Application Note 280

Headspace sampling using HiSorb™ high-capacity sorptive extraction for flavour profiling of foods and beverages

Summary

This study demonstrates the performance of HiSorb high-capacity sorptive extraction probes for flavour profiling of two samples – cider and potato snacks (crisps) – contrasting the unflavoured product with those that have had flavourings added. HiSorb is a solvent-free technique utilising a high-capacity sorptive phase to ensure good extraction efficiency and is readily applicable to both headspace and immersive sampling. In conjunction with the Centri® extraction and enrichment platform, HiSorb is fully automatable.

Introduction

Analysis of the volatile organic compound (VOC) content of foodstuffs is an important tool in the food and beverage industry, with applications in research and development, quality control, shelf-life assessment and even detection of food fraud. HiSorb high-capacity sorptive extraction probes offer a highly sensitive, robust and fully automatable flavour profiling solution, and have provided excellent results in gas chromatography–mass spectrometry (GC–MS)-based analysis of foodstuffs.[1,2,3]

The robust design of HiSorb probes allows for flexibility in sampling method. Probes may be suspended above a sample to extract VOCs from the headspace or immersed directly into a liquid sample so that the sorptive phase is in direct contact with the sample matrix (Figure 1). By removing the requirement for VOCs to partition into the headspace first, immersive sampling can improve extraction efficiency for some compounds.

Following sorptive extraction, HiSorb probes must be desorbed with heat so that analytes can be transferred to the analytical system. The Centri extraction and enrichment platform is the ideal option for coupling HiSorb extraction with GC analysis, fully automating all aspects of sampling and incorporating Markes' leading focusing trap technology (Figure 2) for hands-free, high-throughput analysis with optimal chromatography. Alternatively, HiSorb probes can be used with an off-line agitator for sample extraction. Probes fit inside industry-standard thermal desorption tubes and can be desorbed with dedicated thermal desorption instruments such as Markes' TD100-xr™.

Here, we demonstrate the ability of HiSorb probes to provide comprehensive flavour profiles of foodstuffs, by comparing the VOCs extracted from unflavoured products with those extracted from products after addition of a flavour mix. We show extraction from the headspace of a solid sample (potato snacks) and a liquid sample (cider), detecting a broad range of compounds with both techniques.

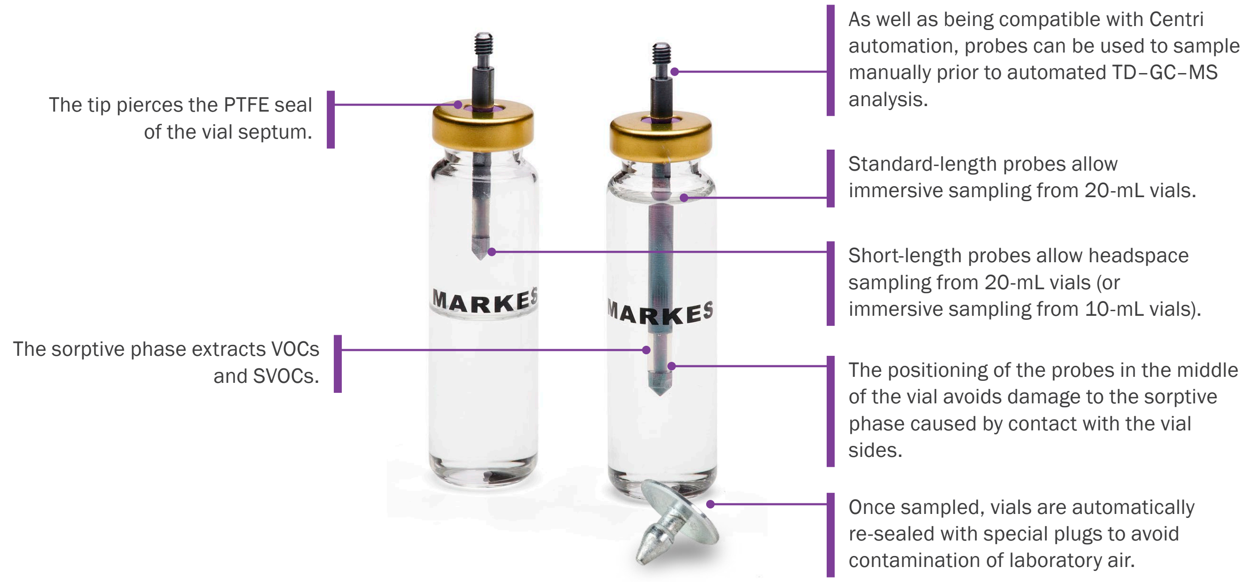

Figure 1: Headspace (left) and immersive (right) sampling with HiSorb probes.

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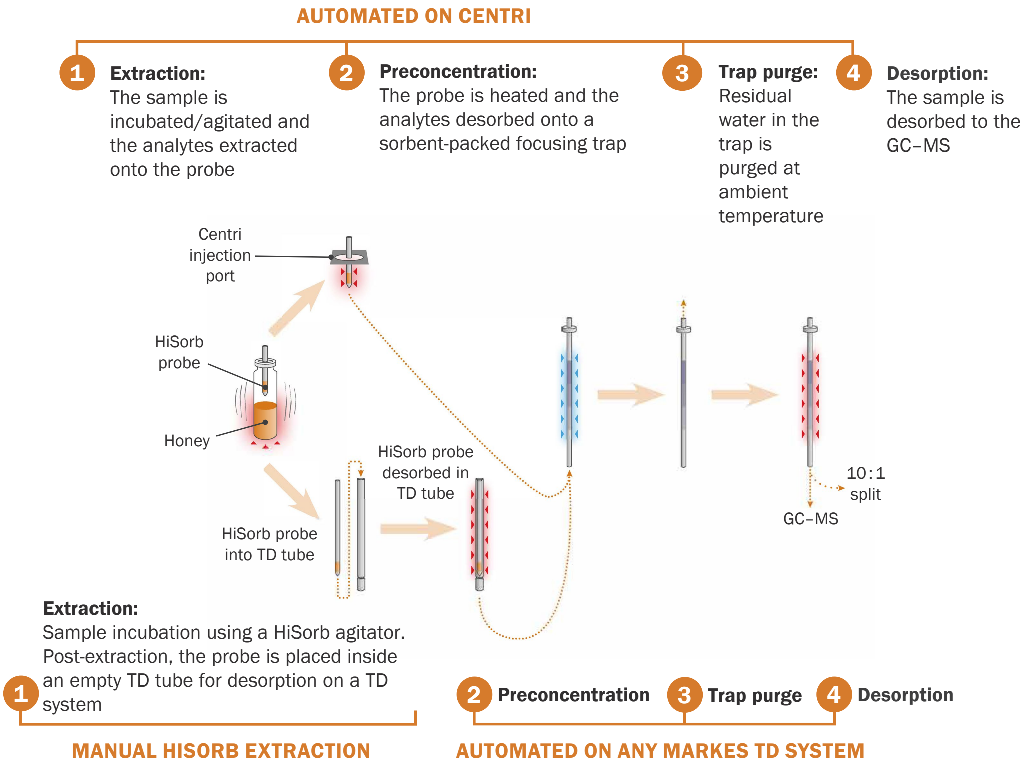


Figure 2: HiSorb extraction workflows using Markes' thermal desorbers. Bottom: offline, manual sample extraction using a HiSorb agitator, followed by probe desorption inside an empty TD tube. Top: fully automated workflow on Centri, from sampling to GC injection.

Experimental

Sample preparation:

Crisps:	3g, ground
Cider:	10 mL undiluted cider

Sampling:

Instrument:	HiSorb Agitator (U-HSAG-20)
HiSorb probes:	PDMS, short length, inert-coated (part no. H1-AXABC)
Incubation:	37°C for 30 min

Thermal desorption:

Instrument:	TD100-xr
Flow path:	180°C
Probe desorption:	270°C for 10 min
Trap:	'Material emissions' (part no. U-T12ME-2S)
Trap temperature:	30°C
Trap dry purge:	1 min at 50 mL/min
Trap desorption:	Max heating rate to 290°C, 3 min
Outlet split:	50 mL/min (26:1)

GC:

Column:	DB-5™ – 30 m x 0.25 mm i.d. x 0.25 µm film thickness
Column flow:	2 mL/min
Oven ramp:	40°C (3 min), 10°C / min to 310°C (10 min)
Inlet:	200°C

MS:

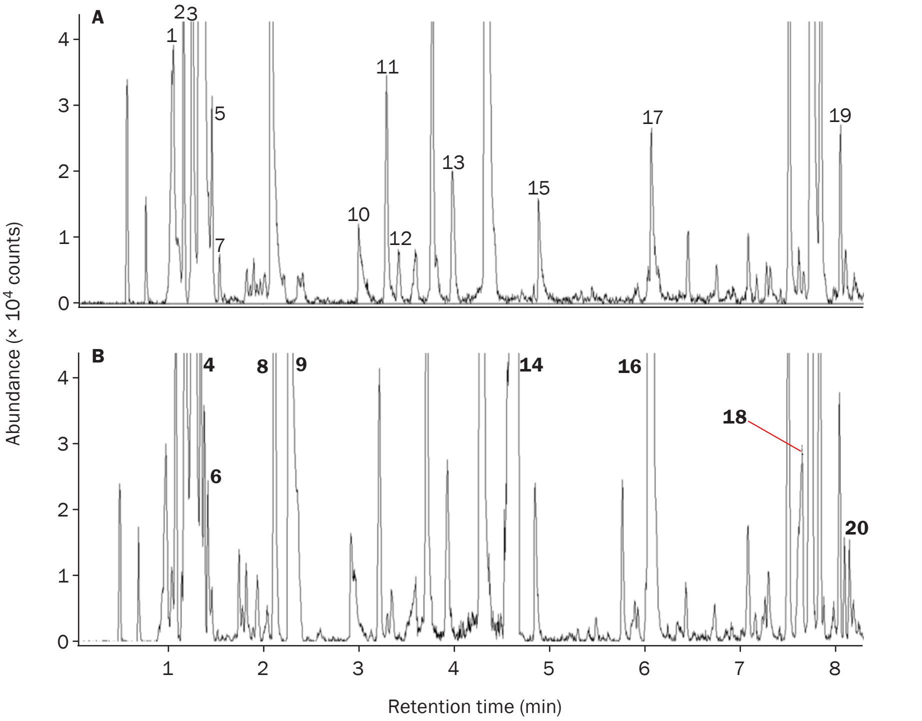
MS transfer line:	310°C
MS source:	250°C
Quad:	180°C
Scan range:	35–350 m/z

Results and discussion

Potato snacks

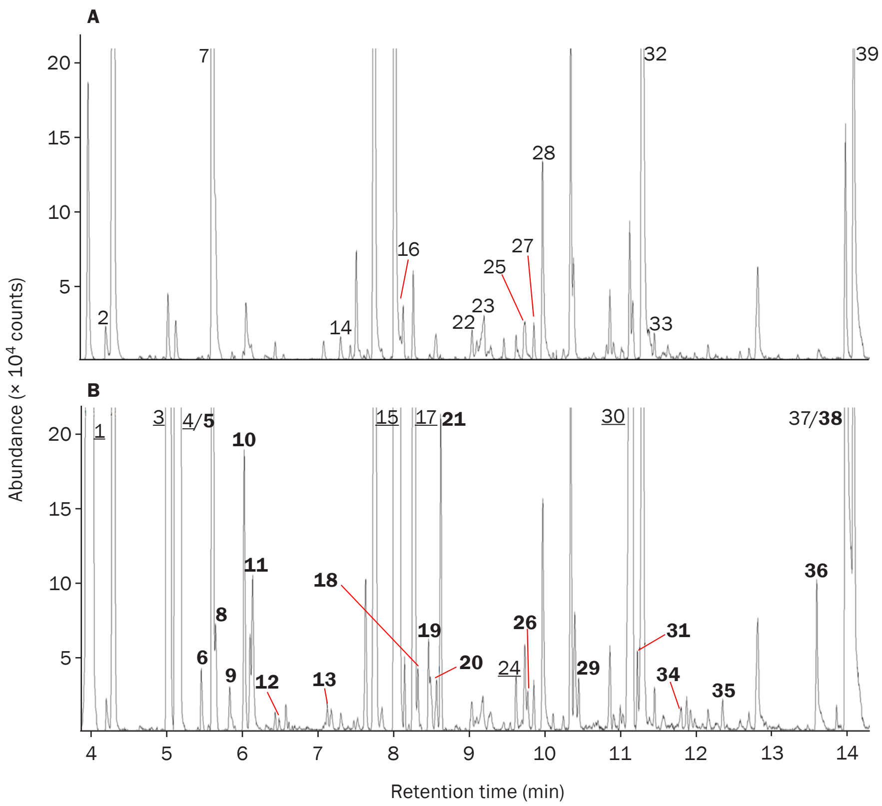
Potato snacks (crisps) were sampled by suspending a HiSorb probe above a dry, homogenised sample for 30 minutes at 37°C (to emulate the temperature inside the mouth). Extracted compounds were subsequently analysed by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS). Data processing was carried out using ChromSpace® (SepSolve Analytical).

Figure 3 shows the total ion chromatograms (TICs) produced from samples of unflavoured crisps (A) and crisps after addition of a cheese flavour mix (B). Peaks are labelled if they were confidently identified and with a NIST match factor (MF) > 750. The 12 peaks labelled in A represent analytes detected in both samples, while the eight peaks labelled in B indicate analytes found only in the flavoured sample (bold labelling). Compounds unique to B typically conferred cheesy- or dairy-like flavours, as expected for compounds in a cheese flavour mix. This highlights the power of HiSorb to extract the important flavour constituents and distinguish between similar, yet distinct products.



1. Butane
2. Acetone
3. Methanesulfonic anhydride
4. **2,3-Butanedione**
5. 2-Ethylacetone
6. **Acetic acid**
7. Ethyl acetate
8. **2,3-Pentanedione**
9. **Acetoin**
10. 1-Ethoxy-2-propanal
11. Toluene
12. 3-Methylheptane
13. Octane
14. **Butyric acid**
15. 1-Propoxy-2-propanal
16. **n-Propyl butyrate**
17. Methyl hydroxybenzenecarboximidate
18. **Benzaldehyde**
19. Decane
20. **Butyl lactate**

Figure 3: Flavour profiles of unflavoured (A) and cheese flavoured (B) potato snacks, obtained by HiSorb extraction. Compounds given in bold were found only in the cheese flavoured sample.



1. Ethyl butyrate
2. Ethyl lactate
3. Ethyl 2-methylbutyrate
4. Ethyl 3-methylbutyrate
5. ***cis*-3-Hexen-1-ol**
6. **1-Hexanol**
7. **Isopentyl acetate**
8. **2-Methylbutyl acetate**
9. **S-Methyl thiobutyrate**
10. **3-Heptanol**
11. **Ethyl pentanoate**
12. **2,4-Hexadiene**
13. **Methylcyclohexanone**
14. Benzaldehyde
15. Ethyl caproate
16. (*E*)-3-Hexenol acetate
17. Hexyl acetate
18. **Isocineole**
19. **2-Octen-4-one**
20. **D-Limonene**
21. **Eucalyptol**
22. Isopentyl butyrate
23. Sorbic acid
24. 2-Nonanone
25. Ethyl-2,4-hexadienoate
26. **Linalool**
27. Nonanal
28. Phenylethyl alcohol
29. ***trans*-3-Hexenyl butyrate**
30. 2-Methyl-3-hexenyl propanoate
31. **Hexyl butanoate**
32. Ethyl caprylate
33. Decanal
34. ***cis*-3-Hexenyl valerate**
35. **Citral**
36. **Nerol acetate**
37. Ethyl-9-decanoate
38. ***trans*-Methyl cinnamate**
39. Ethyl decanoate

Figure 4: Flavour profiles of (A) unflavoured and (B) fruit flavoured cider, obtained by HiSorb. Compounds that were only present (bold) or present in higher abundance (underlined) in the flavoured sample are indicated.

Cider

For liquid samples, HiSorb probes are compatible with extraction from the headspace or *via* direct immersion into the matrix. Here, cider was sampled by suspending a probe in the headspace above a 10-mL undiluted sample, with parameters and downstream analysis as described for the potato snack samples.

Figure 4 compares TIC profiles of an unflavoured cider (A) with cider enriched with a fruit flavouring mix (B). 52 peaks had NIST MF > 750, of which 39 are shown. Substantial differences were observed between the two sample types, with 27 compounds either newly present (bold labels) or present at substantially higher abundance (underlined labels) in the flavoured sample. Notably, most of these compounds had sweet, fruity and/or herbal flavour characters, as expected from additives in a fruit flavouring mix. The 13 compounds not shown in Figure 4 all eluted before the retention window shown and were all present at approximately equal concentrations in the two cider samples.

In conclusion, we have demonstrated good performance of HiSorb extraction and enrichment probes, combined with TD–GC–MS, for the analysis and comparison of flavoured and unflavoured varieties of cider and potato snacks. The extensive flavour profiles generated highlight robust detection of these flavour-active compounds in both solid (potato snack) and liquid (cider) matrices. In addition to this, the high phase loading of HiSorb can provide improved extraction efficiency relative to conventional extraction methods, such as solid-phase microextraction (SPME, ~0.5–1 µL phase loading), which are typically used for flavour and aroma profiling.

References

1. S. Mascrez and G. Purcaro, Exploring multiple cumulative trapping solid-phase microextraction for olive oil aroma profiling, *Journal of Separation Science*, 2020, 43: 1934–1941, https://pubmed.ncbi.nlm.nih.gov/32144941/.
2. Z. Cheng, D.T. Mannion, M.G. O'Sullivan, S. Miao, J.P. Kerry and K.N. Kilcawley, Comparison of automated extraction techniques for volatile analysis of whole milk powder, *Foods*, 10: 2061, https://www.mdpi.com/2304-8158/10/9/2061/htm.
3. Markes International Application Note 275, Authentic or synthetic? Discovering authenticity markers in luxury to low-cost honey varieties using a high-capacity sorptive extraction technique (HiSorb™).

Trademarks

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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