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RESEARCH PAPER

Exploring different high-capacity tools and extraction modes to characterize the aroma of brewed coffee

Damien Eggermont[1] · Natasha Damiana Spadafora[2] · Juan Aspromonte[3] · Rocío Pellegrino[3] · Giorgia Purcaro[1]

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Abstract

In the present work, the potential benefit of using multi-cumulative trapping headspace extraction was explored by comparing the results using solid-phase microextraction (SPME) coated with divinylbenzene/carboxen/polydimethylsiloxane and a probe-like tool coated with polydimethylsiloxane. The efficiency of a single 30-min extraction, already explored in previous work, was compared with that of multiple shorter extractions. We evaluated three different conditions, i.e., three repeated extractions for 10 min each from different sample vials (for both the probe-like tool and SPME) or from the same vial (for SPME) containing brewed coffee. The entire study was performed using comprehensive two-dimensional gas chromatography coupled with mass spectrometry. The two-dimensional plots were aligned and integrated using a tile-sum approach before any statistical analysis. A detailed comparison of all the tested conditions was performed on a set of 25 targeted compounds. Although a single 30-min extraction using the probe-like tool provided a significantly higher compound intensity than SPME single extraction, the use of multiple shorter extractions with SPME showed similar results. However, multiple extractions with the probe-like tool showed a greater increase in the number of extracted compounds. Furthermore, an untargeted cross-sample comparison was performed to evaluate the ability of the two tested tools and the different extraction procedures in differentiating between espresso-brewed coffee samples obtained from capsules made of different packaging materials (i.e., compostable capsules, aluminum capsules, aluminum multilayer pack). The highest explained variance was obtained using the probe-like tool and multiple extractions (91.6% compared to 83.9% of the single extraction); nevertheless, SPME multiple extractions showed similar results with 88.3% of variance explained.

Keywords High capacity (HC) · HiSorb · Solid-phase microextraction (SPME) · Multi-cumulative trapping (MCT) · Multidimensional comprehensive gas chromatography (GC × GC) · Coffee

Introduction

Headspace (HS) analysis mediated by the use of high-capacity (HC) tools for the analysis of volatile and semi-volatile compounds is a highly explored technique in various fields of application such as clinical [1, 2], environmental [3, 4], and food [5–7]. In fact, HC tools are easy to use, solvent free, and, in some cases, easy to automate [8]. Among the different HC techniques, solid-phase microextraction (SPME) is the most widely applied and the most versatile. Nevertheless, over the years, different HC tools have been developed, including stir-bar sorptive extraction (SBSE) [9], SPME Arrow [10–13], a probe-like tool (commercially available with the name of HiSorb) [14, 15], and thin-film solid-phase microextraction (TF-SPME) [16]. The main difference among these HC tools is the sorbent volume, which is positively related to the extraction yield according to the

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✉ Giorgia Purcaro
gpurcaro@uliege.be

[1] Gembloux Agro-Bio Tech, University of Liège, Bât. G1 Chimie Des Agro-Biosystèmes, Passage Des Déportés 2, 5030 Gembloux, Belgium

[2] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, 44121 Ferrara, Italy

[3] Laboratorio de Investigación Y Desarrollo de Métodos Analíticos, LIDMA, Facultad de Ciencias Exactas (Universidad Nacional de La Plata, CIC-PBA, CONICET), 1900 La Plata, Argentina

equation $R = E\beta$, where R is the recovery, E is the enrichment factor, and β is the phase ratio ($\beta = V_e/V_s$, where V_e is the volume of the extractant or sorbent and V_s the volume of the sample) [17]. The sorbent volume of the different tools is around 0.6 µL for SPME (PDMS 100 µm), 24–126 µL for SBSE, 3.8–11.8 µL for SPME Arrow, 63 µL for HiSorb, and 40 µL for TF-SPME. The latter tool, along with a higher sorbent volume, has the advantage of a significantly higher surface-to-volume ratio leading to much faster extraction kinetics [18]. Nevertheless, the two tools exhibiting the highest sorbent volume, i.e., SBSE and TF-SPME, are penalized by a lack of full automation.

On the other hand, alternative approaches have been used to improve the extraction kinetics and the extraction yield of HS-HC. Besides the most classical approach of adjusting the stirring rate and extraction temperature, some attractive alternatives have been suggested. For instance, Psillakis et al. systematically investigated the use of reduced-pressure conditions, named Vac-HS, and formulated its underlying principle [19–23]. Another interesting approach is the use of multi-cumulative trapping (MCT). This approach was presented for the first time in 2000 by Lipinski and collaborators in direct-immersion SPME to enhance the sensitivity for the analysis of pesticides in water [24]. Later, Chin et al. trapped multiple extractions using a cold trap at the head of the chromatographic column to increase the detection limit in GC-O for screening of wine aroma [25]. More recently, the MCT-SPME technique has been successfully applied to discriminate between extra-virgin olive oil, virgin and lampante oil, and among different geographical origins [26–28]. When applying the MCT-SPME approach, multiple sequential extractions from the same vial (or different ones) are cumulated in a cryo-trap and then released together into the GC system. Similarly to vacuum SPME, MCT-SPME applied to a single vial significantly increased the extraction of the semi-volatile and more polar compounds [27]. When working under non-saturated HS conditions, the first extraction reduces the amount of the most volatile analytes, positively changing the equilibrium toward the less volatile ones and reducing the displacement effect when adsorption sorbents are used (e.g., the DVB/CAR/PDMS coating used in the cited studies). This beneficial depletion of the most volatile compounds was reported as an interesting strategy also for the use of TF-SPME, coupling with different coatings [29]. The increased extraction of less volatile compounds improved the discrimination capability for olive oil quality and authenticity by using a fingerprinting approach [28].

The goal of this study is to explore the use of MCT using a HiSorb probe and compare its extraction performance with that of MCT-SPME for brewed coffee volatile characterization. The present work follows a previous one where HiSorb extraction conditions were optimized and the untargeted extraction yield was compared with that of the SPME coated with the same phase (PDMS) and another commonly used sorbent phase, namely, DVB/CAR/PDMS [30]. The MCT or single-extraction approaches are applied to explore their potential in discriminating between brewed coffees obtained from different capsule materials. The results obtained using MCT in combination with HiSorb probes are compared with those obtained using SPME in MCT mode performed from both multiple vials (MV) and a single vial (SV).

Materials and methods

Chemicals and reagents

n-Hexane and alkane mixture (C_7–C_{30}) were from MilliporeSigma® (USA). The alkane mixture was used for quality control of the instrument performance and to calculate the linear retention index (LRI) to support peak identification. The probe-like tool, commercially named HiSorb, was kindly provided by Markes International Ltd. (UK). It consisted of a probe coated with polydimethylsiloxane (PDMS) (H1-XXABC). SPME fibers coated with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) df 50/30 µm/1 cm length were kindly provided by MilliporeSigma® (USA).

Coffee samples and brewing procedure

A local coffee roasting company, Charles Liégeois (Belgium), kindly provided us with 23 coffee samples, consisting of 11 aluminum-pack, 6 aluminum-capsule, and 6 compostable-capsule-packed coffee samples. For method optimization and preliminary comparison, a commercially available ground coffee sample (Arabica 100%) was prepared according to the Turkish method proposed by Bicchi et al. [31] and treated as reported in [30].

The samples provided by the roasting company were prepared using a Nespresso Inissia coffee machine (De'Longhi Appliances S.r.l., Italy). For the coffee samples not already in capsules (named "pack" afterwards), a re-usable aluminum capsule was used to prepare the espresso using the amount of coffee determined in [30].

Headspace high-capacity multi-cumulative trapping extraction

A Centri sample extraction and enrichment platform (Markes International Ltd., UK) was used for sample preparation. Extraction, either using HiSorb or SPME, was performed from a 20-mL vial where 1 mL of brewed coffee was added, following the procedure reported below. Triplicates were used for the MCT and tool comparison.

HiSorb probe extraction

HiSorb probes consisted of a PDMS extraction phase, and the extractions followed the previously optimized method [30]. Briefly, samples were left to equilibrate for 20 min at 60 °C under agitation (350 rpm) before 30 min of extraction. The probes were dried under air flow before desorption at 270 °C for 10 min. The volatiles were focused on an electronically cooled trap (U-T12ME-2S, Markes International Ltd.) set at 0 °C before injection into the GC × GC system at 300 °C for 3 min.

SPME extraction

SPME fibers consisted of a DVB/CAR/PDMS phase and were pre-conditioned as recommended by the manufacturer for 30 min at 270 °C. The sample preparation and extraction procedures were the same as for HiSorb, except for the drying step, which was not applied for SPME. The SPME desorption was limited to 4 min, verifying the absence of carryover.

Multi-cumulative trapping

Multi-cumulative trapping extractions were achieved following two different approaches, namely SV-MCT (repeated extraction from the same vial) and MV-MCT (repeated extraction from different vials containing the same sample). In the first case, several extractions (as previously described) were performed on the same aliquot and trapped all together. In the latter, the extractions were performed on different aliquots of the same sample. The compounds extracted from each exposure step were desorbed at 270 °C in the injector and re-trapped on an electrically cooled focusing trap (U-T12ME-2S, Markes International Ltd.) set at 0 °C. The focusing trap was then heated up at 300 °C to inject the sum of all extractions at once.

SPME fibers can use both MV and SV-MCT approaches since the pierced septum does not exhibit loss of sealing capacity for several subsequent septum piercings (tested up to 6). In the present work, 5 min of enrichment delay was used before performing a new extraction from the same vial, as reported by Mascrez and Purcaro [26]. Regarding HiSorb, the size of the probe does not allow for a re-sealing of the septum and the instrument was not equipped with a re-cap tool. Therefore, only the MV-MCT approach was used for extraction with HiSorb.

The results obtained using three extractions of 10 min (3 × 10 min) in MV (HiSorb and SPME) and SV (SPME only) for the MCT approach were compared with the previously obtained optimal single extraction of 30 min using a HiSorb probe.

GC × GC-qMS analysis

All the samples were analyzed in a Shimadzu GCMS-TQ8050 NX (Shimadzu, Germany), consisting of a GC-2030 and triple-quadrupole mass spectrometer detector (TQ-MS). The system was upgraded to a comprehensive multidimensional system using an INSIGHT differential flow modulator (SepSolve Analytical Ltd., UK).

The first-dimension column (^{1}D) was a 20 m × 0.18 mm i.d. × 0.18 µm SLB-5MS silphenylene polymer capillary column (practically equivalent in polarity to poly(5% diphenyl/95% methylsiloxane)), kindly donated by Millipore-Sigma (USA). The second-dimension column (^{2}D) was an SLB-50 (MilliporeSigma, 5 m × 0.25 mm i.d. × 0.25 µm) equivalent to 50% phenylpolysilphenylene-50% siloxane. The eluent of the second column was diverted into the MS and a VUV detector (VGA-101, VUV Analytics, USA) with a ratio corresponding to 41% and 59%, respectively. The splitting was obtained by connecting the outlet of the second column to two uncoated capillaries, i.e., 1.1 m × 0.18 mm i.d. connected to the MS and a 20 cm × 0.25 mm i.d. to the VUV detector (data not used in this study). The splitting of the flow before entering the MS detector is anyway needed to have a flow rate compatible with the MS detector. The GC temperature program was 40 °C (held 5 min) increased to 280 °C at 6 °C/min. The carrier gas was helium. The flow was regulated through the programmed pressure mode both at the inlet and the auxiliary pressure-controlled module (to regulate the ^{2}D column flow), to generate 0.6 mL/min in the ^{1}D column and 16 mL/min in the ^{2}D column. A 1 m × 0.1 mm i.d. bleeding line from the reversed fill/flush modulator was connected to an auxiliary pressure controlled to generate a 0.6 mL/min flow. Modulation time of 3.5 s was used, including 100 ms of reinjection.

The TQ-MS was used in single-quadrupole mode, setting the electron ionization (EI) at 70 eV. The ion source and transfer line temperatures were 200 °C and 280 °C, respectively. The scan range was set from 45 to 350 m/*z*, with an acquisition frequency of 50 Hz.

Data were acquired using Shimadzu GCMSolution version 4.45 from Shimadzu.

Data treatment and statistical analysis

The ChromCompare + software version 2.1.4 (SepSolve Analytical Ltd., UK) was used for data elaboration after a careful alignment based on the ^{1}D and ^{2}D retention time and the spectral information. A dynamic background compensation (DBC) based on a peak width of 0.6 s was applied before the untargeted tile-based approach. A tile size of 5

modulations (18 s) in ^{1}D and of 1.2 s in ^{2}D with 25% overlap was applied. Artifacts and siloxane were removed by a careful comparison with blank samples.

Chromatographic integration and VOC identification

Chromatograms of the samples were integrated after a DBC pretreatment via ChromSpace GC × GC data processing software (SepSolve Analytical, Peterborough, UK), and incorporated within the ChromCompare + analytical software. Significant compounds were putatively identified based on the NIST17 library similarity ≥ 75% and supported with the experimental linear retention index (LRI) within a ± 30 range compared to the LRI reported on the NIST17 library.

Exploratory classification of the samples

The probabilistic quotient normalization (PQN) [32] and a logarithmic transformation were applied in order to make the distribution of the variables closer to normal [33, 34]. A data reduction based on random forest (RF) was performed using 100 repetitions of 10 decision trees with 15 randomly presented samples and half of the whole features randomly picked presented at each tree with an error threshold of 0.2. The top 30 most significant features were selected. In summary, a data matrix of size 30 × 23 (features × samples) was obtained for each of the methods applied and saved in ASCII format for visualization and further analysis.

Principal component analysis (PCA) was applied to all three feature reduced datasets (single-extraction HiSorb, MCT-HiSorb, and MCT-SPME-SV), in order to explore the classification of the coffee samples based on the type of packaging, that is, aluminum-capsule packed, compostable-capsule packed, and multilayer aluminum pack. Score plots were constructed using the first three principal components (PC).

Further statistical analysis

Further statistical and visualization treatments were performed using Excel (Microsoft Office, version 2016), Minitab (Minitab LCC, version 19.2020.1), Morpheus (https://software.broadinstitute.org/morpheus/), and RStudio (RStudio PBC, version 1.4.1717, R version 4.1.0).

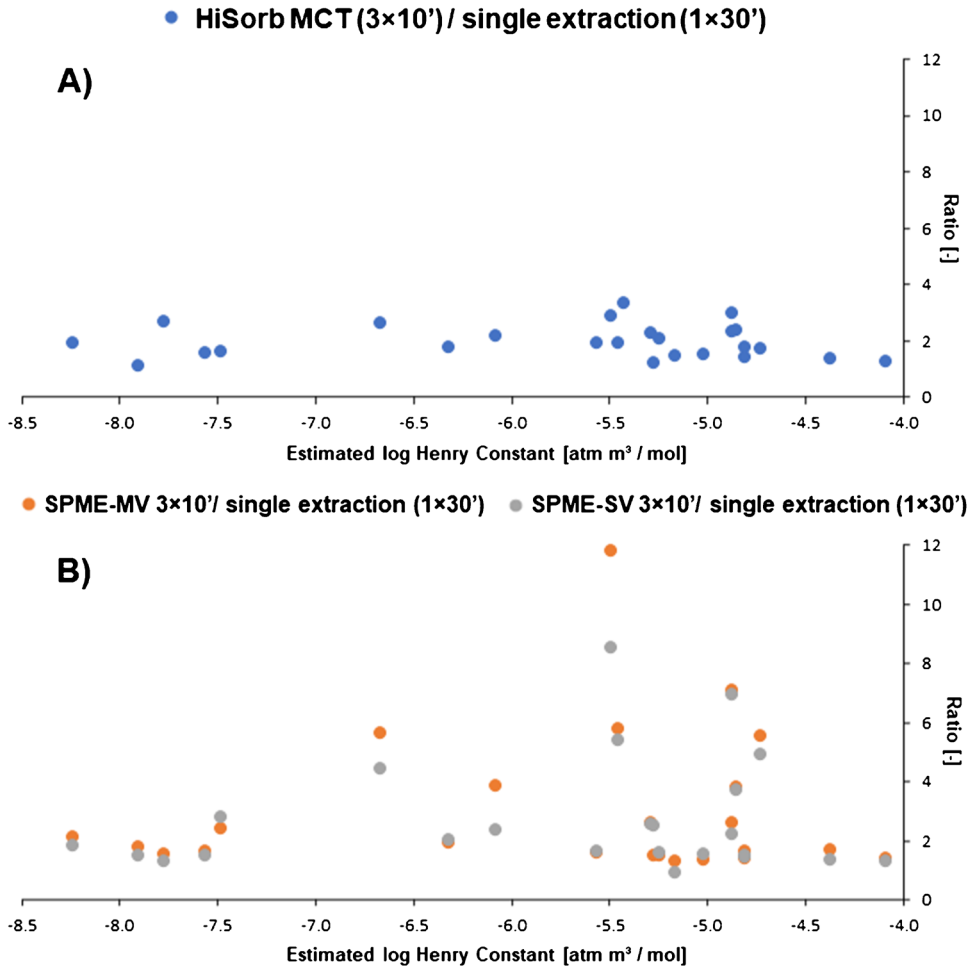

Fig. 1 Ratio of intensity obtained for 25 selected target compounds obtained with (A) MCT-HiSorb MV and (B) MCT-SPME-MV and MCT-SPME-SV using 3 extractions of 10 min, and the reference method of a single extraction of 30 min using either HiSorb or SPME, accordingly; plotted against their log-transformed Henry's constant

Results and discussion

Study of the multi-trapping conditions for HiSorb and SPME

In our recent publication [27], HiSorb was compared, in terms of coverage and analyte response intensity, with the more commonly used SPME approach in characterizing the HS profile of brewed coffee. In this regard, HiSorb showed a higher performance.

Recently, we also investigated the use of the MCT approach, as explained in the introduction, that can be applied to both HiSorb and SPME methodologies. The use of MCT was investigated to study the volatile profile of the espresso coffee samples previously explored using single extraction. Three extraction conditions were evaluated: MCT-SPME-MV, MCT-SPME-SV, and MCT-HiSorb (also MV). One milliliter was used for all experiments, as reported previously [30]. However, as shown by the results discussed below, where negligible differences were observed between MCT-SPME-SV and MCT-SPME-MV, 1 mL of sample led to the saturation of the HS for most of the compounds. However, by using volumes lower than 1 mL, a total volatilization of the sample is likely to occur during the conditioning and sampling times, creating a crust on the vial wall.

In fact, when comparing the extraction capacity between the two SPME approaches, MCT-SPME-MV and MCT-SPME-SV, the results are very comparable. Only few analytes with higher volatility (e.g., methyl pyrazine, 1-(acetyloxy)-2-propanone, 2-furanmethanol) are better recovered when working in MCT-SPME-MV than MCT-SPME-SV (Fig. 1). It is expected that the reuse of the same vial for multiple extractions will cause a depletion of the more volatile analytes, eventually improving the recovery of the less volatile ones [27, 35]. However, in this case, MCT-SPME-SV did not show a clear benefit in the recovery of the less volatile compounds. This is an indication that the HS remained saturated for most of the compounds, and the depletion of the more volatile analytes was not fully achieved under the studied conditions. Therefore, no significative advantage of MCT-SPME-SV over MCT-SPME-MV would be expected.

The MCT extraction conditions were compared with those of the single-step 30-min extraction using either HiSorb or SPME. The 25 compounds already identified in the previous work, which covered a wide range of polarities and volatilities [30], were used to evaluate the potential benefit of MCT. The ratio of the obtained area of these compounds when using MCT and the one obtained when using the single extraction with the same type of probe (HiSorb or SPME) was plotted against Henry's constant of each analyte (Fig. 1(A and B)). The overall recoveries increased in all MCT approaches by roughly twofold (median value). HiSorb probes used with the MCT approach showed a 1–3 times

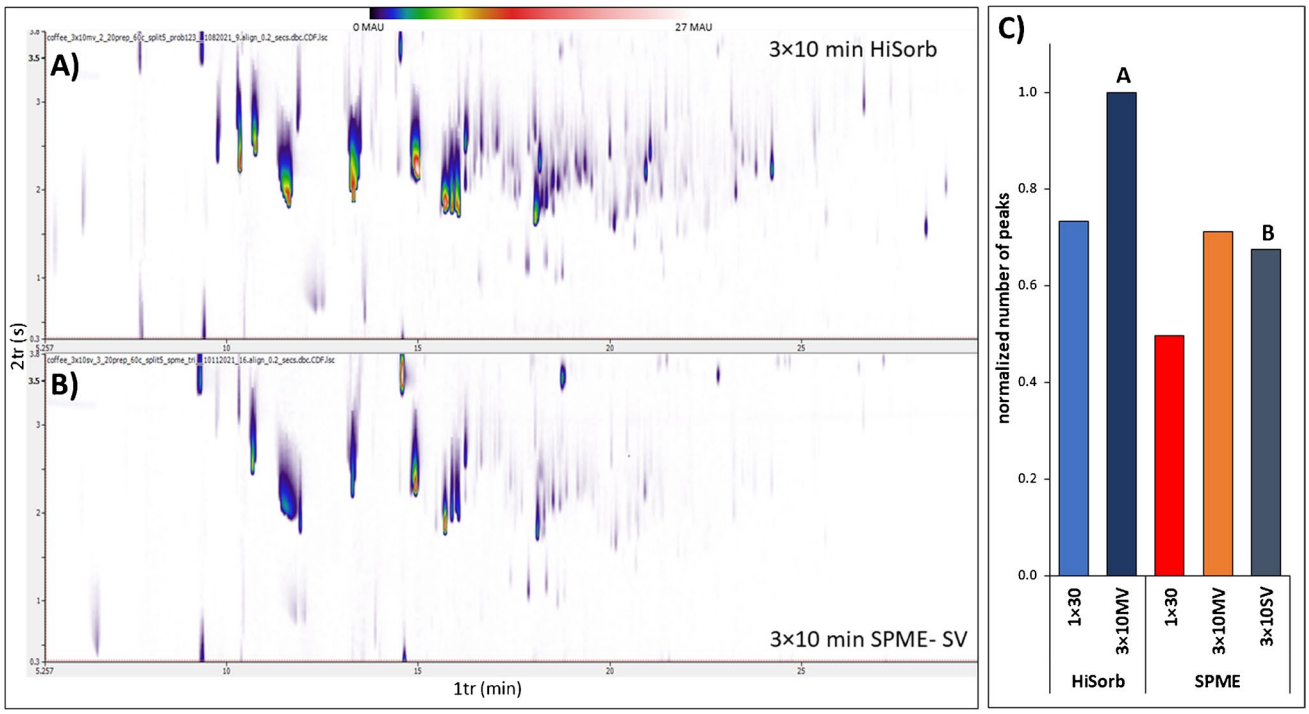

Fig. 2 Comparison of the 2D plot obtained by extracting the same brewed coffee using (A) MCT-HiSorb 3×10 min and (B) MCT-SPME-SV 3×10 min. (C) Normalized comparison of the total number of compounds extracted using HiSorb 1×30 min, MCT-HiSorb 3×10 min (A) and SPME 1×30 min, MCT-SPME-MV 3×10 min, MCT-SPME-SV 3×10 min (B)

higher recovery than when HiSorb probes were used in single extraction for all analytes without any particular trend (Fig. 1(A)). While SPME showed a twice median increment for both MV and SV-MCT approaches, compared to the single-step SPME (Fig. 1(B)). However, there is a broad variability, namely in the ~ 1–12 and 1–9 ratio ranges, for MV and SV, respectively, with a clear trend of increased signal for the more volatile compounds for both extraction modes. This improved extraction of the most volatile compounds with multiple shorter SPME extractions is due to the lower sorbent volume, which is quickly saturated in the first minutes of extraction. The renewal of the vial and concentration of the extracted compounds in the cold trap has a higher impact on sensitivity than a longer exposure time. Therefore, proper analyte extraction can be achieved within a shorter time per vial, with a net gain in the aggregate, thanks to the high capacity of the cold trap. The adsorption process is more favorable in the first few minutes; therefore, having a fresh solid phase has a higher impact on recoveries than extending the extraction time per vial. In this case, this allows for the same total extraction time for single or MCT approaches.

The signal of the compounds obtained with MCT-SPME (either MV or SV) compared with a single HiSorb extraction of 30 min showed a median ratio of 0.6 (ranging between 0.2 and 1.5). Furthermore, almost the same number of total peaks was extracted using MCT-SPME either in SV or MV mode compared to HiSorb 1 × 30 min. MCT-HiSorb 3 × 10 min provided an increase of about 36% of the total number of compounds extracted compared to a single 30-min extraction with HiSorb. Figure 2 shows the comparison between the 2D plot obtained using MCT-HiSorb 3 × 10 min and that using MCT-SPME-SV 3 × 10 min. In the insert box, the normalized (against the highest) total number of peaks for the different extraction conditions is reported. Nevertheless, when investigating the coverage of the key odorants, as reported in our previous work [30], no differences were noted using HiSorb or SPME in both tested modes.

Table 1 Corresponding explained variance for the first three principal components for the HiSorb single extraction, MCT-HiSorb, and MCT-SPME-SV models using the selected features

Mode	Explained variance (%)			
	PC1	**PC2**	**PC3**	**Total**
HiSorb	60.8	14.3	8.8	83.9
MCT-HiSorb	57.0	24.3	10.3	91.6
MCT-SPME-SV	69.6	10.6	7.8	88.3

Classification of brewed coffee based on the capsule material

The ability to obtain an appropriate classification of the samples depending on their packaging, i.e., biodegradable capsules, aluminum capsules, and multilayer aluminum packaging, was also investigated.

MCT-SPME-MV was not tested further as it provided almost superimposable results to HS-SPME-SV

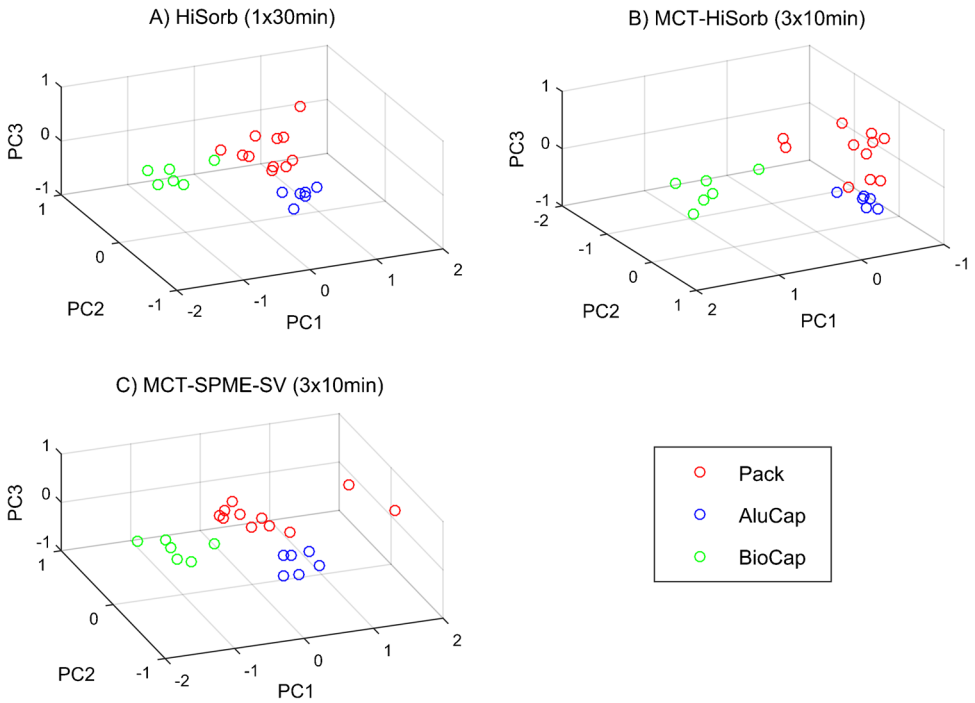

Fig. 3 3D score plot for PC1, PC2, and PC3 for (A) HiSorb single extraction, (B) MCT-HiSorb, and (C) MCT-SPME-SV models using the selected features (red: aluminum multilayer pack, blue: aluminum capsule, green: biodegradable capsule)

Table 2 Tentative identification of the selected features, along with the MS similarity and the linear retention indices calculated experimentally (RI) and reported in the NIST library (NIST RI), for the untargeted approach for HiSorb single extraction, HiSorb MCT, and SPME SV-MCT after removal of redundancy

	1tr (min)	2tr (s)	Features	MS	RI	NIST RI
HiSorb single extraction	3.75	1.5	Unknown			
	6.23	2.4	2,3-Pentanedione	705	483	669
	8.93	0.6	Unknown			
	9.38	1.5	Unknown			
	11.40	1.5	2 furanmethanol	846	826	830
	13.20	3.3	Ethanone, 1-(2-furanyl)-	862	883	889
	13.43	0.6	Pyrazine 2,5 dimethyl	857	885	889
	14.33	0.6	Unknown			
	15.23	0.6	Unknown			
	15.90	3.3	Pyrazine, 2-ethyl-5-methyl-	833	962	975
	15.90	3.3	Pyrazine, 2-ethyl-6-methyl-	823	967	976
	16.13	0.6	Pyrazine, 2-ethyl-3-methyl-	850	978	970
	16.13	2.4	Unknown			
	16.35	3.3	Unknown			
	16.58	2.4	4(H)-Pyridine, N-acetyl-	653	991	1038*
	16.80	0.6	Unknown			
	17.25	2.4	Unknown			
	18.38	2.4	Phenol 2 methoxy	817	1055	1063
	18.83	1.5	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	830	1065	1100
	19.73	2.4	4C-Pyrazine		1095	
	24.23	2.4	2 methoxy 4 vinylphenol	834	1275	1285
	25.80	0.6	Unknown			
HiSorb MCT	3.75	2.4	Unknown			
	4.88	2.4	Unknown			
	7.80	3.3	Unknown			
	10.28	2.4	Pyrazine, methyl-	846	791	801
	13.43	3.3	Butanoic acid, 4-hydroxy-	852	892	933*
	15.00	1.5	Benzaldehyde	833	936	933
	15.00	1.5	2-Furancarboxaldehyde, 5-methyl-	833	936	940
	15.23	3.3	Alkane		944	
	17.93	2.4	Unknown			
	19.50	1.5	Unknown			
	20.85	1.5	1H-Pyrrole, 1-(2-furanylmethyl)-	831	1145	1153
	20.85	0.6	1H-Pyrrole, 1-(2-furanylmethyl)- + unknown	831	1145	1153
	20.85	0.6	Unknown			
	21.75	0.6	Unknown			
	21.98	0.6	Unknown			

Table 2 (continued)

	1tr (min)	2tr (s)	Features	MS	RI	NIST RI
SPME SV-MCT	7.80	3.3	Unknown			
	8.93	2.4	Unknown			
	10.28	3.3	Furan, 2-(methoxymethyl)-	815	622	845*
	10.95	2.4	2/3 furaldehyde	823	689	804
	14.78	3.3	2-Furancarboxaldehyde, 5 methyl	869	928	933
	15.00	3.3	Benzaldehyde	865	932	933
	15.23	0.6	Unknown			
	15.68	1.5	2-Furanmethanol, acetate	838	955	966
	16.13	2.4	Furan, 2-[(methylthio)methyl]-	792	963	980
	16.58	2.4	4(H)-Pyridine, N-acetyl-	720	986	1038*
	17.25	3.3	Unknown			
	17.48	3.3	Unknown			
	18.38	1.5	Unknown			
	19.28	2.4	Unknown			
	19.50	2.4	Unknown			
	21.08	2.4	Unknown			
	24.23	2.4	2-Methoxy-4-vinylphenol	854	1276	1285

*NIST RI calculation based on a semi-standard non-polar column

(Fig. 1(B)). However, MCT-SPME-SV would be expected to bring more useful information than MCT-SPME-MV [26, 28]. Therefore, only MCT-HiSorb, MCT-SPME-SV, and the previously studied single-extraction HiSorb were considered for comparison purposes through PCA.

Comprehensive GC × GC–MS analysis is a very powerful tool when dealing with complex samples because of the wide range of information that can be obtained for each sample. However, the volume and complexity of the acquired data require the use of specific software for its interpretation. To reduce complexity, the top 30 most important features were selected for each of the data sets.

The selected features were used to explore the discrimination capacity of each of the proposed MCT techniques regarding coffee packaging by means of PCA. In all cases, the first three components accounted for more than 80% of the explained variance, while the following ones fell below 5%. Figure 3 shows the corresponding 3D score plots for PC1, PC2, and PC3 for each case, and Table 1 summarizes the explained variance of each component.

PCA analysis showed differences among the coffee packaging types, with samples from the biodegradable capsule being more easily differentiated than those from the other two types in all tested conditions. Samples from the biodegradable capsule packaging are more easily differentiated than the other two classes in all the conditions tested.

Although none of the extraction techniques achieved complete discrimination of the three classes of samples by packaging, the PCA plot for MCT-HiSorb shows an overall better discrimination among classes.

Such a trend can be explained by considering the higher capacity of the solid phase in the HiSorb probe. This allows for the extraction of a wider range of analytes (in particular the more polar and less volatile ones) and suggests that a higher recovery paired with a wider variety of extracted analytes is needed to increase the discrimination capacity of the extraction technique.

The different selected features were tentatively identified (see Table 2). Six components were reported to decrease due to oxidation; i.e., 2,3-pentandione, 2-methoxy-phenol, 2-methoxy-4-vinylphenol (that are 3 potent odorants [36]), 1-(2-furanylmethyl)-1H-pyrrole-, N-acetyl-4(H)-pyridine, and 1-(2-furanyl)-ethanone (previously found also in [37–41]) were found in smaller amounts in the biodegradable cap samples than in the other samples. However, 2-methoxy-4-vinylphenol was also reported to increase with storage time [40, 41]. Furfural was present at a higher concentration in the biodegradable cap sample than in the others. Furfural is an oxidation product

of furfuryl alcohol reported to increase with the storage time [37, 42]. The biodegradable capsules are made of cellulosic material, permeable to air and oxygen, differently from the other two categories of samples. The characteristics of the capsules explain the differences in the volatile profile, characterized mainly by oxidation and a loss of odorants in the biodegradable capsules. Similar results were previously reported analyzing the grounded coffee within different types of capsules [37] [38]. Here, we show that the same trends can be translated into the final product, i.e., the brewed coffee.

Conclusion

In the present paper, the comparison between HiSorb and SPME was performed using both single extraction and shorter MCT extractions. The use of the MCT approach resulted in a higher number of compounds extracted (targeted analysis) and allowed capturing useful information when the fingerprinting approach (untargeted analysis) was applied. Furthermore, the MCT-SPME extraction approach showed similar results to those obtained with HiSorb used in the single-extraction mode. Nevertheless, the use of HiSorb showed a clear advantage in the extraction of less volatile compounds compared to SPME. The employment of the extraction techniques described throughout this manuscript applied to a cross-sample comparison allowed easily discriminating coffee brewed in a compostable capsule from the other two brewing capsule materials, regardless of the tool used, mainly due to the presence of oxidation markers transferred to the brewed drink. However, MCT-HiSorb showed overall better discrimination across the classes of brewed coffee materials.

It is important to highlight that the coatings of the two extraction tools used here, SPME and HiSorb, were not comparable, with DVB/CAR/PDMS for the first one and PDMS for the latter. New coatings for HiSorb have only recently been made commercially available. In a future scenario, it will be very interesting to evaluate their behavior with relevant food applications.

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Declarations

Conflict of interest The authors declare no competing interests.

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