COMPARISON OF HIGH CONCENTRATION CAPACITY HEADSPACE TECHNIQUES FOR BREWED COFFE CHARACTERIZATION FOLLOW BY GC×GC-MS

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Introduction

Volatile and semi-volatile components are highly relevant to characterize different samples, among which food. These compounds contribute to the peculiar aroma profile of foods and are widely used to assess quality and authenticity. The most common technique used to characterize the headspace of food samples is the used of high-concentration capacity (HCC) technique and in particular solid-phase microextraction (SPME). Recently HiSorb™ technique has been introduced, which can be considered an intermediate tool between SPME and stir-bar sorptive extraction (SBSE), allowing an easy automation as SPME but with higher sample capacity as SBSE [1].
The performance of the novel Hisorb™ probe have been compared with the traditional SPME approach. Time and temperature conditions were carefully optimized, and the possibility of performing multiple cumulative trapping was investigated as well. The analyses were performed on a multidimensional comprehensive gas chromatographic system coupled with a quadrupole mass spectrometer (GC × GC-qMS) and equipped with a Flow modulator. The fingerprinting obtained from a series of different coffee was investigated for quality purposes.

Material & Methods

HS-HiSorb™-HCCE: Hisorb™ PDMS; PDMS 100 µm df and 1 cm long 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.).
Multiple cumulative trapping were performed by trapping the volatiles extracted for 3 consecutive 10-min extractions from 3 different vials containing the same sample.

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), 3.5s modulation period.

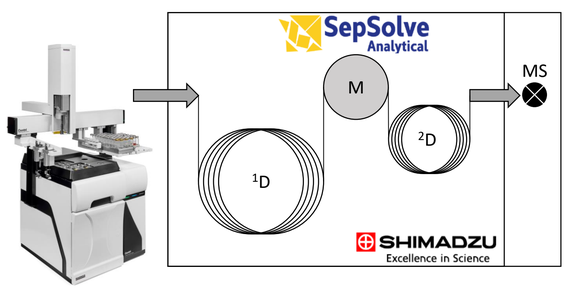
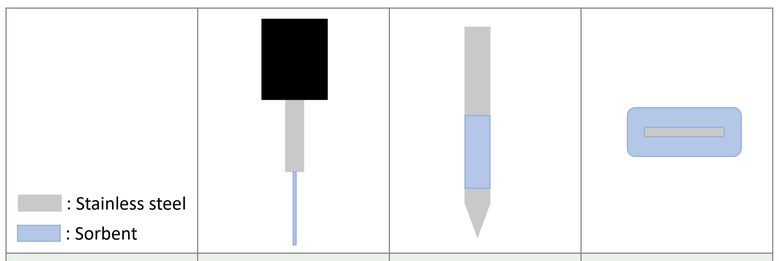


Fig 1. *Sampling technique and instrument schema*



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

Tab 1. *Comparison of different HCC tools*

HiSorb™ optimisation

The sample volume (1 and 4 mL) and extraction time (10-60 min) were evaluated. The profiles obtained using 1 or 4 mL were comparable, increasing up to 30 min after which no further improvement was observed. (**Fig. 2**). In this view, **1 mL extracted during 30 min** were selected.

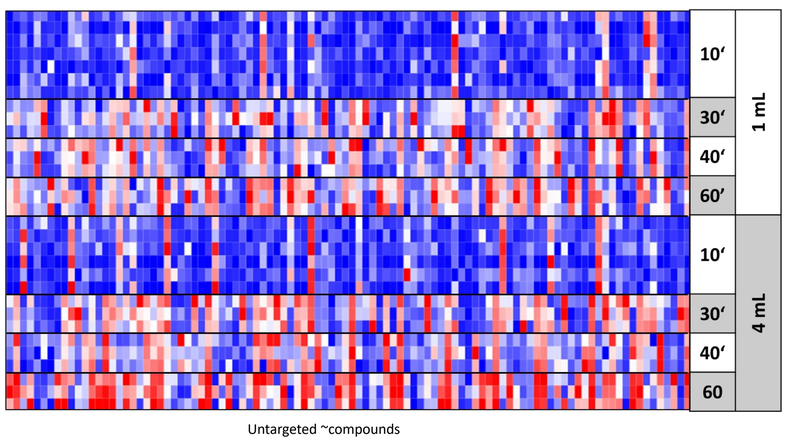


Fig 2. *Time profile (10, 30, 40, 50 min) for 1 and 4 mL sample, extracted at 50 °C*

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].

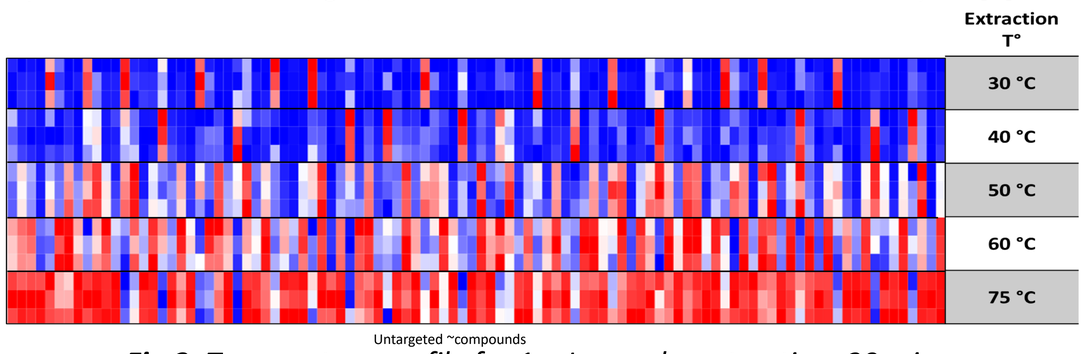


Fig 3. *Temperature profile for 1 mL sample, extraction: 30 min*

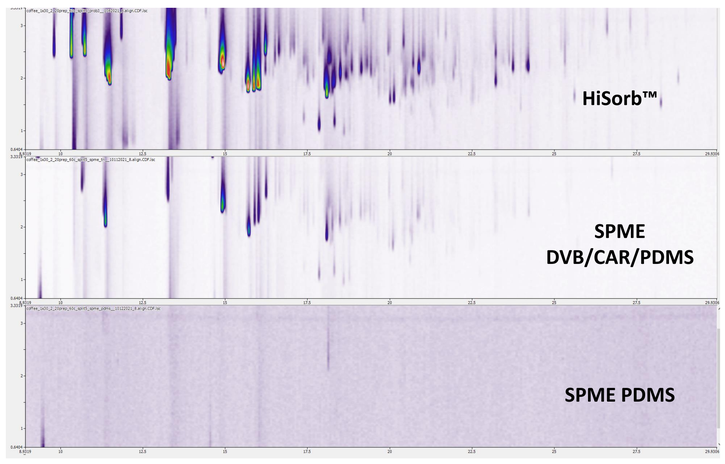


Fig 4. *Chromatogram of 1 mL coffee extracted during 30 min by different HCC tools*

HCC tools comparison

Fig 4. display the comparison of 1 mL coffee chromatogram extracted during 30 min. The number of extracted compounds and the quantity are much higher for HiSorb™ than for both SPME (triphasic then PDMS). This is confirmed by the **Fig 5.** that plot target compounds identify in coffee versus their octanol-water partition coefficients.
This improvement is particularly visible for more polar compounds which is consistent with the PDMS absorption theory described by David *et al.* [3].

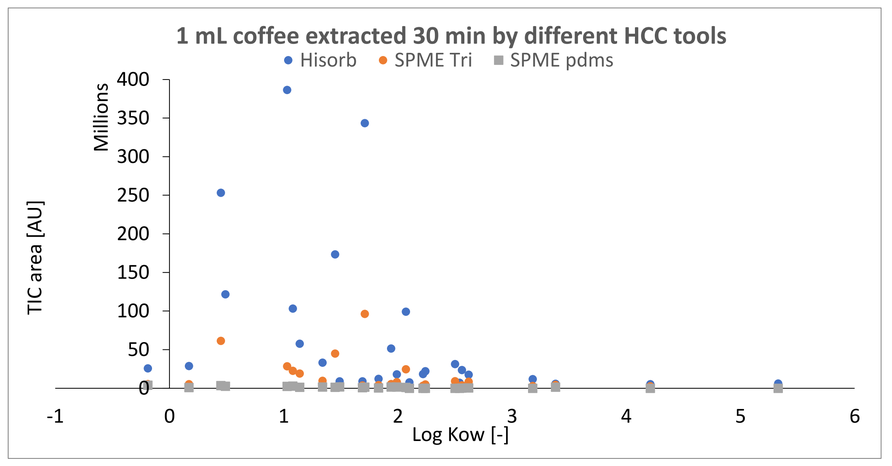


Fig 5. *Comparison of extraction profile (target compounds) of 1 mL coffee extracted during 30 min by different HCC tools*

Application: Packaging impact on the aroma profile

Samples: 6 aluminum and 6 biodegradable coffee capsules, and 11 grinded coffees stored in aluminum bag ("Pack") prepared using a stainless-steel reusable capsule.
Coffee preparation: Nespresso Inissia coffee machine

Fig 5. displays heatmaps of the untargeted models allowing the perfect separation of sample packaging according to their aroma profile. This model permits the identification of discriminant compounds.
This separation is also expressed by the Euclidian distance (**Tab 2.**). The comparison between SPME triphasic and HiSorb™ highlights the potentiality of the HiSorb™ to better discriminate samples based on their volatile profile compared to SPME triphasic.

Tab 2. *Euclidian distance between the different coffee packaging*

Euclidian distance	SPME Tri	HiSorb™
caps_alu vs caps_bio	1.8	2.9
pack vs caps_alu	0.8	0.9
pack vs caps_bio	1.7	3.0

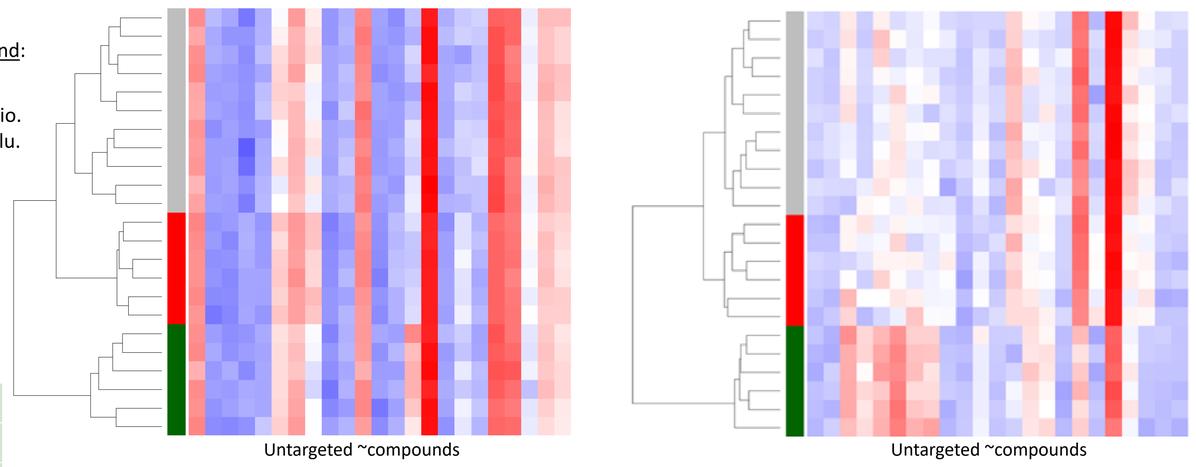


Fig 5. *Heatmaps of model selected ~compounds for 1 mL coffee extracted at 60 °C 3×10' from multiple vials for HiSorb™ and SPME triphasic*

Conclusion

The extraction conditions were optimised using a non-targeted approach. The HiSorb™ performances were compared to usual SPME (Triphasic and PDMS) on a single sample, but also on the capability to capture the fingerprinting to differentiate between different coffee packaging, proving superior performance of the HiSorb™ tool.

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References: [1] Bicchi *et al.*, J. Chromatogr. A., 1071 (2005), 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