Comparison between sensometric and sensomic approaches in the sensory-chemistry relationship definition

Davide Bressanello[a], Erica Liberto[a], Chiara Cordero[a], Barbara Sgorbini[a], Cecilia Cagliero[a] Patrizia Rubiolo[a], Gloria Pellegrino[b], Manuela R.. Ruosi[b], Carlo Bicchi[a]

[a] Dipartimento di Scienza e Tecnologia del Farmaco, Università degli Studi di Torino, Via Pietro Giuria 9, Torino, Italy
[b] Lavazza spa, Strada Settimo 410, 10156 Torino, Italy

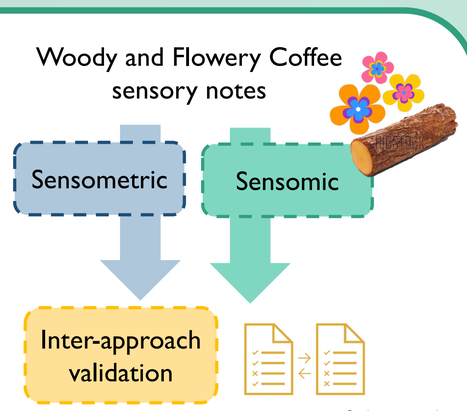
Email: davide.bressanello@unito.it

Aim & Scope

The classification and the objective evaluation of different coffee sensory profiles becomes ever more important since coffee consumption is going towards closer to those of other valuables food products (e.g. terroir for wine). In addition consumers are well aware of what they desire and expect from their daily cup of coffee[1,2]

Several papers have addressed sensory-instrumental relationship on coffee sensory properties to deal with this ambitious objective, however the knowledge of the chemistry behind this sensorial experience is limited, despite the large number of studies on coffee flavor chemistry, because of the complexity of flavor formation, which is greatly not only influenced by roasting but also by the whole production chain.

Although recent studies demonstrated that a relationship can be proven, the sensory testing cannot be completely replaced by machines[3], but the instrumental evaluation can be a useful tool to alleviate the panel of part of the routine work and focusing their expertise on specific and valuable assessments.



Scheme 1

Sensometrics is a bridge linking the sensory properties to the chemical information behind them. This approach can be applied only when high throughput instrumentation is available. The fast and automatic Total Analysis Systems (TAS) afford to screen a high number of samples and in combination with suitable statistical tools (e.g PLS-DA, PLS) make the connection between the classic sensory evaluation and the chemical profile possible.

Nevertheless, the effectiveness of this approach has to be assessed by the molecular sensory science (or sensomics) approach that still is the approach of choice to identify and quantify the molecules responsible for different foods flavors.[4,5]

In these perspectives, "*Woody*" and "*Flowery*" coffee notes have been studied with the two approaches (Sensometrics *vs* Sensomics) to investigate if, despite their differences, the information extracted from the samples with both approaches are coherent. (Scheme 1). The consistency between these approaches might support the sensometrics as a valid tool to face this ambitious challenge also through its cross-validation

Materials & Methods

References:

1.Sunarharum, W. B., Williams, D. J. & Smyth, H. E. Complexity of coffee flavor: A compositional and sensory perspective. *Food Res. Int.* **62,** 315–325 (2014).
2.Folmer, B. How can science help to create new value in coffee? *Food Res. Int.* **63,** 477–482 (2014).
3.Chambers IV, E. & Koppel, K. Associations of volatile compounds with sensory aroma and flavor: The complex nature of flavor. *Molecules* **18,** 4887–4905 (2013).
4.Schieberle, P. & Hofmann, T. in *Food Flavour* 413–438 (2011).
5.Schieberle, P. in *Characterization of Food* 403–431 (1995

More details on the Sensometric approach at: **YSKN14**

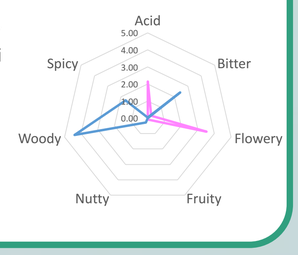
Sensometric

152 Coffee samples of *Coffea arabica* L. (Arabica) and *Coffea canephora Pierre* (Robusta), coming from 27 different origins spread all over the world were kindly supplied by LavazzaSpa(Turin, Italy).

The sensorial description of the different coffee samples was done by the Lavazza trained panel; this sample-set was selected because able to quote the *Woody* note score from 0 to 8.5 and the *Flowery* note from 0 to 7.4.

Sensomic

Starting from the panel sensory evaluation, Vietnam and Burundi coffee samples were chosen as representative of extreme scoring **Woody** and **Flowery** notes respectively.



HS-SPME-GC-MS

Sampling Conditions

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 at a stirring speed of 350rpm. The internal standard was preliminary uploaded 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, stirring speed: 350 rpm.

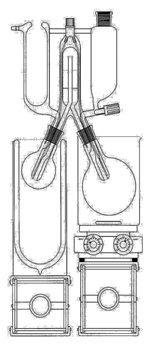
Chromatographic Conditions*:* injector temperature: 230°C; injection mode, splitless; carrier gas, He (2mL/min); fiber desorption time and reconditioning: 5min; column, SGE SolGelwax (100% polyethylene glycol) 30 m x 0.25 mm d_c x 0.25 µm d_f (SGE- Melbourne, Australia); temperature program, from 40°C (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.

Extraction

- 30g coffee powder + 200mL DCM
- 1h Stirring
- Filtration

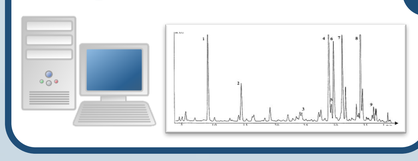
Solvent Assisted Flavour Evaporation (SAFE)



Acid (AV) and Neutral-Basic (NBV) volatiles separation

GC-MS PROFILE — **AROMA ISOLATION** — **AROMA EXTRACT**

Integration

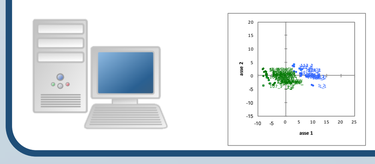


Aroma Extract Dilution Analysis (AEDA)

GC-O/FID conditions*:* injection mode: cold on column; inlet pressure: 80kPa; carrier gas, He; column, DB-FFAP (30 m, 0.32 mm i.d., 0.25 µm film thickness; J&W Scientific, Agilent Technologies, Waldbronn, Germany); temperature program, 40 °C (2 min) to 230 °C (5 min) at 6 °C/min.

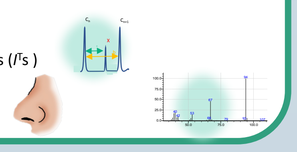
The flow was splitted in two equal parts trasferred via two deactivated fused silica capillaries (50 cm × 0.25 mm) to a sniffing port and a flame ionization detector (FID), respectively. The sniffing port consisted of a cylindrically shaped aluminium device (80 mm length, 25 mm diameter) with a bevelled top and a central drill hole (2 mm) housing the capillary. It was mounted on a detector base of the GC and heated to 230 °C. The FID was operated at 250 °C with hydrogen (20 mL/min) and air (200 mL/min). Nitrogen (30 mL/min) was used as the make-up gas.

PLS-DA Elaboration



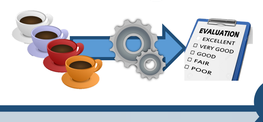
Identification

- Linear Retention Indices (I^Ts)
- ms-spectra
- Odour properties



PREDICTIVE MODELS — **TARGETS LIST** — **AROMA RECOMBINATION**

PLS modelling



Normalized Responses Calculation

ISTD:

5000ng Ethylcycloexanoate

Quantitation (SIDA*)

- Response Factors determination $R_f = \frac{m_{ana} * A_{Std}}{m_{Std} * A_{Ana}}$
- Analytes concentration determination $C_{Ana} = R_f \frac{m_{Std} * A_{Ana}}{g * A_{Std}}$

* Stable Isotopes Dilution Assay

Results & Discussion

Target selection is one of the key points of both methods, the sensometric approach uses chemometric tools (e.g. PLS-DA) to select discriminant variables from a complex data matrix while AEDA (Aroma Extract Dilution Analysis) is used in sensomics starting from the flavour extract.

Twenty-two discriminant odour active compounds were selected by GC-O, after comparison of the Neutro-Basic (NBV) and the Acid Fractions (AV) between the two samples. These compounds differ for at least two dilution steps (FD) between the two samples (Figure 1).

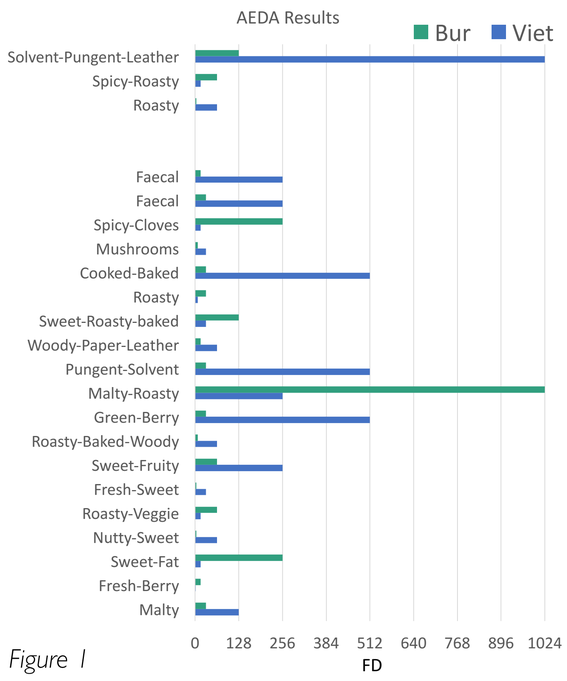


Figure 1

Target odorant peaks selected after the Comparative AEDA

Target peaks were identified using three different criteria: retention indices (I^Ts), mass spectra and odour quality; Table 1 reports the list of identified targets together with, odour description and FD values.

The consistency between the list of target compounds identified with the sensomic approach and those used to develop the *Woody* and *Fruity* prediction models with the sensometric approach has been investigated.

Compounds selected with sensometrics are reported in green; they are also part of the list used in the *Woody* and *Flowery* PLS prediction models. Compounds detected in sensometrics but not directly involved in the prediction models although showing high correlations (corr. coeff >0.7) with those used to develop the PLS models are in yellow.

QUALITATIVE COMPARISON

#	Odour	Viet	Bur	Compound
			AV	
3	Roasty	64	4	3,4 dimethyl-2,5-furandione
4	Spicy-Roasty	16	64	3-methylcyclopentane-1,2-dione
8	Solvent-Pungent-Leather	1024	128	3-methylphenol
			NBV	
	Malty	128	32	3-methylbutanal
3	Fresh-Berry	2	16	Ethylbutanoate
4	Sweet-Fat	16	256	2,3-Pentandione
8	Nutty-Sweet	64	4	4.Methylthiazole
9	Roasty-Veggie	16	64	2,5-dimethylpyrazine
10	Fresh-Sweet	32	4	1-Hydroxy-2-butanone
12	Sweet-Fruity	256	64	Pyrazine 2-ethyl-, 5-methyl + Pyrazine 2-ethyl-, 6-methyl
13	Brown-Cooked	512	-	2-Ethyl-3,5-dimethylpyrazine
14	Roasty-Baked-Woody	64	8	Furfurylthiol
16	Green-Berry	512	32	2,3 Diethylpyrazine
17	Malty-Roasty	256	1024	2,3-diethyl-5-methylpyrazine
18	Pungent-Solvent	512	32	Acethylfuran
20	Woody-Paper-Leather	64	16	Furfuryl Acetate
23	Sweet-Roasty-baked	32	128	1-Methylpyrrole-2-Carboxaldehyde
24	Roasty	8	32	2-Acethyl-1-methylpyrrole
25	Cooked-Baked	512	32	Furfuryl alcohol
29	Mushrooms	32	8	Difurfuryl ether
30	Spicy-Cloves	16	256	4-Ethyl-guaiacol
32	Faecal	256	32	Indole
33	Faecal	256	16	3-methyl-indole

Table 1

Identified targets on both Acid and Neutro-Basic fractions

Further experiments have been carried out to understand also from a quantitative viewpoint, the list of targets that can characterize the two samples.

Moreover, the true quantitation of three compounds (2,3-Pentandione, 4-Ethylguaiacole and Furfurylthiol) has been performed with SIDA (Stable Isotopes Dilution Assay) to investigate in depth the relative distribution of these target compounds in the two samples. True quantitation is a further tool to validate the sensometric results.

Table 2 summarizes data collected over the quantitative measured levels and approaches from the samples under study. i) data on target compounds identified by GC-O with the sensomic approach, ii) the AEDA results to the normalized responses obtained in GCxGC-TOF, iii) the quantitative data obtained by SIDA, and iv) the normalized responses obtained by the HS-SPME-GC-MS of the coffee powder.

QUANTITATIVE TRENDS COMPARISON

Odourant	Sensomic: cAEDA NBV FD vie	cAEDA NBV FD bur	Resp Norm Distillate NBV Vietnam	Resp Norm Distillate NBV Burundi	Quantification SIDA NBV Vietnam µ(g/L)	Quantification SIDA NBV Burundiµ(g/L)	Sensometric: Norm Resp HS- SPME NBV Vietnam	Norm Resp HS- SPME NBV Burundi
2,3-pentanedione	▼ 16	▲ 256	▼ 3.05	▲ 27.21	▼ 2.03	▲ 9.40	▼ 0.007	▲ 0.047
4-methylthiazole	▲ 64	▼ 4	▲ 4.08	▼ 2.63				
2,5-dimethylpyrazine	▼ 16	▲ 64	▼ 98.36	▲ 119.13			▲ 0.364	▼ 0.247
1-Hydroxy-2-butanone	▲ 32	▼ 4	▼ 1.36	▲ 8.83			▼ 0.003	▲ 0.017
Pyrazine 2-ethyl-, 5-methyl + Pyrazine ethyl-, 6-methyl	▲ 256	▼ 64	▲ 30.19	▼ 5.77			▲ 0.309	▼ 0.130
2-Ethyl-3,5-dimethylpyrazine	▲ 512	-	▲ 18.68	▼ 4.85			▲ 0.081	▼ 0.024
Furfuryl thiol	▲ 64	▼ 8	▼ 0.95	▲ 1.00	▲ 1.07	▼ 0.89	▲ 0.027	▼ 0.017
2,3-diethylpyrazine	▲ 128	▼ 32	▲ 2.40	▼ 0.58				
2,3-diethyl-5-methylpyrazine	▼ 256	▲ 1024	▲ 4.22	▼ 0.81				
Acethylfurane	▲ 512	▼ 32	▲ 27.83	▼ 21.94			▼ 0.112	▲ 0.318
Furfuryl Acetate	▲ 64	▼ 16	▼ 14.67	▲ 26.16			▼ 0.233	▲ 0.498
1-methylpyrrole-2-carboxyaldehyde	▼ 32	▲ 128	▼ 34.97	▲ 56.92			▼ 0.105	▲ 0.130
2-Acethyl-1-methylpyrrole	▼ 8	▲ 32	▼ 6.73	▲ 11.90				
Furfuryl alcohol	▲ 512	▼ 32	▼ 188.17	▲ 213.33			▼ 1.19	▲ 2.403
Difurfuryl ether	▲ 32	▼ 8	▼ 11.53	▲ 19.25			▼ 0.013	▲ 0.072
4-Ethyl-guaiacole	▼ 16	▲ 256	▲ 22.11	▼ 3.35	▲ 8.54	▼ 2.05	▲ 0.294	▼ 0.048
Indole	▲ 256	▼ 32	▲ 8.07	▼ 2.42				
3-methyl-indole	▲ 256	▼ 16	▲ 1.79	▼ 0.18				

Odourant	AV FD vie	AV FD bur	AV Vietnam	AV Burundi	AV Vietnamµ(g/L)	AV Burundiµ(g/L)	AV Vietnam	AV Burundi
3,4 dimethyl-2,5 furandione	▲ 64	▼ 4	▲ 8.78	▼ 8.12				
1,2-Cyclopentanedione, 3-methyl-	▼ 16	▲ 64	▼ 1.53	▲ 20.78				
3-methylphenol	▲ 1024	▼ 128	▼ 2.48	▲ 2.80				

Table 2

Comparison of quantitative data obtained with different strategies: AEDA, GCxGC-TOF normalized responses, SIDA quantitation, HS-SPME-GC-MS normalized responses.

Red and Green arrows help to understand trends of data; green arrow indicate the highest values compared to those of the other sample under study.

This table aims to compare the compounds' trends between samples characterized by different sensory note with the two approaches, and not to compare their absolute values.

A good consistency between normalized data obtained from the HS-SPME and quantification of the SAFE distillate can be observed. These data suggest that the overall information on the samples is comparable although they derive from two highly different analytical procedure.

An example of this consistency is 2,3-Pentandione: according to chemometric elaboration it has been found as a compound overexpressed in "*Fruity*" coffees by the HS-SPME normalized responses, for instance it is higher in Burundi (*Flowery)* compared to Vietnam (*Woody)* samples. The normalized responses on the distillate obtained with SIDA confirm this behaviour.

Other compounds (e.g. 4-Ethylguaiacole) show AEDA does not result in agreement with the instrumental data independently of the methods. This unexpected behaviour is probably due to the low performance of the operator with comparative AEDA (cAEDA) that requires intensive training and long experience.

Conclusions

The aim of this work was to validate the sensometric approach in the chemical description of the sensory characteristic aroma notes of coffee samples by investigating how data collected with this high throughput approach behave compared to those obtained with the sensomic approach, assumed as reference standard for molecular sensory science.

The results from the two analytical approaches show a good consistency; a significant number of the compounds identified with sensomics were also in the set of targets used to develop the chemometric prediction models (Note Related Compounds); moreover, other compounds not directly involved in the reported models showed a high correlation with them (table 1).

In addition, from a quantitative viewpoint, a good correspondence has been found between data acquired in sensomics (cAEDA, normalized responses and absolute quantitation) and data from sensometrics (HS-SPME-GC-MS normalize responses). This good agreement suggests that, despite the dramatic difference (sample preparation, volatiles extraction dynamics, target compounds selection criteria etc…) between the two methods, the overall information extracted of the samples is the same.

The good coherence of the results obtained from sensomics cross-validate those obtained with the sensometric. The latter approach affords to analyse a high number of samples, fundamental to correlate chemometrically sensory data to the chemical odor code of the coffee aroma notes.