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2nd ADVANCES IN SEPARATION SCIENCE: from extraction to chromatographic applications, Gembloux 21 June 2023

Potentialities of High-Capacity-Headspace-Extraction followed by GC×GC-qMS to better appreciate coffee brew note

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Introduction

The distinctive scent profile of food is influenced by volatile and semi-volatile organic compounds, which also provide a distinctive fingerprint that may be used to assess the quality and authenticity of foods. Solid-phase microextraction (SPME), which combines the ease of use with a high enrichment factor, is by far the most used sample technique. To increase sample throughput, this approach frequently necessitates a trade-off between sensitivity and extraction time.
New analytical tools have emerged by the time to improve the sensitivity with the arrival of commercial stir-bare sorbent extractor (SBSE) and SPME-arrow system. The letter one having the advantage of being fully automatable as SPME but less sensitive than the SBSE. In 2016, a new probe-like tool (HiSorb), combining the sensitivity of SBSE and the automation of SPME, has appeared. For a long time, this tool was limited to the PDMS-only sorbent phase (which already boasts higher sensitivity than SPME-triphasic), until the recent appearance of new phases.

Material & Methods

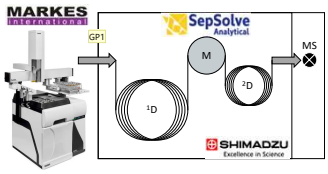
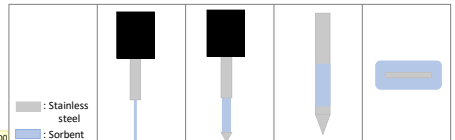


Fig 1. *Sampling technique and instrument scheme*

HS-HiSorb/SPME-HCE: HiSorb PDMS, DVB-PDMS, CWR-PDMS, CWR-DVB-PDMS ; SPME PDMS 100 µm df and 1 cm long SPME DVB/CAR/PDMS 50/30 µm df (**Tab 1.**).
Sample: 350 rpm stirred; 20' pre-equilibrium extraction, trap desorption 3 min at 300 °C (5.6 mL/min), injection (1:9.3) by Centri platform (Markes int.).

GC×GC: Shimadzu GCMS-TQ8050 NX; columns: ^{1}D: BPX-5 20m × 0.18mm i.d. × 0.18 µm df; ^{2}D: BPX-50 5 m × 0.25 mm i.d. × 0.28 µm df (Restek) (**Fig 1.**). Oven prog: 40 °C (5 min) to 180 °C at 6 °C min^{-1}.
Flow modulator: INSIGHT flow modulator (SepSolve Analytical Ltd), 3.5 s modulation period.



	SPME	SPME-Arrow	HiSorb™	SBSE
$V_{sorbent}$ (µL)	< 1	~20	~67	~126
Automation	✓	✓	✓	✗

Tab 1. *Comparison of different HC tools*

HiSorb optimisation

The sample volume (1 and 4 mL) and extraction time (10, 30, 40 and 60 min) conditions were assessed. The profiles obtained using 1 or 4 mL were comparable, the overall uptake increased up to 30 min after which no additional enhancement was observed (**Fig. 2**). Thus **1 mL** and **30 min** were chosen for further experiments[1].

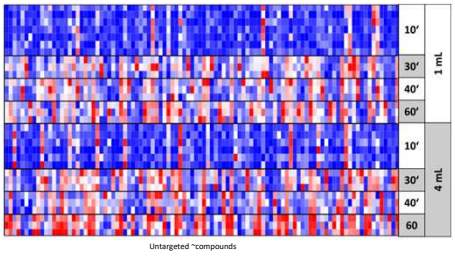


Fig 2. *Time profile (10, 30, 40, 50 min) for 1 and 4 mL sample, extracted at 50 °C*

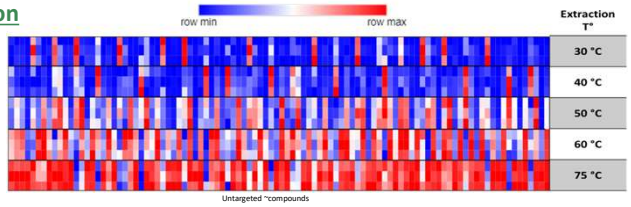


Fig 3. *Temperature profile for 1 mL sample, extraction: 30 min*

The temperature profile (**Fig 3.**) shows an increase of the extraction with the temperature. However, **60 °C** corresponds to the usual consumption temperature of hot beverages, therefore it was selected for further analyses [2].

High-capacity tools comparison vs SPME

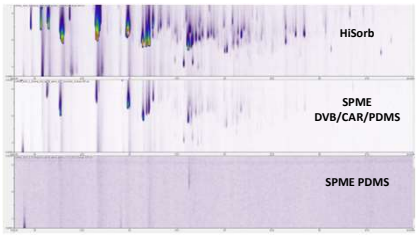


Fig 4. *Chromatograms of 1 mL coffee extracted during 30 min by different HC tools*

The **Fig 4.** displays the different chromatograms obtained from the analysis of 1 mL of coffee extracted for 30 min at 60°C with the HiSorb-PDMS and SPME both PDMS and DVB/CAR/PDMS. The number of extracted compounds as well as their quantity is much higher for HiSorb than for both SPME (triphasic and PDMS). This is confirmed by **Fig 5.** that plots the area of a series of target compounds identified in coffee against their octanol-water partition coefficients.
This enhancement is particularly discernible for more polar compounds which is consistent with the PDMS absorption theory described by David *et al.* [3].

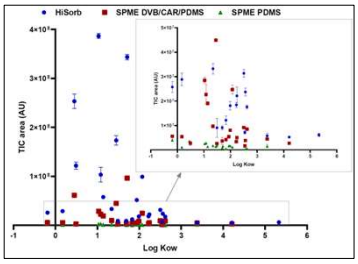


Fig 5. *Comparison of extraction profile (target compounds) of 1 mL coffee extracted for 30 min by different HC tools* *(error bar as SD [n=3])*

Comparison of different Hisorb sorbent phase

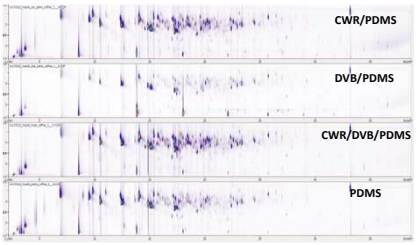


Fig 6. *Chromatograms of 1 mL coffee extracted during 30 min by HiSorb with different sorbent phases*

Different sorbent phases have been compared by analysing the VOC profile of 1 mL of coffee brew for 1 min (60 °C).
The chromatograms obtained using different HiSorb coatings (i.e., CWR/PDMS, DVB/PDMS, CWR/DVB/PDMS, PDMS) are reported in the **Fig 6.** It can be observed that the extraction profile differs in terms of intensity and number of extracted compounds (*e.g.*: DVB/PDMS phase being considerably less efficient than the other coatings).
A more detailed comparison based on the type of chemical compounds extracted is reported in the bar plot of **Fig 7.** PDMS provided the highest extraction, in terms of number of peaks, for the most volatile and both apolar and more polar compounds.
This observation should be seen in relation to the fact that the extraction method was initially optimised for HiSorb PDMS. Consequently, these conditions may not be optimal for other sorbents. Therefore, further optimization may be required.

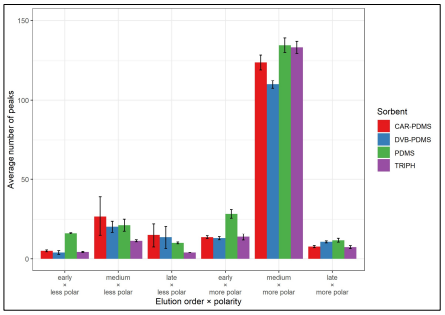


Fig 7. *Comparison of HiSorb ability to extract various classes of compounds with different sorbent phases*
(1 mL coffee extracted during 30 min; error bar represents the standard deviation [n=3])

Conclusion

Further experiments are on-going using a design of experiment to define the optimal time-temperature conditions for all the different HiSorb coating herein tested to have a better comparison of the extraction performance of the coffee volatiles.

Acknowledgments: We would like to thanks to Markes Int., Shimadzu, Supelco and SepSolve Analytical Ltd. for their support.
References: [1] Eggermont *et al.*, ABC, 415, 2511–2521 (2023)., 111–118; [2] J. Abraham, K. Diller, J. Food Sci., 84 (2019), 2011-2014; [3] David *et al.*, Trends Anal Chem, 112 (2019) 102–111

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Slide 1

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GP1 Just for consistency I would add the logo of Markes
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GP2 IN a way you should cite also your two published methods
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ED2 0 I only cited the first paper since I didn't mention any MCT in this poster
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GP3 I suggest using the same figure of the paper, it is more complete with also error bars and the color choice is better to differentiate
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