

# Rapid aroma-profiling of cookies by dynamic headspace sampling and TD-GC-TOF MS



This study shows the value of dynamic headspace sampling and thermal desorption-GC-TOF MS analysis to rapidly profile volatile compounds released from flavoured cookies, and avoid the problems typically encountered when using solvent-extraction methods.

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## Introduction

Within the food industry, there is an increasing need to monitor product safety and quality, typically in relation to flavour composition, taint and contamination. This requires a detailed understanding of individual components, but conventional approaches to sample preparation and GC analysis struggle to provide the necessary level of sensitivity.

For example, a common sampling technique is solvent extraction, whereby the food sample is treated with a solvent such as hexane. Typically, only 1–2  $\mu\text{L}$  of the resulting extract is injected into the GC, with correspondingly high limits of detection and reduced confidence in the detection of trace-level components. While there are approaches to reducing matrix interference and improving detection limits, these are associated with risks. For example, clean-up methods such as solid-phase extraction (SPE) may cause key analytes to be retained, or eluted during the solvent washing steps. A particular problem with any method involving solvent is chromatographic interference from the solvent or associated impurities, as well as the potential for the more volatile compounds to be lost during the process of extraction.

All of the above issues can be solved by using dynamic headspace sampling (DHS) onto sorbent tubes, in conjunction with analysis by thermal desorption (TD) and GC-MS. Firstly, the dynamic extraction process, which is typically conducted at about 40°C, allows far greater levels of compounds to be extracted from the sample than static headspace. Secondly, the two-stage process of analyte focusing on the sorbent tube and then on the focusing trap ('cold trap') within the TD instrument results in analytes being focused in a narrow band of vapour, greatly improving peak shape and detection limits.

A final aspect of the analytical setup to consider is the detector. Quadrupole instruments are widely used in the food industry, but lack sensitivity when used in scan mode and cannot be used to screen unknowns in the more sensitive selected ion monitoring (SIM) mode. Time-of-flight (TOF) mass spectrometers overcome these problems by offering enhanced sensitivity and collection of data across the full mass range in a single run.

This study investigates the potential of these techniques for the rapid analysis of aroma compounds in flavoured cookies. A Micro-Chamber/Thermal Extractor<sup>™</sup> [1] is used for simple dynamic headspace extraction onto sorbent tubes, followed by analysis of the tubes with a TD100-xr<sup>™</sup> thermal desorber,<sup>[2]</sup> GC separation, and detection with a BenchTOF<sup>™</sup> mass spectrometer<sup>[3]</sup>.

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## Experimental

**Samples:** Three types of cookie were purchased from the local supermarket: (A) chocolate-chip, (B) peanut and (C) orange-cream. The cookies were broken into pieces, and a single piece (~3 g) used for each analysis.

**DHS:** Instrument: Micro-Chamber/Thermal Extractor (Markes International); Gas flow: Nitrogen, 100 mL/min (set using flowmeter on a low-flow setting); Chamber temperature: 40°C or 80°C; Equilibration: 5 min; Sampling: 30 min; Sorbent tubes: Stainless steel, packed with Tenax<sup>®</sup> TA (Markes International).

**TD:** Instrument: TD100-xr (Markes International); Flow path: 200°C; Dry-purge: 1 min, 50 mL/min; Pre-purge: 1 min, 50 mL/min; Tube desorb: 300°C (10 min), 50 mL/min, no split; Trap low: -10°C; Pre-trap fire purge: 1 min, 50 mL/min; Heating rate: Max.; Trap high: 320°C (3 min); Trap desorb: 100:1; Re-collection: Onto the same tube, subsequently desorbed with a 20:1 split.

**GC:** Instrument: 7890 GC (Agilent Technologies); Column: Rxi<sup>®</sup>-5Sil MS, 20 m × 0.18 mm × 0.18 µm; Temperature program: 35°C (3.5 min), 3°C/min to 120°C (0 min), 5°C/min to 250°C (0 min), 10°C/min to 330°C (5 min).

**TOF MS:** Instrument: BenchTOF-HD<sup>™</sup> (Markes International); Filament voltage: 1.8 V; Ion source: 200°C; Transfer line: 300°C; Mass range: m/z 40–600; Data rate: 4 Hz at 70 eV.

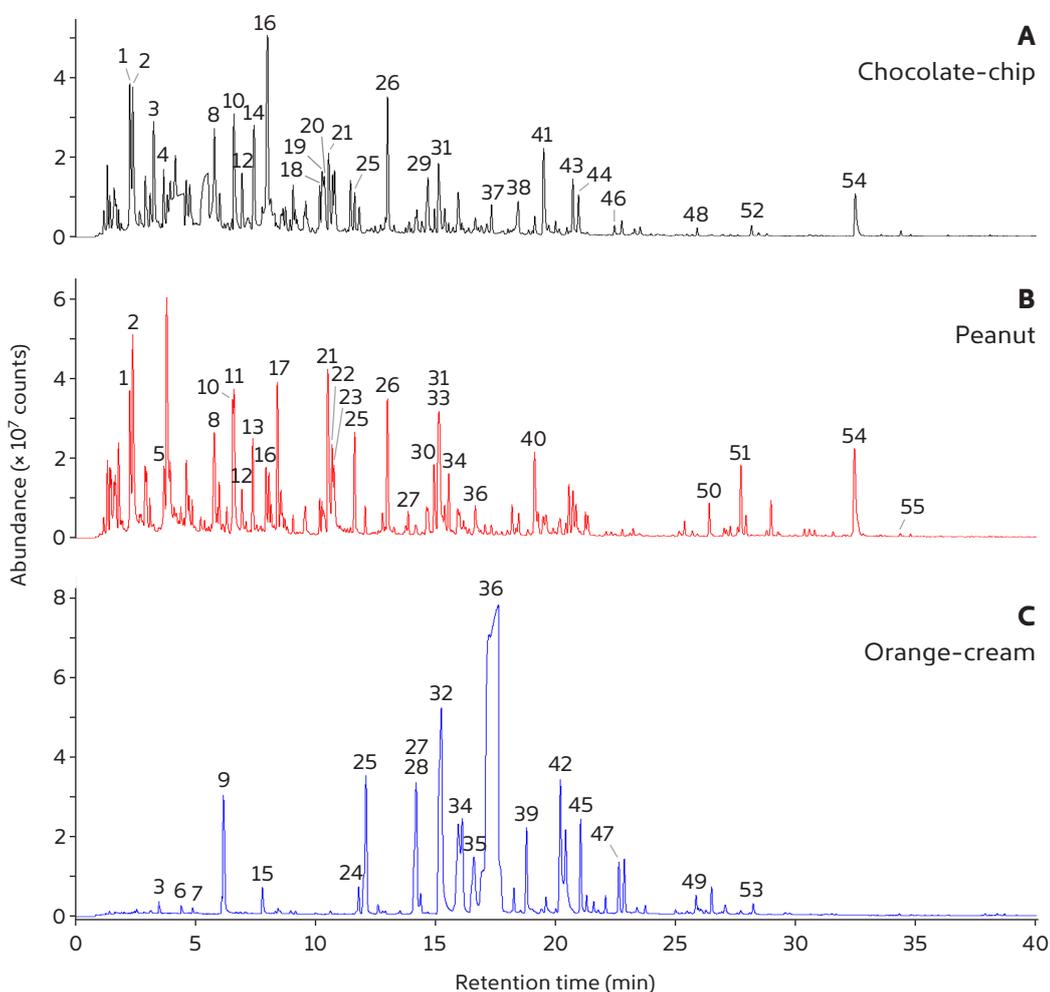
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## Results and discussion

### Example analyses at 40°C and 80°C

Figure 1 shows example analyses of the three types of cookies run at a split ratio of 100:1 with an extraction temperature of 40°C. Many compounds associated with flavours are identified, including a number of pyrazines, alcohols, aldehydes and ketones that may contribute to the aroma. For example, the peanut cookie

contains the largest number of pyrazine derivatives (associated with a 'nutty' aroma), while the orange-cream cookie is characterised by a very high concentration of the citrus-derived compound limonene (#36, Figure 1C).

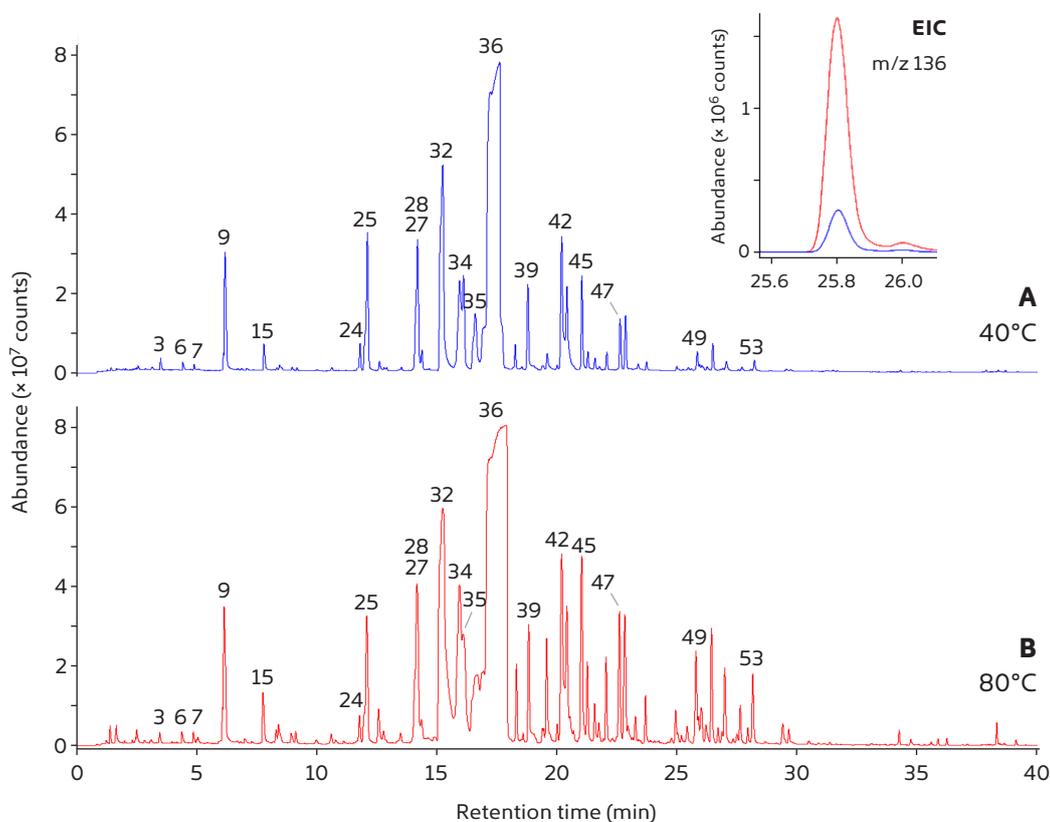


**Figure 1**

DHS-TD-GC-TOF MS analyses of the (A) chocolate-chip, (B) peanut and (C) orange-cream cookies, extracted at 40°C.

1 3-Methylbutanal	17 4-Methyloctane	30 2-Ethyl-6-methylpyrazine	42 Terpinolene
2 2-Methylbutanal	18 Heptanal	31 Trimethylpyrazine	43 Nonanal
3 n-Propyl acetate	19 $\gamma$ -Crotonolactone	32 $\beta$ -Myrcene	44 Phenylethyl alcohol
4 Pyrazine	20 Butyrolactone	33 2-Ethyl-5-methylpyrazine	45 Linalool
5 Methylpyrrole	21 2,5-Dimethylpyrazine	34 3-Carene	46 Pyranone
6 Butane-1,2-diol	22 Ethylpyrazine	35 $\alpha$ -Terpinene	47 Limonene epoxide
7 Toluene	23 2,3-Dimethylpyrazine	36 Limonene	48 Decanal
8 Hexanal	24 $\alpha$ -Thujene	37 Phenylacetaldehyde	49 $\alpha$ -Terpineol
9 Ethyl butanoate	25 $\alpha$ -Pinene	38 Acetophenone	50 2,3-Dihydrobenzofuran
10 Methylpyrazine	26 Benzaldehyde	39 $\gamma$ -Terpinene	51 2,6-Diethylaniline
11 2,4-Dimethylheptane	27 $\beta$ -Pinene	40 3-Ethyl-2,5-dimethylpyrazine	52 $\beta$ -Phenylethyl acetate
12 Furfural	28 $\beta$ -Phellandrene	41 Tetramethylpyrazine	53 Carvone
13 2,4-Dimethylhept-1-ene	29 2-Pentylfuran		54 Triacetin
14 2-Propoxypropan-1-ol			55 Vanillin
15 1-Propoxypropan-2-ol			
16 2-(Hydroxymethyl)furan			

With a higher extraction temperature of 80°C there is (as expected) an increase in the response from compounds across the range (Figure 2), but especially for the higher-boiling compounds, such as  $\alpha$ -terpineol (#49).

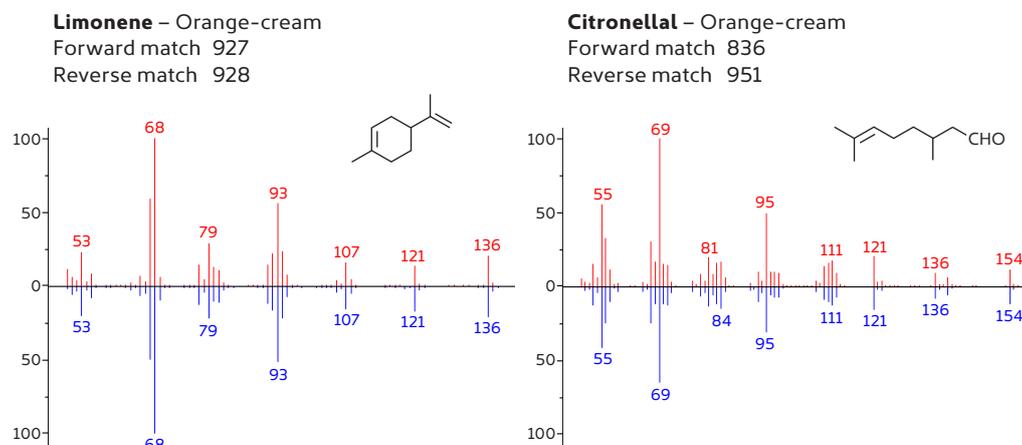


**Figure 2**

DHS-TD-GC-TOF MS analysis of the orange-cream cookie, extracted at (A) 40°C and (B) 80°C. Note the increased response for a range of VOCs and SVOCs at the higher temperature, including the higher-boiling compound  $\alpha$ -terpineol (#49, inset).

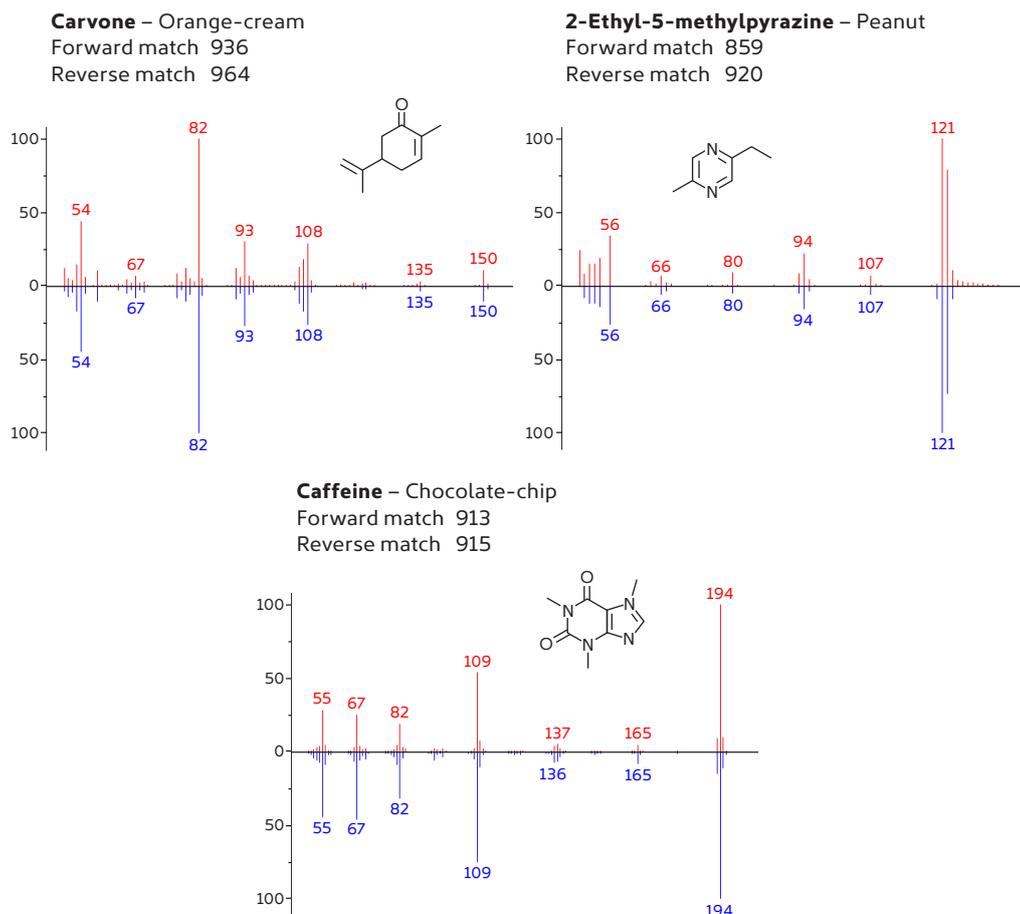
### Spectral quality

One of the advantages of the BenchTOF system compared to other time-of-flight instruments is the ability to produce spectra that closely match the (typically) quadrupole-acquired spectra in commercial libraries such as NIST and Wiley. This ensures strong match factors, as illustrated by Figure 3 for the case of number of key flavour/fragrance compounds found in the cookies.



**Figure 3**

BenchTOF spectra (top, red) and NIST 14 spectra (bottom, blue) for five components found in the cookie samples (*continued on next page*).

**Figure 3**

BenchTOF spectra (top, red) and NIST 14 spectra (bottom, blue) for five components found in the cookie samples (*continued from previous page*).

## Conclusions

In this study, we have shown that the combination of dynamic headspace sampling with TD-GC-TOF MS analysis offers efficient evaluation of volatile compounds from cookies, which avoids the disadvantages of solvent-based methods at the same time as enhancing sensitivity.

The TOF mass spectrometer also plays a key role in this analysis, by enabling flavour/aroma compounds to be identified with greater confidence through the generation of 'reference-quality' spectra.

For more information on this application, or any of the techniques or products used, please contact SepSolve.

## References and notes

- [1] The Micro-Chamber/Thermal Extractor™ from Markes International is a compact device for dynamic extraction of headspace from up to six samples simultaneously. Two versions are available – one with six 44-mL chambers and a maximum temperature of 120°C, and the other with four 114-mL chambers and a maximum temperature of 250°C. All chambers are made from inert-coated stainless steel to minimise sink effects and aid the recovery of very reactive species. Samples are placed into the individual chambers (Figure 4), equilibrated under a flow of air or gas, and the organic vapours then collected on to sorbent tubes connected to the outlet.



**Figure 4**

Example of the Micro-Chamber/Thermal Extractor being used to release volatiles from a food sample.

- [2] The TD100-xr™ thermal desorber from Markes International is a fully-automated instrument for the analysis of up to 100 sorbent tubes in a single sequence. A key feature of the TD100-xr is the ability to re-collect split samples onto clean sorbent tubes. This overcomes the historic ‘one-shot’ limitation of thermal desorption, and can aid method development by allowing a single sample to be re-analysed by the same method for validation purposes, or by other methods such as flame ionisation detection or olfactometry to obtain complementary data about the sample. The same technique can also be used to accurately quantify both high-level and trace-level compounds, by using different split ratios on the original and re-collected samples.
- [3] BenchTOF™ time-of-flight mass spectrometers from Markes International are designed specifically for gas chromatography, and have many advantages over standard single-quadrupole mass spectrometers. Specifically, they offer sensitivities that are comparable to those possible in SIM mode, at the same time as full-range spectra that allow the same level of information to be generated for both targets and unknowns. In addition, the sub-unit mass selectivity provides enhanced data clarity through elimination of matrix interferences.

Unlike other time-of-flight mass spectrometers, BenchTOF instruments produce reference-quality spectra at 70 eV, allowing confident matching against reference libraries such as NIST or Wiley. BenchTOF instruments can also handle 10,000 transient accumulations per second, allowing them to accurately define the narrowest of peaks, making it suitable for GC×GC applications.

A recent addition to the capability of BenchTOF is Tandem Ionisation for simultaneous acquisition of 70 eV and 'soft' electron ionisation spectra across a single GC or GC×GC peak, enabling challenging compounds to be discriminated without impacting laboratory workflows. Soft EI spectra can be collected down to 10 eV, and acquisition is fully automated by the software with no inherent loss in sensitivity or need for manual intervention. Contact SepSolve for more details.

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Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

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