. Chamber temperature: 40°C.
TD (UNITY or TD100): Tube (Material emissions): Desorbed at 150°C (5 min) then 300°C (5 min). Trap (Material emissions): Analytes trapped at 30°C, desorbed at 300°C (5 min). High split: Inlet: 3:1, Outlet 15:1. Low split: Inlet: 2:1, Outlet 3:1.
Analysis: GC–MS.

A ‘High/Low’ analysis of cheese headspace indicated that concentrations on-tube extended from microgram levels for the fatty acids to subnanogram levels for the trace-level compounds.
The key differences between three cheeses become obvious when they are compared side-by-side using the Micro-Chamber/Thermal Extractor. TargetView was used to remove background interference and match peaks against a target library – see page 42.
Analysing samples with high water content

Foods often contain large quantities of water that can interfere with gas chromatography. Obtaining reliable results therefore depends upon selectively removing this water from the sample before analysis commences – which can be time-consuming and may introduce contaminants (or cause analyte loss).

Markes’ Micro-Chamber/Thermal Extractor circumvents these problems by being compatible with aqueous samples, while the choice of sorbent tube and TD focusing conditions can efficiently eliminate water before the start of the GC run.

**Typical analytical conditions:**
Sample: 10 mL natural Greek yoghurt.
Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 70 mL/min for 10 min. Chamber temperature: 70°C.
TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 280°C (10 min).
Trap (General-purpose hydrophobic): Analytes trapped at 30°C, desorbed at 300°C (3 min). Split ratio: Outlet 16:1.
Analysis: GC–MS.

Reactive polar analytes such as aldehydes are successfully analysed in this yoghurt sample, thanks to the options for water management offered by Markes’ TD instruments (and the inertness of the flow path). Use of a trap temperature above 0°C improves analytical reproducibility by completely avoiding problems with ice accumulation.
Potato crisps

Detecting key flavour compounds

Within the food industry, there is an increasing need to monitor product safety and quality, typically in relation to flavour composition, taint and contamination. This requires a detailed understanding of individual components – but without an appropriate pre-concentration step, the sensitivities of GC-based analyses can be insufficient to detect key trace-level compounds.

The two-stage desorption process used in Markes' TD instruments allows vapour concentrations to be raised by a factor of up to $10^6$, enabling detection of flavour components at ultra-low levels. Here, this inherent TD sensitivity enhancement is given an extra boost by the use of relatively large-volume dynamic headspace sampling with Markes' Micro-Chamber/Thermal Extractor.

**Typical analytical conditions:**
Sample: ~5 g of crushed potato crisps.
Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 40 mL/min for 10 min. Chamber temperature: 40°C.
TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 300°C (5 min). Trap (Tenax TA): Analytes trapped at 0°C, desorbed at 320°C (3 min). Split ratio: Outlet 20:1.
Analysis: GC–MS.

**Pyrazines, with their roasted/earthy to potato-like aroma and low odour thresholds,** were a target group in this analysis of potato crisps. The use of dynamic headspace extraction and TD, with MS detection in EIC mode, allowed the detection of two pyrazines despite their presence at trace levels.
Comprehensive analysis of meat products

Comparison between brands is of great importance for manufacturers looking to improve their product range and enhance their existing lines – but to be useful in a busy laboratory, such analyses need to be quick as well as comprehensive.

These needs are met by the ease-of-use and speed of sampling of the Micro-Chamber/Thermal Extractor, complemented here by the use of multi-bed sorbent tubes. The combination of these tubes with the inherent analytical versatility of Markes’ TD systems allows single-run analysis of compounds with widely differing properties (polar, non-polar and reactive species, from C_2–C_{44}) – in contrast to techniques such as solvent extraction and SPME.

Typical analytical conditions:
Sample: ~8 g of uncooked bacon.
Headspace (Micro-Chamber/Thermal Extractor): Flow rate: 5 mL/min for 60 min. Chamber temperature: 30°C.
TD (UNITY or TD100): Tube (Tenax® TA–Carbopack™ X): Desorbed at 280°C (10 min). Trap (General-purpose carbon): Analytes trapped at 25°C, desorbed at 320°C (5 min).
Analysis: GC–MS.

The choice of sorbent-tube and focusing-trap sorbents in this comparison of two bacon brands allows the detection of a wide range of analyte types – from non-polar compounds like hexane, to highly polar components such as acetic acid and levoglucosan.
Improving understanding of shelf-life

The shelf life of foods depends on a complex interplay of factors, and understanding these is of huge importance to the food industry. A key aspect is how the aroma profile varies over time, and whether this has an impact on consumer perception, or can be used to flag spoilage.

The Micro-Chamber/Thermal Extractor, as well as being a versatile instrument suitable for a range of food types, also makes it easy to acquire profiles at different time-points. An added advantage of the dynamic headspace process used is that the relatively large sample volumes further enhance the already high sensitivity levels offered by two-stage TD.

Typical analytical conditions:
Sample: ~8 g of uncooked bacon.
Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 5 mL/min for 60 min. Chamber temperature: 30°C.
TD (UNITY or TD100): Tube (Tenax® TA–Carbopack™ X): Desorbed at 280°C (10 min). Trap (General-purpose carbon): Analytes trapped at 25°C, desorbed at 320°C (5 min).
Analysis: GC–MS.

Application Note 095

The decomposition of bacon is studied in this analysis using a Micro-Chamber/Thermal Extractor with TD. Note that the fully passivated TD sample flow path enables recovery of thermally labile components like methanethiol, dimethyl sulfide and dimethyl trisulfide.
A dynamic headspace analysis of a whole strawberry easily picks out furaneol (#15), a highly polar and unstable compound with a desirable ‘burnt sugar’ aroma and a sub-ppb odour threshold. Also detected were some oxygenated species, and low-level sulfur compounds such as methyl thioacetate (#5), demonstrating the ability to monitor a wide analyte range in a single run.

**Application Note 104**

**Strawberries**

**Understanding the detail of volatile profiles**

Although the aroma of fruits is often determined by the presence of high-abundance esters, some fruits – such as strawberries – owe their distinctive aromas to much lower-abundance compounds. Understanding these differences is vital when characterising different cultivars.

Coupling headspace with efficient TD trapping typically improves headspace sensitivity by one or two orders of magnitude, and extends the analyte volatility range while ensuring complete transfer of analytes through the TD flow path. In this example, a wide range of analytes were detected in one run because multi-bed tubes and traps were used – which is only possible because of the backflush operation of the valve in Markes' thermal desorbers.

**Typical analytical conditions:**

Sample: Whole strawberry.

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

TD (UNITY or TD100): Tube (Odour): Desorbed at 120°C (5 min) then 260°C (5 min). Trap (Material emissions): Analytes trapped at 25°C, desorbed at 300°C (5 min). Split ratio: Outlet 21:1.

Analysis: GC–MS.

The peak listing was generated by an automated library search using TargetView (see Application Note 104 for the full list of 76 compounds).
Assisting quick comparisons of different sample preparations

The inherent batch-to-batch variability of ingredients from natural sources makes it all the more important to maximise reproducibility within the analytical protocol, in order to generate useful results. This is especially true when comparing similar samples, when the main differences may only be in component abundance.

Using the principle of dynamic headspace–TD, Markes’ easy-to-use Micro-Chamber/Thermal Extractor eliminates error-prone sample preparation, and allows quick and meaningful comparison of similar samples – such as between foods stored under different conditions, or (as here) samples prepared in different ways.

**Typical analytical conditions:**
Sample: Whole and chopped strawberry.
Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 50 mL/min for 20 min. Chamber temperature: 40°C.
TD (UNITY or TD100): Tube (Odour): Desorbed at 120°C (5 min) then 260°C (5 min). Trap (Material emissions): Analytes trapped at 25°C, desorbed at 300°C (5 min). Split ratio: Outlet 21:1.
Analysis: GC–MS.

**Easy comparison of the volatiles** released from chopped and whole strawberries using Markes’ Micro-Chamber/Thermal Extractor indicates a tendency for the higher-boiling components (including the key strawberry aroma compound furaneol) to be more prevalent in the aroma profile of the chopped strawberry.
As illustrated by this direct desorption analysis of mushroom powder, TD makes it possible to achieve comprehensive volatile profiling, with minimal sample preparation and unattended operation helping to streamline quality-control procedures.
Comprehensive headspace profiling of melon is achieved by grab-sampling onto two-bed sorbent tubes to maximise the analyte range. Esters are predominant, including some (*) that are known to contribute to the distinctive aroma of melons. Data reproduced courtesy of Hilary Rogers et al., Cardiff University, UK.

Melon

Comprehensive aroma profiling of fresh fruit

In the ready-to-eat food industry, shelf-life is estimated mainly by judging the appearance of the product – an approach that is limited because appearance does not necessarily indicate deficiencies in aroma profile, nutrient content, or the presence of micro-organisms.

Markes has been participating in a 7th Framework Program EU project (‘QUAFETY’) that aims to resolve this by developing tools for the evaluation of food quality and safety. As part of this project, grab-sampling was used with automated TD for detailed analysis of melon aroma profiles.

Typical analytical conditions:

Sample: Cantaloupe melon (Cucumis melo ‘Arapaho’), cleaned, cut into 10 mm cubes and kept in a sealed bag at 20°C for 1 h.
Headspace (Easy-VOC): 2 × 100 mL, collected successively.
TD (UNITY or TD100): Tube (Odour): Desorbed at 280°C (10 min).
Analysis: GC–MS.

Comprehensive headspace profiling of melon is achieved by grab-sampling onto two-bed sorbent tubes to maximise the analyte range. Esters are predominant, including some (*) that are known to contribute to the distinctive aroma of melons.

Application Note 536

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**Meat processing**

**Simplifying the analysis of labile compounds**

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 below ambient 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 sampling: 0.5–2 L.

TD (UNITY or TD100): Tube (Tenax\textsuperscript® 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.

Volatile 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.*
Boar taint

Lowering detection limits for undesirable aromas from pork

Fatty tissue from male pigs – known as ‘fatback’ – can be contaminated with skatole, indole and androstenone, which are naturally-occurring but offensive-smelling hormones that can cause consumer complaints. Castrating male piglets overcomes this problem, but forthcoming restrictions on this practice have highlighted the need for a screening method for these compounds.

Addressing this need, a team at the University of Bonn, Germany, found that combining Markes’ headspace sampling equipment and automated TD delivered limits of detection and quantitation for skatole, indole and androstenone well below the levels set for consumer acceptance.

Typical analytical conditions:
Sample: 500 mg of liquid fat heat-extracted from fatback.
Dynamic headspace (HS5-TD, modified with a dual needle): Equilibration: 40 min at 200°C. Sample volume: 90 mL.
TD (UNITY): Tube (Tenax® TA): Desorbed at 300°C (12 min). Trap (Tenax TA):
Analysis: GC–MS.

Ultra-low limits of detection were achieved for the three key boar taint compounds in this dynamic headspace analysis of pig fatback. An added benefit of TD for this application is that the TD tubes are relatively lightweight compared to other sampling media, making them much easier and cheaper to transport.

Data reproduced courtesy of Peter Boeker and Jan Leppert, University of Bonn, Germany.

http://dx.doi.org/10.1016/j.foodchem.2014.02.113
Betel-nut stimulants

Validating analyte recovery by sample splitting and re-collection

‘Betel nut’ or ‘paan’ is the name given to a number of chewed stimulants popular in south-east Asia. These products have recently attracted attention because of the presence of potential carcinogens, making it particularly important that the analysis is both rigorous and verifiable.

Markes’ thermal desorbers address this challenge by allowing samples to be ‘split’ at a precisely defined ratio, both at the tube and trap desorption stages. The portion of each sample not sent to the GC can be re-collected onto a clean sorbent tube to confirm analyte recovery, or analysed again using a different column or detector to acquire complementary sets of data.

Typical analytical conditions:
Sample: 70.5 mg of crushed areca fruit, placed in an empty TD tube.
TD (UNITY or TD100): Sample: Desorbed at 50°C (10 min).
Analysis: GC–MS.

Repeat desorption under constant split conditions is useful for validating analyte recovery, as illustrated by this example of areca fruit. The response from patchouli alcohol decreases as expected from the 10:1 split ratio used during trap desorption, in a sequence of repeat runs.
Animal feed

Assisting continued quality assurance

The quality of animal feed is vital to ensure healthy livestock, a clean environment, and food products that are safe for human consumption. Consequently, reliable analytical data on the volatile content of feed formulations is essential for quality assurance.

With this in mind, coupling the larger sample volumes of headspace sampling with efficient TD trapping allows significant improvements in sensitivity and analyte range. Using the Micro-Chamber/Thermal Extractor also gives reproducible results while making it easy to vary the sampling conditions for optimum results.

Typical analytical conditions:
Sample: ~5 g soya-based animal feed.
Analysis: GC–MS.

Varying the sampling conditions is straightforward using the Micro-Chamber/Thermal Extractor. In this animal feed sample, it can be clearly seen how greater quantities of lower-level compounds are extracted at 80°C, compared to 40°C.
Fresh herbs

Checking the quality of raw foodstuffs

Herbs are widely used in many food products, but substantial differences in aroma can result from differences in growing conditions or preparation of the plant material. Quick batch comparison is therefore very useful for those in the food industry.

The Micro-Chamber/Thermal Extractor allows rapid collection of the entire vapour profile from vegetable products such as herbs, making it ideal for assessment of quality. In addition, the inertness and adjustable flow-path temperature of Markes’ TD systems ensures reliable analysis of a wide range of analytes in a single run.

Typical analytical conditions:
Sample: 5 g pre-packaged 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.

A large number of mono- and sesquiterpenes were identified in this analysis of basil.
The large number of structurally similar compounds in this analysis of dried peppermint tea leaves demanded sample splitting and re-collection, so that the identity of the key analyte piperitone could be independently verified.
Curry powder

Quick and convenient comparison of samples

Herbs and spices are used in many food preparations, and controlling quality is of paramount importance to food manufacturers. A challenge often encountered when analysing such samples is that the VOC profiles often differ in the relative abundance of key components – differences that can be difficult to assess by traditional methods such as solvent extraction, static headspace, or SPME.

Direct desorption is ideal for relatively homogeneous, finely-divided samples, and offers rapid, simple comparison of everything from powdered spice blends to edible oils.

Typical analytical conditions:
Sample: ~50 mg curry powder, placed in an empty TD tube.
TD (UNITY or TD100): Sample: Desorbed at 50°C (3 min). Trap (Material emissions): Analytes trapped at 10°C, desorbed at 180°C (5 min). Split ratio: Outlet 25:1.
Analysis: GC–MS.

Rapid and simple direct desorption of two brands of curry powder shows a very similar range of analytes, but with large differences in relative abundance.

The cheaper brand shows much higher quantities of some compounds (●) compared to a mid-range brand, but lower concentrations of others (○).
Edible oils

Identifying taint or pinpointing adulteration

Edible oils, because of their liquid nature, are easily contaminated during processing, transport or storage – and there is also the problem of adulteration of ‘virgin’ oils. GC-based monitoring is widely used in such situations, but the sample preparation techniques commonly used (liquid extraction or steam distillation) are laborious, and may result in skewed profiles due to loss of the more volatile species.

In contrast, TD-based methods allow representative vapour profiles to be generated while avoiding tedious sample preparation. Direct desorption is a simple and suitable method for small samples, while dynamic headspace sampling using the Micro-Chamber/Thermal Extractor offers enhanced sensitivity because of the relatively large sample volumes.

Typical analytical conditions:
Sample: A few milligrams of sesame oil, loaded on to a plug of glass wool and placed in an empty TD tube behind a 1 cm bed of Tenax® TA.
TD (UNITY or TD100): Sample: Desorbed at 300°C (10 min). Trap (Tenax TA): Analytes trapped at 10°C, desorbed at 300°C (3 min). Split ratio: Outlet >100:1. Analysis: GC–MS.

Headspace analysis of sesame oil – either by direct desorption (shown here) or using the Micro-Chamber/Thermal Extractor – yields the comprehensive information on the volatile profile of oils needed for quality control.
Drink
Fruit juice

Expanding target analyte range and sensitivity

Understanding the VOC profiles of fruit juices is key to increasing their customer appeal, but characterising juice aroma has historically required cumbersome sample preparation steps such as liquid–liquid extraction, solid-phase extraction and distillation, usually with the additional drawback of organic solvents.

Used with TD to enhance sensitivity and broaden the analyte range, sorptive extraction and headspace sampling offer less labour-intensive, complementary alternatives to such protocols, as illustrated by this example.

Typical analytical conditions:

**Sorptive extraction**
Sample: 20 mL of a 1:20 dilution of freshly-squeezed orange juice.
Sorptive extraction (SPE-tD cartridge): Stirred for 1 h at 20°C. Cartridge then placed in an empty TD tube, and desorbed at 180°C (5 min).
Analysis: GC–MS.

**Headspace**
Sample: 10 mL of a 1:2 dilution of freshly-squeezed orange juice.
Headspace (HS5-TD): Equilibration: 1 min at 50°C. Sample volume: 75 mL. Sample cycles: 2.
TD (UNITY): As opposite.
Analysis: GC–MS.

Headspace and sorptive extraction techniques complement each other in this analysis of freshly-squeezed orange juice. Headspace extracts only the more volatile components, while sorptive extraction provides added sensitivity for the less volatile compounds.

Valencene has been suggested as an easily measurable marker for increased fruit maturity.
Fruit juice

Convenient sorptive extraction of semi-volatile aroma compounds

Liquid–liquid extraction and immersion SPME are the most common ways of analysing semi-volatile organic compounds in aqueous samples, but these can be laborious and have limitations with regard to analyte scope and sensitivity.

Sorptive extraction media such as Markes’ reusable SPE-tD cartridges are easy to use, and have a much larger area of sorbent than SPME fibres, giving them a high analyte capacity and consequently greater sensitivity. The cartridges are simply placed in the liquid and agitation to ensure equilibrium is reached between the polymer adsorbent and the sample. They are then inserted directly into an empty TD tube and desorbed within the TD instrument.

Typical analytical conditions:
Sample: 10 mL of freshly-pressed apple juice.
Sorptive extraction (SPE-tD cartridge): Stirred for 1 h at 20°C. Cartridge then placed in an empty TD tube.
TD (UNITY or TD100): Tube: Desorbed at 180°C (5 min). Trap (General-purpose hydrophobic): Analytes trapped at 25°C, desorbed at 300°C (5 min). Split ratio: Outlet 11:1.
Analysis: GC–MS.

Once sampling is complete, Markes’ SPE-tD cartridges are desorbed within an industry-standard TD tube.

Application Note 088

Alcohols, aldehydes, ketones and esters predominate in these sorptive-extraction analyses of ‘from-concentrate’ and freshly-pressed apple juice. Perhaps surprisingly given their different origin, the range of compounds is very similar in the two samples – and the relative amounts differ only slightly.
Quick identification of ‘Brett’ spoilage

‘Brett’, or Dekkera (Brettanomyces) bruxellensis, is a spoilage yeast found in beer and wine that creates ‘animal’ or ‘phenolic’ off-odours. Screening techniques need to be able to quickly pinpoint the presence of low levels of the compounds responsible – primarily 4-ethylphenol, 4-ethyl-2-methoxyphenol and 3-methylbutanoic acid.

These compounds, being relatively involatile, are best monitored by sorptive extraction using Markes’ SPE-tD cartridges (see page 41). Following release of the vapours from the cartridges within a TD tube, efficient focusing of analytes within the thermal desorber ensures detection of the widest possible analyte range with optimum sensitivity.

**Typical analytical conditions:**
Sample: 20 mL of red wine.
Sorptive extraction (SPE-tD cartridge): Stirred for 1 h at 20°C. Cartridge then placed in an empty TD tube.
TD (UNITY or TD100): Tube: Desorbed at 180°C (5 min). Trap (General-purpose hydrophobic): Analytes trapped at 25°C, desorbed at 300°C (5 min). Split ratio: Outlet 11:1.
Analysis: GC–MS.
Beer

Widening the analyte volatility range

Beer, like many other products of fermentation, contains a large number of chemical components with a wide range of volatilities and concentrations. However, existing techniques such as headspace or SPME struggle to sample this diversity in one run.

Sorptive extraction solves these difficulties because the large volume of PDMS on the cartridges can capture a wide range of analytes with maximum sensitivity for trace-level species. Multi-bed focusing traps and the inert flow path in Markes’ TD instruments enhance this capability by ensuring compatibility with the widest possible analyte volatility range – from C₂ to C₄₄, including reactive species.

Typical analytical conditions:
Sample: 20 mL of bottled beer.
Sorptive extraction (SPE-tD cartridge): Stirred for 10 min at 40°C. Cartridge then placed in an empty TD tube.
TD (UNITY or TD100): Tube: Desorbed at 280°C (10 min). Trap (Air toxics or Material emissions): Analytes trapped at 25°C, desorbed at 280°C (2 min). Split ratio: Outlet 15:1.
Analysis: GC–MS.

A wide range of analytes – from penta-1,4-diene (b.p. 26°C) to decanoic acid (269°C) – are sampled and detected in bottled beer with minimal sample preparation using sorptive extraction with TD–GC–MS.
Minimising sample preparation for accurate brand comparison

The aroma profiles of beer often depend rather critically on the presence or absence of minor components, placing considerable emphasis on the reproducibility of the analytical protocol.

The simplicity of sorptive extraction (see page 41) contrasts with conventional more labour-intensive techniques for sampling of beverages, making it straightforward to ensure that variation in the sampling phase is minimised and therefore that aroma profiles of different samples reflect the actual volatile content.

**Typical analytical conditions:**
Sample: 20 mL of bottled beer.
Sorptive extraction (SPE-tD cartridge):
Stirred for 30 min at 45°C. Cartridge then placed in an empty TD tube.
TD (UNITY or TD100): Tube: Desorbed at 180°C (5 min). Trap (Air toxics):
Analytes trapped at 25°C, desorbed at 300°C (5 min). Split ratio: Inlet: 3:1 (high-split run only), Outlet 11:1 (high-split and low-split runs).
Analysis: GC–MS.

Three brands of beer are compared in this analysis, using sorptive extraction and TD to maximise the sensitivity for minor components. Beer 2 has a distinctly smaller number of components, and a much lower proportion of the floral-smelling phenethyl alcohol.
Avoiding interference from water and ethanol

The large quantities of water and ethanol present in the headspace of spirits can interfere with GC, but sample preparation to remove these bulk components can be time-consuming and may introduce contaminants (or cause analyte loss).

Markes’ TD instruments overcome these problems and so speed up analysis, firstly by using appropriate sorbents to avoid sampling excess water (while of course allowing collection of a range of VOCs and SVOCs). Secondly, residual water and ethanol can be selectively eliminated before desorption. The result is the visualisation of key aroma components that would have otherwise been masked.

Typical analytical conditions:
Sample: Whisky.
TD (UNITY): Trap (Tenax® TA): Analytes trapped at –10°C, desorbed at 280°C (3 min).
Analysis: GC–MS.

Application Note 084

The use of hydrophobic sorbents, and a selective purge of water and ethanol from the focusing trap prior to desorption, unmasks a number of high-volatility components in whisky headspace.
The presence of toluene (#3) and xylene (#5) is a possible cause for concern in this headspace analysis of whole milk, collected by direct injection into the focusing trap of the thermal desorber.
Drinking water

Enabling routine detection of trace-level odorants

Drinking water is prone to contamination by naturally occurring compounds such as geosmin, methyl isoborneol and trihaloanisoles – compounds that can be detected by the human nose at levels as low as ~10 ppt. Although these chemicals don’t pose a health hazard, water companies monitor them because their ‘earthy’ smell frequently leads to customer complaints.

These volatile compounds are best detected by repeated collection of headspace onto the focusing trap of a thermal desorber. This provides a 10–100-fold increase in sensitivity compared to direct GC injection of a single headspace sample, as well as improved performance for less volatile analytes.

Typical analytical conditions:
Sample: 5 mL drinking water, spiked with a mix of common odorants.
Headspace (HS5-TD): Equilibration: 2 min at 45°C. Sample cycles: 10.
TD (UNITY): Trap (General-purpose): Analytes trapped at 30°C (purgeables) or 50°C (odorants): Desorbed at 300°C (3 min).
Analysis: GC–MS.

Repeated headspace sampling onto a single sorbent tube, followed by TD–GC–MS analysis, is used to enhance the sensitivity for key odorants in this sample of drinking water to the low-ppt level.
Drinking water

Sorptive extraction of semi-volatile organics

Headspace is a convenient technique for assessing the odour profile experienced by the consumer, but its sensitivity is limited. In addition, to carry out comprehensive analysis that includes less-volatile contaminants requires time-consuming liquid–liquid extraction, or solid-phase extraction with solvent elution.

Sorptive extraction using Markes’ SPE-tD cartridges speeds up such analyses by entirely avoiding the need for solvent. In addition, the large volume of PDMS on the cartridges ensures maximum sensitivity for trace-level species, while the multi-bed focusing traps and the inert flow path in Markes’ TD instruments allow the widest possible analyte volatility range – from C₂ to C₄₄, including reactive species.

**Typical analytical conditions:**
Sample: 1 L of drinking water, spiked with a mix of common odorants.
Sorptive extraction (SPE-tD cartridge): Stirred for 2 h at 45°C. Cartridge then placed in an empty TD tube.
TD (UNITY or TD100): Tube: Desorbed at 60°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at 30°C, desorbed at 300°C (3 min). Split ratio: Outlet ~6:1.
Analysis: GC–MS.

Despite being at the sub-ppb level, a range of commonly-encountered odorants are easily detected in drinking water using the ability of sorptive extraction with TD to enhance the concentration of semi-volatiles.
Packaging materials
Drinks bottles

Detecting chemicals migrating from product packaging

Plastics have long been highly popular for the packaging of food and drinks, but it is now recognised that some chemicals in the plastic can leach into the product. These may be highlighted because they give rise to a taint in the product, but health concerns are usually the focus of attention, with some chemicals – such as bisphenol A (BPA) and phthalates of particular concern. Identifying any migrating chemicals is therefore important for many food and drink manufacturers.

Markes provides a range of highly sensitive and versatile options for tracking down the sources of chemical migrants, whether from the packaging or elsewhere in the supply chain. The Micro-Chamber/Thermal Extractor is recommended for larger or heterogeneous samples, whereas direct desorption is particularly convenient for small quantities of homogeneous materials such as the polymer illustrated here.

Typical analytical conditions:
Sample: 200 mg of ground polyethylene terephthalate (PET), placed in an empty TD tube.
Analysis: GC–MS.

Direct desorption is a convenient way of comparing similar samples in order to troubleshoot taint. 1,3-Dioxolane and acetaldehyde are clear issues in two of these samples of PET (a polymer widely used in plastic drinks bottles).
Corks used for wine

Detection of trichloroanisole taint

Although polymer or screw-cap closures are now widely used on wine bottles, traditional corks are still popular in many countries, especially for the most prestigious vintages. However, the use of cork does carry a risk of ‘corking’ due to the presence of 2,4,6-trichloroanisole (TCA) – leading to the need for reliable, automated and highly sensitive detection.

TD greatly enhances the sensitivity and analyte range of headspace methods, due to the efficient focusing and release of analytes and the inert, uniformly heated flow path. This makes detection of TCA and other undesirable components straightforward, whether in the final wine (see page 27) or from the corks themselves, as shown here.

**Typical analytical conditions:**

Sample: Whole cork, spiked with TCA to give 5 pg on-column.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 30 mL/min for 5 min. Chamber temperature: 60°C.

TD (UNITY or TD100): Tube (Material emissions): Desorbed at 280°C (7 min). Trap (Tenax® TA): Analytes trapped at 25°C, desorbed at 300°C (3 min). Split ratio: 5.5:1.

Analysis: GC–MS.

An elevated temperature was used to rapidly release the headspace from whole corks using the Micro-Chamber/Thermal Extractor (µ-CTE), leading to the detection of TCA at trace levels despite a complex background.
Packaged steak

Checking for contaminants from packaging using simple grab-sampling

Food safety can be jeopardised if residual chemicals from a poor-quality batch of packaging material migrate into the food. GC analysis can assist in pinpointing such problems, but sample preparation often remains a bottleneck.

Grab-sampling directly on to sorbent tubes is a rapid way of collecting vapours from a variety of containers. TD then ensures that the widest possible range of volatiles are sent to the GC, so a comprehensive profile can be obtained in a single run. To avoid analytical interference from water, a relatively small sample was taken, with the use of hydrophobic sorbents, a dry-purge, and sample splitting used to further reduce the amount of water reaching the detector.

Typical analytical conditions:
Sample: Packaged steak.
Headspace (Easy-VOC): 100 mL.
TD (UNITY or TD100): Tube (Odour): Desorbed at 120°C (5 min) then 260°C (5 min). Trap (Material emissions): Analytes trapped at 25°C, desorbed at 300°C (5 min). Split ratio: Outlet 21:1.
Analysis: GC–MS.

Application Note 107

Rapid and representative sampling of meat headspace was achieved here using Markes’ Easy-VOC grab-sampler. Packing the TD tubes with two hydrophobic sorbents allowed over 30 components to be analysed without interference from water. Removal of baseline interference and compound identification was carried out using TargetView software – see page 42.
Relevant sampling and analytical techniques
Thermal desorption

Thermal desorption (TD) uses heat and a flow of inert gas to desorb volatile and semi-volatile organic compounds (VOCs and SVOCs) from sorbents or sample materials. Extracted vapours are swept onto an electrically-cooled sorbent-packed 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-C_{44}H_{90} and reactive species can all be analysed on a single TD platform.

- **Quantitative re-collection of split flows** enables repeat analysis and simple method validation, overcoming the historical ‘one-shot’ limitation of TD.

- **High sensitivity** – Two-stage desorption using sorbent tubes allows concentration enhancements of up to 10^6.

- **Wide dynamic range** – Two-stage desorption and sample splitting means that Markes’ thermal desorbers can handle analyte concentrations ranging from part-per-trillion up to low-percent levels.

- **Sample compatibility** – As world leaders in TD technology, Markes offers an unmatched range of innovative and labour-saving sampling accessories for liquids, solids and gases.

- **Analytical quality** – The narrow-bore design of the focusing trap ensures that a highly concentrated band of vapour is introduced to the GC, allowing true splitless operation and optimising both resolution and sensitivity.

- **Reduced running costs** – Electrical cooling eliminates the cost of cryogen, and also avoids problems with ice formation, improving retention time stability.

- **Cleaner chromatography** – By circumventing the need for sample preparation, solvent artefacts are eliminated, while unwanted high-abundance components such as water can also be selectively removed.

Markes’ patented inert valving enables C_2–C_{44} and reactive species to be analysed on a single thermal desorption system.

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

For more on the principles, benefits and applications of TD, download Application Note 012.

For more on the single-tube UNITY-xr™ thermal desorber and the multi-tube automated TD100-xr™ instrument, visit www.markes.com.

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Micro-Chamber/Thermal Extractor

Markes' Micro-Chamber/Thermal Extractor™ (µ-CTE™) is a stand-alone sampling accessory for dynamic headspace sampling of organic vapours from a wide variety of materials. Operation is simple, with short sampling times (typically <60 minutes) and the capability to analyse up to four or six samples at once, depending on the model chosen.

The µ-CTE can be used for:
- Quality-control of chemical emissions from products and materials.
- Screening of products before long-term certification tests.
- Checking raw materials.
- Comparing products to those of competitors.
- Monitoring odour and emission profiles.
- Product troubleshooting and R&D.
- Kinetic studies such as shelf-life tests, or monitoring fragrance profiles as they change over time.
- Permeation tests.

Direct desorption

Direct desorption is a highly effective way of sampling organic vapours from homogeneous materials containing relatively high concentrations of volatiles.

A small quantity of the material is placed into an empty TD tube, and the tube placed in the thermal desorber. It is then gently heated in a flow of inert gas to dynamically extract headspace volatiles directly on to the focusing trap.

See pages 6–12, 19, 20, 23 and 36 for applications using the µ-CTE.

For more on the µ-CTE and to download the brochure, visit www.markes.com.

For more on direct desorption, see Application Note 009.
Sorptive extraction

Sorptive extraction, using plain or magnetically-stirred cartridges, is a simple way of sampling less volatile compounds in aqueous samples – applications that would otherwise require manually intensive extraction or distillation before GC analysis.

Markes’ SPE-tD™ cartridges are constructed in the form of a hollow tube, coated inside and out with poly(dimethylsiloxane). In contrast to SPME fibres, this large volume gives them a high sampling capacity, making them ideal for applications demanding high sensitivity.

The cartridge is simply placed into the sample and agitated, before being removed, rinsed, and placed into an empty TD tube for analysis by direct desorption. This allows semi-quantitative analysis of less volatile organics, and direct comparison of organic chemical concentrations in similar samples.

Grab-sampling

Grab-sampling onto sorbent tubes is a convenient alternative to pumped sampling, and is especially suitable for monitoring headspace of packaged goods.

Markes’ Easy-VOC™ is a manually-operated grab-sampler that allows precise volumes of air or gas to be sampled directly onto sorbent tubes. Tubes can be packed with multiple sorbent beds, widening the analyte range detectable from a single sample.

See pages 25–29 and 33 for applications using sorptive extraction.

For more on SPE-tD cartridges, visit www.markes.com.

See pages 15 and 37 for applications using grab-sampling.

For more on Easy-VOC 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 closely-eluting 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.

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

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**As shown in this example of bacon headspace,** 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 quickly and conveniently.

As well as profiling of food and drink, Markes’ products are used extensively in multiple routine and research applications – everything from environmental analysis to metabolomic studies.

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™, Easy-VOC™, HSS-TD™, Micro-Chamber/Thermal Extractor™, μ-CTE™, SPE-ID™, TargetView™, TD100™, TD100-xr™, UNITY™ and UNITY-xr™ are trademarks of Markes International.

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