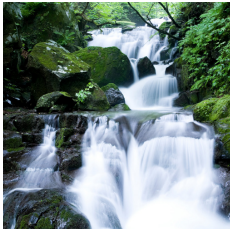
MARKES international

TOF MS Applications Guide



A comprehensive guide to the applications of time-of-flight mass spectrometry for gas chromatography

Introduction

Time-of-flight mass spectrometry (TOF MS) is a versatile and powerful detection method for gas chromatography (GC), which offers considerable advantages for both routine and advanced applications.

In this Applications Guide we highlight this diversity by describing how it can be successfully applied to everything from cheese aroma profiling to crude oil fingerprinting using GC×GC... and much more besides.

For more information on any of these applications, or to discuss how TOF MS 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).

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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).

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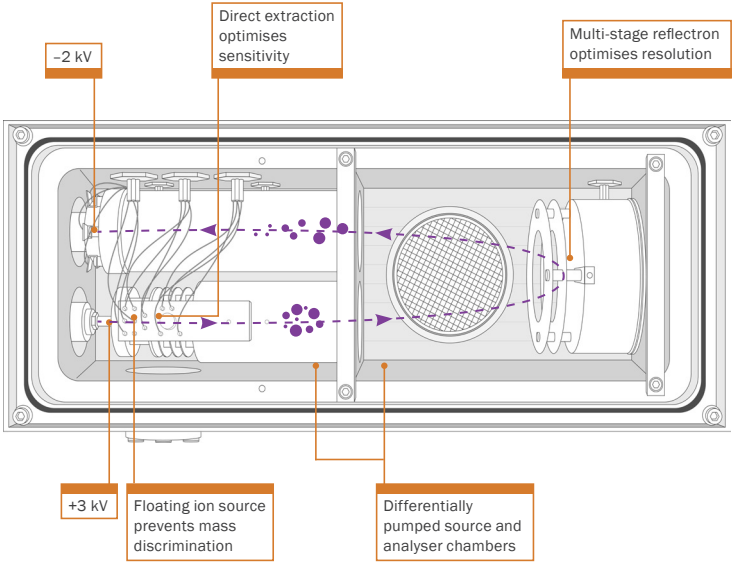
Time-of-flight mass spectrometry

Time-of-flight mass spectrometry (TOF MS) is one of the simplest and most powerful forms of mass spectrometry, and uses the principle that when different ions are imparted with a given energy, the heavier ions will take longer to travel the fixed distance from the ion source to the detector.

In contrast to conventional quadrupole mass spectrometers, which work by mass filtering, TOF instruments simultaneously analyse all ions. This makes them far less wasteful, and so inherently more sensitive.

Although the sensitivity of quadrupoles can be boosted by use of selected ion monitoring (SIM) mode, in this mode only target compounds can be monitored, meaning that full characterisation of the sample is not possible in a single run, and retrospective searching of data is severely limited.

TOF mass spectrometers overcome this issue by providing highly sensitive detection whilst acquiring full-range mass spectra. The result is that they allow identification of trace-level targets and unknowns in a single, rapid analysis.



Schematic of the BenchTOF flight box showing the path travelled by the ions.

BenchTOF technology

Markes' BenchTOF™ time-of-flight mass spectrometers incorporate a highly efficient direct-extraction ion source, which boosts sensitivity to the level normally encountered in selected ion monitoring (SIM) mode, while collecting full-range mass spectra.

BenchTOF instruments also generate 'reference-quality' spectra that do not suffer from the mass discrimination common with other TOF designs. As a result, the spectra can be directly compared to commercial libraries such as NIST or Wiley. This dispenses with the need for the custom weighted libraries needed with other TOF systems, and ensures confident identification of both targets and unknowns.

Three BenchTOF models are available:

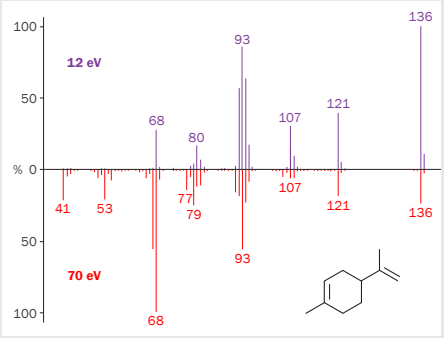
- **BenchTOF-Evolve™** – Complementing conventional GC–MS technology.
- **BenchTOF-HD™** – Featuring TOF-DS™ software for enhanced productivity.
- **BenchTOF-Select™** – Incorporating Select-eV® capability for full sample characterisation in a single sequence.

For more on the BenchTOF range, visit www.markes.com.

Select-eV

Select-eV variable-energy ionisation technology delivers 'soft EI' spectra down to 10 eV with an enhanced molecular ion, reduced fragmentation and minimised chemical background.

The result of this is greater confidence in identification, without the hassle and expense typically associated with soft ionisation techniques.



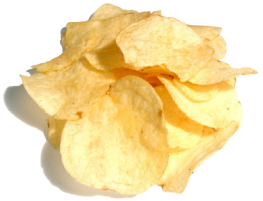
The power of Select-eV is perfectly illustrated by these spectra of limonene. In the 12 eV spectrum, the enhanced molecular ion at m/z 136 helps to confirm compound identity, while the reduced degree of fragmentation enhances the response from the structurally significant higher-m/z fragments.

For more information on Select-eV, download Application Note 528.

Search our library of Select-eV spectra at www.select-ev.com.

Potato crisps

Detecting trace flavour compounds in complex profiles



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 standard GC–MS analyses of foods can yield complex chromatograms in which trace-level compounds are hard to detect.

Detection using BenchTOF provides the sensitivity and data density needed to deconvolve the profiles of trace-level compounds in complex profiles, such as the flavour compounds in this potato-crisp headspace.

Typical analytical conditions:

Sample: 2 g crushed potato crisps.

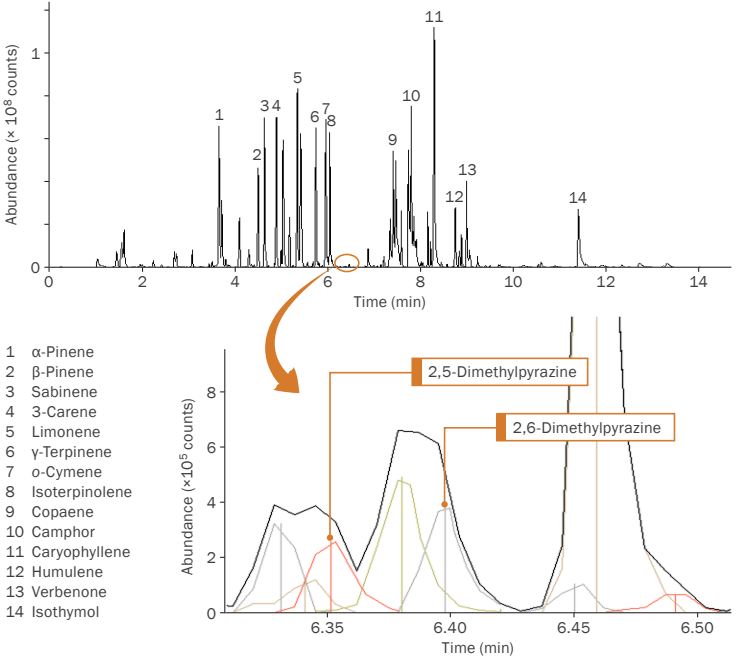
Dynamic headspace (Micro-Chamber/Thermal Extractor™): Flow rate: 40 mL/min for 10 min. Chamber temp.: 40°C.

TD (UNITY™): Tenax® TA sorbent tube, desorbed at 300°C for 5 min. Analytes trapped using a 'General-purpose hydrophobic' trap. Overall split: 20:1.

GC: HP-INNOWax™ column (30 m × 0.25 mm × 0.25 µm). Oven ramp: 40°C (2 min), 20°C/min to 240°C (2 min).

MS (BenchTOF): Transfer line 250°C. Ion source 200°C. Ionisation energy: 70 eV. Mass range: m/z 35–400. Acquisition rate: 2 Hz.

Application Note 502



Pyrazines, with their roasted/earthy to potato-like aroma and low odour thresholds, were a target group in this analysis of potato crisps. Using BenchTOF, two dimethylpyrazines were readily deconvolved from closely-eluting components.

Strawberries

Automated detection of odour taint

In food quality control scenarios, 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.

Solving these problems is Markes' ChromCompare® software module, part of the TOF-DS package for BenchTOF. Using the relative abundances of key olfactory components from BenchTOF, ChromCompare generates 'match factors' indicating the quality of each pairwise sample comparison.

Typical analytical conditions:

Sample: Whole strawberry.

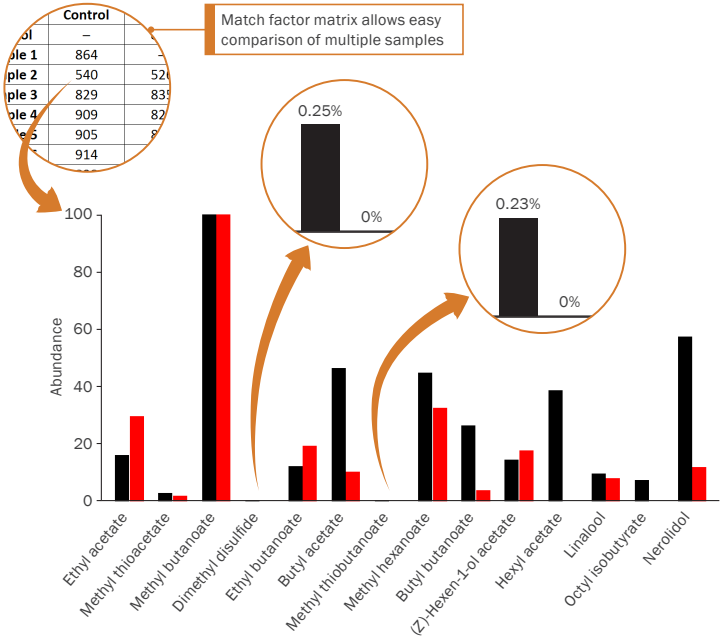
Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 50 mL/min for 20 min. Chamber temp.: 40°C.

TD (UNITY or TD-100™): 'Odour' sorbent tube, desorbed at 120°C for 5 min, then 260°C for 5 min. Analytes trapped using a 'Material emissions' trap. Overall split: 21:1.

GC: Rtx®-5ms column (60 m × 0.25 mm × 0.5 µm). Oven ramp: 40°C (5 min), 10°C/min to 300°C (5 min).

MS (BenchTOF): Transfer line: 200°C. Ion source: 280°C. Ionisation energy: 70 eV. Mass range: m/z 35–350. Acquisition rate: 2 Hz.

Application Notes 515 and 526



In this ChromCompare comparison of a strawberry headspace sample with a control, 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.

Cheese

Identifying ‘hidden’ aroma compounds

A range of compounds are responsible for the wide variation of cheese aroma. Many of these are present at trace levels and have low odour thresholds relative to more abundant components such as fatty acids, making the identification of key aroma components a considerable challenge.

By facilitating the deconvolution of closely-eluting peaks and providing NIST-searchable spectra, BenchTOF allows trace components to be confidently identified. In this example, a minor peak in cheese headspace was found to comprise four co-eluting compounds.

Typical analytical conditions:

Sample: 5 g of grated cheese.

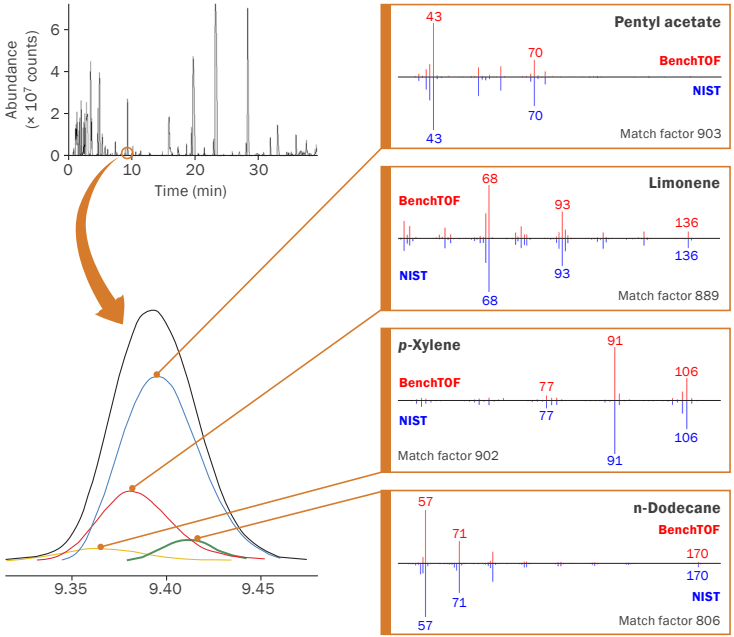
Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 40 mL/min for 20 min. Chamber temp.: 40°C.

TD (UNITY or TD-100): ‘Material emissions’ sorbent tube, desorbed at 150°C for 5 min, then 300°C for 5 min. Analytes trapped using a ‘Material emissions’ trap. Overall split: 6:1.

GC: HP-INNOWax column (30 m × 0.25 mm × 0.25 µm). Oven ramp: 40°C (2 min), 5°C/min to 180°C, 20°C/min to 260°C (6 min).

MS (BenchTOF): Transfer line 265°C. Ion source 260°C. Ionisation energy: 70 eV. Mass range: m/z 33–350. Acquisition rate: 2 Hz.

Application Note 101



In this headspace profile of Cheddar cheese, four closely-eluting components at picogram levels in a single minor peak were deconvolved using TOF-DS – courtesy of the data density and spectral quality of BenchTOF. The mass spectra of the deconvolved components display excellent matches to those in the NIST library.

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.

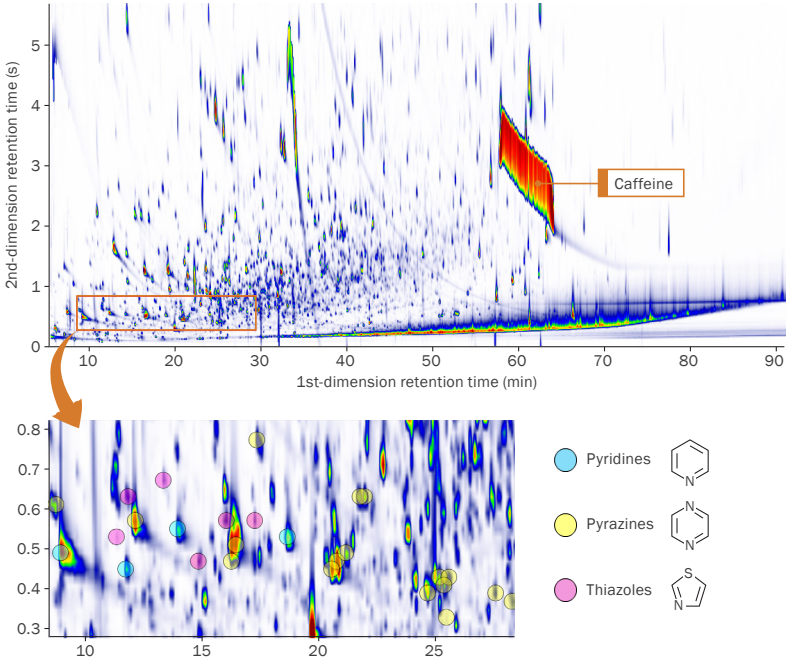
GC×GC with BenchTOF detection provides the enhanced separation capacity to allow the entire composition to be screened in a single analysis – as illustrated in this example of a roasted coffee extract.

Typical analytical conditions:

Sample: 1 µL of roasted coffee extract, injected with a 5:1 split.

GC×GC: DB-50™ 1st-dimension column (30 m × 0.25 mm × 0.25 µm) with Stabilwax® 2nd-dimension column (0.6 m × 0.10 mm × 0.10 µm). Main oven ramp: 40°C (1 min), 3°C/min to 250°C (20 min). No offset for secondary oven. Modulator delay loop: As for 2nd dimension (1 m). Hot jet: 140°C (1 min), 3°C/min to 250°C (20 min). Modulation period: 6 s. Hot-jet pulse 350 ms.

MS (BenchTOF): Transfer line: 240°C. Ion source: 250°C. Ionisation energy: 70 eV. Mass range m/z 35–400. Acquisition rate: 50 Hz.



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.

Beer

Assisting quality control of raw ingredients

Beer contains hundreds of organic compounds, with concentrations spanning many orders of magnitude. Of particular interest to brewers are hop-derived monoterpenes and sesquiterpenes, which provide much of the characteristic flavouring of the finished beer, and generally have low odour thresholds.

Highly sensitive BenchTOF detection combines with the analyte-enriching techniques of sorptive extraction and thermal desorption (TD), to enable comprehensive flavour profiling of minor components in a single sequence. Here this is complemented by Select-eV soft ionisation for enhanced confidence in analyte identification.

Typical analytical conditions:

Sample: Bottled beer in 20 mL vial, capped with zero headspace.

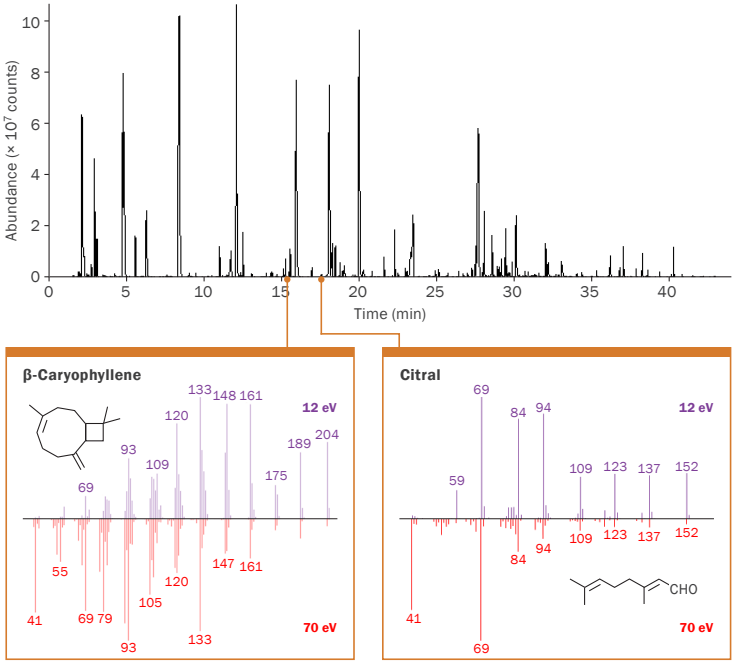
Sorptive extraction (SPE-tD™): 30 mm × 2.5 mm coated with 500 µm PDMS, agitated with magnetic stir-bar at 1100 rpm and 45°C for 30 min.

TD (UNITY or TD-100): SPE-tD cartridge placed in an empty TD tube. Analytes trapped using an 'Air toxics' trap. Overall split: 6:1.

GC: HP-INNOWax column (30 m × 250 µm × 0.25 µm). Oven ramp: 40°C (2 min), 10°C/min to 150°C, 25°C/min to 250°C (3 min).

MS (BenchTOF): Transfer line: 250°C. Ion source: 200°C. Ionisation energy: 70 eV and 12 eV. Mass range: m/z 35–350. Acquisition rate: 2 Hz.

Application Notes 503 and 517



A comprehensive flavour profile is collected in a single sequence in this analysis of a beer, by combining sorptive extraction and BenchTOF with Select-eV ionisation. The mass spectra show the complementary 70 eV and 12 eV spectra of two key terpenoid flavour compounds.

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 detection.

Combining thermal desorption (TD) with the ability of BenchTOF to collect full-range mass spectra at SIM-like sensitivities allows trace levels of TCA to be quantitated, while ensuring that any other taints present are also detected.

Typical analytical conditions:

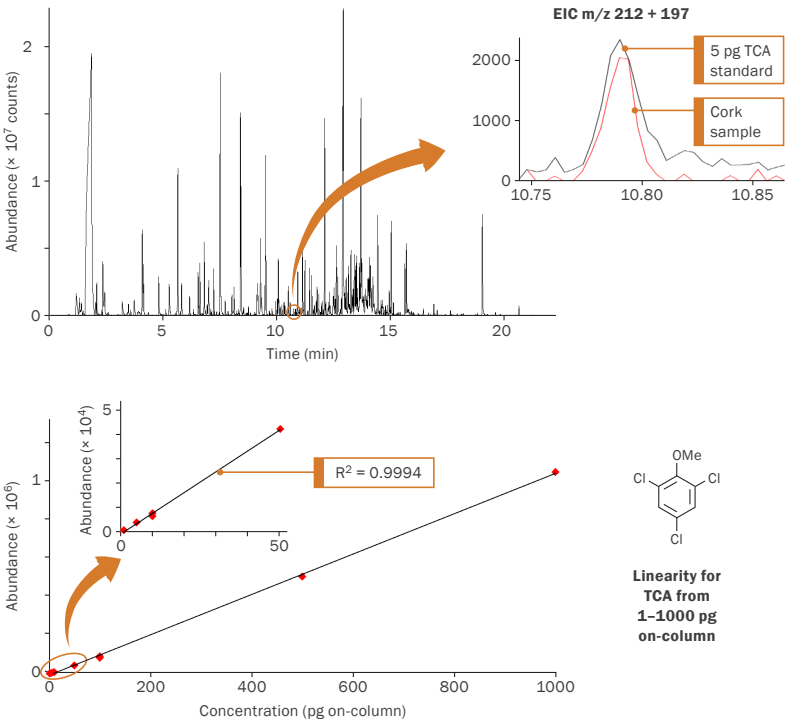
Sample: Whole cork, spiked with TCA to give 1–1000 pg on-column.

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

TD (UNITY or TD-100): 'Material emissions' sorbent tube, desorbed at 280°C for 7 min. Analytes trapped using a Tenax TA trap. Overall split: 5.5:1.

GC: BPX5™ column (30 m × 0.25 mm × 0.25 µm). Oven ramp: 40°C (3 min), 15°C/min to 280°C (5 min).

MS (BenchTOF): Transfer line: 280°C. Ion source: 250°C. Ionisation energy: 70 eV. Mass range: m/z 40–400. Acquisition rate: 4 Hz.



Linearity for TCA from 1–1000 pg on-column

Reliable detection of TCA was achieved at low-picogram levels despite the complexity of this cork headspace profile.

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, Germany, 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.

Typical analytical conditions:

Sample: 500 mg of liquid fat heat-extracted from pig fatback.

Dynamic headspace (HS5-TD™): Flow rate: 30 mL/min for 3 min. Vial temp.: 200°C.

TD (UNITY or TD-100): Tenax TA sorbent tube, desorbed at 300°C for 12 min. Analytes trapped using a Tenax TA trap. Overall split: 7:1.

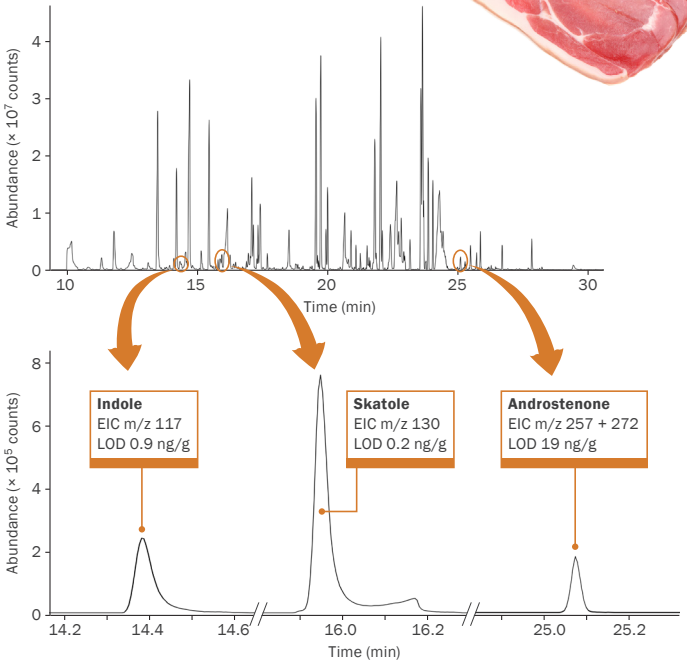
GC: BPX5 column (30 m × 0.25 mm × 0.25 µm). Oven ramp: 40°C (3 min), 15°C/min to 280°C (5 min).

MS (BenchTOF): Transfer line: 280°C. Ion source: 250°C. Ionisation energy: 70 eV. Mass range: m/z 40–400. Acquisition rate: 4 Hz.

http://dx.doi.org/10.1016/j.foodchem.2014.02.113

J. Fischer *et al.*, Fast and solvent-free quantitation of boar taint odorants in pig fat by stable isotope dilution analysis–dynamic headspace–thermal desorption–gas chromatography/time-of-flight mass spectrometry, *Food Chemistry*, 2014, 158: 345–350.

Summarised at: www.markes.com/Resources/Scientific-publications/Featured-paper



Ultra-low detection limits were achieved for the three key boar taint compounds using BenchTOF in this headspace analysis of pig fatback. *Data reproduced courtesy of Peter Boeker and Jan Leppert, University of Bonn, Germany.*

Essential oils

Taking advantage of the separation capacity of GC×GC

Essential oils are used in a variety of personal care products, but exhibit a wide degree of natural variation that can adversely affect the quality of the final product. This demands rigorous quality control and the ability to detect variation in even the most minor of components.

GC×GC–TOF MS is a powerful approach to the screening of complex mixtures such as essential oils. In particular, the high sensitivity of BenchTOF ensures that key components are detected quickly and reliably.

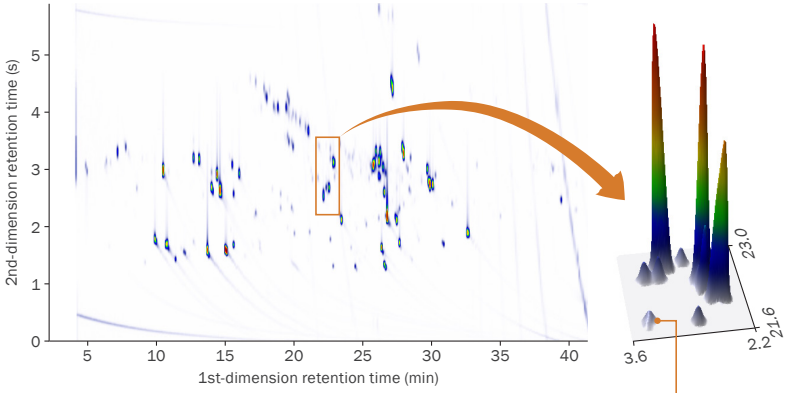
Typical analytical conditions:

Sample: 1 µL of a 200:1 dilution of essential oil in ethyl acetate, injected with a 200:1 split.

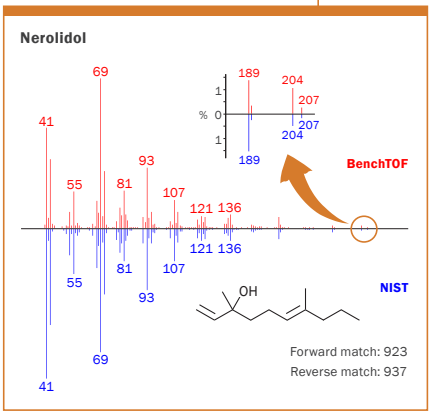
GC×GC: DB-5™ 1st-dimension column (30 m × 0.32 mm × 0.25 µm) with BPX50™ 2nd-dimension column (1.25 m × 0.10 mm × 0.10 µm). Main oven ramp: 50°C (2 min), 5°C/min to 310°C (12 min). No offset for secondary oven. Modulator delay loop: 1.5 m × 0.10 mm fused silica. Modulation period: 6 s. Hot-jet pulse: 350 ms.

MS (BenchTOF): Transfer line: 300°C. Ion source: 280°C. Ionisation energy: 70 eV. Mass range: m/z 40–500. Acquisition rate: 50 Hz.

Application Note 532



Coupling two columns of different selectivity provides enhanced separation capacity and excellent peak shape for this complex essential oil. At the same time, the reference-quality spectra generated by BenchTOF ensure confident identification – exemplified by the high-quality match for the m/z 189/190 and m/z 204–207 signals in nerolidol.



Laundry powder

Combining sensitivity-enhancing techniques to generate comprehensive fragrance profiles

Fragrance plays a major part in market acceptance and consumer satisfaction for personal care products and domestic cleaning materials.

The high sensitivity of BenchTOF, in combination with the sensitivity-enhancing techniques of dynamic headspace sampling and thermal desorption (TD), allows a comprehensive fragrance profile to be obtained for this sample of laundry powder. Select-eV further improves confidence in the identification of challenging analytes that have weak molecular ions and/or similar spectra at conventional 70 eV.

Typical analytical conditions:

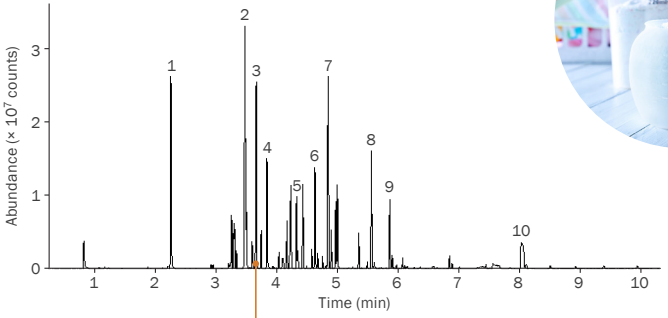
Sample: 1 g of laundry powder.

Dynamic headspace (Micro-Chamber/Thermal Extractor): Flow rate: 50 mL/min for 5 min. Chamber temp.: 40°C.

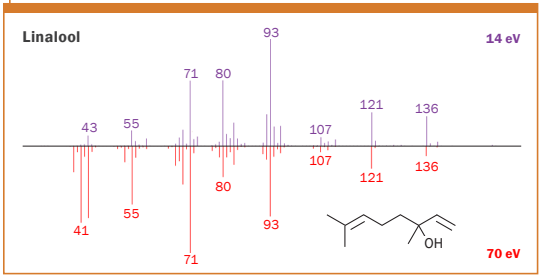
TD (UNITY or TD-100): Tenax TA—Carbograph™ 5TD sorbent tube, desorbed at 250°C for 5 min. Analytes trapped using a 'Material emissions' trap. Overall split: 50:1.

GC: BP5MS™ column (20 m × 0.18 mm × 0.18 µm). Oven ramp: 40°C (2 min), 15°C/min to 250°C (2 min).

MS (BenchTOF): Transfer line 250°C. Ion source 250°C. Ionisation energy: 70 eV and 14 eV. Mass range: m/z 30–400. Acquisition rate: 11 Hz.



1 Hexanol
2 Dihydromyrcenol
3 Linalool
4 Phenylethyl alcohol
5 α-Terpineol
6 Benzylacetone
7 Vertenex
8 Diphenyl ether
9 α-Isomethylionone
10 Dibutyl phthalate



Select-eV adds an extra level of mass spectral information to the comprehensive headspace profiling of this sample of laundry powder. As shown for linalool, molecular ions and structurally-significant ions are enhanced while common ions and chemical noise are reduced, increasing selectivity.

Fragranced cosmetics

Speciating structurally similar isomers

A 2003 EU Directive on the use of potential allergens in fragrances names 27 compounds, and states that they should be labelled in 'wash-off' products when levels exceed 100 ppm, and in 'leave-on' products at levels above 10 ppm. Compliance with this Directive therefore requires that these compounds are identified and quantified accurately – which is all the more important because structurally similar isomers can have very different allergenic properties.

The Select-eV capability of BenchTOF addresses this need by making it possible to speciate isomers that otherwise would require knowledge of retention indices and time-consuming analyst review.

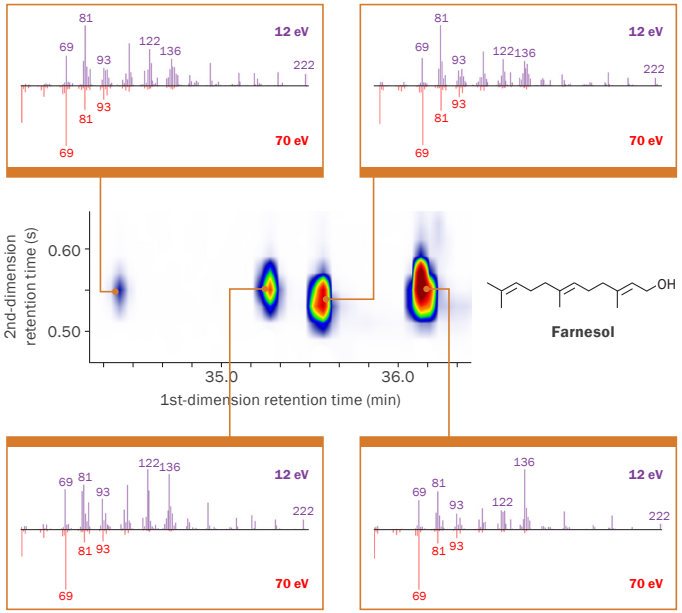
Typical analytical conditions:

Sample: 1 µL of perfume sample spiked with a suite of allergens, injected with a 10:1 split.

GC×GC: SolGel-WAX™ 1st-dimension column (30 m × 0.25 mm × 0.25 µm) with DB-1™ 2nd-dimension column (1.6 m × 0.10 mm × 0.10 µm). Main oven ramp: 50°C (2 min), 5°C/min to 310°C (12 min). No offset for secondary oven. Modulator delay loop: As for 2nd dimension (1 m). Hot jet: 140°C (1 min), 6°C/min to 210°C, 4°C/min to 250°C. Modulation period: 2.5 s. Hot-jet pulse: 350 ms.

MS (BenchTOF): Transfer line: 280°C. Ion source: 250°C. Ionisation energy: 70 eV and 12 eV. Mass range: m/z 40–600. Acquisition rate: 50 Hz.

Application Note 522



Speciation of four farnesol isomers is possible at 12 eV using Select-eV, whereas their very similar spectra at 70 eV would make identification impossible. The enhanced intensities of the heavier, structurally-significant ions is characteristic of Select-eV, and is achieved while retaining the ability to quantitate such allergens at trace levels, due to the inherent sensitivity of BenchTOF.

E-cigarette aerosol

Improving quality control by comprehensive chemical fingerprinting

Intensive studies on the safety of tobacco-replacement devices have identified potentially harmful chemicals in some e-cigarette solutions, including nitrosamines and polycyclic aromatic hydrocarbons (PAHs). The ongoing quality control needed demands confident chemical fingerprinting, for both R&D and regulatory purposes.

The ability of BenchTOF to produce library-searchable spectra enables confident assignment of trace-level targets and unknowns in a single run, aiding quality control. Here it is used with thermal desorption (TD) to achieve sensitivities compatible with toxicological levels of interest.

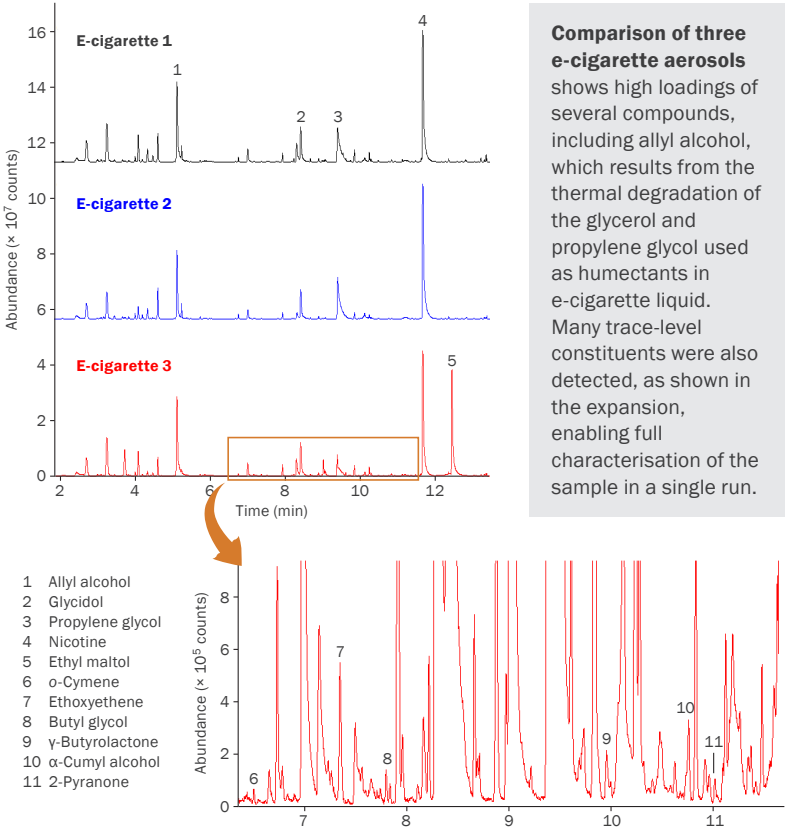
Typical analytical conditions:

Sampling: One 25 mL two-second 'puff' of aerosol from three different e-cigarettes was sampled directly on to sorbent tubes.

TD (UNITY or TD-100): 'Odour' sorbent tube.

GC: Stabilwax column (30 m × 0.25 mm × 0.5 µm).

MS (BenchTOF): Transfer line: 275°C. Ion source: 250°C. Ionisation energy: 70 eV. Mass range: m/z 35–350. Acquisition rate: 4 Hz.

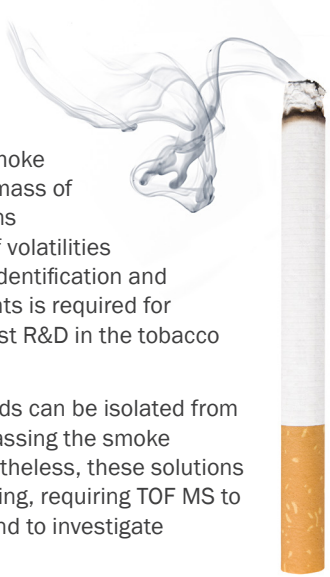


Comparison of three e-cigarette aerosols shows high loadings of several compounds, including allyl alcohol, which results from the thermal degradation of the glycerol and propylene glycol used as humectants in e-cigarette liquid. Many trace-level constituents were also detected, as shown in the expansion, enabling full characterisation of the sample in a single run.

Tobacco smoke

Topic continued on next page

Deconvolving co-eluting components in complex extracts



The vapour phase of tobacco smoke accounts for ~95% of the total mass of mainstream smoke, and contains chemicals with a broad range of volatilities and concentrations. Confident identification and quantitation of these components is required for regulatory purposes and to assist R&D in the tobacco industry.

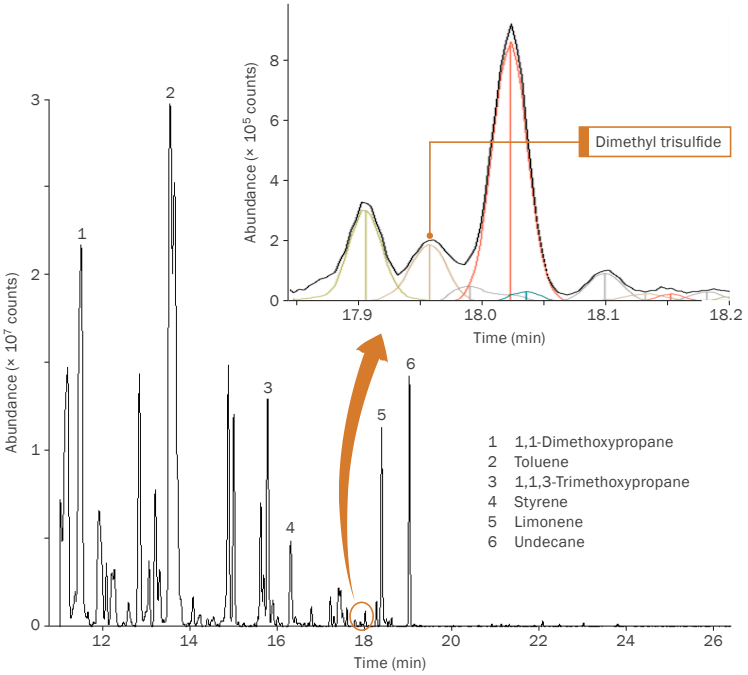
Vapour-phase organic compounds can be isolated from the complex smoke matrix by passing the smoke through organic solvents. Nevertheless, these solutions can still be analytically challenging, requiring TOF MS to deal with multiple co-elutions and to investigate trace-level analytes.

Typical analytical conditions:

Sample: 1 µL of methanol extract (20 mL used to trap the vapour-phase components of a smoke sample), injected with a 10:1 split.

GC: VF-624ms™ column (60 m × 0.32 mm × 1.8 µm). Oven ramp: 40°C (5 min), 8°C/min to 60°C (0 min), 12°C/min to 230°C (5 min).

MS (BenchTOF): Transfer line: 230°C. Ion source: 250°C. Ionisation energy: 70 eV. Mass range: m/z 35–290. Acquisition rate: 4 Hz.



The dual challenge of deconvolving components at trace levels is met by BenchTOF, as illustrated in this example of a smoke extract found to contain the odorous component dimethyl trisulfide.

Application Note 520

Tobacco smoke

Topic continued from previous page

Enhancing separation by GC×GC

GC×GC, with its enhanced separating power, offers considerable advantages over regular GC when investigating highly complex tobacco smoke extracts.

Combining GC×GC with BenchTOF detection and thermal desorption (TD) pre-concentration can significantly increase the number of separable analytes compared to one-dimensional GC analyses, as shown by this example.

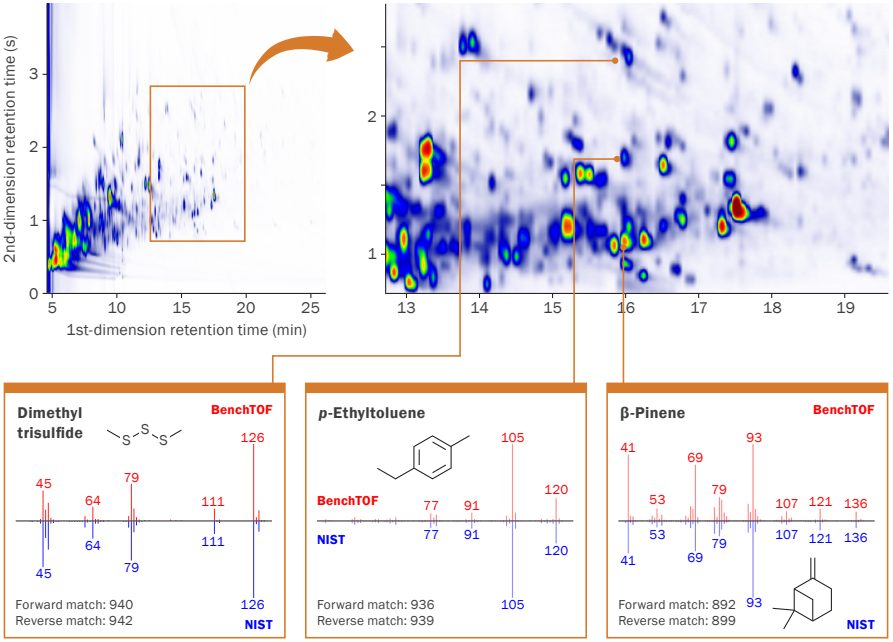
Typical analytical conditions:

Sample: Cigarette smoke collected onto TD tube.

TD (UNITY or TD-100): Sorbent tube desorbed at 290°C for 5 min. Overall split: 151:1.

GC×GC: Rxi®-17 1st-dimension column (20 m × 0.18 mm × 0.18 µm) with BPX1™ 2nd-dimension column (2.0 m × 0.10 mm × 0.10 µm). Main oven ramp: 55°C (2 min), 4°C/min to 310°C (6 min). No offset for secondary oven. Modulator delay loop: As for 2nd dimension (1 m). Hot jet: 155°C (2 min), 4°C/min to 410°C. Modulation period: 6 s.

MS (BenchTOF): Transfer line: 300°C. Ion source: 280°C. Ionisation energy: 70 eV. Mass range: m/z 40–450. Acquisition rate: 50 Hz.



Three compounds that would have co-eluted in a one-dimensional GC–MS analysis are separated using TD–GC×GC–TOF MS, as shown in this colour plot from cigarette smoke. The strong spectral matches against the NIST library show the potential of this technique to screen complex matrices and identify compounds that may escape notice on conventional systems.

Chemical warfare agents

Allowing accurate target-matching in complex matrices

Decomissioning of chemical agent stockpiles is a key aspect of work at demilitarisation ('demil') sites. Safety protocols at these sites are necessarily strict, and as part of this, materials and equipment are monitored for the presence of agent. Such analyses are made extremely challenging by the often complex samples that need to be analysed, while avoiding extensive sample preparation.

BenchTOF is an ideal system for performing such analyses, because it provides the high sensitivity and sub-unit mass selectivity needed to reliably detect trace-level chemical agents in such complex matrices. TOF-DS further simplifies the analytical process with its automated baseline compensation and peak deconvolution capabilities.

Typical analytical conditions:

Sample: 6 mL of diesel-loaded air spiked with HD (~100 ng/L).

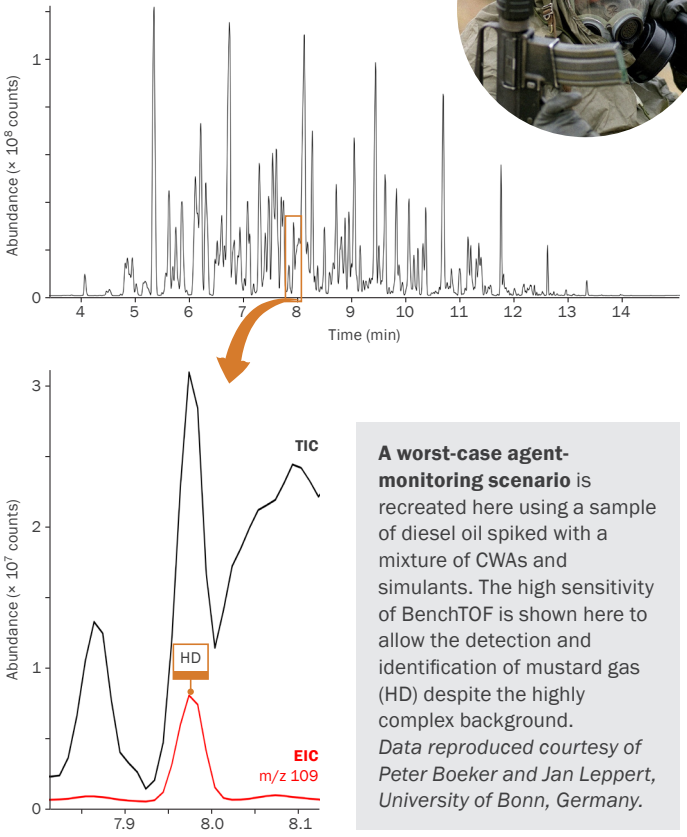
TD (UNITY or TD-100): Tenax TA sorbent tube desorbed at 300°C for 3 min. Analytes trapped using a Tenax TA trap. Overall split: 20:1.

GC: FS-Supreme™-5ms column (30 m × 0.25 mm × 0.25 µm). Oven ramp: 60°C (1 min), 10°C/min to 160°C, 20°C/min to 250°C.

MS (BenchTOF): Transfer line: 220°C. Ion source: 250°C. Ionisation energy: 70 eV. Mass range: m/z 40–500. Acquisition rate: 5 Hz.

http://dx.doi.org/10.1016/j.talanta.2012.09.056

J. Leppert, G. Horner, F. Rietz, J. Ringer, P. Schulze Lammers and P. Boeker, Near real time detection of hazardous airborne substances, *Talanta*, 2012, 101: 440–446.



A worst-case agent-monitoring scenario is recreated here using a sample of diesel oil spiked with a mixture of CWAs and simulants. The high sensitivity of BenchTOF is shown here to allow the detection and identification of mustard gas (HD) despite the highly complex background. *Data reproduced courtesy of Peter Boeker and Jan Leppert, University of Bonn, Germany.*

Tear gas

Detecting trace-level lachrymators on clothing

Increasing illegal use of tear gas and self-defence sprays has meant that forensic analysts have to assess crime-scene materials for their presence – and to use their 'chemical fingerprints' to link suspects with a given crime-scene.

A range of complex matrices are encountered in forensic analyses of lachrymator-containing materials, and in this case GC×GC with BenchTOF was used to enhance separation capacity.

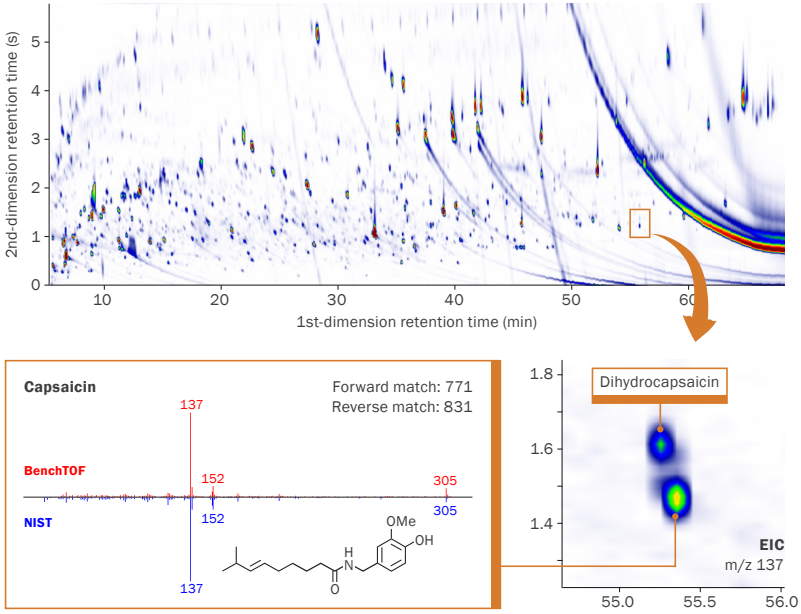
Typical analytical conditions:

Sample: 1 µL of a solvent extract of a section of clothing exposed to tear gas, injected splitless.

GC×GC: Rxi-17 1st-dimension column (20 m × 0.18 mm × 0.18 µm) with BPX1 2nd-dimension column (2.0 m × 0.10 mm × 0.10 µm). Main oven ramp: 55°C (2 min), 4°C/min to 310°C (6 min). No offset for secondary oven. Modulator delay loop: As for 2nd dimension (1 m). Hot jet: 155°C (2.0 min), 4°C/min to 400°C. Modulation period: 6 s. Hot-jet pulse 350 ms.

MS (BenchTOF): Transfer line: 300°C. Ion source: 280°C. Ionisation energy: 70 eV. Mass range m/z 40–450. Acquisition rate: 50 Hz.

Application Note 527



Identification and quantitation of the lachrymators capsaicin and dihydrocapsaicin within a clothing extract was achieved using GC×GC with BenchTOF, as shown in the expanded region. This is a remarkable achievement given their presence in trace amounts within this complex matrix (64 and 72 ppb respectively), and the extensive fragmentation that both compounds undergo within the mass spectrometer.

Drugs of abuse

Improving reliability of urine screening

Analysing urine for drugs of abuse such as marijuana, cocaine, heroin and amphetamines, as well as their metabolites, is commonly performed by GC–MS. However, high matrix effects and frequent co-elutions can compromise reliability of identification, particularly for trace-level analytes.

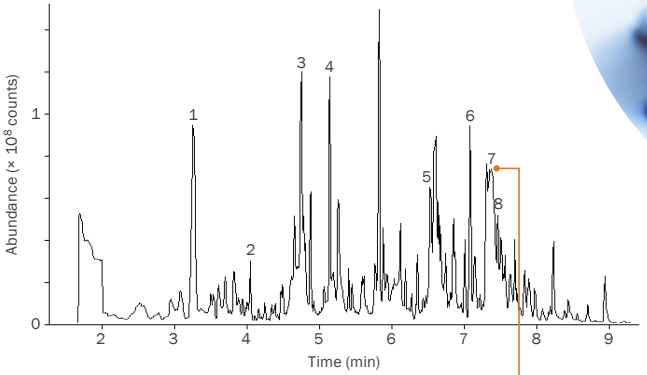
BenchTOF, by providing high sensitivity and spectral quality for all compounds, including those at trace levels, improves the quality of results for complex samples such as urine.

Typical analytical conditions:

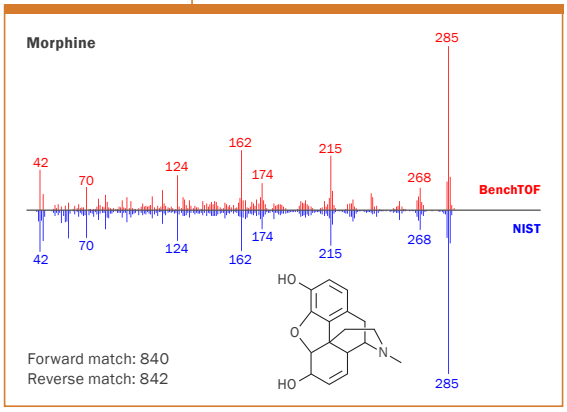
Sample: 1 µL of a concentrated methanol extract of urine, injected splitless.

GC: OPTIMA® 5 Accent column (10 m × 0.2 mm × 0.35 µm). Oven ramp: 80°C (1 min), 30°C/min to 290°C (2 min).

MS (BenchTOF): Transfer line: 250°C. Ion source: 260°C. Ionisation energy: 70 eV. Mass range: m/z 35–635. Acquisition rate: 2 Hz.



1 2-Nicotine
2 Ibuprofen methyl ester
3 Cotinine
4 Hydrocotarnine
5 Dioxepin
6 Codeine
7 Morphine
8 6-Monoacetylmorphine



An excellent spectral match is obtained for morphine in this analysis of a urine sample, collected from a participant in a drug substitution programme.

Application Note 507

Plastics

Speeding up routine sample analysis

The release of VOCs and SVOCs from products and materials is increasingly subject to regulation in many countries, and is driving a need for more comprehensive analyses of a wide range of everyday consumer products.

The inherent sensitivity of BenchTOF – assisted by thermal desorption (TD) pre-concentration – makes it possible to flag up trace-level toxic or odorous components that other GC–MS systems might miss. Near-real-time screening of chromatograms against a target library also speeds up sample processing, which is vital for routine production-line screening.

Typical analytical conditions:

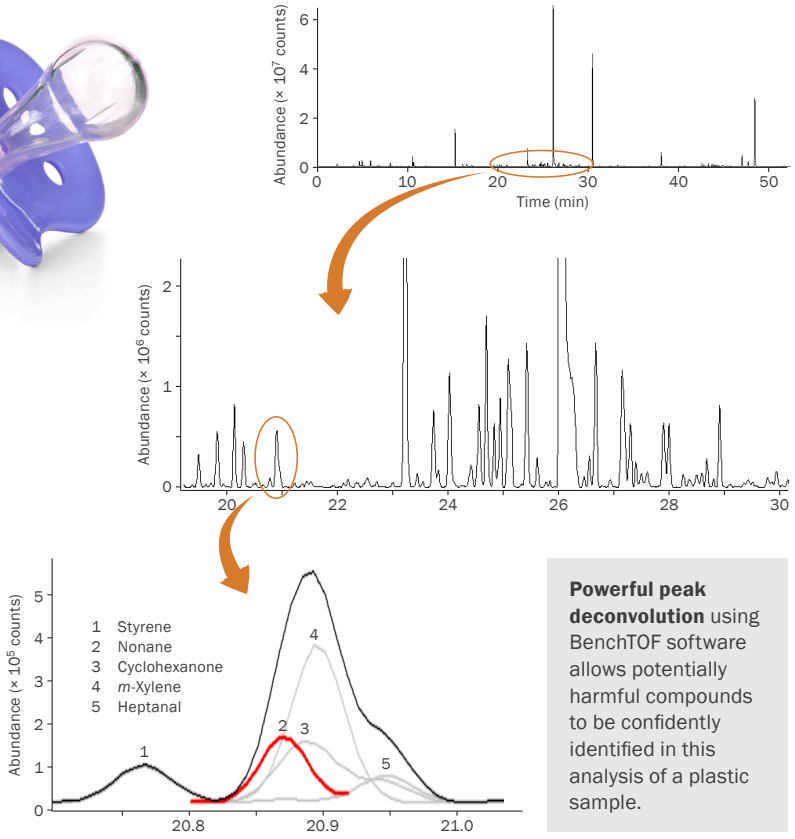
Sample: Section of plastic used in footwear.

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

TD (UNITY or TD-100): 'Material emissions' sorbent tube, desorbed at 300°C for 7 min. Analytes trapped using a 'Material emissions' trap. Overall split: 21:1.

GC: Rtx-5ms column (60 m × 0.25 mm × 0.5 µm). Oven ramp: 40°C (5 min), 5°C/min to 200°C, 15°C/min to 280°C (10 min).

MS (BenchTOF): Transfer line: 200°C. Ion source: 200°C. Ionisation energy: 70 eV. Mass range: m/z 20–350. Acquisition rate: 2 Hz.



Powerful peak deconvolution using BenchTOF software allows potentially harmful compounds to be confidently identified in this analysis of a plastic sample.

Building materials

Improving detection of trace-level indoor air pollutants

In order to comply with stringent limit levels relating to indoor air quality, building material manufacturers are increasingly being expected to measure emissions of VOCs and SVOCs from their products.

BenchTOF provides the high sensitivity needed to detect priority pollutants at such levels, while minimising post-processing time by providing NIST-matchable spectra. The sensitivity is given a further boost in this example by the use of thermal desorption (TD) pre-concentration.

Typical analytical conditions:

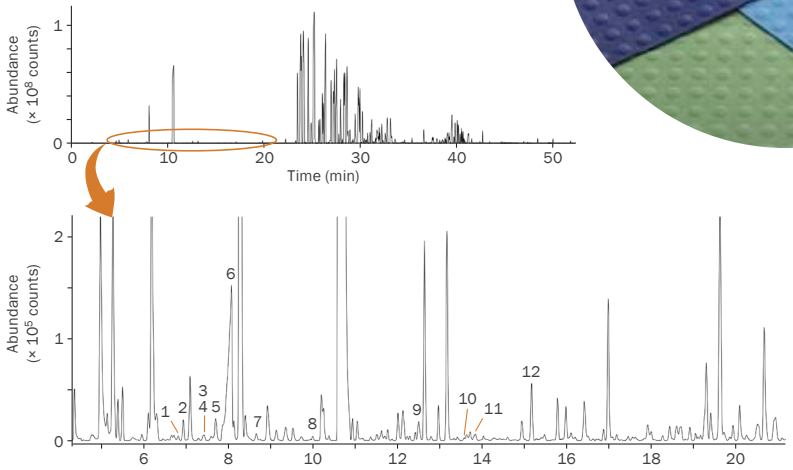
Sample: A section of vinyl flooring tile.

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

TD (UNITY or TD-100): Carbograph 1TD–Carbograph 5TD sorbent tube, desorbed at 300°C for 7 min. Analytes trapped using a 'Material emissions' trap. Overall split: 21:1.

GC: Rtx-5ms column (60 m × 0.25 mm × 0.5 µm). Oven ramp: 40°C (5 min), 5°C/min to 200°C, 15°C/min to 250°C (10 min).

MS (BenchTOF): Transfer line: 200°C. Ion source: 200°C. Ionisation energy: 70 eV. Mass range: m/z 20–350. Acquisition rate: 2 Hz.



Hazardous emissions from flooring tiles that would elude detection on other systems are easily detected using BenchTOF. The results, generated in an easy-to-read table format, illustrate high match factors against the NIST 14 library, reflecting the ability of BenchTOF to generate classical spectra.

No.	Target compound	Time (min)	Match factor	Peak area (× 10⁶)
1	Dichloromethane	6.60	0.997	1.32
2	Carbon disulfide	6.77	0.998	0.53
3	Methacrolein	7.40	0.999	0.21
4	Methyl *tert*-butyl ether	7.42	0.998	0.63
5	Ammonium acetate	7.82	0.987	20.5
6	Butanal	8.00	0.984	34.8
7	Ethyl acetate	8.71	0.978	2.98
8	Crotonaldehyde	10.01	0.996	1.50
9	Methyl methacrylate	12.54	0.982	1.09
10	Propylene glycol	13.53	0.975	15.3
11	Methyl isobutyl ketone	13.78	0.996	44.3
12	Toluene	15.18	0.996	3.77

Odorous industrial air

Detecting labile trace-level odorants

Odorous compounds released from waste-processing facilities can cause a public nuisance, as well as being bad for health. However, they can have very low (often sub-ppb) odour thresholds, and may be difficult to identify within complex polluted air samples. Certain species, particularly sulfur compounds and terpenes, can also decompose during analysis.

The inherent sensitivity of BenchTOF allows automated detection of trace-level compounds in such samples, assisted in the example shown by the use of suitably inert sampling media with thermal desorption (TD) pre-concentration.

Typical analytical conditions:

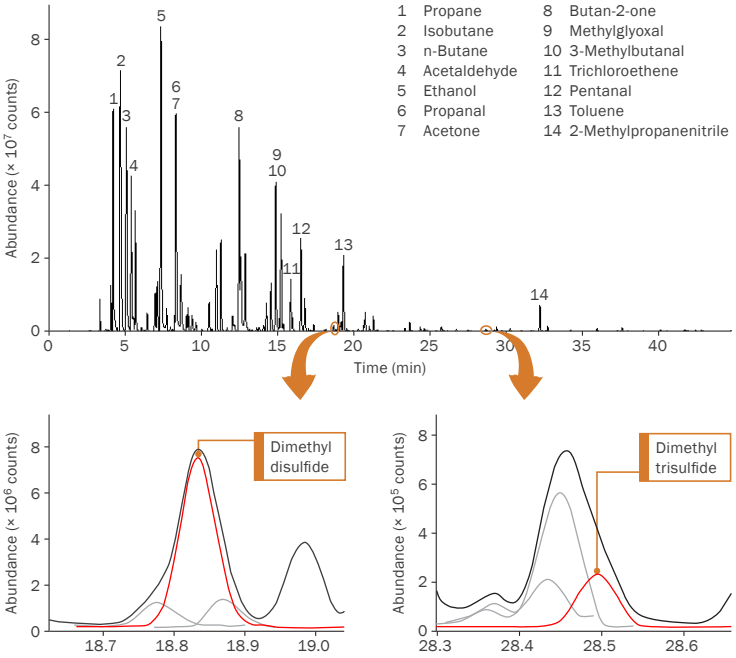
Sample: Air from a waste processing plant, collected in a Nalophan® bag.

TD (UNITY or TD-100): 'Odour' sorbent tube, desorbed at 120°C for 5 min, then 260°C for 8 min. Analytes trapped using a 'Sulfur' trap. Overall split: 30:1.

GC: VF-624ms column (60 m × 0.32 mm × 1.8 µm). Oven ramp: 40°C (0.5 min), 5°C/min to 230°C (5 min).

MS (BenchTOF): Transfer line: 240°C. Ion source: 240°C. Ionisation energy: 70 eV. Mass range: m/z 15–350. Acquisition rate: 2 Hz.

Application Note 521



The use of a fully inert analytical system, with detection by BenchTOF, allows identification of these trace-level sulfur compounds in polluted air. Near-real-time deconvolution and library-searching in TOF-DS speeds up the process of sample screening.

Environmental contaminants

Speeding up the detection of priority pollutants in environmental samples

Recent EU legislation has led to a demand amongst analysts for improved methods for the identification of pesticides and other environmental pollutants. However, developing such methods is challenging because of the large and continually increasing number of toxic compounds that may need to be monitored in a single GC–MS analysis.

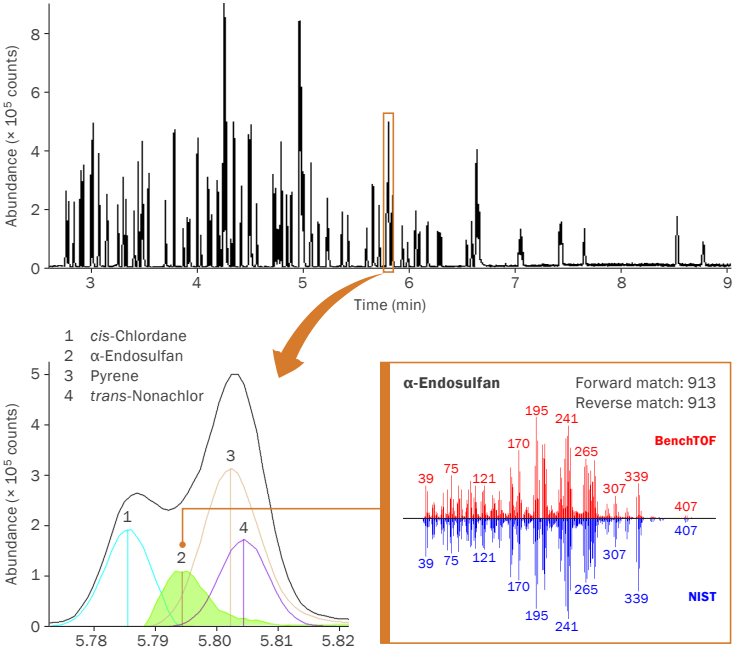
As illustrated in this example, the information-rich data sets generated by BenchTOF provide the raw material for spectral deconvolution algorithms, allowing detection of trace co-eluting or matrix-masked compounds. Such analyses would be difficult using conventional GC–MS methods.

Typical analytical conditions:

Sample: 1 µL of a 1 ppm solution of 92 common contaminants in dichloromethane, injected with a 50:1 split.

GC: BP5MS column (20 m × 0.18 mm × 0.18 µm). Oven ramp: 40°C (0.7 min), 55°C/min to 240°C, 28°C/min to 330°C (2 min).

MS (BenchTOF): Transfer line: 300°C. Ion source: 280°C. Ionisation energy: 70 eV. Mass range: m/z 35–500. Acquisition rate: 16 Hz.



A complex set of co-eluting peaks does not hinder detection of the pesticide α-endosulfan (at 20 pg on-column) in this environmental standard mix. An excellent match against the NIST database confirms the quality of the spectra generated by BenchTOF.

Application Note 525

Hazardous air pollutants

Improving sensitivity for ‘air toxics’

Vapour-phase organic ‘air toxics’, also known as ‘hazardous air pollutants’ (HAPs), are monitored in many industrial and urban environments as a measure of air quality. They span a wide range in volatility and polarity, making their sampling and subsequent analysis a challenge.

The two conventional methods of achieving the necessary sub-ppb detection levels – class-specific detectors and quadrupoles in SIM mode – rely on a limited number of characteristic ions and stable retention times. This makes it difficult to achieve full characterisation of the sample in a single analysis. Detectors such as BenchTOF overcome this limitation by monitoring all ions simultaneously across the mass range, significantly improving sensitivity and allowing identification of other compounds of potential concern.

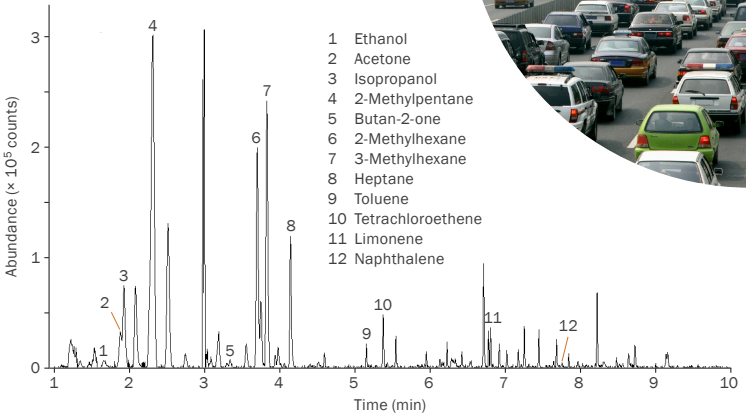
Typical analytical conditions:

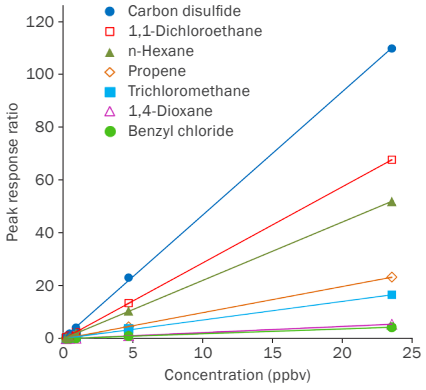
Sample: 50 mL of semi-rural air.

TD (CIA *Advantage*-HL™): Analytes trapped using an ‘Air toxics’ trap.

GC: DB-624™ column (20 m × 0.18 mm × 1.0 µm). Oven ramp: 35°C (1.5 min), 20°C/min to 110°C (0 min), 35°C/min to 210°C (0.3 min).

MS (BenchTOF): Transfer line: 210°C. Ion source: 250°C. Ionisation energy: 70 eV. Mass range: m/z 40–300. Acquisition rate: 6 Hz.





Detection of limonene (in addition to a range of known ‘air toxics’) in semi-rural air is possible at sub-ppb levels using a combined TD–GC–TOF MS system. An average R^2 value of 0.997 for five example analytes illustrates the excellent linearity obtained.

Application Note 529

Watercourse pollutants

Enabling comprehensive screening of environmental samples

Protocols for monitoring water quality need to be robust, adaptable, and scalable to the processing of multiple samples. In addition, monitoring all relevant analytes in one run demands high sensitivity across the entire sampling and analytical system.

BenchTOF facilitates such comprehensive screening by being compatible with GC×GC, and by making retrospective screening possible. Here, the analysis is enhanced by using novel passive samplers, which lower detection limits by concentrating pollutants over time.

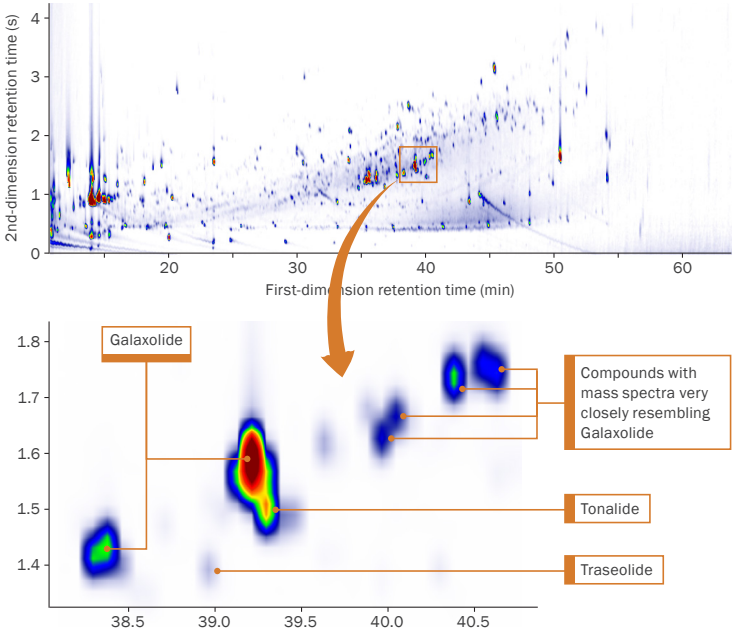
Typical analytical conditions:

Sample: 1 µL of river water extract (spiked with a mix of PCBs, PAHs, and pesticides), and injected splitless.

GC×GC: BPX5™ 1st-dimension column (30 m × 0.25 mm × 0.25 µm) with BPX50 2nd-dimension column (2 m × 0.1 mm × 0.1 µm). Main oven ramp: 50°C (2 min), 5°C/min to 320°C (8 min). No offset for secondary oven. Modulator delay loop: As for 2nd dimension (1 m). Hot jet: 150°C (2 min), 5°C/min to 400°C. Modulation period: 5 s. Hot-jet pulse 350 ms.

MS (BenchTOF): Transfer line: 300°C. Ion source: 300°C. Ionisation energy: 70 eV. Mass range m/z 40–500. Acquisition rate: 50 Hz.

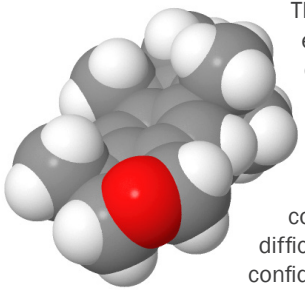
Application Note 518



In this comprehensive screen of a pesticide-spiked water sample, BenchTOF enables detection of non-target compounds such as polycyclic musks with little additional effort. Unlike triple-quadrupole GC–MS methods, targets and unknowns are acquired simultaneously, and retrospective data searching can be performed.

Emerging contaminants

Reducing fragmentation for improved speciation



There is currently rising concern about environmental contamination caused by domestic chemicals that pass unhindered through water-treatment plants – so-called 'emerging contaminants'. Like many other environmental pollutants, these are often structurally complex, leading to extensive fragmentation at conventional 70 eV ionisation. This often makes it difficult to find sufficiently intense quantifier ions for confident speciation and quantitation.

Select-eV addresses the disadvantages of existing 'soft' ionisation techniques used to detect such analytes – by providing variable-energy electron ionisation without compromising sensitivity, and without the need for any hardware changes.

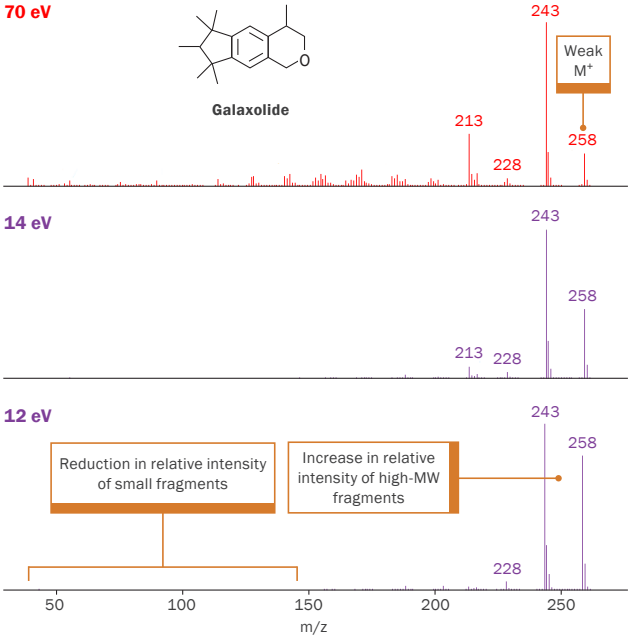
Typical analytical conditions:

Sample: 1 µL of river water extract, injected splitless.

GC×GC: BPX5 1st-dimension column (30 m × 0.25 mm × 0.25 µm) with BPX50 2nd-dimension column (1.95 m × 0.1 mm × 0.1 µm). Main oven ramp: 60°C (2 min), 2.5°C/min to 320°C (10 min). No offset for secondary oven. Modulator delay loop: As for 2nd dimension (0.95 m). Hot jet: 150°C (2 min), 2.5°C/min to 410°C. Modulation period: 4 s. Hot-jet pulse 350 ms.

MS (BenchTOF): Transfer line: 300°C. Ion source: 280°C. Ionisation energy: 70 eV, 14 eV and 12 eV. Mass range m/z 40–500. Acquisition rate: 50 Hz.

Application Note 525



Galaxolide has a relatively weak molecular ion at 70 eV, but its relative intensity rises substantially at lower ionisation energies, along with reduced fragmentation. The result is a set of complementary soft-ionisation spectra that aid identification in complex matrices.

Organotins

Trace quantitation of tributyl tin in water

Organotins (stannanes) find widespread use as disinfectants, additives to paints and plastics, and agricultural pesticides. However, many organotins are endocrine disruptors, with the EU Water Framework Directive stating a maximum allowable concentration of just 1.5 ng/L. This calls for highly sensitive detection methods.

The inherently high sensitivity of BenchTOF provides unparalleled performance for the analysis of organotins, with the example here showing how detection limits can be lowered to just 0.1 ng/L using the soft electron ionisation capability of Select-eV.

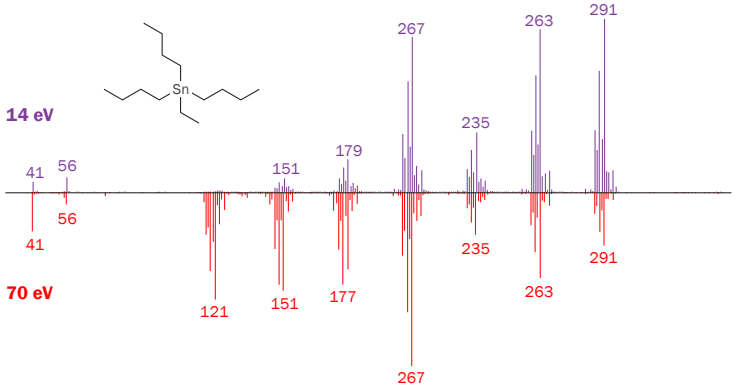
Typical analytical conditions:

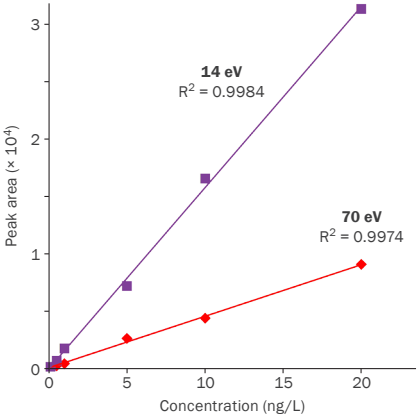
Sample: 1 µL of an extract of an environmental water sample (spiked with organotins and ethylated with sodium tetraethylborate prior to extraction), injected splitless.

GC: Rxi®-5Silms column (20 m × 0.18 mm × 0.18 µm). Oven ramp: 50°C (2.5 min), 20°C/min to 300°C (1 min).

MS (BenchTOF): Transfer line: 280°C. Ion source: 250°C. Ionisation energy: 70 eV and 14 eV. Mass range: m/z 40–500. Acquisition rate: 4 Hz.

Application Note 531





Outstanding sensitivity is obtained for Bu_3SnEt using BenchTOF. Importantly for environmental monitoring, the application of Select-eV gives an increased response for m/z 291 at 14 eV, resulting in a steeper calibration curve and a lowering of the quantitation limit to 0.1 ng/L.

Crude oil hydrocarbons

Confident identification of branched alkanes

Some crude oil hydrocarbons can have adverse effects on engine performance if present in high quantities in the final product. However, the similar spectra of these compounds at 70 eV often leads analysts to use ‘group-type’ classifications, which may not accurately reflect oil content.

The superior separation of GC×GC goes a long way to overcome this difficulty, but despite this, certain compound classes (such as branched-chain hydrocarbons) can remain challenging. Select-eV resolves these problems by providing another ‘dimension’ of information, leading to more confident speciation of these analytes.

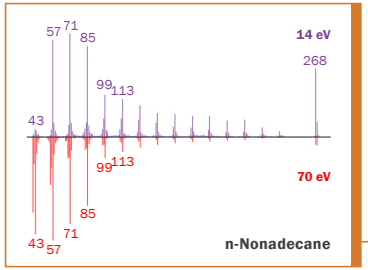
Typical analytical conditions:

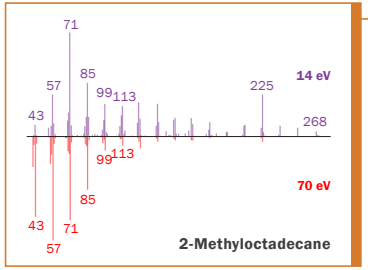
Sample: 1 µL of a 100 mg/mL solution of crude oil in dichloromethane, injected with a 100:1 split.

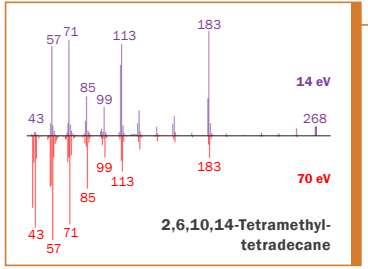
GC×GC: DB-5 1st-dimension column (28 m × 0.25 mm × 0.25 µm) with BPX50 2nd-dimension column (2.3 m × 0.1 mm × 0.1 µm). Main oven ramp: 50°C (1 min), 4°C/min to 325°C (10 min). Secondary oven: 75°C (1 min), 4.2°C/min to 340°C (hold time matched to total run time). Modulator delay loop: As for 2nd dimension (1 m). Hot jet: 150°C (1 min), 4°C/min to 400°C (hold time matched to total run time). Modulation period: 6 s. Hot-jet pulse 350 ms.

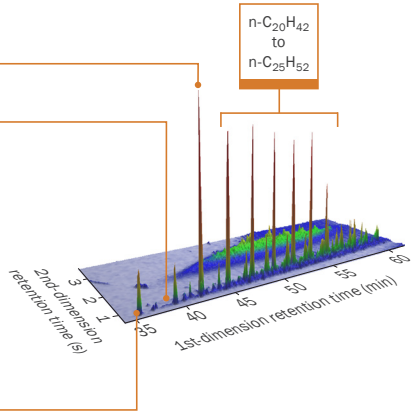
MS (BenchTOF): Transfer line: 325°C. Ion source: 250°C. Ionisation energy: 70 eV and 14 eV. Mass range: m/z 40–600. Acquisition rate: 50 Hz.

Application Note 524









Select-eV soft ionisation allows these nonadecane ($C_{19}H_{40}$) isomers in crude oil to be distinguished, overcoming the problems caused by their similar spectra and weak molecular ions at 70 eV.

Crude oil biomarkers

Improving source apportionment for environmental forensics

Petrochemical biomarkers are breakdown products of the biomolecules in the original oil-producing organisms. As a result of their resistance to degradation, they are of increasing importance for tracing marine oil pollution back to its source. However, because of their similar structures and ease of fragmentation, they are very challenging to distinguish at conventional 70 eV ionisation energies.

Use of Select-eV overcomes the inherent difficulty in confidently identifying these analytes. Unlike some soft ionisation techniques that provide only the molecular ion, it preserves the larger fragments that aid structural elucidation while minimising the common fragments, so improving selectivity. Detection limits are also improved by reducing the chemical noise caused by ionisation of background/carrier gases.

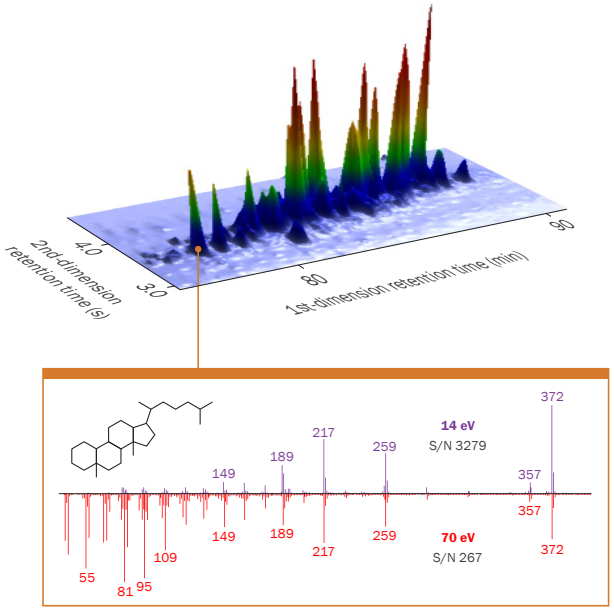
Typical analytical conditions:

Sample: 1 µL of a 100 mg/mL solution of crude oil in dichloromethane, injected with a 100:1 split.

GC×GC: DB-5 1st-dimension column (28 m × 0.25 mm × 0.25 µm) with BPX50 2nd-dimension column (2.3 m × 0.1 mm × 0.1 µm). Main oven ramp: 50°C (1 min), 4°C/min to 325°C (10 min). Secondary oven: 75°C (1 min), 4.2°C/min to 340°C (hold time matched to total run time). Modulator delay loop: As for 2nd dimension (1 m). Hot jet: 150°C (1 min), 4°C/min to 400°C (hold time matched to total run time). Modulation period: 6 s. Hot-jet pulse: 350 ms.

MS (BenchTOF): Transfer line: 325°C. Ion source: 250°C. Ionisation energy: 70 eV and 14 eV. Mass range: m/z 40–600. Acquisition rate: 50 Hz.

Application Note 524



Fragmentation is drastically reduced at 14 eV, as shown by the Select-eV mass spectra of this diasterane biomarker from crude oil. As well as dramatically reducing fragmentation, the molecular ion signal is enhanced, resulting in an improved signal-to-noise value and a lowered limit of detection.

High-boiling compounds

Pioneering the use of TOF MS with high-temperature GC

Full characterisation of certain environmental, biological and petrochemical samples depends on being able to overcome the restriction imposed by the temperature limit of conventional GC columns, and detect compounds heavier than C_{35-40}. To achieve this, specialist high-temperature columns are employed.

Such high-temperature GC is typically used with flame ionisation detection (FID), because of technical challenges surrounding coupling to MS. However, a team at Plymouth University have shown how BenchTOF can be used as the detector for a range of very challenging samples containing high-MW analytes. Remarkably, this was possible with no ion-source cleaning other than that carried out during the annual instrument maintenance.

Typical analytical conditions:

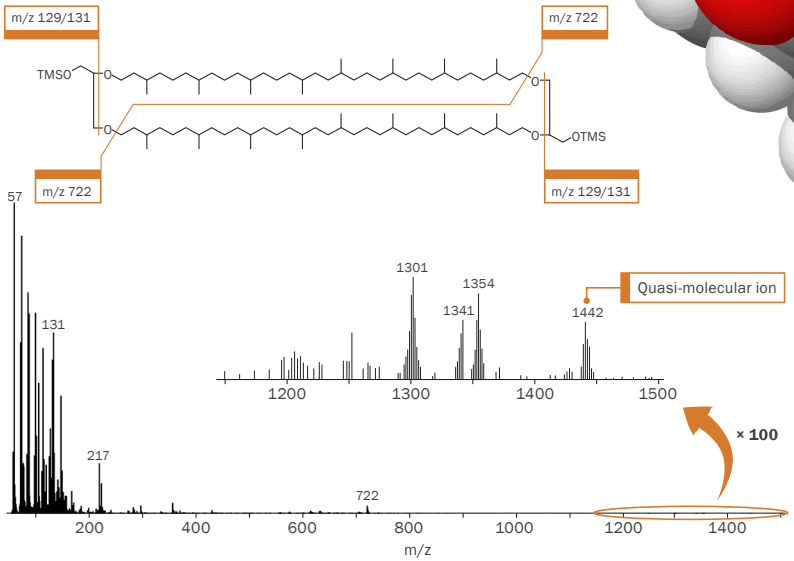
Sample: 0.5 µL of lipid extract, with cool on-column injection.

GC: VF-5ht column (15 m × 0.25 mm × 1.0 µm). Oven ramp: 40°C, 20°C/min to 430°C (10 min).

MS (BenchTOF): Transfer line: up to 430°C. Ion source: up to 380°C. Ionisation energy: 70 eV. Mass range: m/z 50–1500.

http://dx.doi.org/10.1016/j.chroma.2012.04.044

P.A. Sutton and S.J. Rowland, High temperature gas chromatography–time-of-flight-mass spectrometry (HTGC–ToF-MS) for high-boiling compounds, *Journal of Chromatography A*, 2012, 1243: 69–80.



A C_{80} tetraether lipid of the caldarchaeol family is successfully identified from a trimethylsilylated lipid extract of the Archaeon *Thermococcus waiotapuensis* – the first time that such an analyte has been detected by GC–MS. Acquisition of data over the range m/z 1–1500, combined with reference-quality spectra from BenchTOF, allows the quasi-molecular ion at m/z 1442 to be reliably detected, aiding confidence in identification.

Data reproduced courtesy of Paul Sutton and Steve Rowland, University of Plymouth, UK.

Breath

Detection of disease biomarkers

Breath monitoring has attracted much attention for its potential to non-invasively diagnose a range of physiological and pathological conditions. However, detection of breath volatiles at the necessary part-per-trillion sensitivities has historically required time-consuming sample preparation.

Pre-concentration by thermal desorption (TD) coupled with highly sensitive GC–TOF MS overcomes this issue, allowing comprehensive measurement of trace-level targets and unknowns in a single run. An additional benefit of BenchTOF is the productivity enhancement resulting from the ability to carry out deconvolution and library-searching in near-real-time.

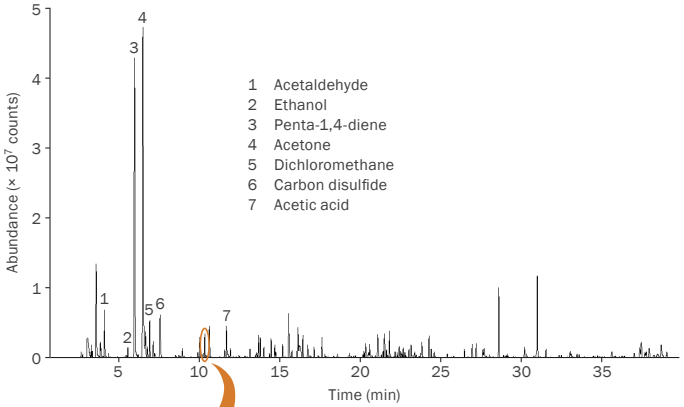
Typical analytical conditions:

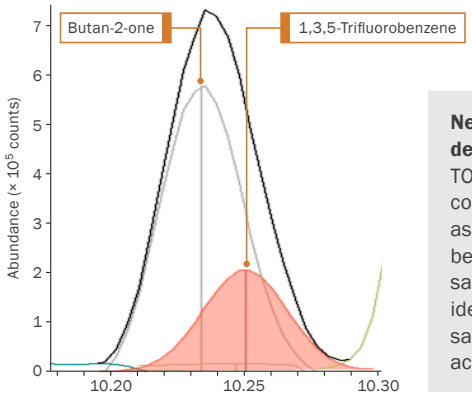
Sample: 500 mL breath, collected onto a sorbent tube using a ReCIVA™ breath sampler (Breathe Free).

TD (UNITY or TD-100): Tenax TA—Carbograph 5TD sorbent tube, desorbed at 270°C for 8 min. Analytes trapped on a 'Material emissions' trap. Overall split: 15:1.

GC: DB-624 column (60 m × 0.32 mm × 0.18 µm). Oven ramp: 40°C (6 min), 8°C/min to 240°C (20 min).

MS (BenchTOF): Transfer line: 250°C. Ion source: 250°C. Ionisation energy: 70 eV. Mass range: m/z 40–400. Acquisition rate: 4 Hz.





Near-real-time deconvolution using TOF-DS allows co-eluting peaks such as the 1,3,5-trifluoro-benzene in this breath sample to be identified while the sample is still being acquired.

Breast implants

Detecting organic pollutants in unusual matrices

Reliable data on the bodily burden of persistent organic pollutants (POPs) is very difficult to obtain, because of the complexity of the biological matrices and the inherent variability in chemical uptake between individuals.

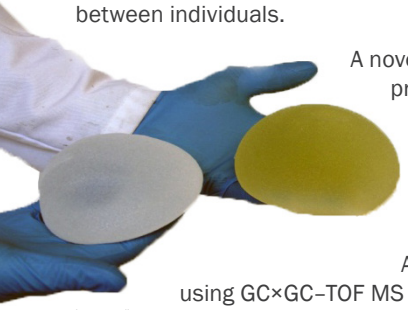


Image credit: NIVA, Norway

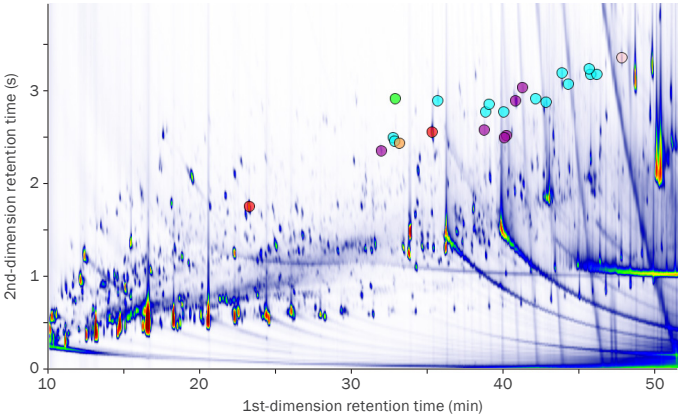
A novel solution to this problem has been proposed by researchers from the UK and Norway, who have found that silicone breast prostheses sequester a comprehensive range of environmental pollutants while implanted in the body. Analysis of extracts of these implants using GC×GC–TOF MS enabled meaningful assessment of bio-accumulated substances in samples and controls.

Typical analytical conditions:

Sample: 1 µL of a cyclohexane extract from a breast implant, injected splitless.

GC×GC: BPX5 1st-dimension column (30 m × 0.25 mm × 0.25 µm) with BPX50 2nd-dimension column (2 m × 0.1 mm × 0.10 µm). Main oven ramp: 65°C (2 min), 5°C/min to 315°C (5 min). No offset for secondary oven. Modulator delay loop: As for 2nd dimension (1 m). Modulation period: 4 s.

MS (BenchTOF): Transfer line: 300°C. Ion source: 250°C. Ionisation energy: 70 eV. Mass range m/z 40–500. Acquisition rate: 50 Hz.



The complexity of this extract from a used breast implant required the enhanced separation provided by GC×GC with the confident identification of BenchTOF. A number of POPs (highlighted) were not found in the control samples, meaning that they most likely accumulated in the implant while it was *in situ* in the body.

http://theanalyticalscientist.com/issues/0415

L. McGregor, A. Gravell, I. Allan, G. Mills, D. Barden, N. Bukowski and S. Smith, The softly-softly approach, *The Analytical Scientist*, 2015, article #0415-501.

Relevant sampling and analytical techniques

GC×GC

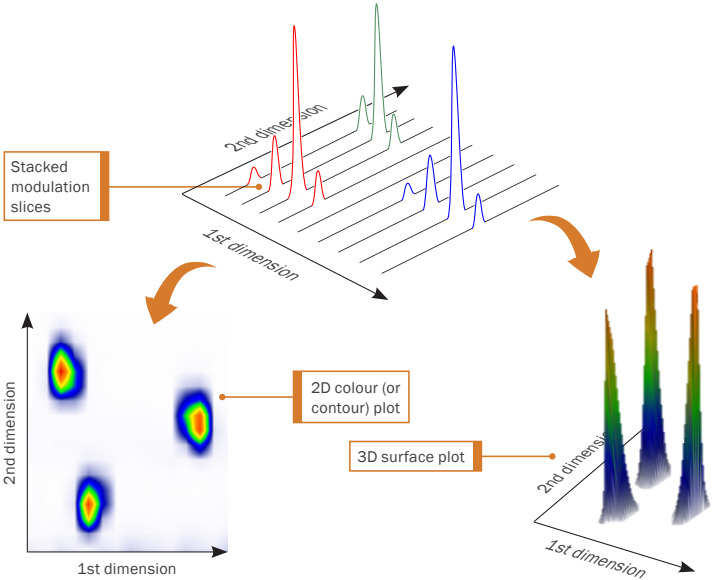
Comprehensive two-dimensional gas chromatography (GC×GC) is an advanced analytical technique with an increased separation capacity suitable for the analysis of complex samples.

The process involves the use of two columns with different stationary phases. This allows separation of mixtures that co-elute on the first column, so enabling an order of magnitude more compounds to be resolved. The *entire* sample is subjected to both separations, and so it is deemed a 'comprehensive' technique.

One of the most critical parts of the GC×GC system is the modulation device, which focuses the first-column eluent into narrow bands before injecting them into the faster-eluting secondary column. The individual chromatograms from the secondary column ('modulation slices') are then stacked side-by side to give the characteristic GC×GC contour and surface plots.

There are several types of modulation device available, and the BenchTOF, being platform-neutral, allows coupling to a range of these.

See pages 9, 13, 15, 18, 20, 27, 28, 30, 31 and 34 for applications using GC×GC.



In GC×GC, the eluent from the 1st-dimension column is split into portions that are individually fed into a much faster-eluting 2nd-dimension column. The resulting chromatograms are 'stacked' to form surface plots, which in turn can also be viewed 'from above' as colour (contour) plots.

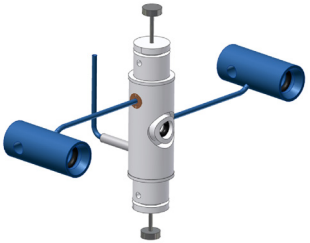
Thermal desorption

Thermal desorption (TD) is a pre-concentration technique for volatile and semi-volatile organic compounds (VOCs and SVOCs) that lowers the detection limits for gas chromatography (GC). Through the use of valving in the flow path, it also allows high-concentration samples to be split, avoiding column overload and extending the detection limit in this direction too.

Markes' thermal desorbers offer numerous benefits, including:

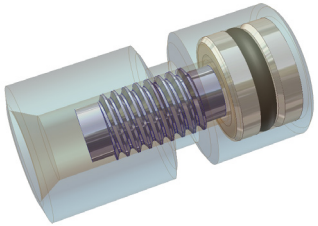
- **High sensitivity** – Two-stage desorption using sorbent tubes allows concentration enhancements of up to 10^6.
- **Analytical quality** – The narrow-bore design of the focusing trap ensures that a highly concentrated band of vapour is introduced to the GC, keeping peaks narrow and allowing true splitless operation.
- **Reduced running costs** – Electrical cooling eliminates the cost of cryogen, and also avoids problems with ice formation.
- **Cleaner chromatography** – By eliminating sample preparation steps, interferences (such as solvent artefacts) are eliminated. Unwanted high-abundance components such as water are also easily eliminated.
- **Wide dynamic range** – Two-stage desorption and sample splitting means that modern thermal desorbers can handle analyte concentrations ranging from part-per-trillion up to low-percent levels.
- **Analyte range** – Analytes ranging in volatility from acetylene to semi-volatiles such as n-$C_{40}H_{82}$ can be monitored.
- **Sample compatibility** – TD is compatible with sampling equipment that allows a wide range of sample types to be examined.

See pages 6, 7, 8, 10, 11, 12, 14, 16, 18, 19, 22, 23, 24, 26 and 33 for applications using TD.



Markes' patented inert valving enables C_2–C_{40} *and* reactive species to be analysed on a single thermal desorption system.

Markes' diffusion-locking SafeLok™ tubes and DiffLok™ caps enhance sample integrity and permit robust automation.



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

For more on the the single-tube UNITY™ thermal desorber and the multi-tube automated TD-100™ instrument, visit www.markes.com.

TOF-DS

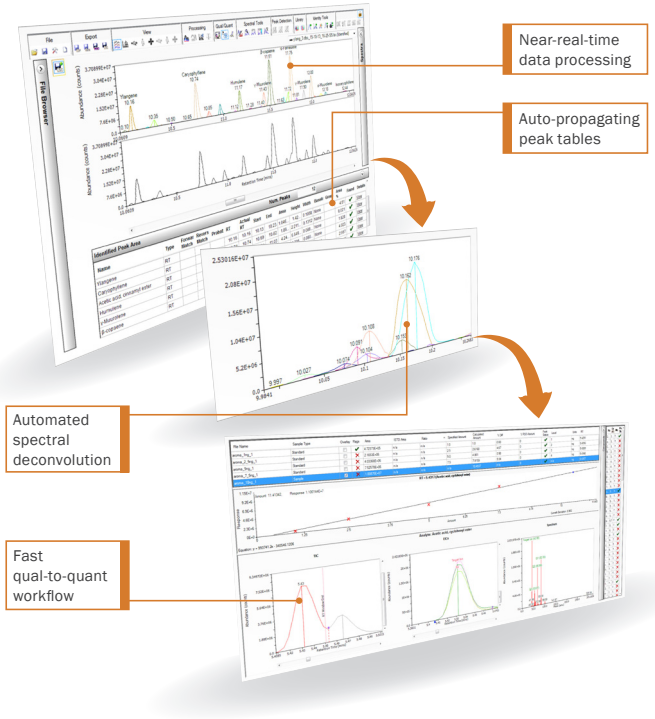
Available as standard with BenchTOF-HD and BenchTOF-Select is TOF-DS™, a powerful software platform for control and data processing of GC–BenchTOF systems.

TOF-DS features:

- **Full instrument control**.
- **Near-real-time data-processing** for reporting of results while the sample is still acquiring.
- **Dynamic baseline compensation** (DBC) to remove column bleed and unwanted background interference.
- **Advanced spectral deconvolution** for confident identification of co-eluting or masked peaks.
- **'Unlockable' method parameters** for simplified method development.
- **A streamlined qual-to-quant workflow**.
- **The ChromCompare® module** for rapid and objective automated comparison of GC–MS chromatograms.

To watch the TOF-DS tutorial videos, visit www.tof-ds.com.

For more information on ChromCompare, download Application Note 526.



The innovative features of TOF-DS complement the speed and spectral quality of BenchTOF, while the near-real-time capability aids on-the-fly method development.

TargetView

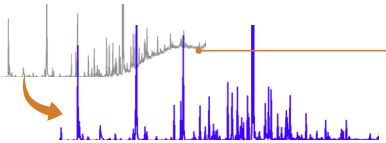
Supplied as standard with every BenchTOF-Evolve (and also available as a stand-alone package) is TargetView™, an easy-to-learn package for accurate and automated identification of trace compounds in complex GC–MS profiles.

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.
- **Compatibility with GC–MS file types** from most major vendors.

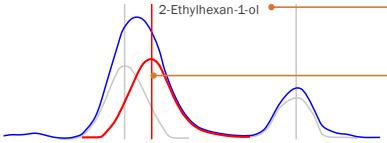
For more on TargetView, visit www.markes.com.

1 Import your chromatogram



Intelligent removal of unwanted baseline interference from chromatograms.

2 Run TargetView



Compounds are identified against a chosen list of targets or the entire NIST database.

Deconvolution algorithms accurately identify hidden compounds.

3 Output your report

Target compound	CAS No.	Retention time (min)	Match factor	Peak area
2,4-Dimethylheptane	2213-23-2	17.511	0.743	466333
beta-Pinene	127-91-3	17.598	0.894	156723
Octanal	124-13-0	17.732	0.773	41416
2-Ethylhexan-1-ol	104-76-7	18.051	0.869	64671
Benzyl alcohol	100-51-6	18.471	0.879	140629
Limonene	138-86-3	18.494	0.888	776248

Fully-automated report generation.

Simple tabular format makes it easy to see the compounds identified.

Easy-to-understand graphical and tabular formats are used by TargetView to display information on the key compounds present in a complex data set.

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 set the benchmark for quality and reliability for well over a decade. 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 and TD-100, a wide range of high-quality sorbent tubes, and innovative accessories that allow representative vapour profiles to be collected with minimal inconvenience.

In addition to our long-established reputation for thermal desorption, we also develop and manufacture the ground-breaking BenchTOF range of time-of-flight mass spectrometers for GC, featuring innovative and labour-saving software, and revolutionary Select-eV technology for hassle-free soft ionisation.

As well as flavour and fragrance profiling, our 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.

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

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