AN OMIC APPROACH TO REVEAL THE CHEMISTRY BEHIND THE COFFEE FLAVOR EVOLUTION OVER TIME

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An omic approach to reveal the chemistry behind the coffee flavor evolution over time

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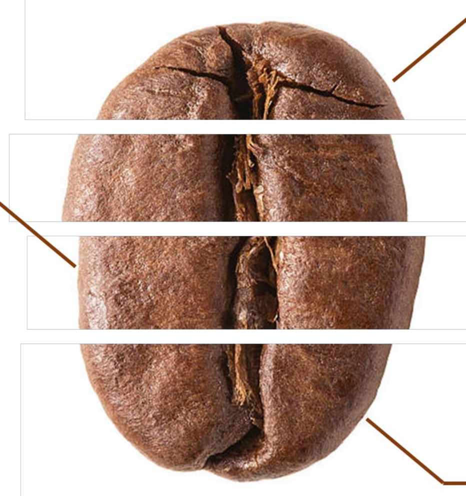
Flavor perception is a multimodal assessment of the interaction between different and complex stimuli and the (bio)chemical and physiological responses. This work deals with the investigation of a flavoromics approach to study the chemistry behind the changes in coffee flavor during storage. The chemical data of the investigated coffee samples were obtained by analysing both volatile and non-volatile profiles (i.e. lipids and phenolic fractions including alkaloids) using different analytical measurements and instruments and related them with the sensory evaluation.

Introduction



The smell of coffee, responsible for a palette of sensory features. Volatiles (VOCs) released and perceived orthonasally and retronasally.

Light or heavy perception of a beverage's texture and mouthfeel on the tongue.

The sensation of sourness, astringency, bitterness and acidity

The pleasure related to drink a good cup of coffee is due to its unique sensory **quality**. This is due to the potent **taste** and **aroma** given off by coffee during the roasting process. The balance of the these two chemical senses constitutes the most important determinant of what is defined as **flavour** perception [2,5-7].
Due to coffee sensory properties and its important financial value, it is essential to preserve and maintain its quality, especially during storage [1-4].

INTRINSICS	EXTRINSICS	
Geographical	Moisture	speed-up the kinetic of degradative reactions
Species	Oxigen	determine a quality deterioration of coffee
Agricultural practices	Temperature	promote the loss of volatiles
Post-harvest processing	Packaging	physical and chemical changes pack dependent
Roasting		
Extraction		

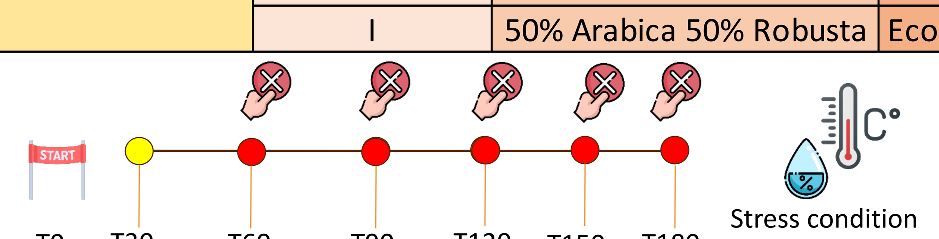
Impacting on the quality of coffee flavour

The quality of coffee flavor is a key step of the coffee production, since it determines the **consumer's acceptability** and delineate the **shelf-life** of the product. Nowadays the estimation is made by using cupping protocols, but this kind of procedure is time-consuming, requiring panel training and aligned professional panelists and often it suffers of a too subjective evaluation. Due to the ever-increasing demand of coffee, there is a need for analytical techniques suitable for routine control (QC). For these reasons, nowadays, we are looking for potential alignment with the analytical instrumental measurements, capable to sample, separate, identify and extract chemical information in a complex food matrix [2,8,9]. In particular, gas chromatography coupled with **mass spectrometry** is used in **foodomics for the quality control**, authentication and characterization of the products of interest.

This work aims to study the chemical changes of coffee flavour investigating the contemporary evolution over time of the coffee volatilome and of non-volatile fraction.

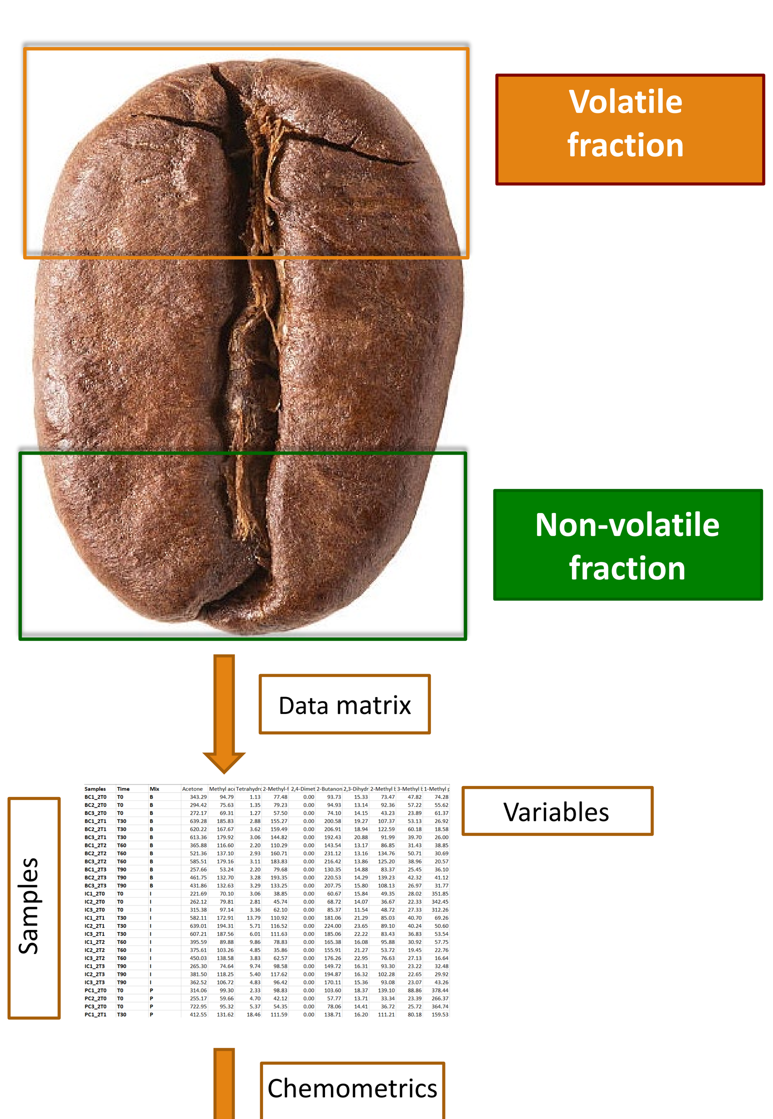
Methods

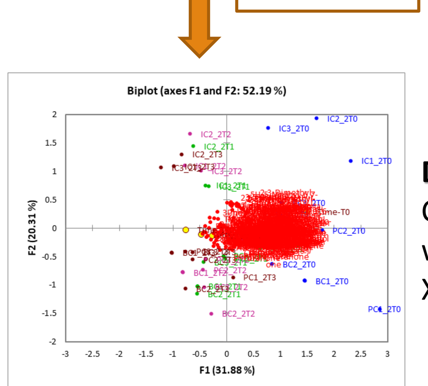
Coffee Type	Blends	Species	Packs
3 lots each			
Capsules available for Espresso coffee	B	100% Arabica	Eco, standard*
	P	100% Arabica	Eco, standard*
	I	50% Arabica 50% Robusta	Eco, standard*



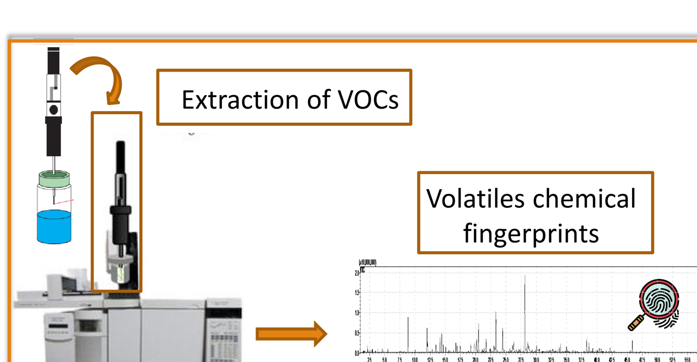
*Standard: multilayer foil with aluminium barrier

Sensorially not good, at T60 for B Eco caps; T90 for P and I Eco caps; T150 for P and B Standard caps and T180 for I Standard caps.

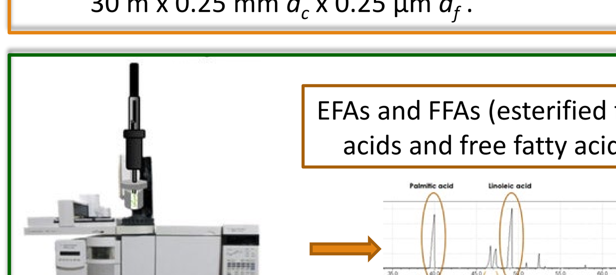




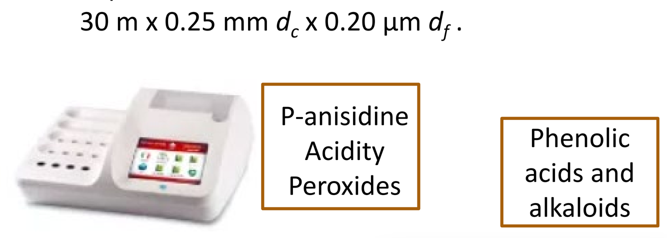
Data elaboration
Chemometric analysis was performed with XLSTAT® (Addinsoft).



HS-SPME-GC-MS (PDMS/DVB) using a Combi-PAL AOC 5000 assembled on-line in a Shimadzu QP2010 GC-MS system, capillary column SGE SolGelwax 30 m x 0.25 mm d_c x 0.25 µm d_f.



GC-MS Agilent 6890 GC-MS system, capillary column Supelco SLB™-IL 76 30 m x 0.25 mm d_c x 0.20 µm d_f.



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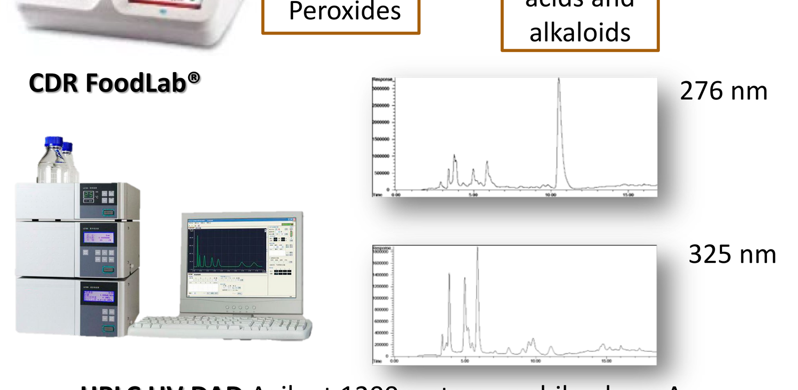
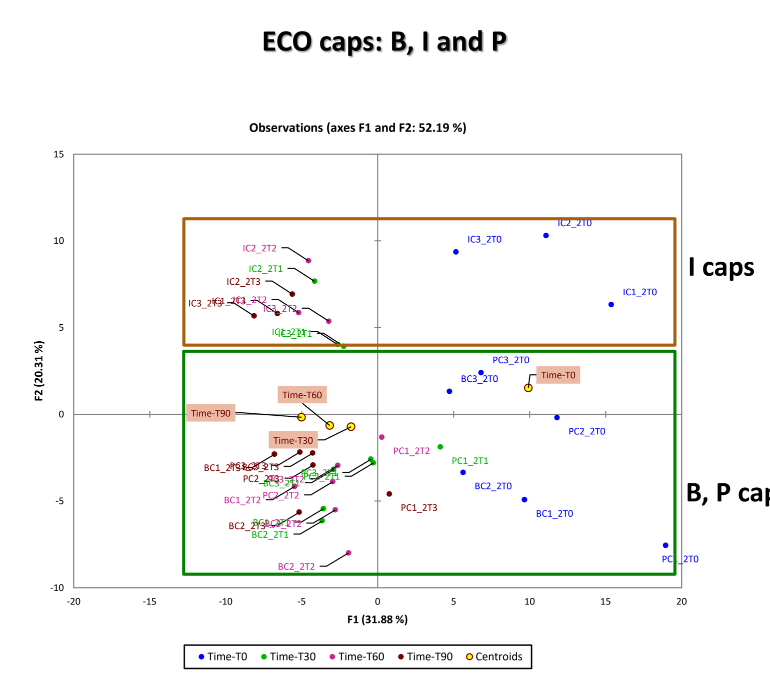


HPLC UV DAD Agilent 1200 system, mobile phase A: water/formic acid (999: 1, v/v) and B: acetonitrile/formic acid (999: 1, v/v). Column Platinum EPS C18 reversed phase (250 x 4.6 mm, 80 Å, 5 µm), (Alltech, Deerfield).

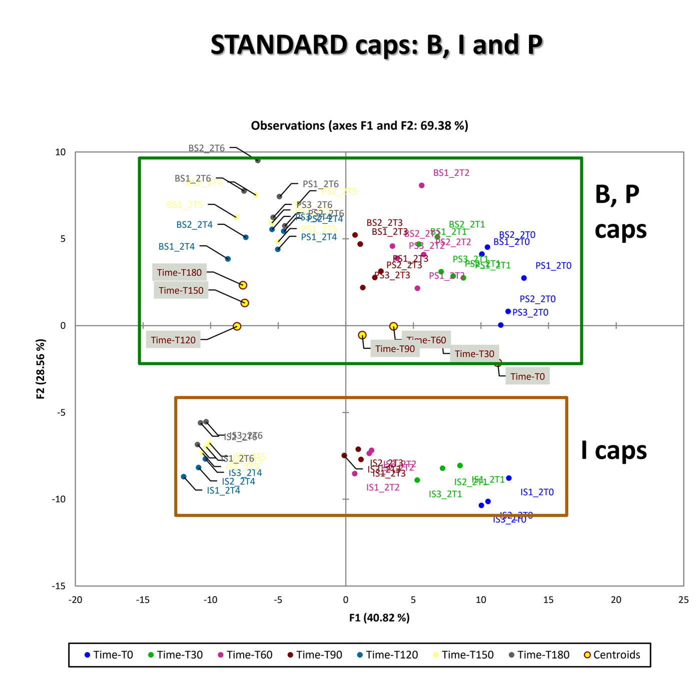
Results

Aroma

GC-MS data set were explored by **unsupervised multivariate analysis** to investigate diagnostic patterns.



PCA (Principal component analysis) score plots on **Eco caps**

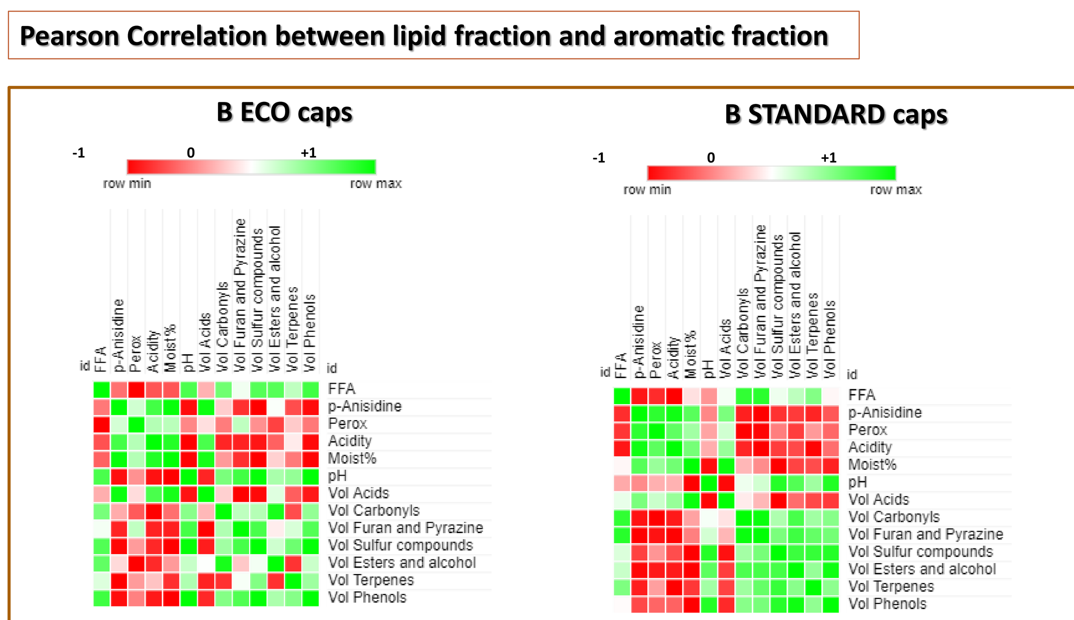


PCA (Principal component analysis) score plots on **Standard caps**

The analytical data of the normalized responses for the Eco and standard capsules report a spread, along the F1 component from right to left, between the reference (T0) and the samples aged from T30:
In the **Eco caps**, at the initial monitoring time (T0), it is possible to notice a heterogeneous distribution, subsequently, however, from the time T30 the samples tend to cluster.
In **standard caps**, samples result more homogeneous although a tendency to stand out among the starting times (from T0 to T90) and aged samples (from T120 to T180).
PCA of the Eco and standard caps, highlighted discrimination in terms of blends. I samples (50% of Robusta and 50% of Arabica), in brown, are separated from the other blends, P and B, in green, that are 100% Arabica.

Taste

Pearson Correlation between lipid fraction and aromatic fraction



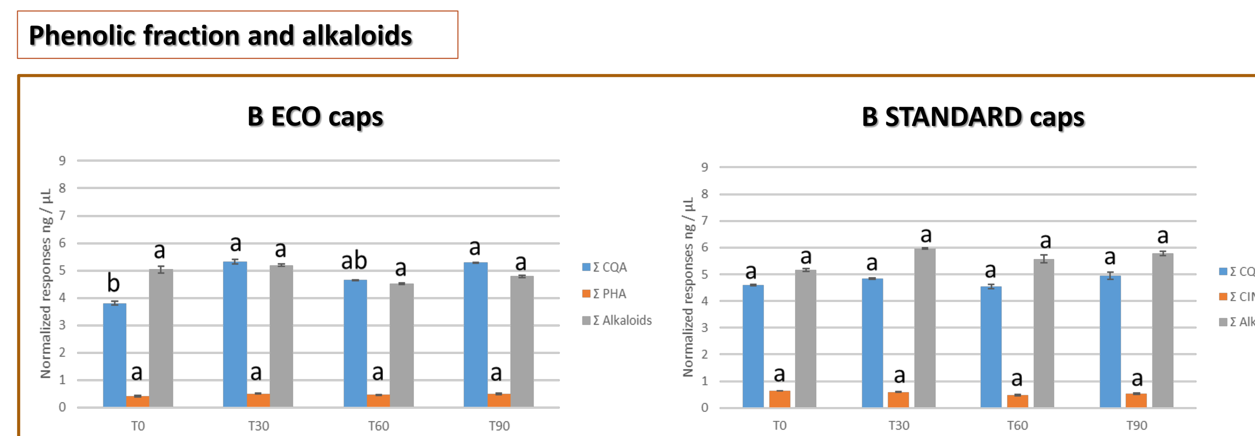
Pearson correlations between: Peroxides value, p-Anisidine, the sum of the free fatty acids (FFAs), acidity, moisture %, pH and the principal classes of volatiles compounds. Data were pre-processed by autoscaling.

Trend from T0 to T90 for the Eco caps and from T0 to T150 for Standard caps for the moisture % and pH for B caps.

For **B Eco caps** is reported the Pearson correlation between the different measures that show an inverse correlation (in red) between FFAs with p-Anisidine, Peroxides value, volatiles acids and acidity, meaning that the degradation of FFAs, for oxidative reactions, consequently to hydroleses of TAGs (data not shown), is related to an increase in acidity and a contemporary formation of oxidative secondary products.

This behaviour highlights that in the Eco packaging, some chemical transformations might have affected the FFAs content during the storage period, due to the packaging, which promotes easier permeation to moisture in particular. The increase of the moisture content in the capsules and a decrease of the pH of the brew can be the responsible to produce an environment that triggers hydrolysis and speeding-up oxidative reactions. In **B standard caps**, the environment is less favourable to degradation as shown in the correlation map in which, FFAs decay (data not shown) is softer and the correlation with volatile acids, pH and moisture % is null or negligible.

Phenolic fraction and alkaloids



Comparison between Eco and Standard caps in equal time. Variation in time of the sum of CQAs that include the esterified chlorogenic acids (3-CQA; 4-CQA and 5-CQA) and di-chlorogenic acids (3,4-di-CQA; 3,5-di-CQA; 4,5-di-CQA); the sum of the CINN which group all the non-esterified hydroxycinnamic acids (ferulic, isoferulic, caffeic and p-coumaric acids) plus quinic acid and the sum of ALK that group trigonelline and caffeine in the time. Same letters correspond to no variation (p value >0.05).

In the phenolic fraction, composed by chlorogenic acids (CQAs), hydroxycinnamic acids (CINN) and alkaloids, the compounds do not vary significantly (p>0.05). The fraction is very stable during time independently to the packaging.

Conclusions

These results attempt to comprehensively explore the chemical changes that occur during storage of different commercial coffee blends when packed in different packaging: standard and eco-friendly. The aroma constitutes the dominant fraction to explain what happens in aged coffee, despite the various types of volatile chemical ingredients and their modest amount, as the result of the final expression of different chemical modifications occurring also in the other fraction investigated. Among the volatiles, in fact, chemical markers that correlate with the sensory aspects describing the coffee aging have been identified. Chlorogenic acids and alkaloids are the non-volatile groups that do not change substantially with storage over time, while lipids have the greatest effects on aged coffee and the fatty acid fraction undergoes the most substantial age-related oxidative reactions. From these studies emerges, also, that moisture is the main responsible for the compositional change of packed coffee quality during storage. Its increase associated with a pH decrease creates a favourable environment to speeding up of degradation reactions. In terms of packaging, standard capsules offer the longer shelf life of coffee, but at a significant environmental cost. On the other hand, Eco-capsules are a good alternative to reduce the environmental impact of single-serve coffee consumption while keeping the sensory quality of the powder, albeit with a shorter shelf life.

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