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Inter-species interactions: Studying the role of VOCs in multitrophic relationships

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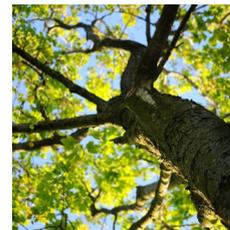
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Thermal Desorption Applications Guide: Biological profiling

A comprehensive guide to using thermal desorption to study human health, atmospheric chemistry and chemical ecology



Introduction

Human health

The study of volatile chemicals from humans has recently attracted increasing attention, particularly regarding the potential of breath volatiles to rapidly and non-invasively diagnose diseases such as cancer.



Ecosystems and the atmosphere

Biogenic volatile organic compounds (BVOCs) contribute substantially to atmospheric concentrations globally, and understanding the factors involved in their release is vital for accurate atmospheric modelling.



Chemical ecology

Many species use volatile chemicals to influence other organisms. This can simply involve the release of volatiles from plants to attract pollinators, or far more complex interactions involving multiple species.



In this Applications Guide, we describe how thermal desorption (TD) is being applied to advanced research into each of the above areas – covering everything from the effect of stress on breath VOC profiles to the ecological role of herbivore-induced plant volatiles.

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



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

What is thermal desorption?

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

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

TD can be used:

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

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

Launched in May 2016, Markes' new 'xr' series of instruments offer performance at least equal to earlier models, with the additional benefits of extended re-collection capability, wider analyte range, and improved reliability. See page 22 and our website for more details.



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

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

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Human health

Breath monitoring

Simple, non-invasive sampling of VOCs in breath



Biological monitoring is well-established for assessing personal exposure to chemicals, but recent research is now showing its potential to assist understanding of medical conditions more generally. However, traditional blood and urine monitoring is invasive, and can require time-consuming, error-prone sample preparation prior to GC analysis of volatiles.

Sampling breath using devices like Markes' Bio-VOC is more appropriate for large-scale studies, because it is much easier for the participants, and doesn't require trained medical personnel. Capturing the volatiles directly onto sorbent tubes, with analysis by thermal desorption, completely circumvents laborious sample preparation (and consequent potential bias) common with techniques such as solvent extraction of aqueous samples.

Typical analytical conditions:

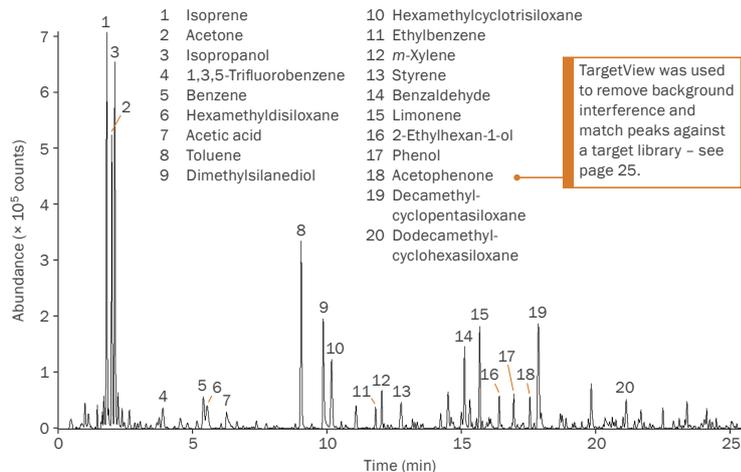
Sample: 411 mL breath, collected onto a sorbent tube using a Bio-VOC breath sampler.

TD (UNITY or TD100): Tube (Bio-monitoring): Desorbed at 270°C (8 min).

Trap (Material emissions): Analytes trapped at 10°C, desorbed at 290°C (3 min). Split ratio: Outlet 3:1.

Analysis: GC-MS.

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



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

Disease diagnosis

Studying potential disease biomarkers in breath

Breath sampling of VOCs has gained prominence as a potentially useful approach to the early diagnosis of many diseases. As well as studies of VOCs with direct links to disease, an important aspect of research in this area involves investigating how other factors such as diet and environment may affect breath volatiles.

As part of this effort, UK researchers have been using TD-GC-MS to study the effect of stress on breath VOCs. The backflush capability of Markes' TD instruments allows multi-bed tubes and traps to be used,

widening the range of compounds that can be reliably monitored from a single sample. An added advantage of sorbent tubes for this study was that samples could be stored until there were sufficient to analyse a large batch in one run, making it easier to schedule GC-MS instrument time.

Typical analytical conditions:

Sample: 4 L end-exhaled breath, collected onto a sorbent tube using a sampling mask.

TD (UNITY or TD100): Tube (Hydrophobic); Desorbed at 300°C (5 min). Trap (General-purpose hydrophobic); Analytes trapped at 10°C, desorbed at 300°C (5 min). Split ratio: Splitless.

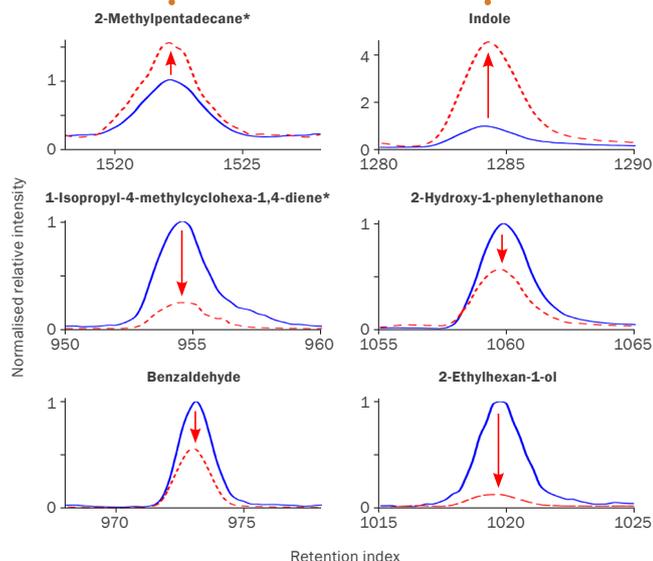
Analysis: GC-MS.



<http://dx.doi.org/10.1088/1752-7155/7/1/017102>

C.L.P. Thomas *et al.*, The effect of a paced auditory serial addition test (PASAT) intervention on the profile of volatile organic compounds in human breath: A pilot study, *Journal of Breath Research*, 2013: 017102.

As shown by these EIC responses from one participant, levels of 2-methylpentadecane and indole rose during a stressful mental-arithmetic test (---), compared to when they listened to relaxing music (—), while levels of four other compounds fell. * Id tentative.



Using breath monitoring with analysis by TD-GC-MS, six stress-sensitive compounds were identified in a group of 22 volunteers. *Image adapted from Journal of Breath Research with permission from IOP Publishing and the authors.*

Skin volatiles

Identifying mosquito-attracting chemicals from skin

Skin volatiles are a major factor determining the attractiveness of humans to mosquitoes, and hence to the risk of exposure to diseases such as yellow fever and malaria. This attractiveness varies markedly between individuals, and is not only determined by genetic differences, but is also thought to be related to the presence of certain microorganisms on the skin.

To examine these factors, researchers at Wageningen University have collected skin emanations using glass beads, analysis of which eliminates the effect of confounding factors like skin temperature or humidity. Subsequent direct desorption of the beads in a TD instrument, as well as being quicker than solvent extraction, also allows a pre-desorption dry-purge to remove residual water and oxygen, which would otherwise interfere with the GC analysis.

Typical analytical conditions:

Sample: Volunteers were asked to rub the sole of their foot over 100 glass beads (4 mm diameter) on a PTFE tray for 10 min. Twenty beads were then placed in an empty TD tube.

TD (UNITY or TD100): Sample: Desorbed at 150°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at -10°C, desorbed at 250°C (3 min). Split ratio: Outlet 6:1.

Analysis: GC-MS.



<http://dx.doi.org/10.1016/j.meegid.2013.05.009>

N.O. Verhulst et al., Relation between HLA genes, human skin volatiles and attractiveness of humans to malaria mosquitoes, *Infection, Genetics and Evolution*, 2013, 18: 87-93.

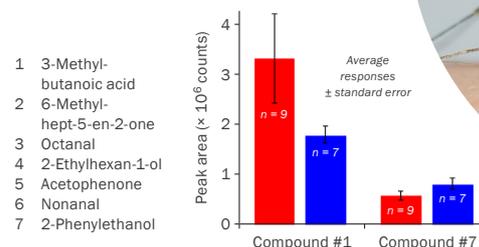
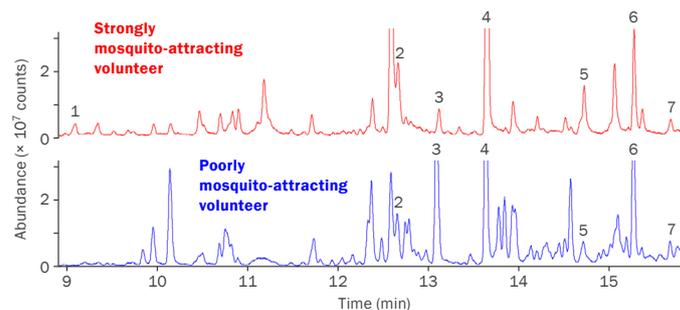


Image credit:
Hans Smid
(Bugs in the Picture)



Desorbing skin volatiles from glass beads, with TD-GC-MS analysis, proved to be a straightforward approach to identifying compounds that attracted (#1) and repelled (#7) mosquitoes (*Anopheles gambiae*) across a group of volunteers. The researchers suggest that this information may be useful in developing new malaria prevention strategies. *Data courtesy of Niels Verhulst, Wageningen University and Research Centre, The Netherlands.*

Ecosystems and the atmosphere

Analysing plant terpenoids

Inert systems for analysis of reactive monoterpenes

Monoterpenes dominate amongst the VOCs emitted from many plants, and are consequently important in atmospheric chemistry, but some of these compounds are highly reactive and prone to rearrangement within TD analytical systems.

The inertness and adjustable flow-path temperature of Markes' TD systems ensures reliable analysis of monoterpenes (in addition to single-run analysis of compounds from C₂ to C₄₄). Use of porous-polymer sorbents such as Tenax® TA avoids on-tube decomposition of certain analytes, while inert-coated stainless steel tubes are used for the most reactive compounds, such as sulfur species. Validating recovery of these reactive species is made possible by the splitting and re-collection capability of Markes' TD systems.

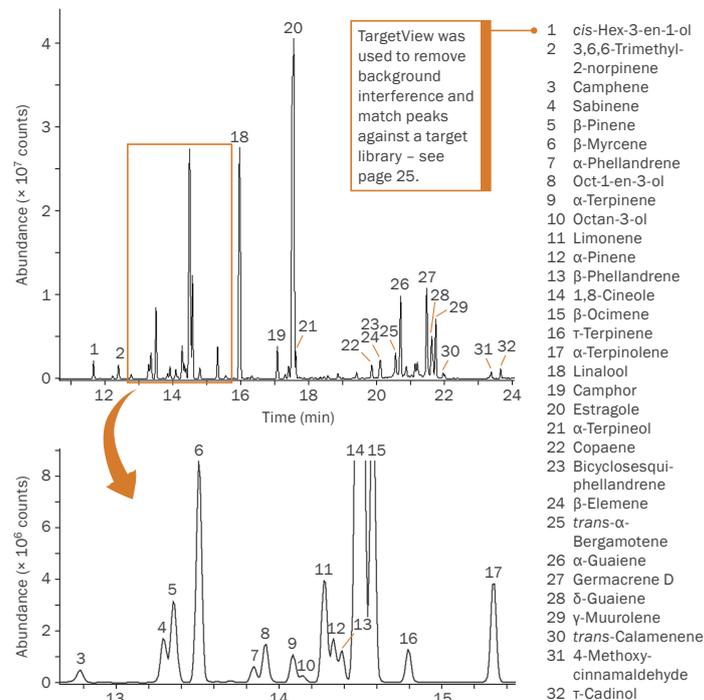
Typical analytical conditions:

Sample: 5 g fresh Basil leaves (*Ocimum basilicum*).

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

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

Analysis: GC-MS.



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

Heathland volatiles

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

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

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

Typical analytical conditions:

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

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

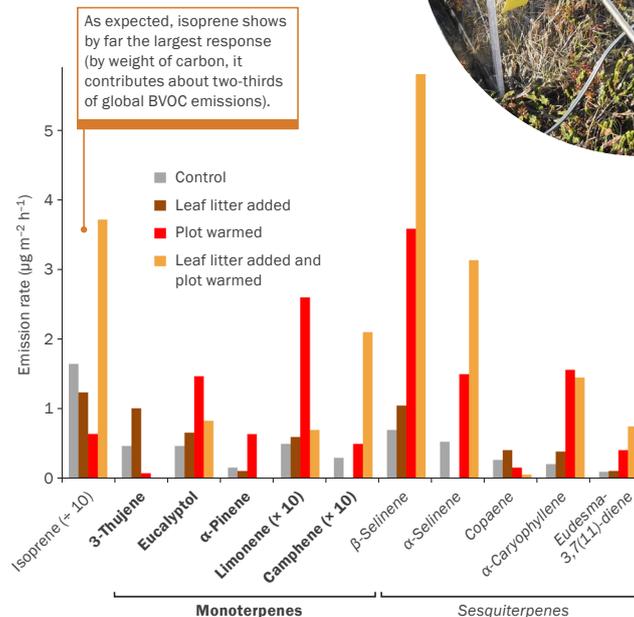
TD (UNITY or TD100): Tube (Hydrophobic): Desorbed at 250°C (10 min). Trap (General-purpose hydrophobic): Analytes trapped at -10°C, desorbed at 300°C (3 min). Split ratio: Outlet 10:1.

Analysis: GC-MS.



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

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



Comparison of four different treatments, sustained over a period of 12 years, shows that warming, and to a lesser extent the addition of leaf litter, causes significant alterations in the emission rates of certain mono- and sesquiterpenes. *Data and photo reproduced courtesy of Rikka Rinnan, University of Copenhagen, Denmark.*

Rainforest monoterpenes

Secure, straightforward sampling of reactive VOCs

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



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

Typical analytical conditions:

Sample: Air in the rainforest canopy, 60 km NNW of Manaus, Brazil.

Grab-sampling (Easy-VOC): 1000 mL.

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

Analysis: GC-MS.



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

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

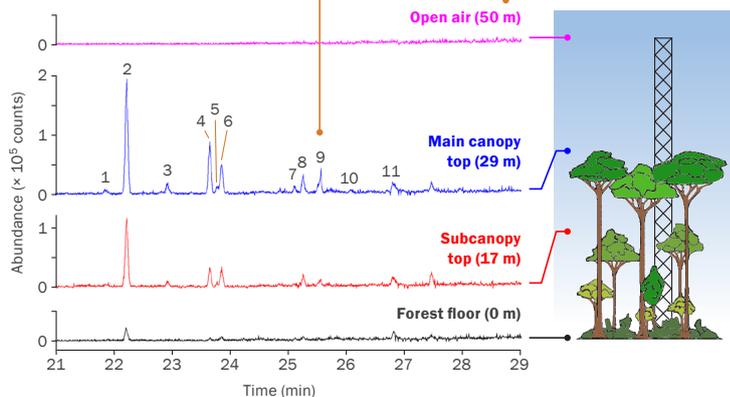
SafeLok tubes contain narrow helical channels that stop analytes escaping or contaminants entering, so avoiding sole reliance on caps for sample security.



- | | | | |
|---|------------------|----|---------------------------------|
| 1 | β -Thujene | 7 | <i>trans</i> - β -Ocimene |
| 2 | α -Pinene | 8 | Limonene |
| 3 | Camphene | 9 | <i>cis</i> - β -Ocimene |
| 4 | Sabinene | 10 | γ -Terpinene |
| 5 | β -Myrcene | 11 | Terpinolene |
| 6 | β -Pinene | | |

The highest monoterpene levels were found in the hot, bright conditions at the canopy top, but levels were much lower further up.

The robust design and manual operation of Easy-VOC make it ideal for field monitoring in remote locations.



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

Emissions from pine forests

Studying responses of plant VOCs to environmental factors

Elucidating the role of plant volatiles in atmospheric processes (and in chemical ecology) relies on first understanding how factors such as light, temperature and availability of water affect VOC production.



Image credit: Gerry/Wikimedia Commons (CC BY-SA 2.0)

Researchers in the USA have been investigating such issues, using Markes' TD equipment to study the compounds released from pine needles *in situ*. Their approach not only allowed the effects of light, temperature and stomatal conductance to be deconvolved, but (combined with $^{13}\text{C}_2$ feeding studies), enabled them to show that a significant proportion of the total monoterpenes are biosynthesised in direct response to light.

Typical analytical conditions:

Sample: A glass cuvette 12.5 cm in diameter was used to enclose fascicles of Ponderosa Pine (*Pinus ponderosa*) growing in the Manitou Experimental Forest, USA.

Pumped sampling: ~200 mL/min for 20–30 min (total volume 4–6 L).

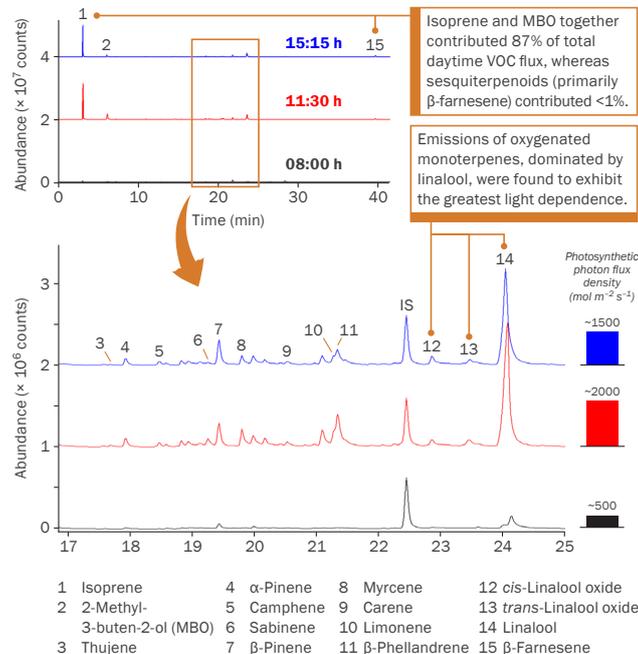
TD (UNITY or TD100): Tube (Bio-monitoring): Desorbed at 275°C (10 min). Trap (Material emissions): Analytes trapped at 0°C, desorbed at 300°C (3 min). Split ratio: Splitless.

Analysis: GC–MS.



<http://dx.doi.org/10.1007/s00442-014-3008-5>

P. Harley, A. Eller, A. Guenther and R.K. Monson, Observations and models of emissions of volatile terpenoid compounds from needles of ponderosa pine trees growing *in situ*: Control by light, temperature and stomatal conductance, *Oecologia*, 2014, 176: 35–55.



A wide diurnal variation in VOC emissions from pine needles was found using *in situ* pumped sampling with TD–GC–MS.

Data reproduced courtesy of Peter Harley, formerly of the National Center for Atmospheric Research, Boulder, CO, USA.

Marine halocarbons

Canister sampling of short-lived very volatile compounds

Marine organisms such as seaweeds and phytoplankton are major sources of certain highly volatile halocarbons, and some of these are believed to play key roles as stratospheric ozone depletants. Levels of these compounds, often termed very short-lived substances (VSLs) vary substantially with location and time, and the factors governing this are the subject of current research.

Low-boiling compounds such as halocarbons and organic nitrates are typically monitored on-line, or by canister grab-sampling. In both cases, the cryogen-free trap cooling and efficient trap desorption of Markes' instruments ensure sharp peaks and maximum sensitivity for splitless samples.

Typical analytical conditions:

Sample: Air from the marine boundary layer, collected in the Galapagos Islands.

Canister sampling (Air Server or CIA Advantage): 500 mL.

TD (UNITY): Trap (Greenhouse gases): Analytes trapped at -15°C , desorbed at 250°C (10 min). Split ratio: Splitless.

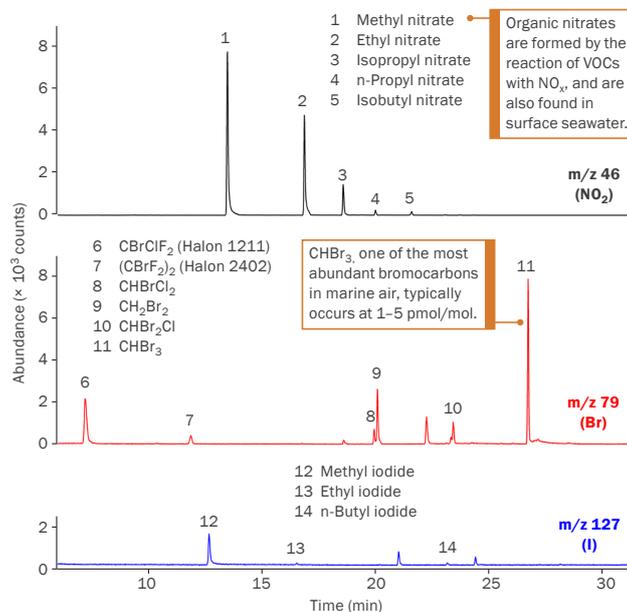
Analysis: GC-MS (negative-ion chemical ionisation).

A published paper describing a similar study in South-East Asia is cited below.

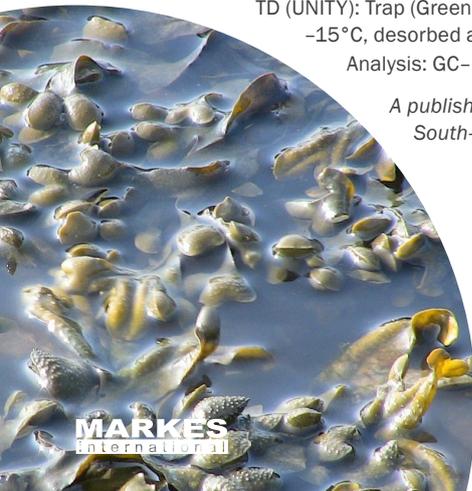


<http://dx.doi.org/10.5194/acp-14-8137-2014>

M.S. Mohd Nadzir et al., Bromocarbons in the tropical coastal and open ocean atmosphere during the 2009 Prime Expedition Scientific Cruise (PESC-09), *Atmospheric Chemistry and Physics*, 2014, 14: 8137–8148.



Highly volatile compounds of biogenic origin (as well as anthropogenic 'Halon' fire-retardants) are easily detected in oceanic air using canister sampling with TD pre-concentration. *Data reproduced courtesy of David Oram & Graham Mills (University of East Anglia, UK) and Shahrul Mohd Nadzir (University Malaya and Universiti Kebangsaan Malaysia).*



A photograph of a honeybee in flight, positioned in the upper right quadrant. The bee is shown in profile, facing left, with its wings spread. The background is a soft-focus field of white flowers with yellow centers. A purple rectangular box is overlaid on the left side of the image, containing the text 'Chemical ecology'.

Chemical ecology

Flower scents

Understanding the effect of ozone on floral volatiles

As well as visual cues, plants use volatiles released from flowers to attract insects, and so achieve pollination. Ozone, generated by the action of sunlight on air pollutants, may interfere with this process by reacting with certain components of the flower scent.

A research group from Spain is investigating the potential impact of ozone by studying how the volatile blends from flowers change when treated with ozone. Using a continuous-flow apparatus to control the reaction time, vapour-phase mixtures were pumped onto sorbent tubes, and analysed using Markes' TD equipment. Under the splitless conditions used, rapid trap heating optimises desorption efficiency, so providing sharp peaks and helping to maximise sensitivity.

Typical analytical conditions:

Sample: Vapours from cut flowering stems of Black Mustard (*Brassica nigra*) in a glass container, flushed with clean air (900 mL/min), and exposed to 0 or 120 ppb ozone during passage through a 4.5 m flow tube.

Pumped sampling: 200 mL/min for 30–40 min (total volume 6–8 L).

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

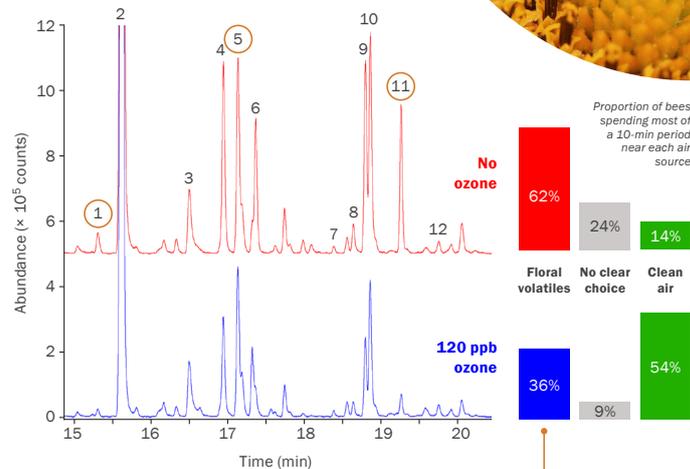
Analysis: GC-MS.

 <http://dx.doi.org/10.1111/nph.13620>

G. Farré-Armengol, J. Peñuelas, T. Li, P. Yli-Pirilä, I. Filella, J. Llusia and J.D. Blande, Ozone degrades floral scent and reduces pollinator attraction to flowers, *New Phytologist*, 2016, 209: 152–160.



- | | | | |
|---|------------------------|----|-----------------------|
| 1 | α -Phellandrene | 7 | α -Terpinene |
| 2 | α -Pinene | 8 | <i>p</i> -Cymene |
| 3 | Benzaldehyde | 9 | Limonene |
| 4 | Sabinene | 10 | β -Thujene |
| 5 | β -Pinene | 11 | (Z)- β -Ocimene |
| 6 | β -Myrcene | 12 | γ -Terpinene |



Levels of floral monoterpenes fell by about 25% when exposed to ozone, with substantial changes being observed in the relative amounts of some compounds (circled). Data reproduced courtesy of Gerard Farré-Armengol, *Global Ecology Unit, CSIC, Barcelona, Spain*.

The ozone-degraded blend was less attractive to Buff-tailed Bumblebees (*Bombus terrestris*) in a two-way behavioural test against clean air.

Beehives

Using diffusive sampling to monitor beehive air

Honeybees (*Apis mellifera*) play a key role in the natural world as pollinators of plants, including crops of commercial significance. Bees' foraging exposes them to environmental pollutants (which are often brought back into the colony), making them of considerable value as 'sentinel' species for monitoring ecosystem health.



Diffusive monitoring of beehive air using sorbent tubes is a useful approach to such research, because it is easy to set up, non-intrusive, and provides qualitative information on important compounds present at trace levels. It can also be used quantitatively when an uptake rate for compound in question is known on the sorbent used.

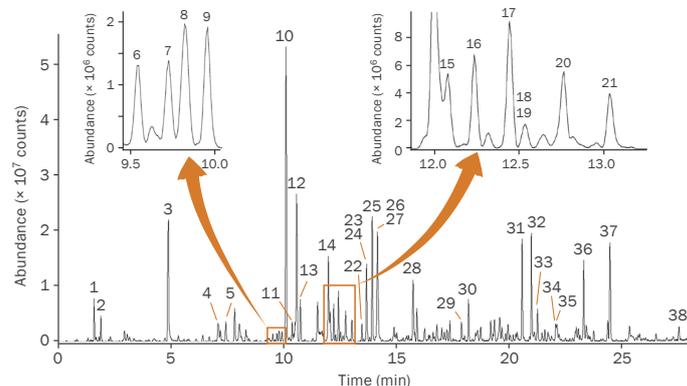
Typical analytical conditions:

Sample: Air within a beehive.

Diffusive (passive) sampling: 1 week.

TD (UNITY or TD100): Tube (Tenax® TA): Desorbed at 270°C (10 min). Trap (Tenax TA): Analytes trapped at 20°C, desorbed at 290°C (2 min). Split ratio: Outlet 2.7:1.

Analysis: GC-MS.



1 Acetone	13 2-Butoxyethanol	26 Methyl benzoate
2 Dichloromethane	14 Benzaldehyde	27 Nonanal
3 Acetic acid	15 3-Carene	28 Decanal
4 3-Methylbut-3-en-1-ol	16 6-Methylhept-5-en-2-one	29 Hexadecane
5 Octane	17 3,3-Dimethylhexane	30 Triacetin
6 <i>p</i> -Xylene	18 <i>o</i> -Cymene	31 Nerolidol
7 Nonane	19 β -Phellandrene	32 4-Hydroxyacetophenone
8 6-Methylhepta-3,5-dien-2-one	20 (Z)-Ocimene	33 Guaiol
9 Isopentyl acetate	21 2-Ethylhexan-1-ol	34 α -Eudesmol
10 Styrene	22 Phenyl formate	35 Cadalene
11 Heptan-2-one	23 Benzyl alcohol	36 Benzyl benzoate
12 α -Pinene	24 Octan-1-ol	37 Benzyl 2-hydroxybenzoate
	25 Acetophenone	38 Heneicosane (n-C ₂₁ H ₄₄)

Compounds covering a wide volatility range were analysed in beehive air using passive samplers packed with Tenax TA. Those found include environmental pollutants (●), plant terpenoids (●), bee pheromones (●) and components of propolis ('bee glue') (●).

Inter-species interactions

Studying the role of VOCs in multitrophic relationships

Research into the role of plant volatiles within entire species communities promises to shed light on how evolutionary pressures have shaped the ability of plants to release VOCs. Interactions between species forming part of a food chain ('trophic levels') are a key aspect of this fascinating area. For example, the volatile profiles of many plants change substantially upon being eaten by herbivores such as caterpillars, and in some cases these modified profiles can attract predators of the herbivores.



Researchers at the Netherlands Institute of Ecology and Wageningen University have pioneered work in this complex field, using TD-GC-MS techniques to investigate the shifts in VOC blends emitted by plants in response to herbivory. As in other studies of this kind, volatile profiles are typically captured from the plants *in situ*, using pumped sampling onto tubes packed with hydrophobic sorbents.

Typical analytical conditions:

Sample: 20 cm of a branch of Crab Apple (*Malus sylvestris*) in a polythene bag.

Pumped sampling: 200 mL/min for 120 min (total volume 24 L).

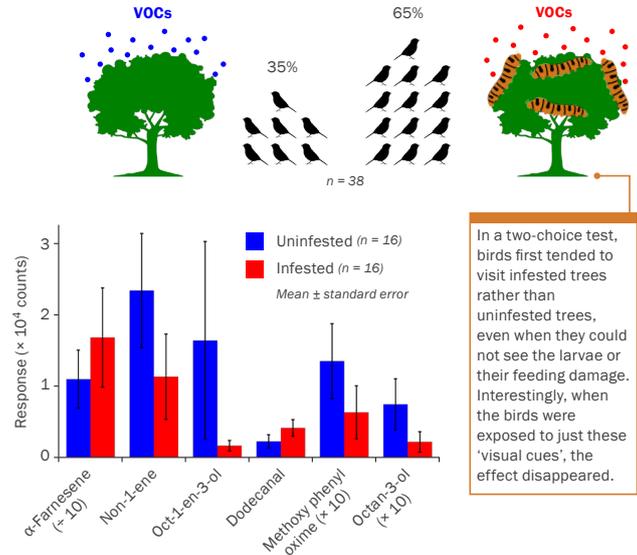
TD (UNITY or TD100): Tube (Hydrophobic): Desorbed at 200°C (12 min). Trap (Tenax®

TA): Analytes trapped at -10°C, desorbed at 270°C (3 min). Split ratio: Outlet 4 : 1. Analysis: GC-MS.



<http://dx.doi.org/10.1111/ele.12177>

L. Amo, J.J. Jansen, N.M. van Dam, M. Dicke and M.E. Visser, Birds exploit herbivore-induced plant volatiles to locate herbivorous prey, *Ecology Letters*, 2013, 16: 1348-1355.



In a rare example of a tritrophic interaction involving birds, apple trees infested by larvae of the Winter Moth (*Operopthera brumata*) were more attractive to Great Tits (*Parus major*) than uninfested trees. The researchers inferred that differing emissions of herbivore-induced plant volatiles (HIPVs), studied here with TD-GC-MS, may underlie this preference.

Image generated from tabulated data in *Ecology Letters* with the permission of the authors.

Decomposing organic matter

Conducting research into soil-gas volatiles



Decomposing material releases a wide range of VOCs, and understanding these can be important in everything from crime-scene investigation to dealing with the aftermath of natural or man-made disasters. However, there is a lack of information regarding which volatiles are released from decomposing remains and which arise naturally from microbial action in the soil. Understanding soil-borne VOCs is therefore a valuable area of study.

Australian researchers have been developing methods to investigate such issues, by studying VOCs in the soil near pig carcasses. Using a VOC-Mole sampler with TD-GC-MS, they were able to speed up sampling and identify more compounds compared to methods such as solvent extraction.

Typical analytical conditions:

Sample: Soil air at 30 cm depth, adjacent to the abdomen of a pig carcass after 17 days of decomposition.

Pumped sampling (VOC-Mole): 100 mL/min for 30 min (total volume 3 L).

TD (UNITY or TD100): Tube (Bio-monitoring): Desorbed at 300°C (4 min). Trap (Air toxics): Analytes trapped at -10°C, desorbed at 300°C (3 min). Split ratio: Outlet 21:1.

Analysis: GC-MS.



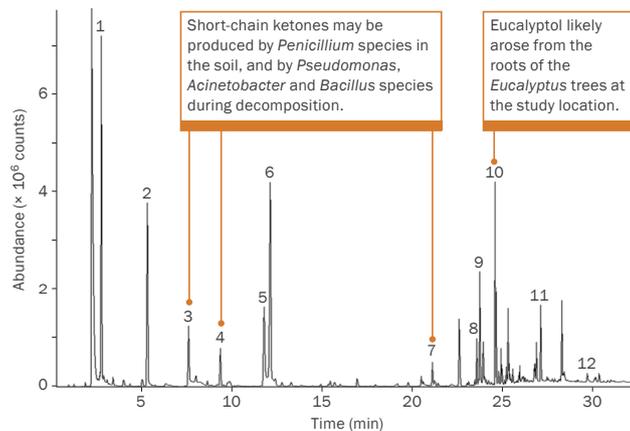
<http://dx.doi.org/10.1371/journal.pone.0095107>

S.L. Forbes and K.A. Perrault, Decomposition odour profiling in the air and soil surrounding vertebrate carrion, *PLOS One*, 2014, 9: e95107.



VOC-Moles are driven into the soil, and can be configured for pumped or passive sampling (shown).

- | | | |
|-------------------|-----------------------|----------------------------------|
| 1 Pentane | 5 Cyclohexanone | 9 Phenol |
| 2 Butan-2-one | 6 Dimethyl disulfide | 10 Eucalyptol |
| 3 3-Methylbutanal | 7 Heptan-2-one | 11 Indole |
| 4 Pentan-2-one | 8 Dimethyl trisulfide | 12 N,N-Diethyl-4-methylbenzamide |



Pumped sampling with a VOC-Mole onto two-bed sorbent tubes allows a wide range of VOCs to be collected from soil gas.

Data reproduced courtesy of Shari Forbes and Katelynn Perrault, University of Technology, Sydney, Australia.

Animal scents

Studying odorous secretions using direct desorption



Many members of the animal kingdom (notably insects) use signalling chemicals to communicate with each other and with other species, but the phenomenon is not well-documented in vertebrates. Investigating these pheromones is important to help understand population dynamics, but the complex mixes of trace odorants present in glandular secretions can make this challenging using solvent extraction.

A team based in Tasmania, Australia, has overcome these difficulties by using direct desorption with TD-GC-MS to investigate potential signalling chemicals from the Brushtail Possum. This is the first such detailed study amongst marsupials, and may help to manage populations of this sometimes over-abundant species more effectively.

Typical analytical conditions:

Sample: A glass microfibre filter-paper was used to swab the cloacal glands of the Brushtail Possum (*Trichosurus vulpecula*), and a 5 mm × 5 mm section was placed in an empty inert-coated stainless steel TD tube.

TD (UNITY or TD100): Sample: Desorbed at 150°C (10 min). Trap (Sulfur):

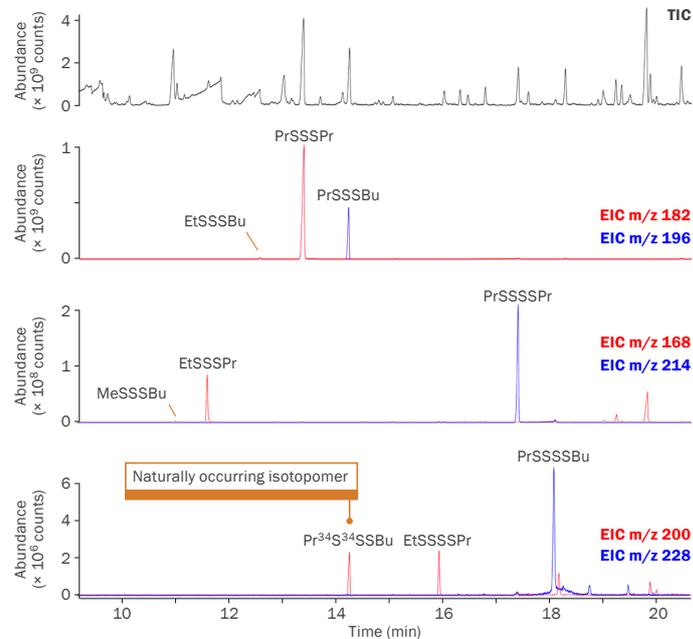
Analytes trapped at 25°C, desorbed at 290°C (3 min). Split ratio: Splitless.

Analysis: GC-MS.



<http://dx.doi.org/10.1007/s10886-012-0188-5>

S. McLean, N.W. Davies and N.L. Wiggins, Scent chemicals of the Brushtail Possum, *Trichosurus vulpecula*, *Journal of Chemical Ecology*, 2012, 38: 1318-1339.



Nearly 40 sulfur compounds were detected in the glandular secretions of the Brushtail Possum, some of which are shown here. Use of TD avoided loss of reactive species typical of solvent-based methods, while splitless analysis maximised sensitivity for trace-level analytes. *Data and photo courtesy of Stuart McLean, University of Tasmania.*



Relevant sampling and analytical techniques

Thermal desorption

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

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

- **Analyte range** – Compounds ranging in volatility from acetylene to $n\text{-C}_{44}\text{H}_{90}$ and reactive species can all be analysed on a single TD platform.
- **Quantitative re-collection of split flows** enables repeat analysis and simple method validation, overcoming the historical 'one-shot' limitation of TD.
- **High sensitivity** – Two-stage desorption using sorbent tubes allows concentration enhancements of up to 10^6 .
- **Wide dynamic range** – Two-stage desorption and sample splitting means that Markes' thermal desorbers can handle analyte concentrations ranging from part-per-trillion up to low-percent levels.
- **Sample compatibility** – As world leaders in TD technology, Markes offers an unmatched range of innovative and labour-saving sampling accessories for liquids, solids and gases.
- **Analytical quality** – The narrow-bore design of the focusing trap ensures that a highly concentrated band of vapour is introduced to the GC, allowing true splitless operation and optimising both resolution and sensitivity.
- **Reduced running costs** – Electrical cooling eliminates the cost of cryogen, and also avoids problems with ice formation.
- **Cleaner chromatography** – By circumventing the need for sample preparation, solvent artefacts are eliminated, while unwanted high-abundance components such as water can also be selectively removed.



Markes' patented inert valving enables $\text{C}_2\text{-C}_{44}$ and reactive species to be analysed on a single thermal desorption system.

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



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



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

Pumped sampling

Pumped sampling onto sorbent tubes is a versatile option for simultaneous monitoring of multiple compounds, whether in the open air or contained within bell-jars, sampling bags, or other headspace containers.

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

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

- **ACTI-VOC™** is a lightweight, compact low-flow pump specifically optimised for TD tubes, which can operate in constant-flow or constant-pressure modes.
- **Easy-VOC™** is a manually-operated grab-sampler that allows precise volumes of air or gas to be sampled directly onto sorbent tubes. By avoiding the need for batteries or electrical power, it is ideal for field sampling.



➔ See pages 11, 12, 13, 16, 18 and 19 for applications using pumped sampling.

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

Canister and on-line sampling

Canisters are a useful approach to monitoring ultra-volatile compounds that are too volatile to be retained on sorbent tubes at ambient temperature. The same applies to on-line monitoring (the collection of vapours directly into the focusing trap of the thermal desorber), which also allows continuous sampling and near-real-time monitoring.

Three canister/on-line systems are available from Markes:

- The **Air Server-xr™** samples air on-line (or from canisters), and delivers it to the focusing trap of the UNITY-xr thermal desorber.
- The **CIA Advantage™**, used with a UNITY-xr thermal desorber, is perfect for canisters, but can also handle sorbent tube or on-line samples.
- The **TT24-7™** on-line thermal desorber uses two focusing traps, working alternately, to sample and analyse air continuously.



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

Micro-Chamber/Thermal Extractor

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

The μ -CTE can be used for:

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

➔ See page 10 for an application using the μ -CTE.

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

Now available with humidifier accessory



The sampling pots of the μ -CTE have volumes of 44 or 114 cm³, depending on the model chosen.

Direct desorption

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

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



Direct desorption is a simple way of releasing organic vapours from a sample. It can use metal tubes, but glass ones are preferred by many analysts because it is easier to position the sample and monitor its state before and after analysis.

➔ See pages 8 and 20 for applications using direct desorption.

📄 ➔ For more on direct desorption, see Application Note 009.

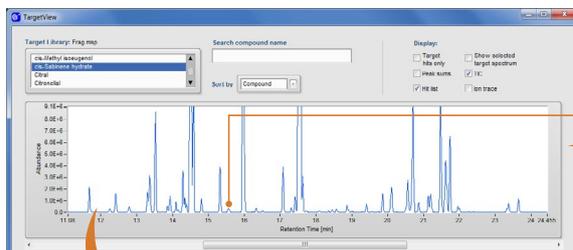
Compound identification software

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

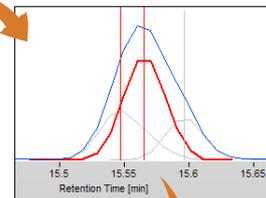
TargetView features:

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

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



Clicking on a peak pulls up the deconvoluted profile of the target – cis-sabinene hydrate in this case – and any nearby peaks.



Target compound	CAS no	Retention time (min)	Expected retention time (min)	Area	Search Index	Peak ratio (%)	Peak ratio (exp)	Retention Index
Carbazole	415030	14.1036	-	-	495156	0.047	100.0000	-
beta-9-epoxy-Dopamine	3770-91-1	14.6547	-	-	602156	0.024	42200550	-
gamma-8-epoxy-Dopamine	96630-2	14.0041	-	-	1090	0.030	4007905	-
Hydroquinone	206450-9	15.2652	-	-	0	0.022	1401905	-
cis-sabinene hydrate	111-81-0	15.5414	-	-	0	0.022	500710	-
trans-sabinene hydrate	12000-05-1	15.2655	-	-	1000	0.019	90270	-
Urethane	78106	15.9783	-	-	0	0.027	130179228	-
1,3-bisphenolpropane	21185-08-5	16.2289	-	-	0	0.087	150204	-
Thiourea	471-15-8	16.6165	-	-	1097	0.087	411038	-
Carbazole	76222	17.0868	-	-	0	0.022	18107449	-
1,4-bisphenol	66573-1	17.5616	-	-	0	0.015	161456	-

Simple report allows key components to be identified quickly.

The acquired mass spectrum (top) is readily compared against the library spectrum (bottom).



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

About Markes International

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

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

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

As well as biological profiling, Markes' products are used extensively in multiple routine and research applications – everything from to vehicle interior air quality to food analysis.

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



ACTI-VOC™, Air Server™, Air Server-xr™, Bio-VOC™, CIA Advantage™, Easy-VOC™, HSS-TD™, Micro-Chamber/Thermal Extractor™, µ-CTE™, TargetView™, TD100™, TD100-xr™, TT24-7™, UNITY™, UNITY-xr™ and VOC-Mole™ are trademarks of Markes International.

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

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