COFFEE AROMA INVESTIGATION: A CHEMOMETRIC COMPARISON OF THE INFORMATION PROVIDED BY THREE HCC SAMPLING TECHNIQUES CHEMICALLY DESCRIBING THE SENSORY PROPERTIES OF THE CUP

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Aim & Scope

Aroma and flavor are very powerful hedonic aspects of a good coffee. They should therefore be carefully considered in coffee classification during coffee-bean selection, in addition to their physical aspects, such as size, color and defective beans. The International Cupping Protocol of the Specialty Coffee Association of America (SCCA) evaluates comprehensively the cup sensory properties scoring the aroma by smelling the dry milled sample and its water infusion (Steps 1 and 2), and the flavor by tasting the brew [2] (Step 3).
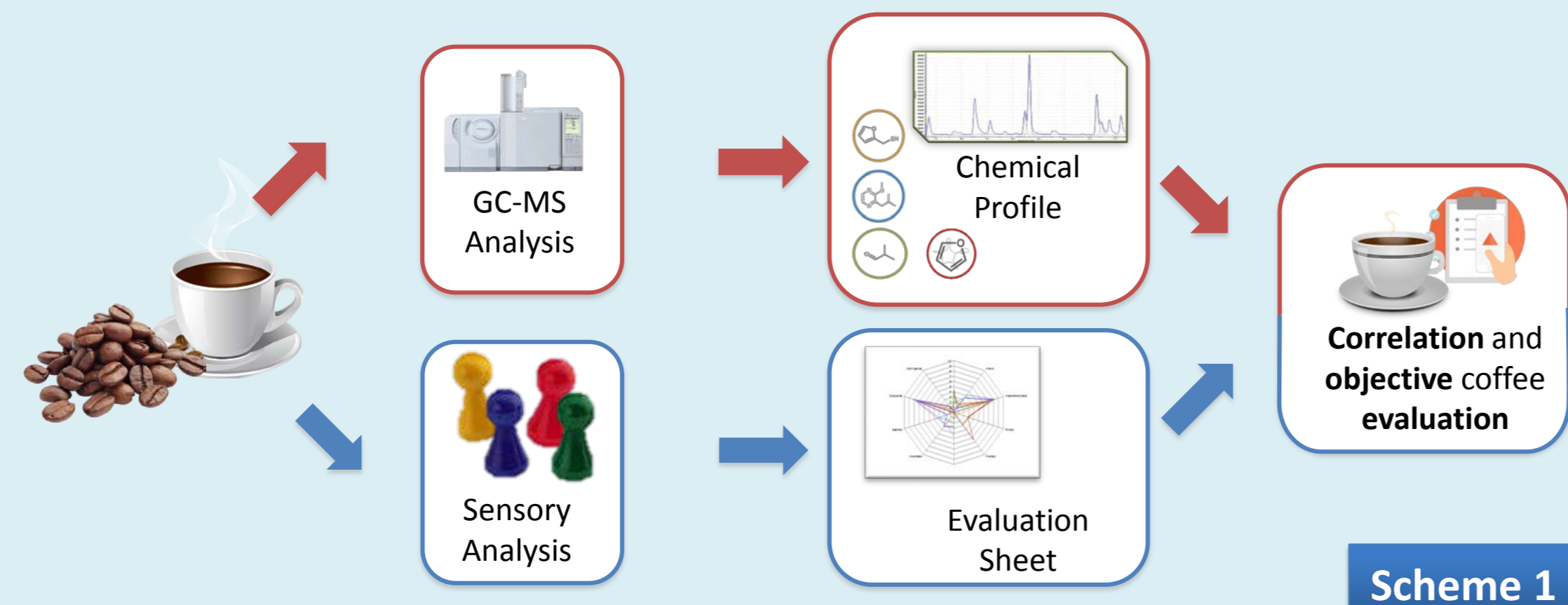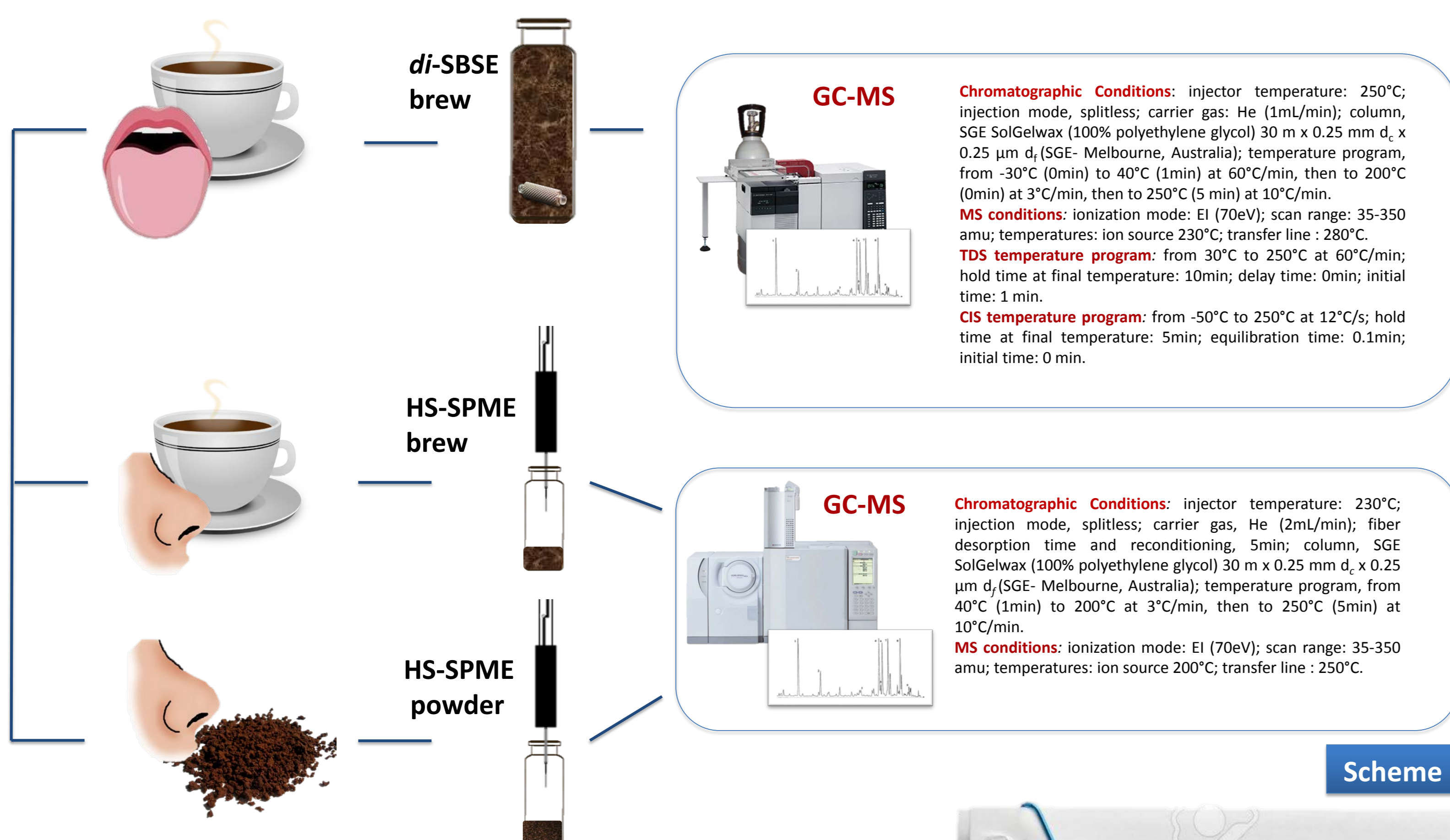

Scheme 1

The objectivation of sensory evaluation by instrumental analysis is a hard task requiring the analytical instrumental platform to provide information as close as possible to the human experience [3] [4] **(Scheme 1).**

The literature reports several approaches to analyze aroma components; however, whatever the approach, sample preparation is still the bottle-neck of the analytical process, since it must provide a consistent and meaningful picture of the sensory-informative components. An effective sample preparation technique needs some key requisites, including (a) possibility to tune extraction selectivity by modifying physico-chemical characteristics of extractants and sampling conditions; (b) flexibility of extraction efficiency, (c) use of methods involving mild interactions to limit artifact formations (e.g. partition (sorption) *versus* adsorption as extraction mechanism); (d) possibility of full automation, and to integrate the extraction step within the analytical system (T.A.S.). Because of the complexity of the coffee matrix (wide range of volatility, water solubility and concentration of the most significant components), three different sampling approaches were considered for a reliable characterization of the final aroma and flavor profiles suitable for coffee quality control at the same time close to the cupping evaluation. [5]

Aroma evaluation (steps 1 and 2 of the SCAA cupping protocol) was associated to Headspace Solid Phase Microextraction (HS-SPME) of roasted coffee powders and the corresponding brews; aroma and taste evaluation (step 3) was combined with in-solution sampling of the brews by SBSE (Stir Bar Sorptive Extraction) **(Scheme 2)**. The ability of each optimized method to discriminate and describe the chemical profiles the investigated samples was compared by multivariate analysis, to determine whether it provided consistent and/or complementary information also in connection to the sample sensory properties defined by a trained panel.

Materials & Methods

Scheme 2

GC-MS

Chromatographic Conditions: injector temperature: 250°C; injection mode, splitless; carrier gas: He (1mL/min); column, SGE SolGelwax (100% polyethylene glycol) 30 m x 0.25 mm d$_c$ x 0.25 µm d$_f$(SGE- Melbourne, Australia); temperature program, from -30°C (0min) to 40°C (1min) at 60°C/min, then to 200°C (0min) at 3°C/min, then to 250°C (5 min) at 10°C/min.
MS conditions: ionization mode: EI (70eV); scan range: 35-350 amu; temperatures: ion source 230°C; transfer line : 280°C.
TDS temperature program: from 30°C to 250°C at 60°C/min; hold time at final temperature: 10min; delay time: 0min; initial time: 1 min.
CIS temperature program: from -50°C to 250°C at 12°C/s; hold time at final temperature: 5min; equilibration time: 0.1min; initial time: 0 min.

GC-MS

Chromatographic Conditions: injector temperature: 230°C; injection mode, splitless; carrier gas, He (2mL/min); fiber desorption time and reconditioning, 5min; column, SGE SolGelwax (100% polyethylene glycol) 30 m x 0.25 mm d$_c$ x 0.25 µm d$_f$(SGE- Melbourne, Australia); temperature program, from 40°C (1min) to 200°C at 3°C/min, then to 250°C (5min) at 10°C/min.
MS conditions: ionization mode: EI (70eV); scan range: 35-350 amu; temperatures: ion source 200°C; transfer line : 250°C.

Scheme 2

Preparation of the Brew:

The coffee brew was prepared from 18g of coffee powder and 300mL of water, using a "Xlong" coffee filter machine.

HS-SPME sampling

SPME fiber: 1 cm long, 65-µm thick polydimethylsiloxane/divinylbenzene (PDMS/DVB)
Sampling Procedure: 1.500 ± 0.010 g of powder or 4.5mL of the brew in a septum-sealed gas vial (20mL) were sampled through the SPME fiber for 40 minutes at 50°C with an agitation speed of 350rpm. The internal standard was preliminary loaded onto the fiber by sampling 5µL of a 1000mg/L solution of n-C$_{13}$ in DBP into a 20mL HS vial for 20 min at 50°C, agitation speed: 350rpm.

SBSE sampling

SBSE Twister®: 1cm long, 0,5mm PDMS film coated (Gerstel GmbH & Co. KG)
Sampling Procedure: 13mL of the brew in a 20mL septum-sealed glass vial were added to 5mL of the 1mg/L n-C$_{13}$ water solution and sampled with a PDMS Twister® for 40 min at 50°C.
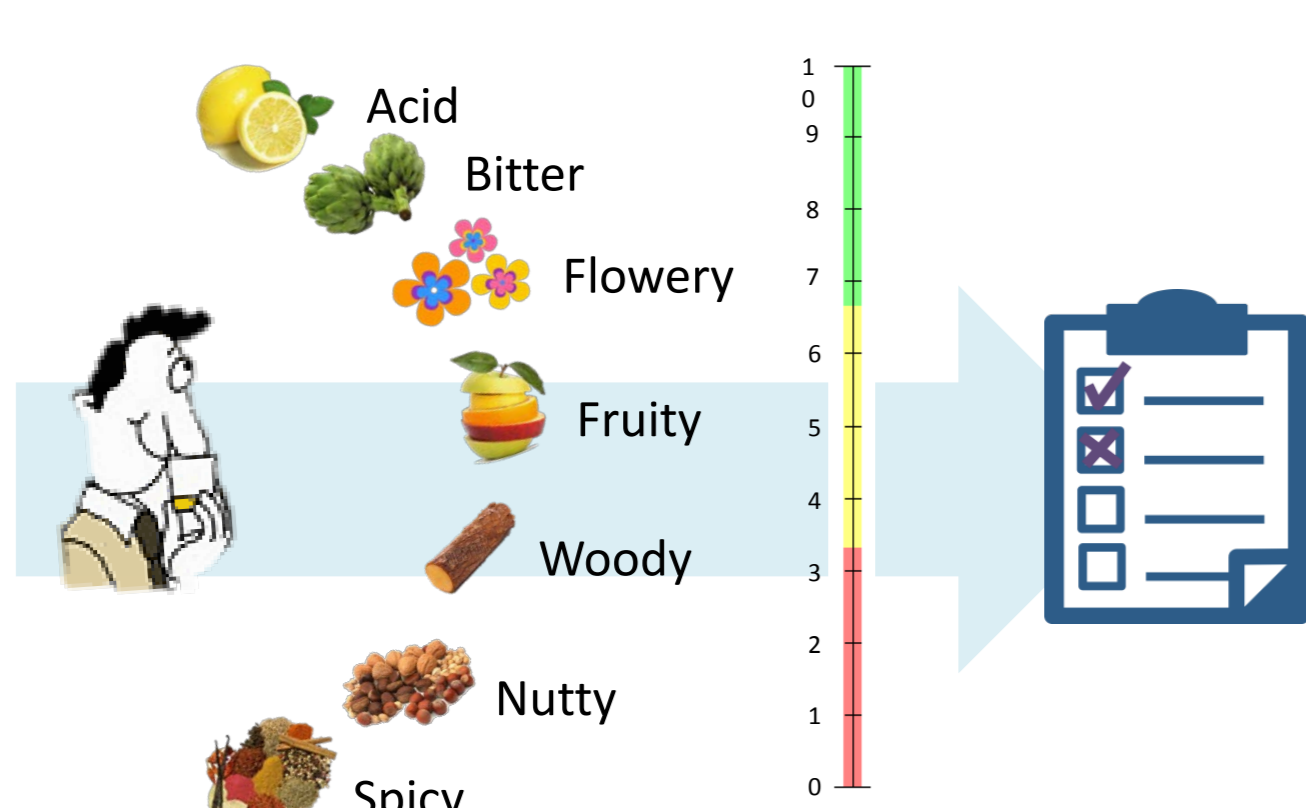
Coffee Samples

Coffees samples, consisting of roasted coffee ground to suit a coffee-filter machine, were kindly supplied by Lavazza Srl (Turin, Italy) over a period of 9 months .

Eight coffee samples with distinctive sensory notes, originating from different countries (Ethiopia, Papua New Guiney, Colombia, Brazil, India, Indonesia, Java, and Uganda), of the species *Coffea Arabica* L. (Arabica) and *Coffea canephora Pierre* (Robusta), were analyzed. Each coffee origin was analyzed in five replicates; each replicate was produced by a fresh cycle of roasting and grinding, starting from the same batch of green coffee beans.

Sensory Analysis

The sensorial description of the different coffee samples was done by the Lavazza trained panel. The panelists classified each characteristics (scheme 1) on a 0-10 scale, where 0 meant none and 10 a strong existence of the characteristic **(Scheme 3)**.

Scheme 3

Results & Discussion

A chemometric approach by PCA (Principal Components Analysis) has been chosen to explore data collected with each analytical platform. The score plot (Figure 1) shows two different groups according to the species and as a consequence to their different sensory profiles. The only exception in this separation is represented by INDIA samples; they are close to "Robusta" samples although they belong to the "Arabica" species.
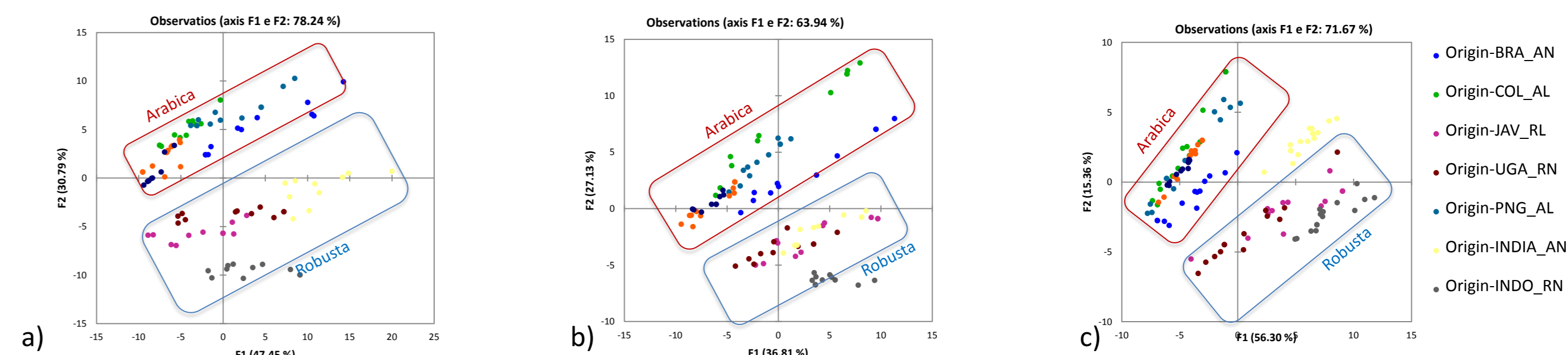

Figure 1 PCA score plots a) HS-SPME of the coffee powder; b) HS-SPME brew; c) SBSE brew.

Figure 1

Within the "Robusta" samples, coffees from Indonesia (INDO), the most woody and bitter samples, are well distinguished from the others two origins (JAV and UGA)
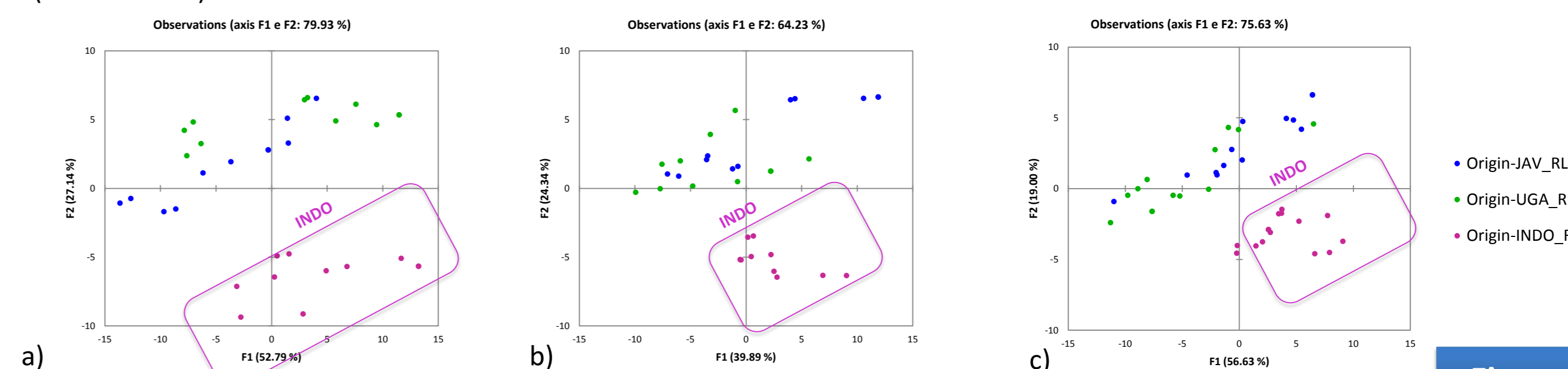

Figure 2 Robusta scores plots: a) HS-SPME of the powder; b) HS-SPME of the brew; c) SBSE of the brew.
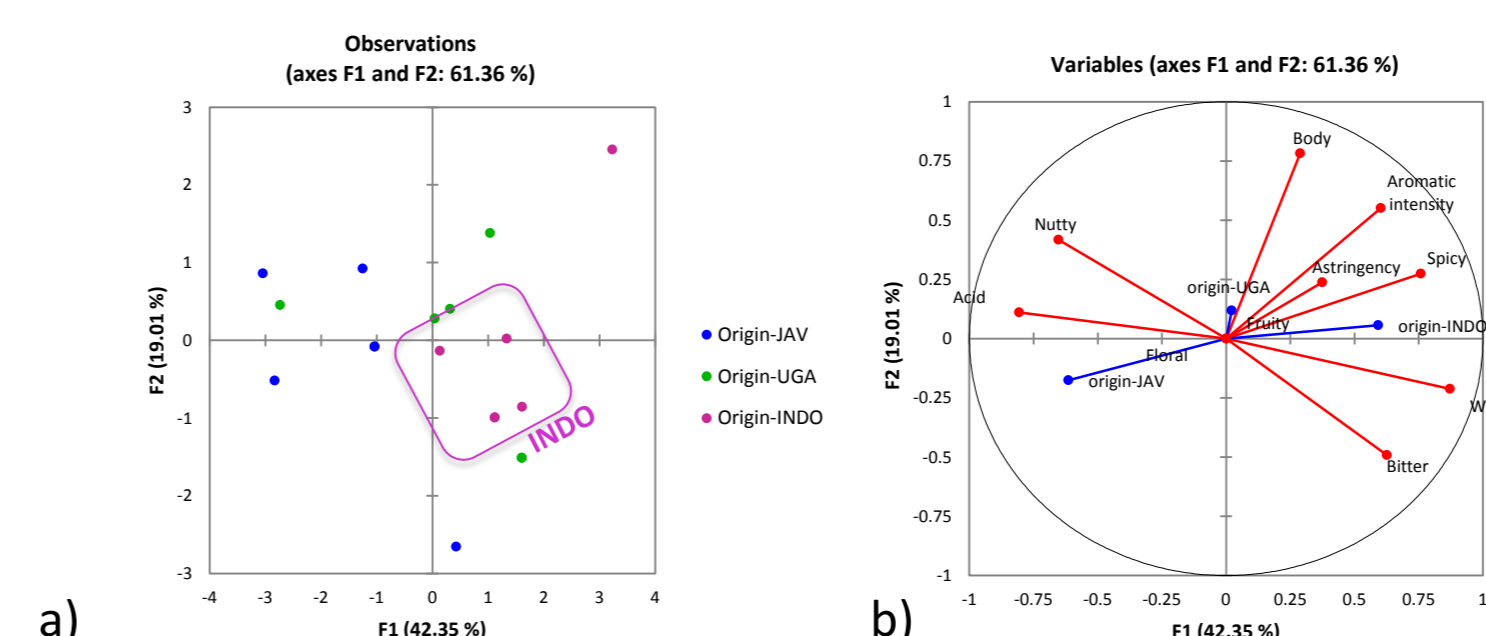
Figure 2

Figure 3

The elaboration of sensory data (figure 3b) shows that the samples distribution is pretty consistent to what has been observed with the chemical data and INDO samples are characterized by Bitter and Woody notes. **Table 1** reports the Direct Discriminant Compounds (DDCs) for INDO samples selected from the elaboration of the HS-SPME-GC-MS of the powder together with their Odor Description.

Compound Name	Odor Description*
1H-Pyrrole-2-carboxaldehyde	Musty
1-Hydroxy-2-butanone	sweet coffee musty grain malt butterscotch
2,3-Butanedione	Buttery
2,3-Pentanedione	Buttery
2-oxopropylpropanoate	-
2-Butanone, 3-hydroxy-	Buttery
2-Furfurylfuran	Roast
2-Propanone, 1-hydroxy-	Caramellic
2-Vinyl-5-methylfuran	-
3(2H)-Furanone, 2,5-dimethyl-	fruity ester caramel
5 METHYL FURFURAL	Caramellic
Acetaldehyde	pungent ethereal aldehydic fruity
Acetic acid	sharp pungent sour vinegar
Acetoxyacetone	Fruity
Furfural	sweet woody almond fragrant baked bread
Hexanal	fresh green fatty aldehydic grass leafy fruity sweaty
Pyridine, 3-ethyl-	Tobacco

*The Good Scents Company

Table 1

RV coefficients:

	HS-SPME pow	HS-SPME_bre	SBSE_bre	MFA
P_HS-SPME	1	0.597	0.534	0.808
B_HS-SPME	0.597	1	0.781	0.911
B_SBSE	0.534	0.781	1	0.893
MFA	0.808	0.911	0.893	1

Table 2

Further elaboration by mean of the Multiple Factorial Analysis (MFA) confirms the consistency and the interchangeability of the three techniques (Table 2)

PCA determined different DDCs for each sampling method, according to the vectors projections of the original variables on PC1 and PC2. This occurs because the three sampling approaches are based on different principles, adopt different sampling materials (PDMS/DVB SPME fibers for headspace, and PDMS Twisters® for in-solution sampling), are applied to different matrices (coffee powder and brew) and involve compounds with different intrinsic physical-chemical properties. Table 3 listed the DDCs pointed out in each sampling technique together with their physical-chemical properties.

Compound Name	Water solubility (mg/L)*	Log K$_{O/W}$	VP (mm Hg at 25 °C]	Henrys LC (VP/Wsol) [atm-m3/mole])
1-acetyl-1,4-dihydropyridine (C)	-		-	
1H-Pyrrole-2-carboxaldehyde (A; B; C)	3.43E+04	0.6	0.09	3.13E-07
1-Hydroxy-2-butanone (B)	7.21E+05	-0.29	0.77	1.24E-07
2,3-Butanedione (B)	1.00E+06	-1.34	56.8	7.95E-06
2,3-Pentanedione (B; C)	6.16E+05	-0.85	31.1	6.65E-06
2-Butanone, 3-hydroxy- (B)	8.33E+05	-0.36	2	2.78E-07
2-cyclopenten-1-one, 2-hydroxy-3-methyl- (C)	8.50E+03	1.29	0	6.68E-08
2-Furancarboxaldehyde, 5-methyl- (A)	2.91E+04	0.67	1.38	
2-furfuryl-5-methylfurane (B)	2216	1.96	2.89	1.96E-04
2-Furfurylfuran (B; C)	217.2	2.99	0.26	2.36E-04
2-Oxopropylpropanoate (B)	1.10E+04	1.2	31.5	4.02E-04
2-Propanone, 1-hydroxy- (B)	1.00E+06	-0.78	1.74	1.70E-07
2-Vinyl-5-methylfuran (B; C)	2216	1.96	2.89	1.96E-04
3(2H)-Furanone, 2,5-dimethyl- (B)	4.63E+04	0.43	1.66	5.29E-06
4-Ethylguaiacol (A)	6.94E+02	2.38	0.02	
5 Methyl Furfural (B;C)	2.91E+04	0.67	0.69	3.41E-06
Acetaldehyde (B)	2.57E+05	-0.34	910	1.72E-04
Acetic acid (B)	4.76E+05	-0.17	15.7	2.86E-06
Acetoxyacetone (A; B; C)	1.52E+05	-0.19	1.49	1.50E-06
Benzaldehyde (A)	6.10E+03	1.71	1.01	
Butanal, 3-methyl- (C)	1.12E+04	1.23	51.6	5.21E-04
Difurfuryl ether (C)	711.3	2.22	0.02	7.48E-06
Furan, 2-(2-(furanylmethyl)-5-methyl- (A)	6.41E+01	3.53	0.07	
Furan, 2,2'-methylenebis- (A)	2.17E+02	2.99	0.26	
Furfural (A; B; C)	5.36E+04	0.83	2.32	5.48E-06
Furfuryl methyl sulphide (A)	1.84E+03	2	1.37	
Guaiacol (C)	2.09E+03	1.88	0.06	5.16E-06
4-ethyl-guaiacol (C)	6.94E+02	2.38	0.02	7.16E-06
4-vinyl-guaiacol (C)	9.26E+02	2.24	0.01	1.64E-06
Hexanal (B)	3527	1.78	9.57	3.58E-04
Pyridine, 3-ethyl- (A; B; C)	8.48E+04	1.84	2.53	3.29E-06
Unknown 1 (B)				
Unknown 12 (B)				
Unknown 13 (B)				
Unknown 14 (B)				
Unknown 17 (B)				
Unknown 2 (B;C)				
Unknown 21 (B;C)				

Letters in brackets highlight that DDCs are different in the three considered sampling techniques.: A=SBSE; B=HS-SPME pow; C=HS-SPME brew

*EPI Suite v3.10 developed by the EPA's Office of Pollution Prevention Toxics NS Syracuse Research Corporation (SRS) 2000 U.S.
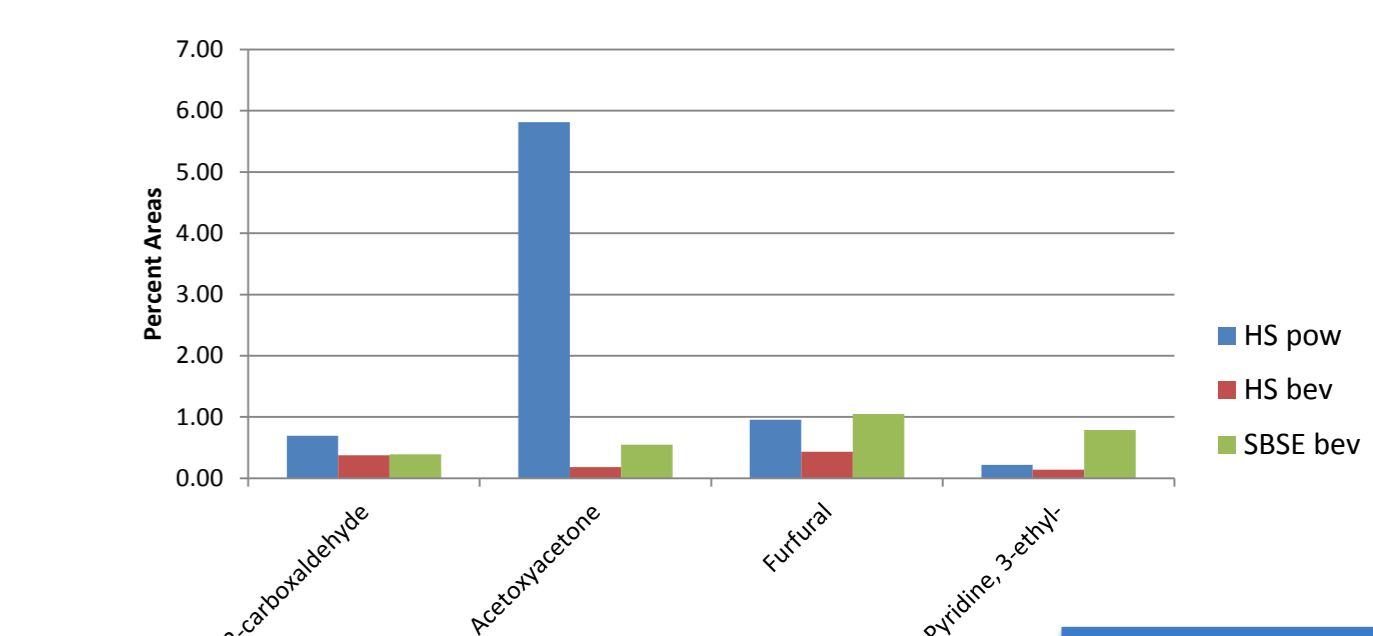
Table 3

Figure 4

SBSE of the brew may be considered the most representative sampling technique for flavor evaluation. Most DDCs are slightly soluble in water and relatively apolar, all with high k$_{O/w}$. Conversely, DDCs in the HS-SPME volatile fraction of the coffee powder generally present high volatility (expressed as Vapour Pressure, VP) and low k$_{O/w}$ (below 1) (Table 3).

These considerations are clearly illustrated by the comparison of normalized percent areas of some DDCs obtained with the three sampling approaches **(Figure 4)**.
3-Ethyl pyridine and furfural (i.e. two DDCs with similar physico-chemical characteristics) are differently recovered by SBSE, 3-ethyl pyridine predominating because of its higher k$_{O/w}$, while furfural, more polar, is less retained by the fatty matrix and more easily released into the HS.
Conversely, by comparing HS-SPME of the brew to SBSE, the more polar furfural is less recovered than 3-ethyl pyridine from the HS and recovered to a greater extent by SBSE .
Acetoxyacetone is highly concentrated in the HS of coffee powder, and is better recovered by SBSE than by HS-SPME from the brew, because of its high solubility in water.
1-H-Pyrrole-2-carboxaldehyde similarly contributes to HS-SPME from coffee powder and brew, but because of its medium-low k$_{O/w}$, good water solubility and low VP, its accumulation in HS is limited.

Conclusions...

Coffee samples were analyzed with three sampling techniques (HS-SPME of the coffee powder, HS-SPME of the brew, and SBSE of the brew) in combination with GC-MS; each technique can simulate a part of the sensory experience perceived during cupping coffee evaluation. Despite the differences between the three sampling approaches, data processing showed that the three methods provide the same kind of chemical information useful for sample discrimination, and that they could interchangeably be used to sample coffee aroma and flavor. Comparison of the multivariate analysis of the sensory data with the chemical fingerprint of the investigated samples showed that: a) sensory and chemical data are in good agreement, and b) sensory evaluation can be related to the different chemical composition of the samples investigated. The choice of sampling technique used for this purpose may thus be guided by factors such as simplicity, sensitivity, reliability, and possibility of automation. As a consequence, HS-SPME of the coffee powder is the easiest and more friendly approach in this respect.

...and Future Perspectives

Further in-depth studies will be necessary to correlate groups of compounds to a specific sensorial note characterizing coffee samples, and to enable the development of a predictive model to support predictive panels in their sensory evaluation of coffee samples. In addition, knowledge on the odor active compounds correlated to a characteristic note, the concentrations of these compounds and their interactions, may open new perspectives in understanding the biological mechanisms underlying the pleasure related to the aroma and flavor of coffee.

References
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