Food and beverages

A guide to comprehensive VOC profiling for aroma, quality and authenticity studies

Contents

For more information on any of the applications described, or to discuss how our aroma discovery technologies could benefit you, please contact our applications specialists at hello@sepsolve.com, or by telephoning any of our regional offices (see back cover for details).

Introduction

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

In this Applications Guide, we describe how access to a range of sampling options, coupled with 1D or 2D gas chromatography (GC) and time-of-flight mass spectrometry (TOF MS), can help provide valuable insights into everything from red wine to fresh-cut fruit.

Discover more – Deliver more

SepSolve Analytical is part of the Schauenburg Analytics Group, alongside Markes International, and together we have many hundreds of years of combined experience at the forefront of GC–MS applications and system engineering. With our wealth of knowledge and expertise, we are the ideal strategic partners to provide the support you need to advance your laboratory's success. We make your life easier, by integrating our products into complete end-to-end workflows – for streamlined analysis, from sample introduction through to data analysis.

SAMPLE INTRODUCTION

Automated sample extraction and enrichment with Markes' Centri® and thermal desorbers:
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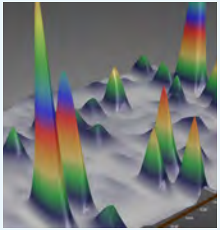
SEPARATION



Advanced separations of complex mixtures using INSIGHT® flow modulation:
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MASS SPECTROMETRY

BenchTOF2™ with uniquely confident identification by Tandem Ionisation®:
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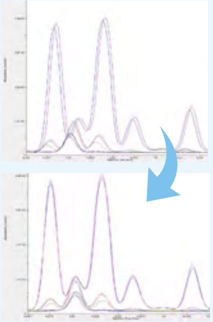
DATA ANALYSIS



Alignment & advanced data mining using the ChromSpace® software platforms:
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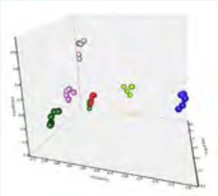
CHEMOMETRICS



Transform complex data into useable results with ChromCompare+™:
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Beverages

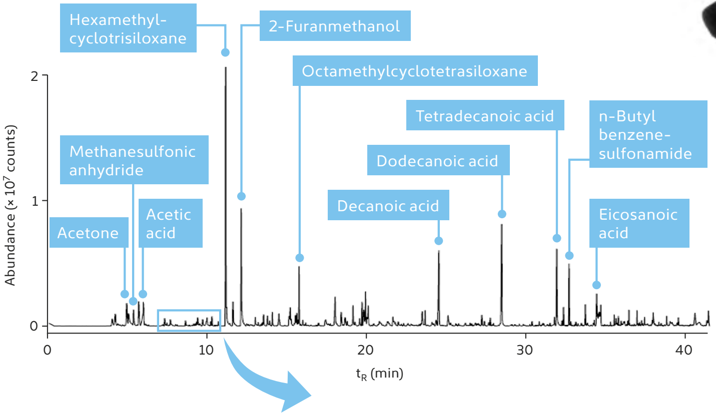
The complex aroma and flavour profiles of beverages such as wine, milk and beer have long presented analytical challenges. These are now being tackled, thanks to novel sampling methods and enhanced separation techniques such as those described here.

Milk

Robust quality control with immersive sorptive extraction

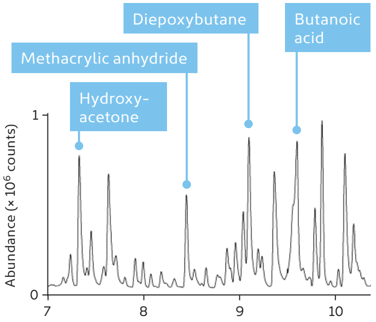
Milk, like many other beverages, contains a wide variety of VOCs and SVOCs with a range of chemical structures and concentrations spanning several orders of magnitude. Many of these compounds are important for their organoleptic and/or health properties. However, current analytical methods lack sensitivity, and struggle to deal with this wide analyte range in a single run.

Immersive sorptive extraction using high-capacity HiSorb™ probes combines high sensitivity with the ability to capture VVOCs, VOCs and SVOCs within a single experiment, allowing robust quality control. Centri® fully automates this process, including a crucial wash/dry step to remove any matrix.



Analytical details

- **Sample:** Semi-skimmed milk (3 mL), diluted with 15% NaCl solution (15 mL).
- **Sorptive extraction and preconcentration:** Inert HiSorb™ probe, used in immersive mode and automated on Centri®. Trap: 'Material emissions'.
- **GC–MS:** Mass range: m/z 35–350.
- **Software:** ChromSpace® 1D.



Excellent chromagraphy is achieved across a wide volatility range in this analysis of milk, using HiSorb™ sorptive extraction followed by GC–MS. Selected peaks are indicated, and the excellent peak shape is shown in the expansion.

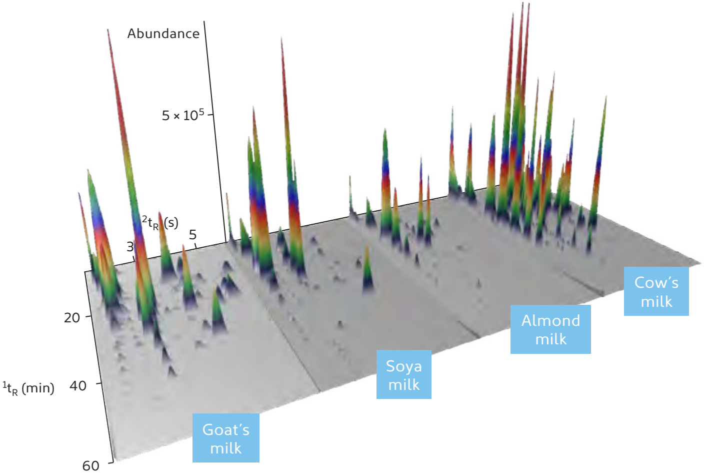
Milk

Continued from previous page

Easily-visualised comparison of milk brands using GC×GC

To cater for customers with different preferences or dietary requirements, a variety of alternatives to traditional cow's milk are now available. These range from milk from other animals to flavoured drinks made with grains, nuts or other non-dairy sources. Achieving reliable comparison of such wide-ranging products calls for sampling and analytical methods with wide applicability.

Addressing this challenge, immersive sorptive extraction in conjunction with TD preconcentration and GC×GC–TOF MS offers unparalleled flavour profiling and the ability to easily visualise differences between sample types.



Comprehensive screening of aroma profiles and robust comparison of milk samples is demonstrated using high-capacity sorptive extraction and TD with GC×GC–TOF MS analysis.

Analytical details

▶ **Sample:** Milk (10 mL). ▶ **Sorptive extraction:** Inert HiSorb™ probe, used in immersive mode. ▶ **TD:** TD100-xr™. Trap: 'General-purpose hydrophobic'. ▶ **GC×GC:** Split 100:1. Modulation period: 3.8 s. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 40–300. Tandem Ionisation®: 70/14 eV. ▶ **Software:** ChromSpace®.

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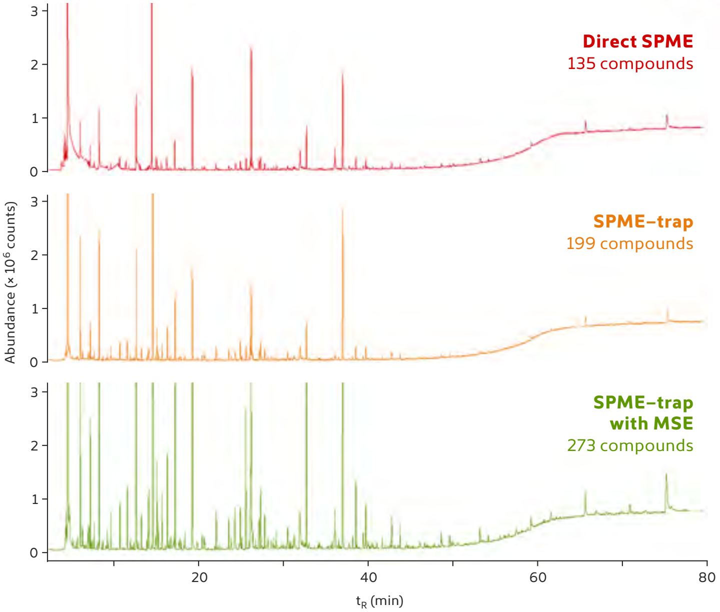
Tea

Sample enrichment for improved sensitivity

Accurate characterisation of the aromas of foods and beverages requires the reliable detection of minor components, but some conventional sampling techniques – such as regular SPME – can struggle to achieve the necessary sensitivity.

Fortunately, SPME sensitivity can be greatly improved by using a process known as 'multi-step enrichment' (MSE). This works by desorbing the sampled SPME fiber onto a sorbent-packed focusing trap. The fiber is then returned to the sample vial for a second round of extraction, followed by desorption onto the same trap. This process is then repeated multiple times, allowing exhaustive analyte extraction.



Increased sample loading and improved detection of trace-level analytes is the benefit of using the multi-step enrichment (MSE) approach – as exemplified by the SPME analysis of a tea suspension.

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Analytical details

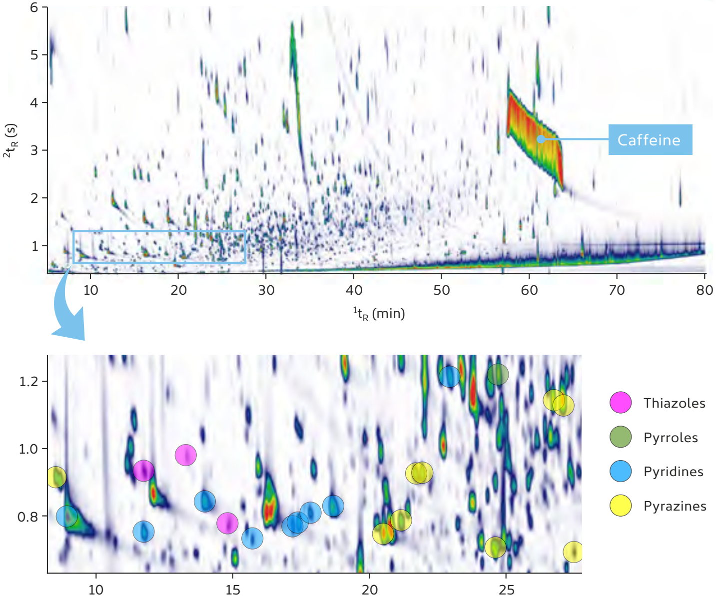
▶ **Sample:** Black tea. ▶ **SPME and preconcentration:** Centri®. Trap: 'Material emissions'. ▶ **GC–MS:** Mass range: m/z 35–350. ▶ **Software:** ChromSpace® 1D.

Coffee

Expanding separation capacity with GC×GC

Almost 1000 compounds have been identified in roast coffee extracts, with chemical composition varying due to a number of factors, such as coffee bean origin and degree of roasting. Such complexity can make efficient screening of coffee samples very difficult or impossible using conventional GC with quadrupole MS detectors.

Addressing such difficulties, GC×GC with BenchTOF™ detection provides the enhanced separation capacity to allow the entire composition. Importantly, this can be achieved within a single analytical run, as illustrated in this example of a roasted coffee extract.



Analytical details

▶ **Sample:** Coffee extract. ▶ **GC×GC:** Thermal modulator. Modulation period: 6.0 s. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 35–400. ▶ **Software:** ChromSpace®.

A number of nitrogen-containing compounds – including pyridines, pyrazines, and thiazoles – contribute to the aroma of coffee, and are identified in this GC×GC run of a ground coffee extract. Such detailed analysis would be extremely difficult to achieve in a regular GC–MS run.

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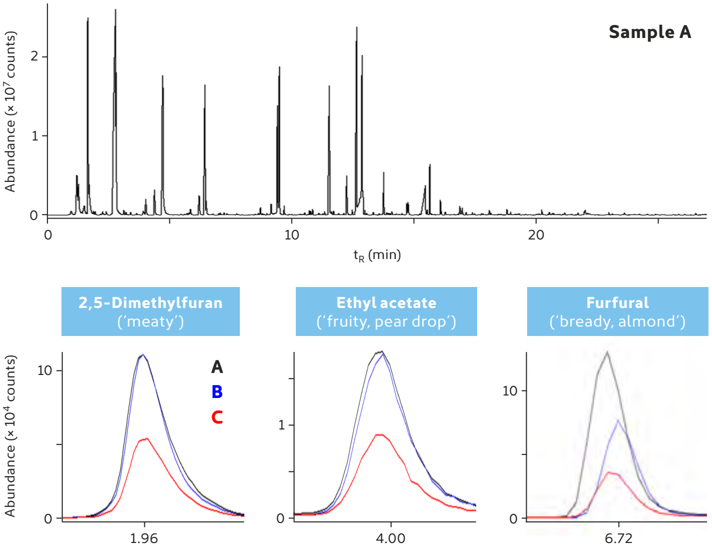
Red wine

Reliable comparison of aroma profiles

Across the wine sector, aroma and flavour profiling is valued, both for quality control, and for understanding the molecular origin of the characteristics that make particular vintages highly desirable.

High-capacity sorptive extraction – used immersively or in headspace mode – is a powerful sampling approach that enables side-by-side comparison of brands, and the elucidation of key differences.

In the case of the three Cabernet Sauvignon wines shown, the aroma compounds present were similar, but abundances varied. Such differences can have a significant impact on the overall aroma.



Key differences are apparent in the abundances of three aroma compounds between three Californian red wines (A, B, C). The main image shows the overall profile of Sample A.

Analytical details

▶ **Sample:** Three Californian Cabernet Sauvignon red wines (AVA region).
▶ **Sorptive extraction and preconcentration:** Inert HiSorb™ probe, used in headspace mode and automated on Centri®. Trap: 'Material emissions'.
▶ **GC–MS:** Mass range: m/z 50–300. ▶ **Software:** ChromSpace® 1D.

Red wine

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Improving analyte separation in complex aroma profiles

Aroma profiles, such as those for wine, are often highly complex, with important odorants frequently masked by higher-concentration components when using conventional 1D gas chromatography.

Because of the enhanced separation it provides, GC×GC is an excellent choice for aroma profiling of complex samples, and use of the INSIGHT® flow modulator provides the additional benefit of eliminating the use of cryogen.

In this example, coupling GC×GC with inherently sensitive TOF MS provides confident identification of both targets and non-targets.

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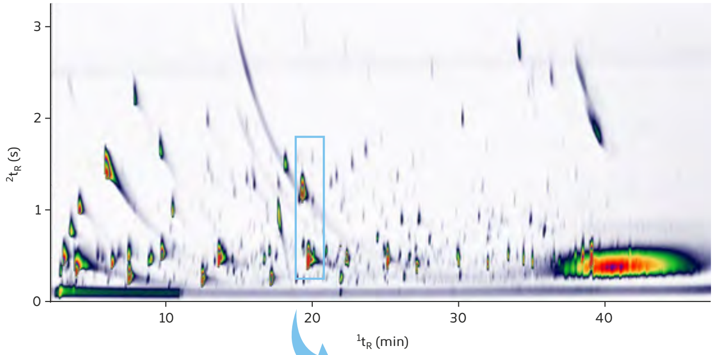
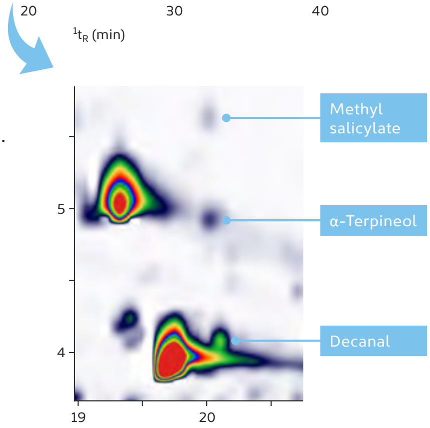


Analytical details

- **Sample:** Pinot Noir red wine.
- **Sorptive extraction:** Inert HiSorb™ probe, used in headspace mode and automated on Centri®.
- **GC×GC:** Flow modulator: INSIGHT®. Modulation period: 5.5 s.
- **TOF MS:** BenchTOF™. Mass range: m/z 35–600
- **Software:** ChromSpace®.



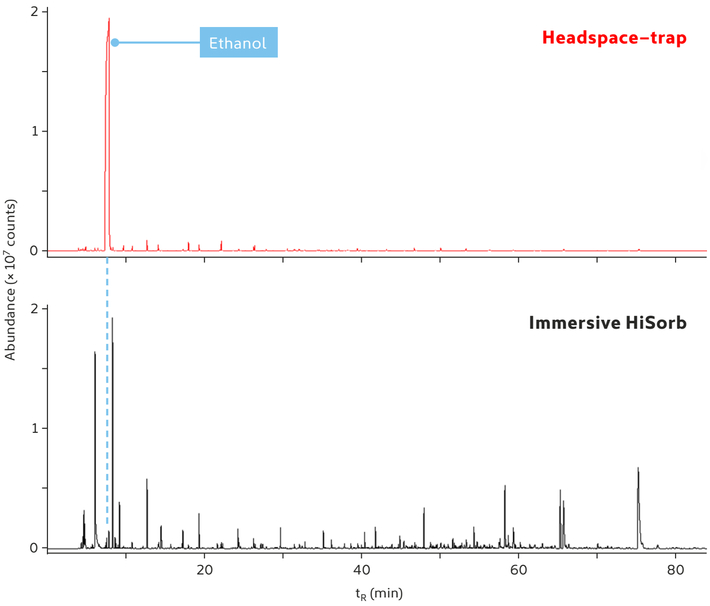
In this headspace analysis of red wine, a co-elution that would have occurred in 1D GC is avoided thanks to the additional separation of GC×GC – meaning more confident identification of a wider range of components.

Vodka

Avoiding interference from ethanol using sorptive extraction

Historically, a wide variety of sampling methods have been used to extract volatiles from alcoholic spirits, with key drivers being the need to improve upon inefficient solvent extraction methods and to cope with high alcohol content.

In such cases, HiSorb™ sorptive extraction has a major advantage over traditional headspace sampling, because the low partition coefficient of ethanol (log $K_{o/w}$ −0.14) means that it is less likely to dominate the aroma profile, as illustrated in this example.



Use of PDMS-based HiSorb™ probes to sample vodka headspace reduces the relative reponse from ethanol, as shown in these GC–MS profiles, both acquired on Markes' Centri® platform. Note the additional detail obtained using immersive mode, especially for high-boilers.

Analytical details

▶ **Sample:** Vodka. ▶ **Sorptive extraction:** Inert HiSorb™ probe, used in immersive mode and automated on Centri®. Trap: 'Material emissions'. ▶ **GC–MS:** Mass range: m/z 35–350. ▶ **Software:** ChromSpace® 1D.

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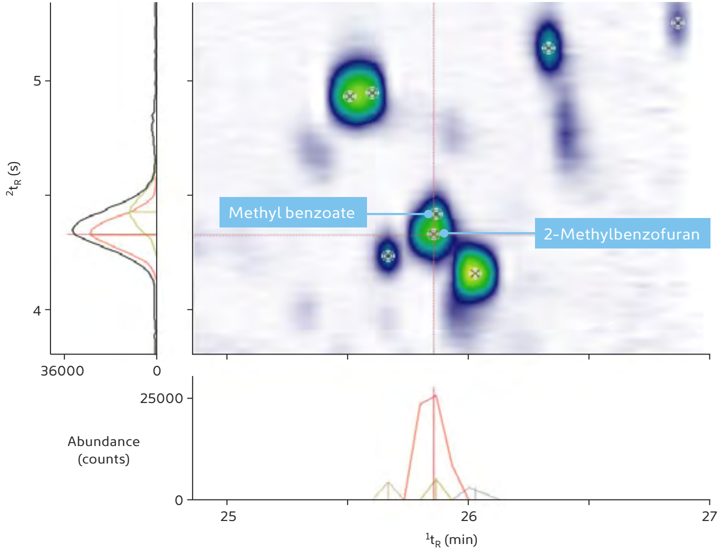
Whisky

Uncovering ‘hidden’ aroma compounds

Hundreds of compounds from a wide range of chemical classes contribute to the aroma of whisky. It is important to be able to confidently identify these volatiles, for quality control and authentication, as well as in the engineering of new aromas.

GC×GC–TOF MS is ideal for the analysis of such complex samples, because the enhanced separation capacity allows screening of the entire composition in a single analysis, with confident identification of compounds that would ordinarily co-elute.



This expanded GC×GC colour plot of a whisky sample shows how ChromSpace software allows two co-eluting aroma-active species to be confidently identified against the NIST database (match factors >890).

Analytical details

▶ **Sample:** Whisky, diluted 3:1 with water. ▶ **SPME:** Fiber: DVB/Car/PDMS StableFlex™ (Sigma-Aldrich). Incubation: 35°C for 10 min, automated using a Sample Preparation Robot. ▶ **GC×GC:** Split: 5:1. Modulation period: 4.0 s. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 40–350. ▶ **Software:** ChromSpace®.

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Hard seltzers

Uncovering unique flavour-active components

After the commercial success of hard seltzers in 2019, over 50 brands are now available. Flavour profiling is vital for maintaining brand quality and consistency during production to ensure longevity in the market.

A variety of compounds contribute to the overall perceived flavour of seltzers, with some being unique to each brand. Low-volatility flavour-active compounds typically require immersive techniques for efficient extraction from the liquid phase.

Here, immersive sorptive extraction with GC–MS provided profiles covering a wide volatility range, with automated brand comparison using ChromCompare+™ enabling fast and simple classification, for checking product quality and brand authenticity.

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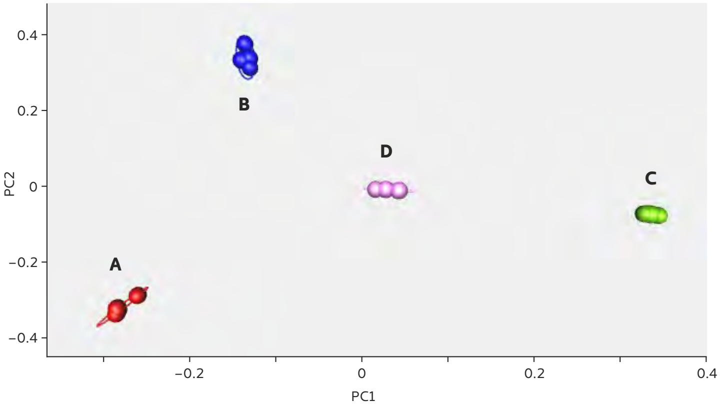
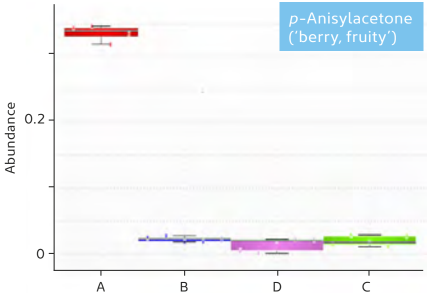


Analytical details

▶ **Sample:** 4 mL of store-bought hard seltzers in 16 mL HPLC-grade water. ▶ **Sorptive extraction:** Inert HiSorb probe (PDMS/DVB) used in immersive mode, and automated on Centri®. ▶ **GC–MS:** Mass range: m/z 35–350. ▶ **Software:** ChromCompare+™.



Four brands of flavoured hard seltzers are clearly differentiated in a PCA score plot in ChromCompare+™ (top), with one flavour component being much more abundant in the most popular brand (A), as shown in the box-and-whisker plot (bottom).

Fruit

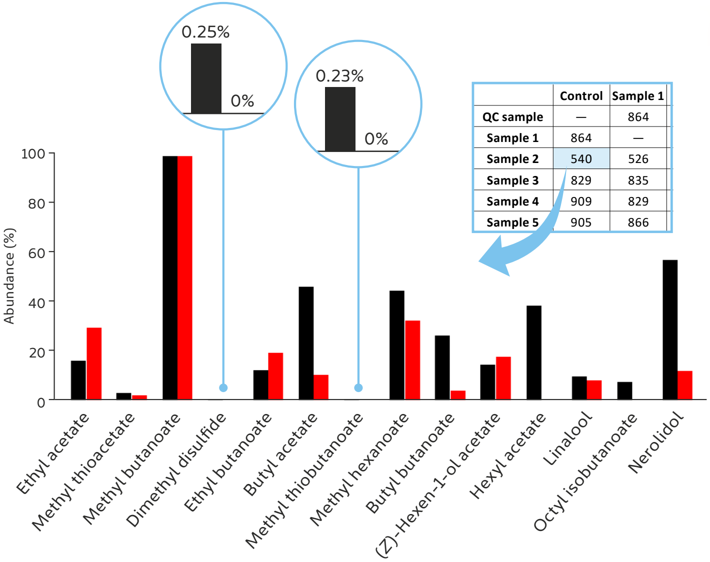
The analysis of volatiles from fresh fruit is particularly important because conditions during packing, transport and storage can affect shelf-life and the consumer perception of the final product. To improve fruit quality, it's therefore imperative to have analytical information on how these key volatiles vary.

Strawberries

Automated comparison of aroma profiles

In food quality control, reliable results are needed quickly. However, visual comparison of complex chromatograms is extremely subjective, while automated methods generally rely on retention-time alignment, which may introduce error.

ChromCompare+™ chemometrics software solves these problems by displaying trends and differences between samples using easy-to-understand visualisations. Using the relative abundances of key olfactory components from BenchTOF™, ChromCompare+ generates tables of simple 'match factors' indicating the quality of each pairwise sample comparison, so speeding up the review process.



	Control	Sample 1
QC sample	—	864
Sample 1	864	—
Sample 2	540	526
Sample 3	829	835
Sample 4	909	829
Sample 5	905	866

Analytical details

▶ **Sample:** Whole strawberries. ▶ **Dynamic headspace:** Micro-Chamber/Thermal Extractor™. Sampling: 40°C for 30 min onto an 'Odour' sorbent tube. ▶ **TD:** TD100-xr™. Trap: 'Material emissions'. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 35–350. ▶ **Software:** ChromCompare+™.

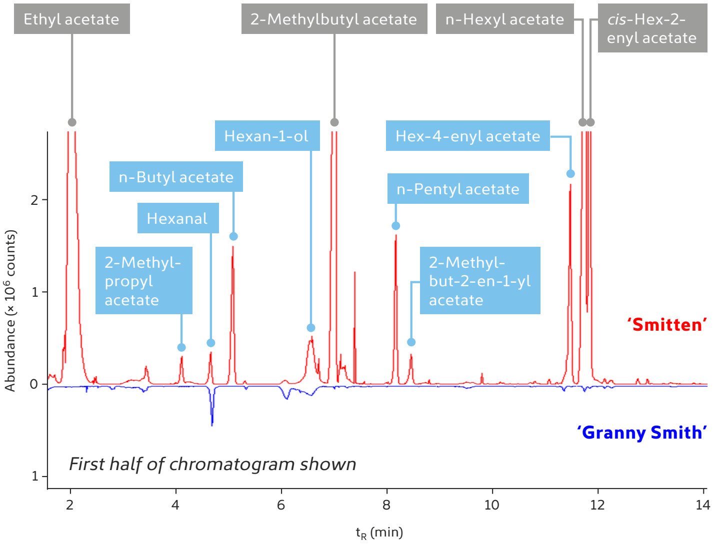
In this comparison of strawberry headspace (black) with a QC sample (red), the responses of two trace-level aroma-active sulfur species were weighted. As shown here, this ensures that any deviation from the control generates a low match factor, so flagging a potential QC issue.

Apples

Using VOC profiles as a measure of fruit quality

The analysis of food aroma is particularly important for fresh fruit, because conditions during packing, transport and storage can affect shelf life and perceived 'freshness'. However, obtaining objective comparisons of such inherently variable samples can be difficult.

Dynamic headspace solves this problem, by allowing relatively large (and hence more representative) samples to be taken. Using this approach in conjunction with trap-based focusing provides better GC–MS peak shape and sensitivity than standard static-loop or syringe injection of headspace.



First half of chromatogram shown

Analytical details

▶ **Sample:** 'Smitten' and 'Granny Smith' apples (six pieces, each ~8 cm^3).
▶ **Dynamic headspace:** Micro-Chamber/Thermal Extractor™.
Sampling: 37°C for 10 min onto an 'Odour' sorbent tube.
▶ **TD:** Centri®. Trap: 'Sulfur/labile'. ▶ **GC–MS:** Mass range: m/z 35–350.
▶ **Software:** ChromSpace® 1D.

Sampling from relatively large amounts of apple enabled acquisition of representative profiles in this pair of analyses. 'Smitten' has a substantially more complex profile than 'Granny Smith', with higher responses from major components and a larger number of minor components.

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Pears

Evaluating fruit quality using ChromCompare+

Quality management enables the food and beverage industry to meet consumer expectations and maintain brand reputation and product safety.

Analytical instrumentation is constantly evolving, allowing us to gain greater insights into sample compositions than ever before, but data processing remains a bottleneck of analytical workflows.

Here, we use ChromCompare+™ software to automatically identify key differentiators across five pear cultivars using all the raw GC–MS data. This innovative approach minimises laborious pre-processing steps, and enables automated workflows to be adopted in quality control labs.

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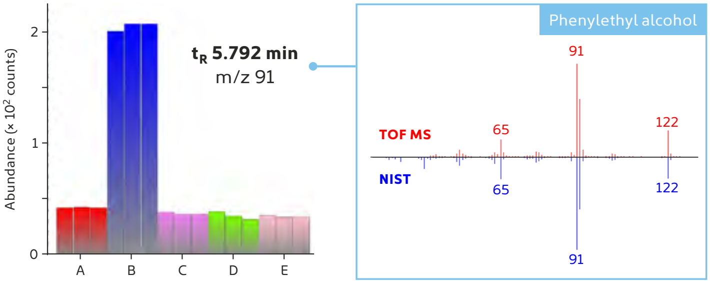
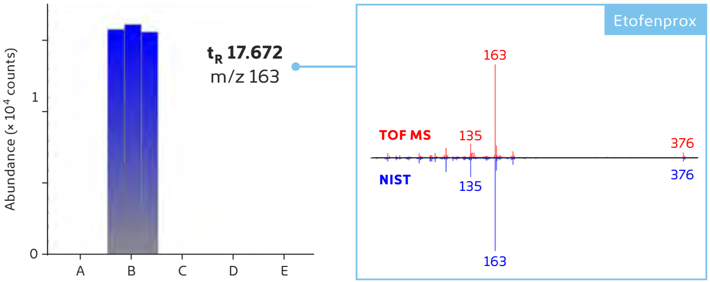




Analytical details

▶ **Sample:** Five pear extracts prepared by QuEChERS extraction and analysed in triplicate. ▶ **TOF MS:** BenchTOF™. ▶ **Software:** ChromCompare+™.

Two features are automatically highlighted as key differentiators between five pear cultivars in these ChromCompare+™ feature summary charts (with identifications made using NIST library screening). These differences are important, as phenylethyl alcohol contributes a floral, sweet flavour, while etofenprox is an insecticide.

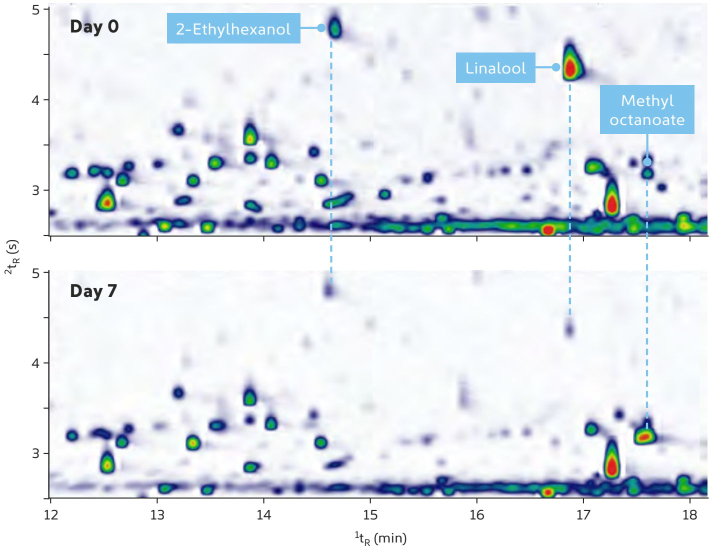
Peaches

Determining post-harvest fruit quality

The FRUIT qualitY (FRUITY) multi-organisation collaboration aims to provide new predictive technologies and a better understanding of physiological changes in fruit for objective quality assessment during post-harvest storage.

Here, the enhanced separation and high sensitivity of TD–GC×GC–TOF MS was used to capture comprehensive VOC profiles from peach cultivars. The results show how individual cultivars reacted differently to cold storage, with different changes in VOC profiles seen after seven days (the typical time taken for shipping from southern Italy to northern Europe).

View *Scientific Reports* journal article



Changed levels of three peach volatiles are apparent in this comparison of two expanded TD–GC×GC–TOF MS chromatograms, acquired before storage, and after storage for 7 days.

Analytical details

▶ **Sample:** Whole peaches sampled directly after harvest (Day 0) and after storage (Day 7) by placing in a roasting bag and drawing 600 mL headspace directly onto an ‘Odour/Sulfur’ sorbent tube. ▶ **TD:** TD100-xr™. ▶ **GC×GC:** Flow modulator: INSIGHT®. Modulation period: 4.0 s. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 45–350. ▶ **Software:** ChromSpace®.

Processed food

Within the food industry, and particularly for processed products, there is a growing need to monitor product quality. This requires a detailed understanding of individual components, and the following examples show how this can be achieved.

Cookies

Improving sensitivity with dynamic headspace extraction and GC–TOF MS

Monitoring product quality typically involves screening for flavour composition, taint and contamination. This requires an in-depth analysis of a sample's chemical constituents, but conventional approaches to sample preparation and analysis struggle to provide the necessary level of sensitivity.

Combining three inherently sensititive techniques – dynamic headspace, thermal desorption and TOF MS – addresses this issue, as demonstrated for this analysis of cookie aroma.

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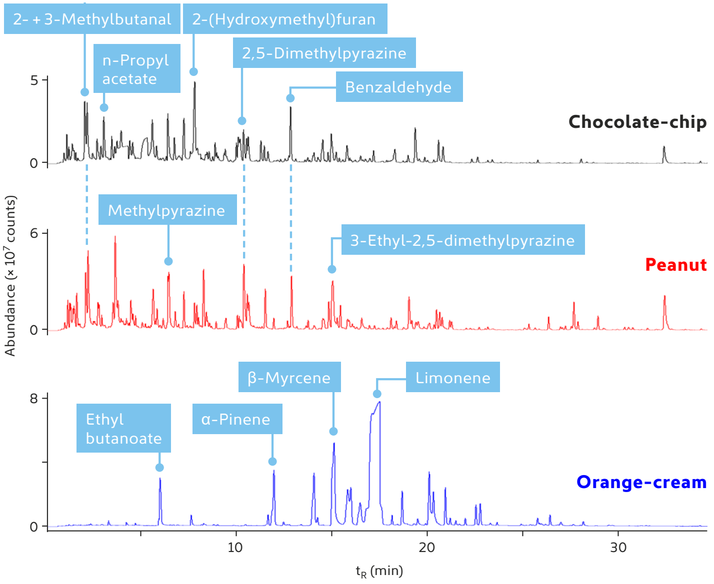


Analytical details

▶ **Sample:** Cookie (3 g). ▶ **Dynamic headspace:** Micro-Chamber/ Thermal Extractor™. Sampling: 40°C for 30 min onto a 'General-purpose' sorbent tube. ▶ **TD:** TD100-xr™. Trap: 'General-purpose'. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 40–600. ▶ **Software:** ChromSpace® 1D.

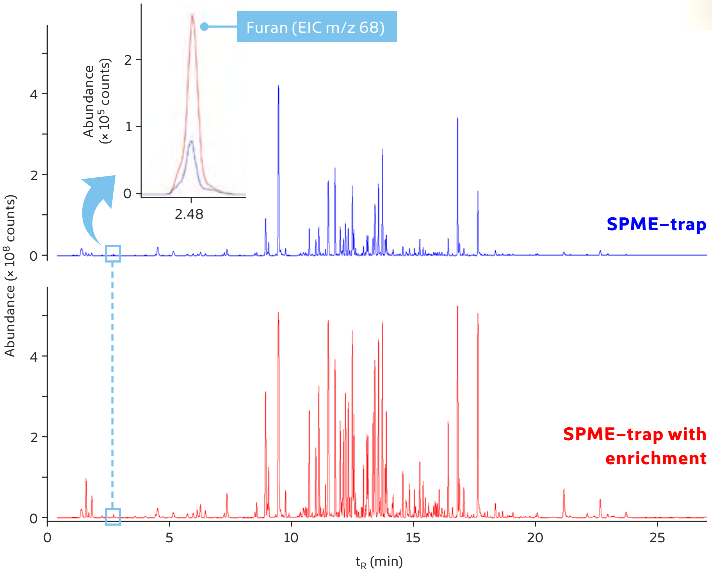
Fast and efficient profiling of trace aromas in cookies is achieved by use of microchamber sampling with TD–GC–TOF MS. Profiles of three cookie flavours show markedly different responses for a range of aroma compounds.

Cereal

Improved sensitivity with sample enrichment

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 conventional approaches to sample preparation and GC analysis struggle to provide the necessary level of sensitivity.

Here, we couple SPME–trap with highly sensitive GC–TOF MS for comprehensive aroma profiling and identification of odour taints and contaminants in a single analytical run.



SPME–trap with enrichment by 'sample stacking' from three vials enabled the detection of over 100 more peaks than SPME–trap alone, and can improve limits of detection for compounds of concern, such as furan.

Analytical details

▶ **Sample:** 1 g of a store-bought cereal, homogenised prior to addition of 2.5 g NaCl and 10 mL distilled water. ▶ **SPME:** DVB/CWR/PDMS SPME fiber (80 µm/10 mm) automated on Centri®. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 33–300. ▶ **Software:** ChromSpace® 1D.

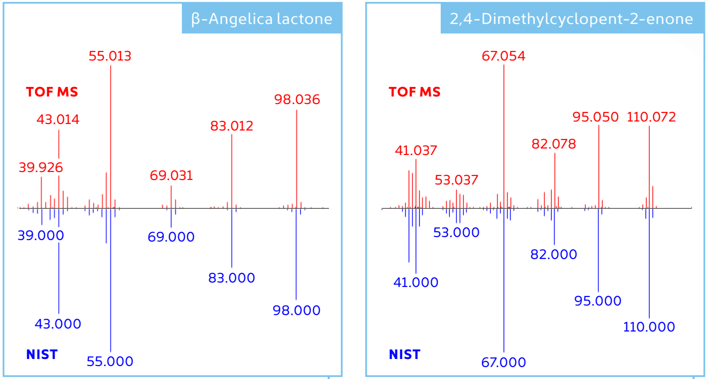
Liquid smoke

Comprehensive chemical fingerprinting

‘Liquid smoke’ is the name given to flavouring products that claim to enhance food by adding a ‘smoked’ flavour, to mimic the traditional smoking process.

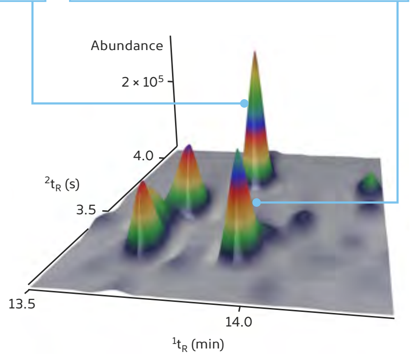
Due to the complex nature of liquid smoke, the European Food Safety Authority (EFSA) issued new guidelines in February 2021 for the analysis of such products prior to authorisation. The new guidelines call for full chemical characterisation of the primary product, meaning that non-target analysis is required.

Here, GC×GC–TOF MS provides comprehensive chemical fingerprinting of liquid smokes, with confident identification of analytes using the excellent spectral quality and improved mass accuracy (<50 ppm) of BenchTOF2™ mass spectrometers.



Analytical details

▶ **Sample:** Store-bought ‘applewood’ liquid smoke, prepared using liquid–liquid extraction into dichloromethane.
▶ **GC×GC:** Flow modulator: INSIGHT®. Modulation period: 3.0 s. ▶ **TOF MS:** BenchTOF2™. Mass range: m/z 30–600. ▶ **Software:** ChromSpace®.



Confident identification of analytes in an ‘applewood’ liquid smoke was achieved by comparison of BenchTOF2™ spectra against commercial libraries (top), following GC×GC–TOF MS analysis (bottom).

Plant-based meat substitutes

Reverse-engineering of aroma

To maximise the customer appeal of plant-based meat substitutes, it is desirable to mimic the sensory experience of cooked meats by 'reverse-engineering' the aroma.

However, ground meat may release hundreds of VOCs during cooking, many of which are odour-active and cover a wide range of chemical classes. It is therefore challenging to capture a comprehensive VOC profile.

Here, the combination of sensitive sorptive extraction, enhanced separation by GC×GC–TOF MS and sophisticated data analysis in the ChromCompare+™ chemometrics platform enables differences in aroma profiles to be identified quickly and easily.

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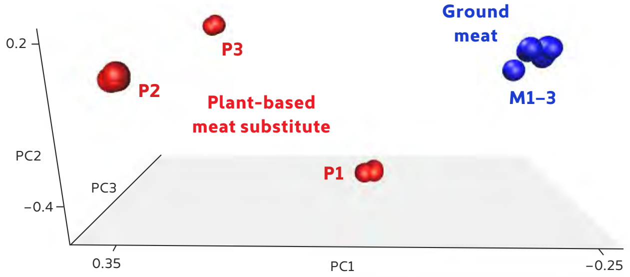

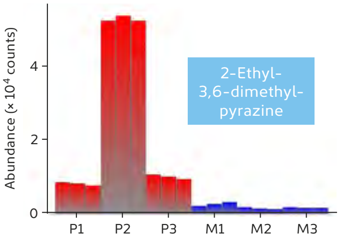

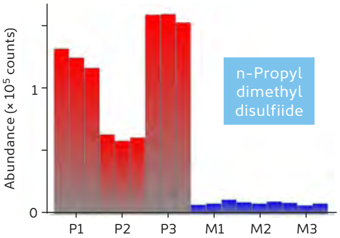

A sulfur compound and a pyrazine are amongst the key differentiators uncovered in this analysis of three ground meat products (M1–3) and three plant-based meat substitutes (P1–3), as illustrated in the PCA plot (top).

Analytical details

▶ **Sample:** Three ground meat products and three plant-based substitutes (4 g each) from different food manufacturers. ▶ **Sorptive extraction:** HiSorb™ probes, used in headspace mode and automated on Centri®. ▶ **GC×GC:** Flow modulator: INSIGHT®. Modulation period: 4 s. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 35–450. ▶ **Software:** ChromCompare+™.

Cheese

Quantifying high- and low-concentration components

A range of compounds are responsible for the wide variation of cheese aroma, and these can be present at high or low concentrations, presenting a challenge for the analyst.

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.

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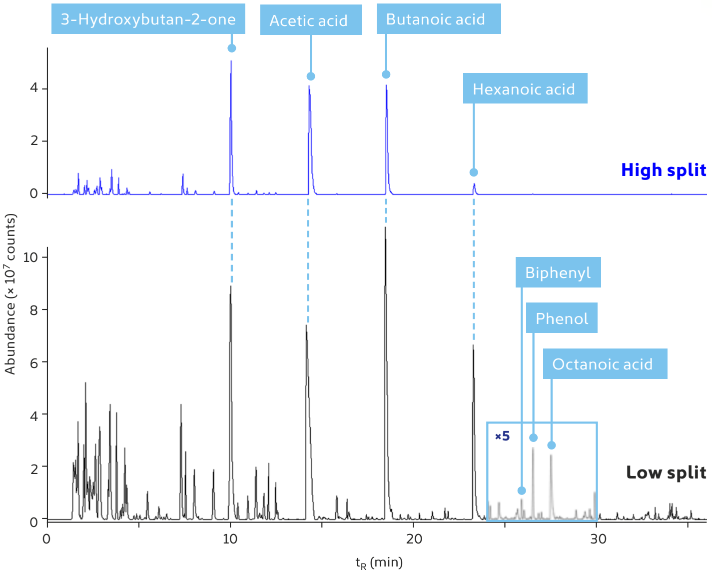


Analytical details

▶ **Sample:** 3 g of grated mature Cheddar. ▶ **Dynamic headspace:** Micro-Chamber/Thermal Extractor™. Tube: 'Material Emissions'. Cold trap: 'Material Emissions'. High split: Inlet: 3:1, Outlet 15:1. Low split: Inlet: 2:1, Outlet 3:1. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 33–350.

A 'High/Low' analysis of cheese headspace allows quantitative measurement of trace phenolic compounds and major fatty acids despite their wide concentration range.

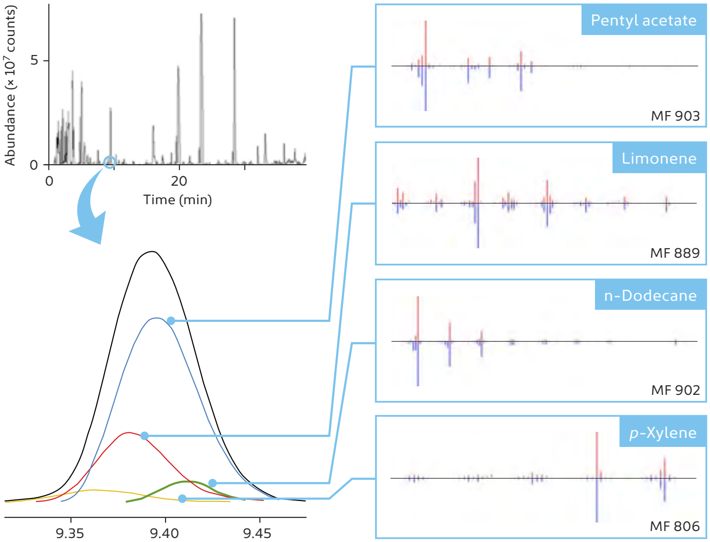
Cheese

Continued from previous page

Identifying ‘hidden’ aroma compounds

Many of the aroma-active compounds found in cheese are often present at trace levels alongside much more abundant components such as fatty acids, making the identification a considerable challenge.

By facilitating the deconvolution of closely-eluting peaks and providing NIST-searchable spectra, BenchTOF™ detection and ChromSpace® 1D software allow trace components to be confidently identified. This is clearly demonstrated in the accompanying profile.



A minor peak in the headspace of Cheddar cheese was found to comprise four closely-eluting compounds at picogram levels. The quality of BenchTOF™ spectra (red) and resulting data density allowed deconvolution using ChromSpace® 1D, enabling excellent matches to NIST library spectra (blue) to be obtained.

Analytical details

▶ **Sample:** Grated Cheddar cheese (5 g). ▶ **Dynamic headspace:** Micro-Chamber/Thermal Extractor™. Sampling: 40°C for 30 min onto a ‘Material emissions’ sorbent tube. ▶ **TD:** TD100-xr™. Trap: ‘Material emissions’. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 33–350. ▶ **Software:** ChromSpace® 1D.

Edible oils

Full separation of FAMEs

The analysis of fatty acid methyl esters (FAMEs) in food is important for assessing nutritional content, and quantitation of both *cis*- and *trans*-fatty acids is particularly important. However, conventional 1D GC struggles to resolve all components.

As shown in this example, GC×GC is capable of separating FAMEs based on carbon number, degree of unsaturation and *cis*/*trans* isomerism. Use of INSIGHT® flow-modulation provides sharp, symmetrical peaks and excellent repeatability across large sample batches.

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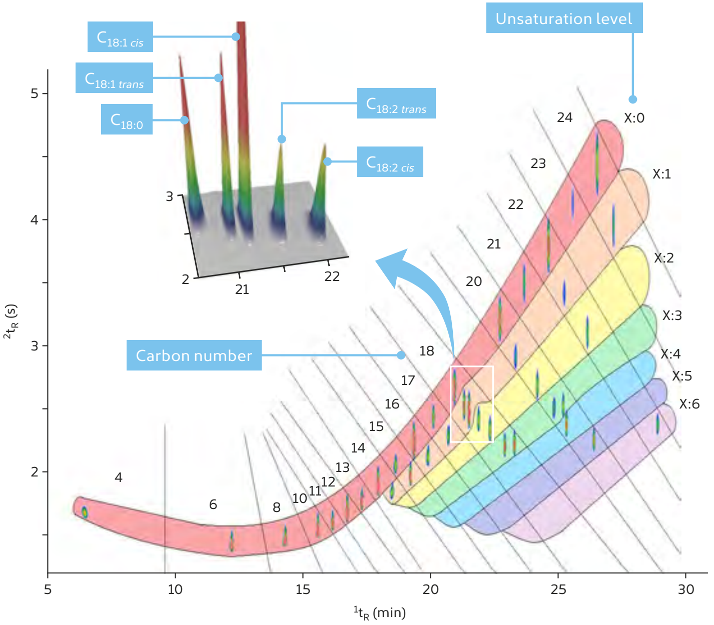


This excellent separation of FAME isomers reveals an additional benefit of GC×GC – the structured ordering of chemical classes. Here FAMEs are separated by their carbon number as well as their degree of unsaturation, simplifying identification and enabling eludication of individual isomers.

Analytical details

- **Sample:** FAME standard in CH_2Cl_2 (37-component, 200 ppm, 200:1 split).
- **GC×GC:** Flow modulator: INSIGHT®. Modulation period: 3.8 s. ▶ **FID**.
- **Software:** ChromSpace®.

Edible oils

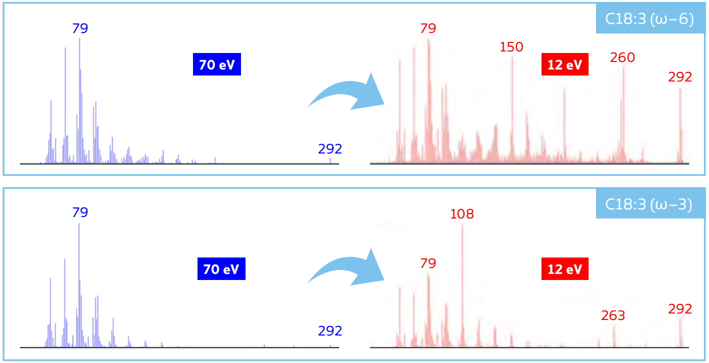
Continued from previous page

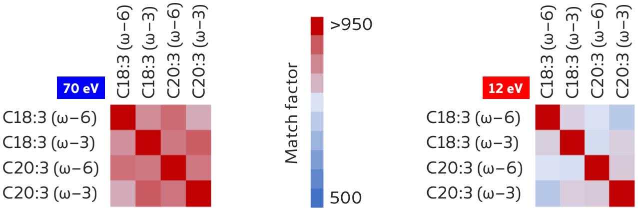
Improved confidence in identification of FAME isomers

Despite the benefits of GC×GC shown on the previous page, certain FAMEs can be challenging to identify using standard 70 eV ionisation alone, due to the high degree of fragmentation, weak molecular ions making it difficult to confirm the carbon chain length, and similar spectra for isomeric compounds.

Tandem Ionisation® at 70 eV and 12 eV can assist discrimination between isomers, as shown here for two C_{18} FAMEs, with their 12 eV spectra showing enhanced molecular ions and structurally-significant fragments.

When comparing spectra against libraries, the greater range of match factors for the 12 eV data provides improved confidence in identification with no added analysis time.





Analytical details

▶ **Sample:** FAME standard in CH_2Cl_2 (37-component, 200 ppm, 200:1 split). ▶ **GC×GC:** Flow modulator: INSIGHT®. Modulation period: 3.8 s. ▶ **TOF MS:** BenchTOF™ at 70 eV and 12 eV. ▶ **Software:** ChromSpace®.

Improved discrimination between two pairs of FAME isomers is demonstrated by the greater disparity in match factors at 12 eV, leading to a reduced risk of incorrect identification and greater data confidence.

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Food packaging

Sensitive sampling of residual solvents

The vast majority of foodstuffs consumed today use packaging to convey information about the product and to protect it during shipping and storage. However, the packaging itself can be a source of contaminants, including residual solvents, monomers and additives.

Screening food packaging for these contaminants is easy to achieve by combining headspace sampling with sensitivity-enhancing trap-based preconcentration. This example shows use of this approach to identify residual solvents in a composite polymer, with ethanol at 1.92 mg/m^2 being a significant constituent.

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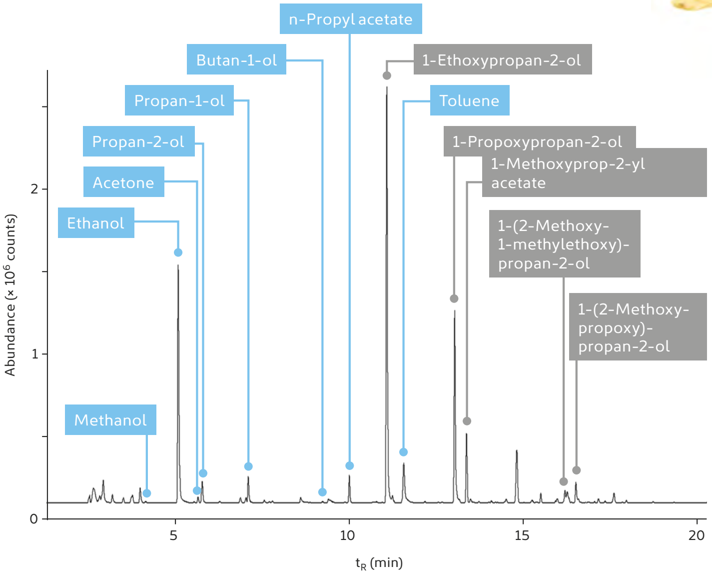


Analytical details

▶ **Sample:** Unused thin composite polymer for packaging baked savoury snacks. ▶ **Headspace–trap:** Centri®. Sampling: 100°C for 60 min. Injection volume: 1 mL. Trap: 'TO-15/TO-17 Air toxics'. ▶ **GC–MS:** Mass range: m/z 15–300. ▶ **Software:** ChromSpace® 1D.

Using the headspace–trap capability of Centri®, a number of volatile compounds resulting from the manufacturing process were identified in this sample of food packaging, including solvents (blue).

Odour taints & additives

Within the food industry, there is an increasing need to monitor product safety and quality, typically in relation to odour taints, adulteration and contamination. Here we show how to overcome the challenges posed by conventional approaches to sample preparation and analysis.

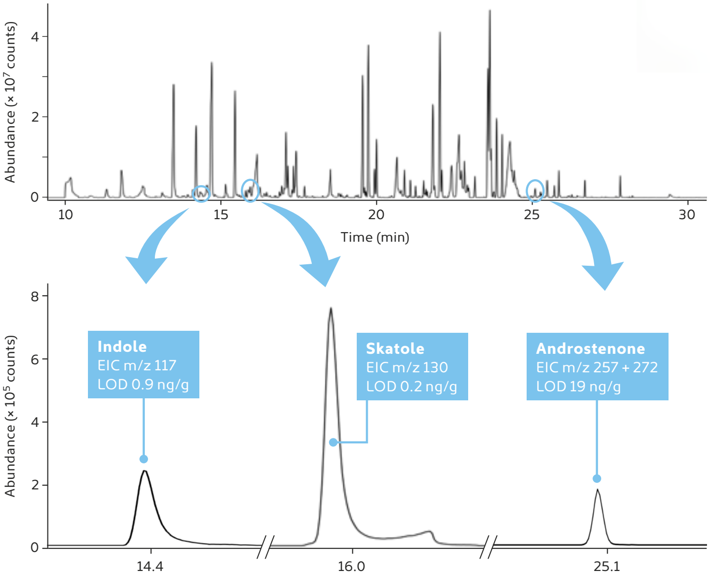
Boar taint

Lowering detection limits for undesirable aromas

Fatty tissue from male pigs – known as 'fatback' – can be contaminated with 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 boar taint screening.

Addressing this need, a team at the University of Bonn have used BenchTOF™ to deliver limits of detection and quantitation for the three key taint compounds well below the levels set for consumer acceptance, with a high degree of precision and accuracy.

View *Food Chemistry* journal article



Indole
EIC m/z 117
LOD 0.9 ng/g

Skatole
EIC m/z 130
LOD 0.2 ng/g

Androstenone
EIC m/z 257 + 272
LOD 19 ng/g

Analytical details

▶ **Sample:** Liquid fat heat-extracted from pig fatback (500 mg).
▶ **Dynamic headspace:** Sampling: 200°C and 30 mL/min for 3 min, onto a Tenax® TA sorbent tube. ▶ **TD:** UNITY-xr™ or TD100-xr™. Trap: Tenax TA.
▶ **GC–MS:** BenchTOF™. Mass range: m/z 40–400.

Ultra-low detection limits were achieved for indole, skatole and androstenone using BenchTOF™ in this headspace analysis of pig fatback.
Data reproduced courtesy of Peter Boeker and Jan Leppert, University of Bonn, Germany.

Wine taint

Enhancing sensitivity with high-capacity sorptive extraction

The yeast *Brettanomyces* (*Dekkera*) *bruxellensis* is commonly found in wineries, and produces volatile phenolic compounds that can impart unpleasant odours and cause desirable fruity aromas to be masked by a ‘drying/metallic’ aftertaste. However, achieving the necessary sensitivity can be challenging for some analytical systems.

Addressing this is sampling with high-capacity HiSorb™ probes, followed by trap-based focusing on Centri®. In this example, we show that two key ‘Brett’ compounds – 4-ethylphenol (4-EP) and 4-ethylguaiacol (4-EG) – can be detected at levels well below their odour thresholds.

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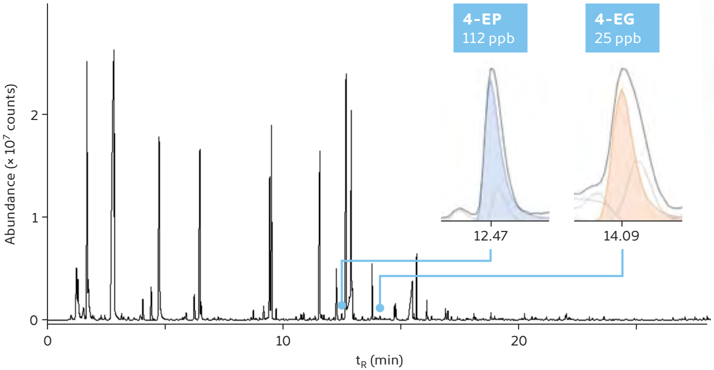
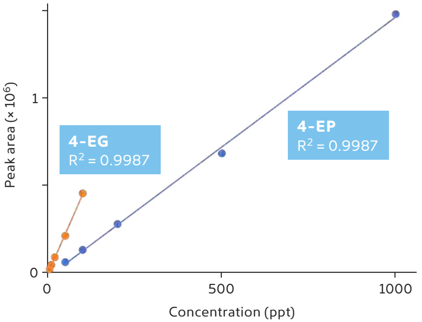


Analytical details

▶ **Sample:** Red wine. ▶ **Sorptive extraction and preconcentration:** Inert HiSorb™ probe, used in immersive mode and automated on Centri®. Trap: ‘Material emissions’. ▶ **GC–MS:** Mass range: m/z 35–350. ▶ **Software:** ChromSpace® 1D.



Excellent linearity was achieved for both 4-EP and 4-EG in this HiSorb™-based analysis of red wine, allowing reliable detection at levels below their odour thresholds of 600 ppb and 50 ppb, respectively.

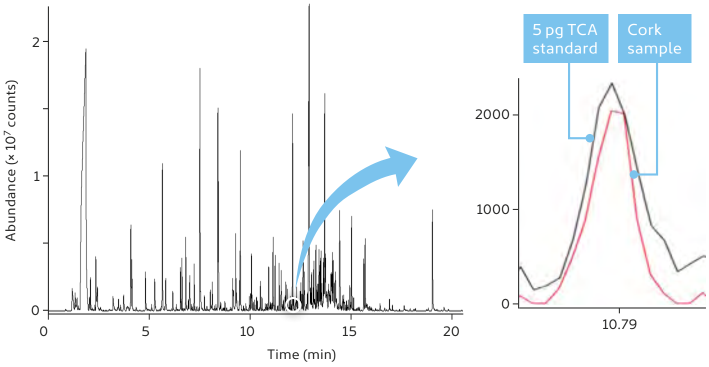
Corks used for wine

Detection of trichloroanisole taint

Traditional cork closures for wine bottles are still popular in many countries, especially for the most prestigious vintages. However, their use does carry a risk of ‘corking’ due to the presence of 2,4,6-trichloroanisole (TCA).

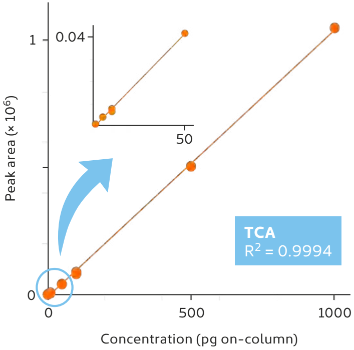
A combination of two technologies addresses the consequent need for reliable, automated detection of TCA. Thermal desorption enhances sensitivity by improving GC–MS peak shape, while the ability of BenchTOF™ to generate full-range mass spectra at SIM-like sensitivities ensures reliable identification.

The result is that trace levels of TCA can be quantitated, at the same time as ensuring that any other taints present are detected.



Analytical details

▶ **Sample:** Whole cork, spiked with TCA to give 1–1000 pg on-column. ▶ **Dynamic headspace:** Micro-Chamber/Thermal Extractor™. Sampling: 60°C for 5 min onto a ‘Material emissions’ sorbent tube. ▶ **TD:** UNITY-xr™ or TD100-xr™. Trap: Tenax® TA. ▶ **GC–TOF MS:** BenchTOF™. Mass range: m/z 40–400. ▶ **Software:** ChromSpace® 1D.



Reliable detection of TCA in cork at low-picogram levels is achieved, despite the complexity of the overall headspace profile.

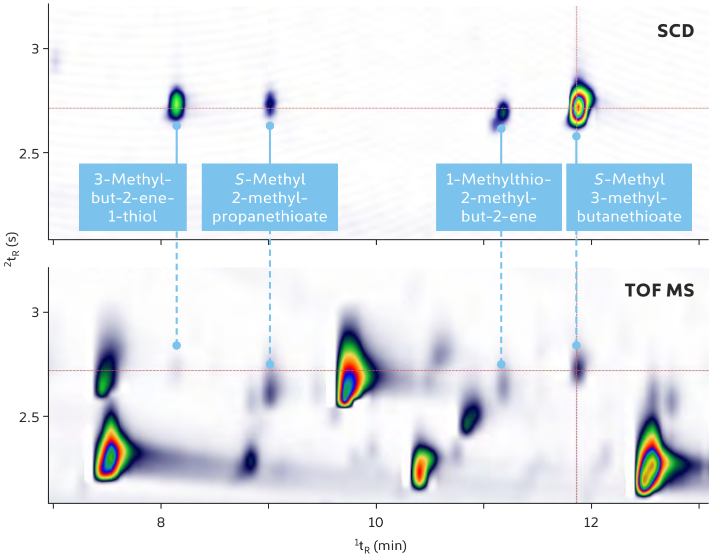
Trace sulfur odorants

Combining SCD and TOF MS for targeted detection

The presence of sulfur compounds in food and beverages is often the cause of undesirable odour taints, but locating these species at trace levels can be difficult.

Sulfur chemiluminescence detection (SCD) provides highly selective and sensitive analysis of sulfur species. By using this detection method alongside TOF MS, it is possible to locate trace sulfur species in cases where they may otherwise have been overlooked or hidden by higher-loading peaks.

In addition, using a dual-detection configuration also allows comprehensive screening of targets and unknowns, all in a single run.



Using a dual-detection approach on samples such as this pale ale allows SCD to be used as a 'guidance system' to uncover key sulfur odorants, which are then confidently identified using TOF MS.

Analytical details

▶ **Sample:** American pale ale. ▶ **Sorptive extraction and preconcentration:** Inert HiSorb™ probe, used in immersive mode and automated on Centri®. ▶ **GC×GC:** Flow modulator: INSIGHT®. Modulation period: 3.0 s. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 35–600. ▶ **Software:** ChromSpace®.

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Authenticity

High-value food products, such as honey, spices and olive oil, are often prone to food fraud. Typically, a less desirable product is misrepresented as a more desirable one, or low-cost substitutes are used to add bulk to the original product. Here, we demonstrate how robust analytical techniques can be used to identify markers of quality and authenticity.

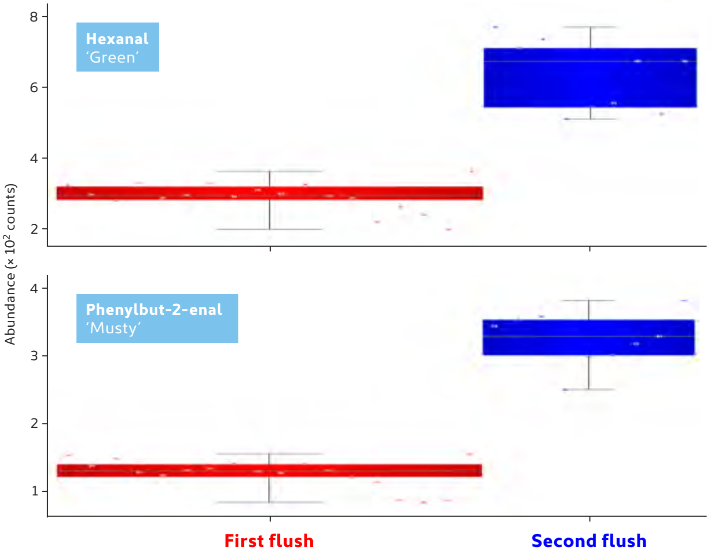
Tea

Evaluating quality of Darjeeling tea

Darjeeling tea is highly sought after, but many factors – such as harvest time – can affect the aroma characteristics of the tea and thus its perceived quality.

Here, automated immersive sorptive extraction coupled with GC×GC–TOF MS provides comprehensive characterisation of tea volatiles, while ChromCompare+™ enables untargeted data analysis to automatically identify the significant differences between the complex flavour profiles, for fast and efficient quality evaluation.

In this case, ChromCompare+ revealed clear distinctions between the higher-quality 'first flush' teas and those of the later 'second flush' harvest.



Two key differentiators between 'first flush' and 'second flush' Darjeeling teas, with different organoleptic properties, were identified using ChromCompare+™, following untargeted GC×GC–TOF MS analysis.

Analytical details

▶ **Sample:** Nine brands of brewed Darjeeling tea (six 'first flush' and three 'second flush'), analysed in triplicate. ▶ **Sorptive extraction:** Inert HiSorb™ probe, used in immersive mode and automated on Centri®. ▶ **GC×GC:** Flow modulator: INSIGHT®. Modulation period: 4.8 s. ▶ **TOF MS:** BenchTOF2™. Mass range: m/z 25–450. ▶ **Software:** ChromCompare+™.

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Curry powder

Uncovering chemical markers of quality

Identifying markers of quality in herbs and spices is of particular interest to manufacturers, for quality control, authenticity studies and in the comparison of competitive products.

The volatile profiles of herbs and spices can be very complex – hundreds of odour-active compounds from a wide range of chemical classes may contribute to the overall perceived aroma.

Here, the combined power of sensitive sorptive extraction, enhanced separation by GC×GC, confident identification by BenchTOF™ MS and novel data analysis in ChromCompare+™ provides an end-to-end workflow to uncover markers of quality.

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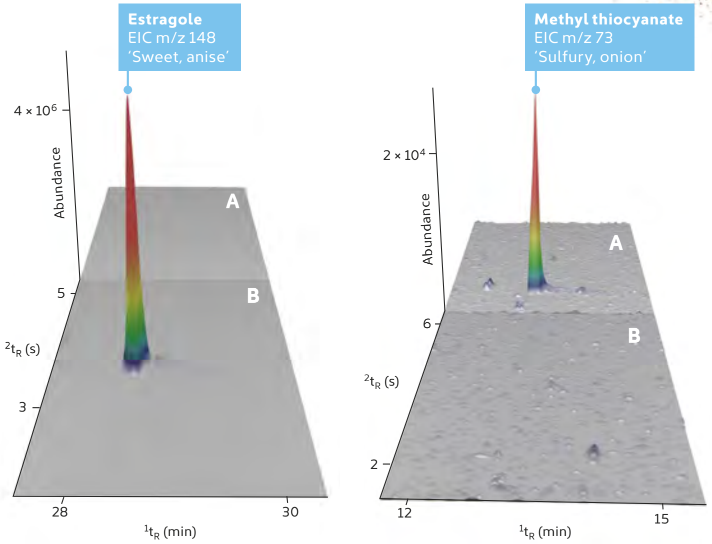


Using GC×GC–TOF MS and ChromCompare+™ software, two compounds with markedly different abundances were automatically identified in the colour plots for an inexpensive (**A**) and expensive (**B**) curry powder.

Analytical details

▶ **Sample:** Two curry powders of different quality added to 10 mL water. ▶ **Sorptive extraction:** HiSorb™ probe, used in immersive mode and automated on Centri®. ▶ **GC×GC:** Flow modulator: INSIGHT®. Modulation period: 5 s. ▶ **TOF MS:** BenchTOF™. Mass range: m/z 35–400. ▶ **Software:** ChromCompare+™.

Honey

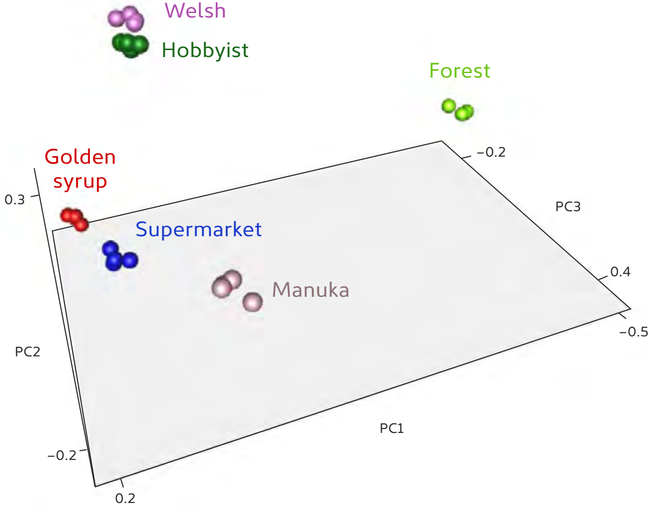
Discovering authenticity markers in honey

Honey is prone to food fraud, where less desirable honey is often misrepresented as a more desirable one, or cheap substitutes are used to add bulk to the original product.

Traditional authentication techniques are becoming obsolete because they involve time-consuming sample preparation and pollen analysis by specially trained analysts.

Here, we show how high-capacity sorptive extraction coupled with GC–MS provides comprehensive VOC profiles across a wide analyte range. ChromCompare+™ software then automatically uncovers key authenticity markers between low- and high-cost honey, enabling fast and simple classification of honey samples of unknown origin.

Download Markes Application Note



A PCA score plot in ChromCompare+™ shows distinct clustering of the honey varieties. Furfural was found to be present at higher levels in the cheap supermarket honey and golden syrup, whereas calamenene was only present in the manuka honey, making it a potential marker of quality.

Analytical details

▶ **Sample:** Five brands of honey and a golden syrup (~ 1 g of each, four replicates). ▶ **Sorptive extraction and preconcentration:** Inert HiSorb™ probe (DVB/CWR/PDMS), used in headspace mode and automated on Centri®. Trap: 'Material emissions'. ▶ **GC–MS:** Mass range: m/z 35–450. ▶ **Software:** ChromCompare+™.

Relevant analytical products

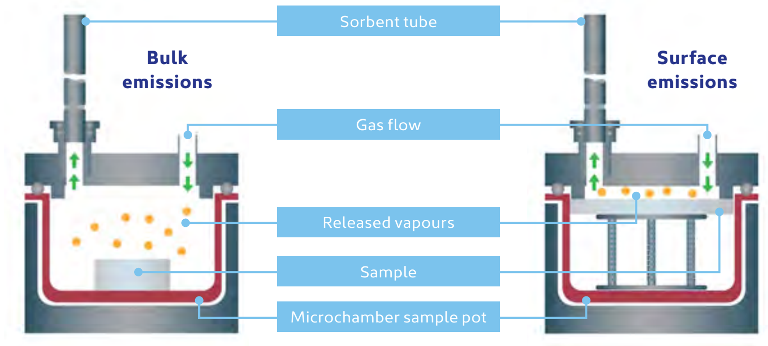
The following pages describe the key products used in the applications shown in this guide. At SepSolve, we can combine these products into single packages that precisely fit your analytical needs.

Micro-Chamber/Thermal Extractor

Rapid dynamic headspace sampling

Headspace sampling has long been a valuable tool for analysis of volatiles, with particular benefits for 'dirty' or viscous samples.

Markes' Micro-Chamber/Thermal Extractor™ (μ-CTE™) improves on the sensitivity of gas-syringe injection, and allows rapid dynamic headspace sampling from a variety of sample types. This makes it exceptionally useful for food odour profiling and shelf-life studies.



Key features of the μ-CTE

- Materials are simply placed in one of the chambers, and equilibrated at the sampling temperature.
- Dynamic sampling onto sorbent tubes followed by TD analysis (see page 30) results in high sensitivity.
- Sampling is usually complete within 30 minutes, aided by raising the chamber temperature.
- Vapours can also be sampled onto DNPH cartridges for formaldehyde monitoring.
- The inert-coated stainless steel chambers are compatible with reactive or thermally labile chemicals.
- Results can be correlated with long-term reference methods.
- Two models are available:
  - Six-chamber, max. 120°C, chamber size 44 cm^3
  - Four-chamber, max. 250°C, chamber size 114 cm^3.

A great advantage of the μ-CTE™ is its versatility – as well as sampling emissions from bulk samples, surface emissions from flat samples can be investigated using dedicated spacers. A permeation accessory is also available.

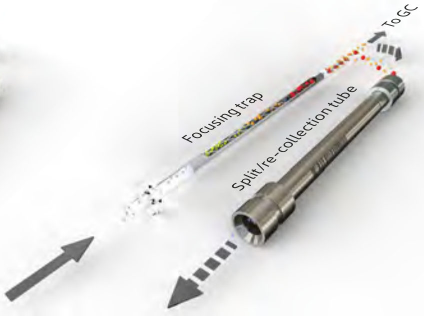
TD100-xr

World-leading thermal desorption

SepSolve offers the entire range of thermal desorbers from Markes International for analysis of samples collected onto sorbent-packed TD tubes, including the flagship TD100-xr™.

Markes' TD platforms use a two-stage process (below) with backflush desorption, for single-run analysis of VOCs & SVOCs (from C_3 to n-C_{44}, including reactive species), using multi-bed tubes and traps.

Step 1
Samples are desorbed onto the cryogen-free focusing trap.



Step 2
The focusing trap is rapidly heated in a reverse flow of carrier gas, to transfer analytes to the GC.

Key features of TD100-xr

- Cryogen-free trapping reduces running costs.
- Re-collection of split flows onto clean sorbent tubes overcomes the 'one-shot' limitation of other TD systems, and allows samples to be re-analysed for simple method/data validation.
- Empty tubes can be used to contain small samples of solids for direct desorption.
- Integrates with all major makes of GC and GC–MS.
- DiffLok™ caps remain in place on tubes through the entire automated TD sequence on the TD100-xr, preserving sample integrity while overcoming the need to uncap and recap tubes.
- Selective removal of water ensures optimal results when analysing food and beverages with high water content.
- Compatible with wide concentration ranges through splitting and re-collection capabilities.

Efficient trap operation (shown here) is central to the performance of Markes' thermal desorbers, while also enabling samples to be split and re-collected for repeat analysis.

HiSorb

High-capacity sorptive extraction

HiSorb™ probes use high-capacity sorbent polymer to extract and concentrate a wide range of organic compounds from liquid and solid samples.

As well as being compatible with Centri® automation, probes can be used to sample manually prior to automated TD–GC–MS analysis, using systems like the TD100-xr™.

Standard-length probes allow immersive sampling from 20 mL vials

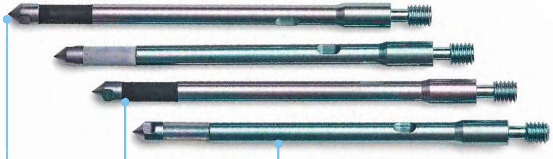
Short-length probes allow headspace sampling from 20 mL vials (or immersive sampling from 10 mL vials)

The positioning of the probes in the middle of the vial avoids damage to the sorptive phase caused by contact with the vial sides

Once sampled, vials can be re-sealed with special plugs to avoid contamination of laboratory air

Key features of HiSorb

- Robust, easy-to-use probes allow unattended sample preparation and maximum productivity.
- HiSorb sampling and analysis is fully automated on the Centri® extraction & enrichment platform for GC–MS.
- Availability of different phases allows the user to select the optimal phase for analytes of interest.
- Detection limits are lower than for SPME because of the larger capacity of the sorptive phase.
- Compatible with headspace and immersive sampling.
- Re-usable probes and tubes minimise the cost per sample.
- The cost of solvent consumption and disposal is eliminated.



Tip pierces PTFE seal of headspace vial

High-capacity sorptive phase extracts VOCs and SVOCs

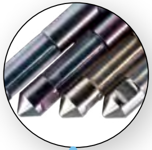
Metal shaft provides intrinsic robustness and allows automated operation on Centri® (and also manual operation if desired)

Centri

Automated sample extraction and enrichment

Common sample introduction techniques such as headspace and SPME are popular due to their simplicity and ease of operation. However, they generally lack sensitivity, and are 'one-shot' techniques requiring duplicate sampling for replicate analysis.

The Centri® platform from Markes International is the first system to offer fully automated, unattended sample extraction and enrichment of VOCs and SVOCs in liquid, solid and semi-solid samples, as well as tube-based analysis of gaseous samples. Using Markes' advanced trapping technology, Centri enhances the sensitivity and extends the performance of several popular sample introduction techniques, including HiSorb™ high-capacity sorptive extraction.



High-capacity sorptive extraction

Headspace and headspace–trap

Thermal desorption

SPME and SPME–trap

Key features of Centri

- A single platform for all GC sample preparation.
- Analyte trapping (optional for headspace and SPME) provides high sensitivity by delivering a sharp, concentrated band of vapour to the GC.
- Cryogen-free operation reduces running costs.
- Enrichment by 'sample stacking' improves sensitivity for trace analyses.
- Selective elimination of water and other interferences improves confidence in data.
- Prep-ahead mode increases productivity.
- Robust HiSorb sorptive extraction probes further extend sampling capability, by allowing immersive sampling and providing 100× more phase than SPME.
- Sample splitting and re-collection allows repeat analysis without the need to repeat extraction steps.
- An automatic tool-change option allows rapid switching between sampling modes.

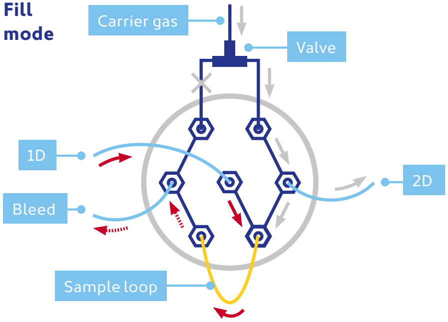
All sampling modes on Centri® can benefit from analyte refocusing using Markes' trapping technology.

INSIGHT

Flow-modulated GC×GC

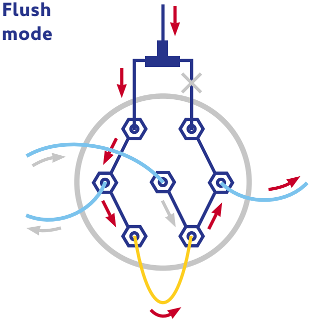
The modulation device is the most critical part of GC×GC – systems with ineffective modulation can suffer from broad, tailing peaks in the second-dimension, which limits peak capacity.

SepSolve's INSIGHT® flow modulator overcomes the practical and performance difficulties experienced with other modulator designs, such as volatility restrictions.



Fill mode

The primary column eluate enters the sample loop (with any overfill directed to a bleed line), while the modulation valve directs auxiliary carrier gas to the secondary column.



Flush mode

The valve switches, and the contents of the sample loop are flushed rapidly onto the secondary column as a narrow band.

Key features of INSIGHT

- Flow-modulation technology allows efficient modulation of volatiles – unlike thermal modulators, which struggle with analytes boiling below C_5 because of their reliance on a cold jet.
- Cryogen-free operation lowers running costs for routine GC×GC.
- Excellent repeatability for routine applications – peak area RSDs are typically <5%.
- Flexible configuration options:
  - GC×GC
  - Heart-cut GC–GC
  - Backflushing
  - Parallel detection, e.g. TOF MS and FID.
- Retrofittable to all popular GCs.
- A compact design allows two INSIGHT devices to be configured in a single GC oven for enhanced productivity through dual-channel acquisition.

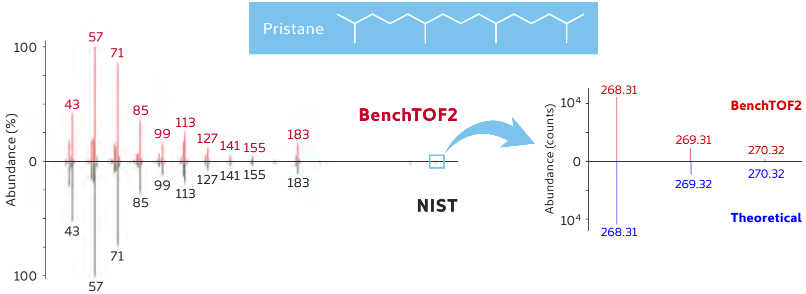
Differential flows in the INSIGHT® modulator are used to 'fill' and 'flush' a sample loop – meaning low running costs for routine GC×GC and none of the logistical issues associated with liquid cryogen.

BenchTOF2

High-definition time-of-flight mass spectrometers

BenchTOF2™ mass spectrometers are the next generation of the successful BenchTOF series of time-of-flight (TOF) mass spectrometers, allowing labs to adapt to increased workloads and new challenges, while improving data confidence and reducing costs.

Like all TOF instruments, BenchTOF2 simultaneously analyses all ions, maximising sensitivity and providing full-range spectra for both target compounds and unknowns in a single run.



Key features of BenchTOF instruments

- Identify analytes confidently through an unbeatable combination of SIM-level sensitivity, high-quality spectra, excellent selectivity and smart software tools.
- Improve detection limits with full spectral information, to detect a wide range of trace-level species in a single analysis, with the option for retrospective searching.
- Extend dynamic range across five orders of magnitude to accurately quantify high-concentration compounds while maintaining low detection limits – removing the need for dilutions or repeat analyses.
- Compatible with fast GC and GC×GC thanks to BenchTOF2's fast acquisition speeds.
- Increase productivity through use of H2 carrier gas, for lower cost of ownership, fast return on investment, and faster chromatographic separations.
- Simultaneously acquire hard and soft EI spectra using patented Tandem Ionisation® technology, and so confidently identify challenging compounds (e.g. isomers) in streamlined workflows.

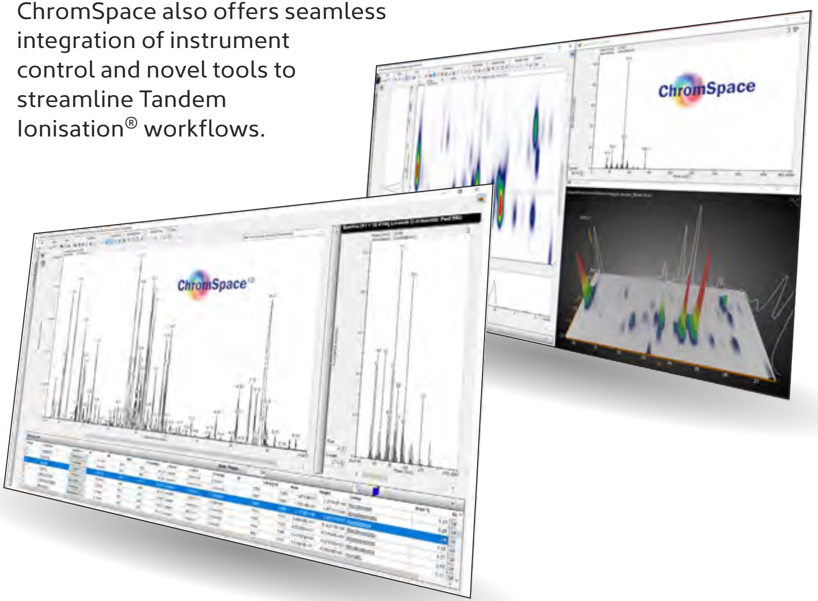
An exact isotope pattern match against the theoretical spectrum is achieved for a C_{19} alkane using BenchTOF2™.

ChromSpace

Intuitive data analysis for 1D and 2D GC and GC–MS

ChromSpace® provides streamlined qualitative and quantitative analysis of 1D and 2D GC(–MS) data, with optional modules for alignment and powerful chemometrics, all in a single, intuitive user interface.

When coupled with BenchTOF2 mass spectrometers, ChromSpace also offers seamless integration of instrument control and novel tools to streamline Tandem Ionisation® workflows.



Key features of ChromSpace

- Intuitive processing of GC(–MS) data for a range of file types (including .lsc, .d, .raw, .rsd and .cdf).
- Easy-to-learn workflows with fast method creation and batch processing, quantitation, and reporting/exporting.
- Automated background subtraction of interferences, and uncovering of ‘hidden’ compounds with easy-to-use deconvolution.
- Time-saving features such as one-click library hits and saved EIC sets.
- Fast screening for compounds (or classes) of interest using the Compound Explorer toolkit.
- Automatically align chromatograms and find significant differences between samples by adding ChromCompare+ chemometrics module.
- Fast group-type analysis with easy-to-use stencils and reporting.
- Network licensing to easily unify lab processing.

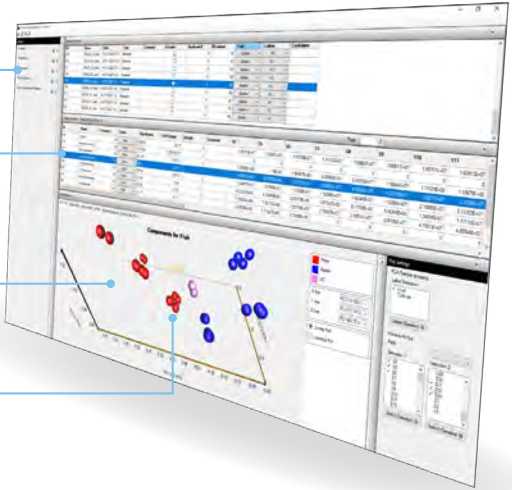
ChromSpace® 1D offers intuitive tools for qualitative & quantitative GC–MS analysis, while ChromSpace lets you evolve your lab’s capabilities and harness the power of GC×GC.

ChromCompare+

A powerful chemometrics platform for GC, GC–MS and GC×GC

ChromCompare+™ is a powerful, easy-to-use data-mining and chemometrics platform for comparing multiple chromatograms and extracting useful insights into the constituents present.

ChromCompare+ offers the flexibility to process a range of file formats using various data-mining strategies. The innovative untargeted approach used by ChromCompare+ allows maximum analytical information to be extracted from the raw data when you don't know what you are looking for.



Flexibility to import peak lists or raw data in a range of file formats

Automatic discovery of the most significant differences

Easy visualisation of patterns and trends

Automatic classification of samples using prediction models

Key features of ChromCompare+

- Account for retention time drift using automated alignment of chromatograms.
- Uncover significant differences between sample classes.
- Accelerate data analysis using automated untargeted workflows.
- Process a range of data file formats for both 1D and 2D GC and GC–MS data.
- Fast classification of unknown samples using prediction models.
- Incorporates all of ChromSpace's efficient qualitative and quantitative data mining tools.
- Benefit from a host of advanced visualisation tools to display the key trends and relationships between your samples.

With ChromCompare+™ you don't have to be a statistician to gain greater insight into your complex datasets, and you don't have to know what compounds are important.

About SepSolve Analytical

SepSolve Analytical provides analytical platforms for separation scientists, including equipment for automated sample introduction, advanced GC separation, state-of-the-art mass spectrometry and powerful data analysis.

Together, these tools enable you to discover more about your sample, and to deliver higher throughput for both research and routine applications. To ensure you get the best from your investment, our experienced application chemists provide access to the training and support you need, at support centres around the globe.

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