TDTS 105

Near-real-time profiling of fragrance components and potential allergens released from an air freshener using TD–GC/TOF MS

Summary

In this Application Note we describe the use of a continuously-sampling thermal desorber in conjunction with GC/TOF MS to monitor the build-up and decay of fragrances and potential allergens released into indoor air from a plug-in air freshener.

Introduction

Air fresheners emit numerous volatile organic compounds (VOCs), amongst which are many fragrance compounds. Developing a near-real-time method of monitoring their build-up and decay in indoor air is of potential interest for manufacturers when formulating their products. Such studies are of particular value in light of a report showing the presence of carcinogens, allergens and other hazardous VOCs amongst the fragrance components in air fresheners[1].

In this Application Note we look at the near-real-time (NRT) analysis of the compounds released from a plug-in air freshener, using the TT24-7™ Series 2 thermal desorber combined with gas chromatography (GC) and time-of-flight mass spectrometry (TOF MS). The fragrance was allowed to diffuse into a room, and the air was sampled continuously to monitor the compounds released as their concentrations changed over time.

Background to twin-trap thermal desorption

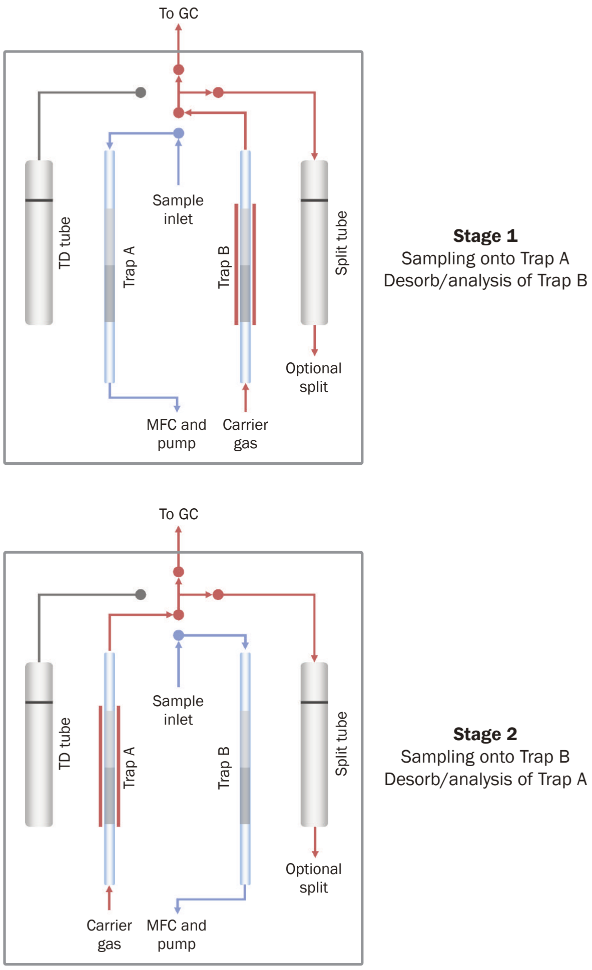
Near-real-time (NRT) analysis based on sample pre-concentration using Markes' TT24-7 Series 2 thermal desorber (Figure 1) involves the use of two electrically-cooled sorbent traps working in tandem[2]. The use of the second focusing trap enables 100% data capture (*i.e.* no sampling blind spots), as there is always one trap available for sample collection.

Figure 1: Markes' TT24-7 Series 2 thermal desorber for continuous monitoring.

The TT24-7 Series 2 is the latest development in twin-trap thermal desorption technology, featuring:

- Dual-trap continuous monitoring – 100% data capture
- Inert, uniformly-heated flow path offers compatibility for C_2–C_{40} compounds and reactive species
- Wide range of sampling flows (up to 800 mL/min) with quantitative trapping offers high sensitivity
- Highly time-resolved data – cycle times as low as 3–5 minutes if required.

During the sampling process, air is collected onto Trap A, at flow rates between 50 and 800 mL/min. At the end of the designated sampling time the sampling flow is switched to Trap B, and Trap A is desorbed (Figure 2). The cycle is then repeated until the sampling sequence is stopped.



Stage 1
Sampling onto Trap A
Desorb/analysis of Trap B

Stage 2
Sampling onto Trap B
Desorb/analysis of Trap A

Figure 2: The two-stage operation of the TT24-7 Series 2.

Background to time-of-flight mass spectrometry (TOF MS)

The TOF MS used in this study, BenchTOF-dx™ [3], is designed specifically for gas chromatography. A key advantage of TOF mass spectrometers for near-real-time monitoring is their high rate of data acquisition (10,000 full-range spectra per second for BenchTOF-dx). This results in a wealth of detailed spectral information that can either be examined immediately, or retained for future reference – such as screening for previously unsuspected trace-level compounds in complex profiles.

BenchTOF-dx is also extremely sensitive, providing full spectral information at levels equivalent to that of quadrupole instruments running in selected ion monitoring (SIM) mode. This makes BenchTOF-dx ideal for trace-level applications.

Another advantage of BenchTOF-dx is its production of reference-quality 'classical' EI spectra. This allows matching against commercial databases, greatly enhancing the detection and analysis of unknowns as well as target compounds.

Experimental

A laboratory blank was first collected using the TT24-7 Series 2, with desorption and analysis of the first trap commencing at $t = 0$. At the same time a commercial plug-in air freshener was switched on (at full power) and collection of the fragranced laboratory air commenced on the other trap. The initial chromatogram was therefore representative of the unmodified laboratory air, with each subsequent analysis reflecting the changing fragrance profile in the room. At $t = 75$ min, the air freshener was switched off and the decay of the fragrance profile determined over 15 subsequent cycles.

To maintain cycle times below 20 minutes while ensuring good chromatographic resolution, a relatively short column was used. Trapping parameters were then selected to ensure quantitative retention of the less volatile components that were the key focus of this study, whilst less emphasis was placed on quantitative retention of compounds more volatile than n-hexane. Injection of each sample took place as soon as the GC had returned to its 'ready' state after the previous run, giving a new data point every 19 min.

TD:

Instrument:	TT24-7 Series 2 (Markes International)
Flow path:	200°C
Continuous sampling mode:	19 min at 158 mL/min (3 L sampled in total)
Focusing traps:	Packed with Tenax® TA
Trap low:	25°C
Trap desorption:	300°C for 3 min
Split flow:	20 mL/min
Overall TD split ratio:	29:1

GC:

Column:	Rxi-5Sil MS, 20 m × 0.18 mm × 0.18 µm
Constant flow:	0.72 mL/min
Oven program:	40°C (1.5 min), 25°C/min to 140°C (0 min), 35°C/min to 300°C (2 min)

MS:

Instrument:	BenchTOF-dx (ALMSCO International)
Transfer line:	250°C
Ion source:	220°C
Mass range:	35–350 amu
Acquisition rate:	4 Hz with 2500 spectra per data point

Software:
Removal of consistent background signals from the total ion chromatogram, deconvolution of co-eluting components, and identification of target compounds was performed using TargetView™ (ALMSCO International)[4].

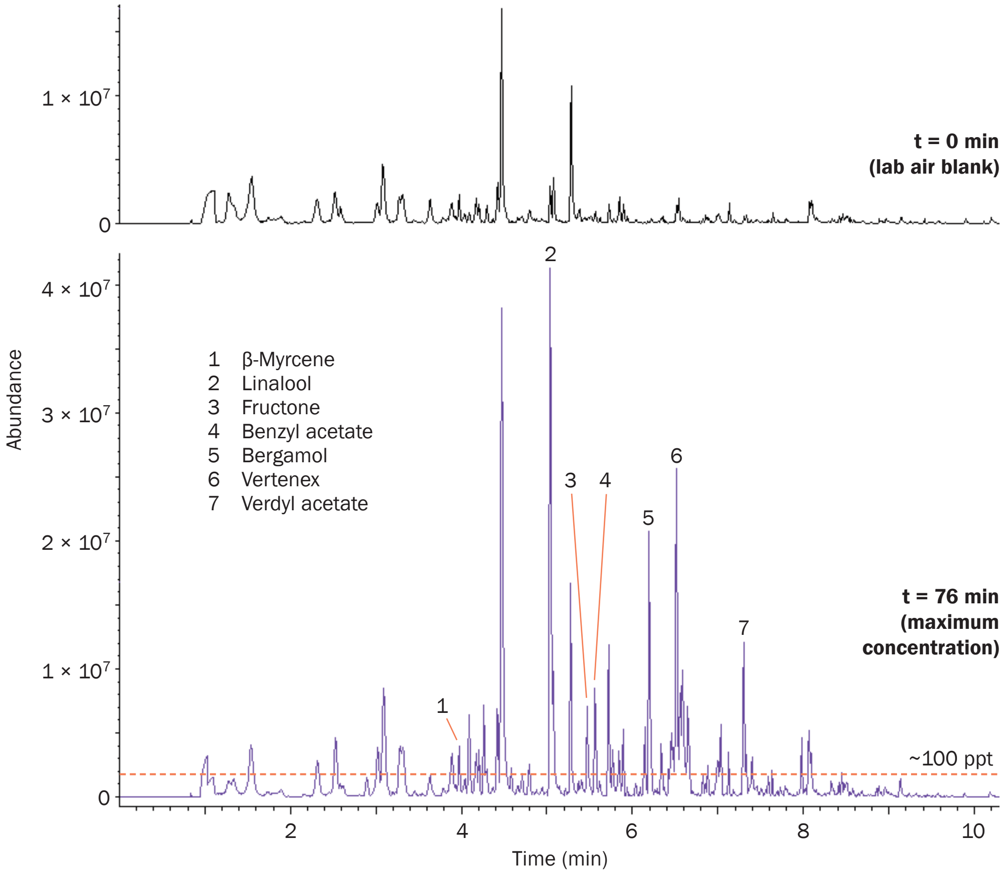


Figure 3: Comparison of VOC profiles at t = 0 and t = 76 min. Emissions were sampled using the TT24-7 Series 2 onto focusing traps packed with Tenax TA, before desorption and analysis by TD–GC/TOF MS. The dotted line indicates a peak height corresponding to an approximate abundance in air of 100 ppt (toluene equivalents).

Results and discussion

Time profiling of fragrance compounds

Figure 3 shows two chromatograms – the first from the laboratory blank taken at the start of the sampling run, and the second after 76 minutes, when the VOC response was at a maximum.

Figure 4 presents the complete (6-hour) data set for seven fragrance compounds. None of these were found in the lab blank, indicating that they were all emitted by the air freshener. The results clearly show how the concentrations of these components increased during the period that the air freshener was active, and subsequently decayed after it was switched off.

Linalool (a terpene alcohol with a pleasantly floral odour) generated by far the largest response. Although its concentration decreased fairly rapidly after the peak signal, it nevertheless remained detectable in the laboratory air until the end of the experiment, 4.75 hours after the air freshener was turned off.

In contrast, fructone (a synthetic fragrance compound with an apple-like smell), gave a relatively small response, with levels falling to near-zero just 2 hours after the air freshener was turned off.

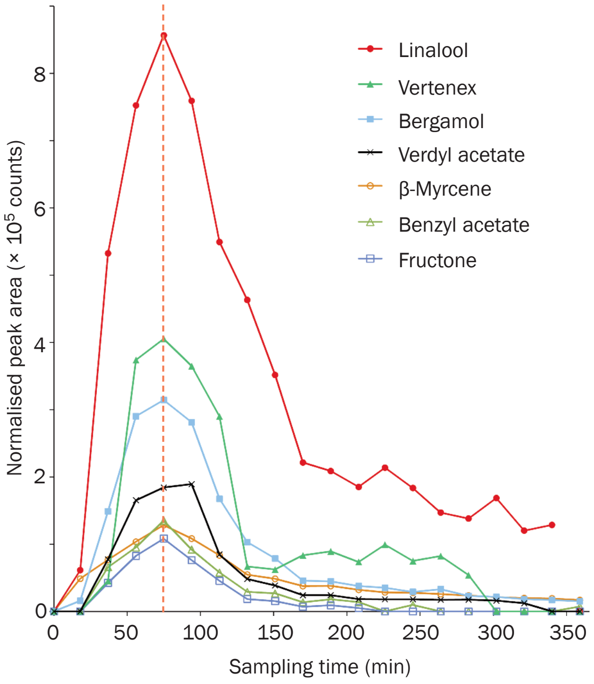


Figure 4: Time profiles of seven identified compounds. The dotted line indicates when the air freshener was turned off.

Library-matching using TargetView

In addition to time-profiling, a valuable feature of any GC/MS method is the ability to rapidly screen samples for compounds of interest. To illustrate this, a library of 24 suspected allergens was created using TargetView, and used to screen the fragrance profile taken at the point of maximum response (t = 76 min). Six compounds were confidently identified (Table 1).

TargetView allows the deconvolved peak profiles for individual compounds to be identified within a complex chromatographic profile, as illustrated for α-isomethyl ionone and lilial in Figure 5. Comparison of the corresponding mass spectra with those in the NIST library (Figure 5C) demonstrates the ability of BenchTOF-dx to produce 'reference-quality' spectra.

Target compound	Retention time (min)	Match coeff.	Peak sum (TIC)
Limonene	4.47	0.884	250 534 613
Linalool	5.04	0.902	256 584 676
Citral	6.34	0.867	18 258 573
Citronellol	6.83	0.786	3 540 439
α-Isomethyl ionone	7.56	0.850	2 305 904
Lilial	7.82	0.772	1 861 836

Table 1: Report identifying the six target compounds in the fragrance profile obtained at t = 76 min, following processing against a customised library using TargetView.

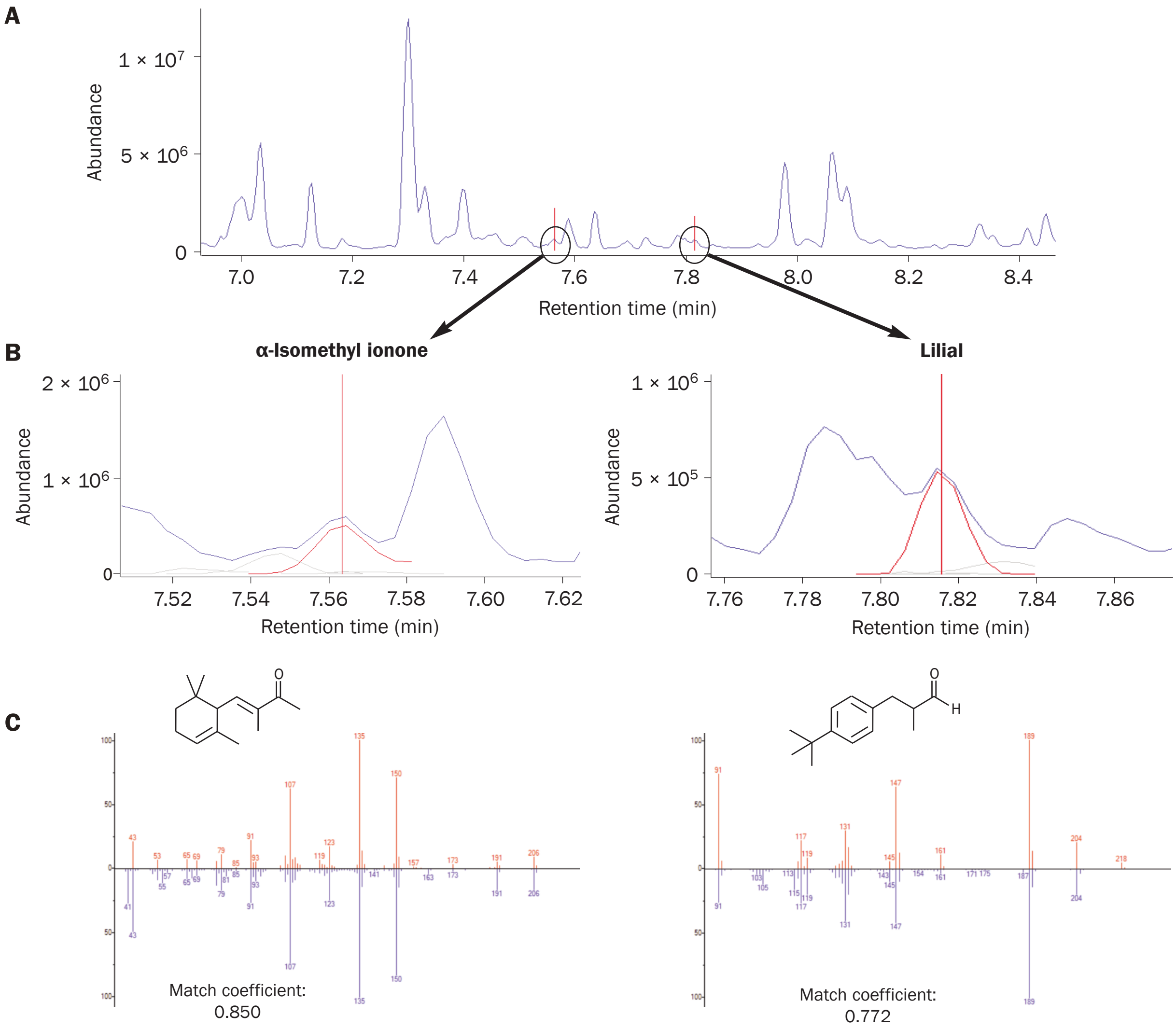


Figure 5: (A, B) Expansions of Figure 3, showing detection of the deconvolved peaks from the trace-level potential allergens α-isomethyl ionone and lilial (red traces) alongside co-eluting peaks (grey traces). (C) The corresponding mass spectra (red, top) compared to those in the NIST library (blue, bottom), demonstrating excellent matches in both cases.

Conclusions

The TT24-7 Series 2 continuous monitoring TD system has successfully profiled a variety of compounds released from a plug-in air freshener in near-real-time. Such data has clear application in the consumer products and fragrance industries, for example in understanding the role that individual components play in contributing to customer perception. Rapid screening of chromatograms against customised target libraries using TargetView can also be useful to rapidly identify compounds of interest, such as potential carcinogens or allergens.

The power of continuous near-real-time monitoring using the TT24-7 Series 2 has been enhanced in this study by use in conjunction with the inherently sensitive BenchTOF-dx time-of-flight mass spectrometer. The 'reference quality' mass spectra it produces, combined with TargetView software, has allowed confident identification of trace-level compounds in this complex air sample, without the need for time-consuming manual data processing by a GC/MS expert.

References

1. Natural Resources Defense Council, Press release, 19 September 2007, http://www.nrdc.org/media/2007/070919.asp.
2. For further details of the TT24-7 Series 2, visit http://www.markes.com/Instrumentation/TT24-7-Series-2.aspx.
3. For further details of the BenchTOF-dx, visit http://www.almsco.com/Products/BenchTOF-dx/default.aspx.
4. For more information about TargetView, visit http://www.almsco.com/Products/TargetView/.

Trademarks

TT24-7™ is a trademark of Markes International, UK.

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