Application Note 250

Correlating consumer sensory experience of apple aroma with VOC profiles acquired by automated TD–GC–MS

This study shows that data acquired using the new Centri® automated multi-mode sampling and concentration system for gas chromatography–mass spectrometry (GC–MS) can be used to generate useful insights into the aroma profiles of foods. In the example investigated, the headspace profiles of two apple cultivars are sampled onto sorbent tubes, which are then analysed on Centri. The results of this analysis are then correlated with consumer sensory experience to highlight key volatiles of interest.

Analysis of food aroma profiles is essential for research into new products and for routine quality control. The latter issue is particularly important for fresh food, because conditions during packing, transport and storage can affect shelf life and the perceived 'freshness' of the final product.

In this study we correlate user sensory experience of two cultivars of fresh apple ('Smitten' and 'Granny Smith') with VOC headspace profiles, sampled onto sorbent-packed tubes using a stand-alone dynamic headspace instrument and analysed using the new Centri automated multi-mode analytical platform, in conjunction with GC–MS.

A total of 29 VOCs were identified across the two samples, and these are shown in Figure 1; a full compound listing is presented in Table 1. It is clear that the profile of 'Smitten' is substantially more complex than 'Granny Smith', with higher responses from major components and a greater number of minor components. As expected, esters comprised a large number (20) of the compounds identified, with 'Smitten' showing a very large response for ethyl acetate (#1). An interesting feature of both profiles was the presence of the sesquiterpene γ-himachalene (#29, $C_{15}H_{24}$) in substantial quantity – an indication of the ability of the sampling and analytical system to monitor less volatile species.

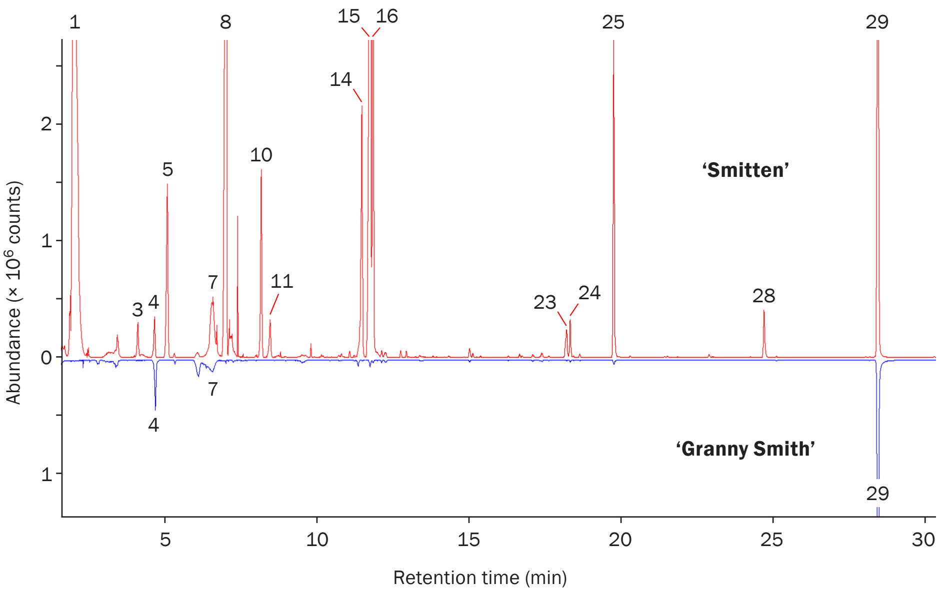

Figure 1: Aroma profiles of 'Smitten' (top) and 'Granny Smith' (bottom). Major compounds are labelled.

No.	Target compound	t_R (min)	Peak sum (TIC)	
			'Smitten'	'Granny Smith'
1	Ethyl acetate	2.05	2.02×10^8	–
2	2-Methylbutan-1-ol	3.14	2.30×10^6	8.99×10^5
3	2-Methylpropyl acetate	4.10	4.09×10^6	–
4	Hexanal	4.65	3.90×10^6	5.72×10^6
5	n-Butyl acetate	5.07	2.30×10^7	–
6	Hex-2-enal	6.07	1.03×10^6	–
7	Hexan-1-ol	6.55	2.00×10^7	3.93×10^6
8	2-Methylbutyl acetate	7.01	1.94×10^8	–
9	n-Butyl propanoate	7.98	1.41×10^5	–
10	n-Pentyl acetate	8.16	2.01×10^7	–
11	2-Methylbut-2-en-1-yl acetate	8.46	5.33×10^6	–
12	n-Butyl butanoate	11.07	6.19×10^5	–
13	3-Carene	11.41	1.16×10^6	–
14	Hex-4-enyl acetate	11.47	3.03×10^7	–
15	n-Hexyl acetate	11.74	1.95×10^8	7.28×10^5
16	*cis*-Hex-2-enyl acetate	11.84	6.62×10^7	2.67×10^5
17	Limonene	12.12	5.25×10^5	2.04×10^5
18	n-Butyl 2-methyl-butanoate	12.75	5.78×10^5	–
19	2-Methylbutyl butanoate	13.37	1.34×10^5	–
20	n-Hexyl propanoate	15.12	3.74×10^5	–
21	n-Heptyl acetate	15.37	1.22×10^5	–
22	n-Hexyl 2-methyl-propanoate	16.66	3.07×10^5	–
23	n-Hexyl butanoate	18.20	2.59×10^6	–
24	Estragole	18.32	3.98×10^6	–
25	n-Hexyl 2-methyl-butanoate	19.75	3.48×10^7	4.98×10^5
26	n-Pentyl hexanoate	21.50	7.98×10^4	–
27	n-Hexyl tiglate	22.89	3.54×10^5	–
28	n-Hexyl hexanoate	24.70	5.12×10^6	–
29	γ-Himachalene	28.44	1.28×10^8	7.06×10^7

Table 1: List of target analytes identified in the headspace of the two apple cultivars (Figure 1) by a search against the customised library generated from the NIST 2017 database.

Four features of this analysis combine to provide excellent sensitivity for trace-level compounds:

- The large quantities of sample analysed increase the quantities of volatiles released. The headspace sampler used has chamber volumes of 114 cm^3, meaning that they can easily accommodate six pieces of apple (each ~8 cm^3).
- The use of dynamic headspace sampling at human body temperature (37°C), as well as being physiologically relevant, enhances the release of volatiles in a short time-frame (10 minutes).
- The use of analyte re-focusing on the Centri focusing trap improves the GC–MS peak shape and sensitivity, compared to standard static loop or syringe injection of headspace.

Background to Centri®

Markes International's Centri system for GC–MS is the first platform to offer high-sensitivity unattended sampling and pre-concentration of VOCs and SVOCs in solid, liquid and gaseous samples.

Centri allows full automation of sampling using HiSorb™ high-capacity sorptive extraction, headspace, SPME, and tube-based thermal desorption. Leading robotics and analyte-trapping technologies are used to improve sample throughput and maximise sensitivity for a range of applications – including profiling of foods, beverages and fragranced products, environmental monitoring, clinical investigations and forensic analysis.

In addition, Centri allows samples from any injection mode to be split and re-collected onto clean sorbent tubes, avoiding the need to repeat lengthy sample extraction procedures and improving security for valuable samples, amongst many other benefits.

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

- The use of a very low 2:1 split ratio for the injection means that a large proportion of the sample is sent to the GC–MS. On many TD systems, the use of such a low ratio would result in poor peak shape, but this is avoided with Centri because of the optimised design and highly efficient backflush desorption of the focusing trap.

Evaluation of the sensory characteristics of the apples was performed using samples prepared in the same way as the headspace studies. This showed distinct differences in acceptability between the two cultivars, with 'Smitten' having significantly higher hedonic scores on all ten characteristics (Figure 2).

Two-dimensional hierarchical cluster analysis (HCA) was next used to assess differences between the cultivars, VOC classes and sensory experience. These show significant positive correlations between high 'Taste/Flavour', 'Fruitiness' & 'Aroma/Smell' scores and five of the esters identified in the headspace analysis. These compounds are (with their odour as described in an olfactometry study of apple cultivars[1]): 2-methylpropyl acetate (#3 – pear, apple), n-butyl acetate (#5 – sweet, fruity), 2-methylbutyl acetate (#8 – fruity, apple), n-pentyl acetate (#10 – fruity, banana), and n-hexyl acetate (#15 – fruity, pear). In that study, the first three of these compounds were identified as 'principal odorants'.

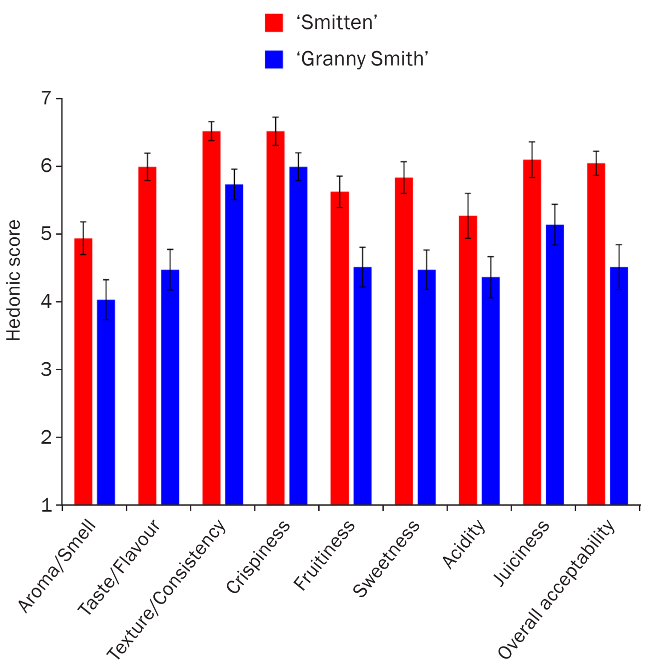

Figure 2: Mean hedonic scores (n = 20) obtained for 'Smitten' and 'Granny Smith' for each of nine attributes, categorised from 1 (dislike very much) to 7 (like very much).

These sensory correlations indicate that that these esters could be used as objective markers for the consumer appreciation of fresh apples, enabling optimum conditions for processing and storage of individual cultivars to be identified without recourse to expensive sensory panels in every case. Such tests could also be used as part of routine quality control by the producer and retailer, reducing costs and eliminating waste due to batches of inferior product.

In conclusion, we have shown the ability of Centri to generate useful insights into the aroma profiles of foods, by allowing automated pre-concentration of dynamic headspace samples collected onto sorbent tubes. This capability is complemented by the other sampling modes available with Centri – HiSorb high-capacity sorptive extraction, headspace and SPME – all of which can benefit from cryogen-free trapping for enhanced sensitivity. In addition, by allowing unattended sequential analysis of multiple sample types using different injection modes, Centri greatly improves efficiency for high-throughput laboratories.

Experimental

Sample:
Ripe, undamaged apples obtained from a supermarket were washed, deskinned and decored, and the flesh cut into pieces approximately 2 cm × 2 cm × 2 cm.

Sensory testing:
Twenty panellists (7 male and 13 female, with a median age of 33) were asked to rate the apple samples according to nine sensory characteristics (Aroma/Smell, Taste/Flavour, Texture/Consistency, Crispiness, Fruitiness, Sweetness, Acidity, Juiciness, Overall acceptability), using hedonic scores ranging from 1 (dislike very much) to 7 (like very much). Samples were presented in a randomised order, and panellists were free to take as many bites as necessary to complete the assessments.

Dynamic headspace:

Sample:	Six pieces of apple
Instrument:	Micro-Chamber/Thermal Extractor™ (µ-CTE™) (Markes International)
Equilibration:	37°C for 15 min
Sampling:	50 mL/min nitrogen for 10 min
Sorbent tubes:	'Odour/Sulfur' inert-coated stainless steel (part no. C2-CAXX-5314)

TD:

Instrument:	Centri (Markes International)
Cold trap:	'Sulfur/labile' (part no. U-T6SUL-2S)
Tube desorption:	280°C (10 min)
Trap flow:	40 mL/min
Trap desorption:	25°C to 300°C (5 min)
Outlet split:	3 mL/min
Flow path:	200°C

GC:

Column:	BP5MS™, 30 m × 0.25 mm × 0.25 µm
Column flow:	~2 mL/min
Oven program:	40°C (3 min), 4°C/min to 220°C (1 min), 10°C/min to 250°C (5 min)
Inlet:	250°C
Aux heater:	280°C

Quadrupole MS:

Scan mode:	m/z 35–350
Source:	200°C
Transfer line:	250°C

Software:
TargetView™ GC–MS software (Markes International) was used to selectively remove unwanted background noise and to deconvolve analyte peaks, improving the identification of lower-level analytes during subsequent automated comparison against a customised library generated from spectra in the NIST 2017 database. TargetView also generated peak-area information that allowed the amounts of each analyte to be compared.

Reference

1. E. Mehinagic, G. Royer, R. Symoneaux, F.R. Jourjon and C. Prost, Characterization of odor-active volatiles in apples: Influence of cultivars and maturity stage, *Journal of Agricultural and Food Chemistry*, 2006, 54: 2678–2687, http://dx.doi.org/10.1021/jf052288n.

IngenieríaAnalítica
Chromatography & Spectrometry
Avda. Cerdanyola, 73 4º izquierda 08172 Sant Cugat del Vallés (Barcelona) SPAIN
Tel. +34 902 45 66 77 | www.ingenieria-analitica.com | e-mail: inf@ingenieria-analitica.com