Packaging and coffee aroma: a kinetic evolution

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Aim and Scope

Coffee is a complex and "evolutive" food whose sensory quality is affected by endogen chemical reactions involving the characteristic reactive aroma components mostly influenced by pH, water activity and the external effects of temperatures, storage and packaging.

Packaging has an important influence in coffee processing, storage and marketing. Controls of possible interactions between coffee products and packaging are therefore necessary because of its possible influence on the sensory quality of the final product over time [1-2].

The shelf-life is defined in function of a tolerable decrease of the coffee quality and determines the time limit within which the progressive reactive events produce not perceivable modifications of its sensory properties and/or it is still acceptable in terms of safety of use [3-4]. Its definition is product-depending and it is related to specific quality markers that are able to correctly describe the sensory decay over time.

This approach must be based on the direct measure of product shelf-life under the conventional conditions of storage of the product(s) and can easily be developed for perishable foods in which the decay occurs quickly, but it is more complex for a stable food such as roasted coffee powder that has longer shelf-life. In this case, the shelf-life is artificially speeded up by acting on factors that may influence the quality depletion (Fig1).

This study aims to define the evolution of coffee aroma stored under different conditions (stressed and conventional) as a function of packaging through an untargeted aroma fingerprinting and targeted profiling approaches by a HS-SPME-GC-MS method. In particular, this project aims 1) to propose a model of the kinetic evolution of aroma active compounds, and 2) to look at the chemical markers of coffee degradation that could be used in combination with sensory data to define a prediction model of coffee shelf-life.

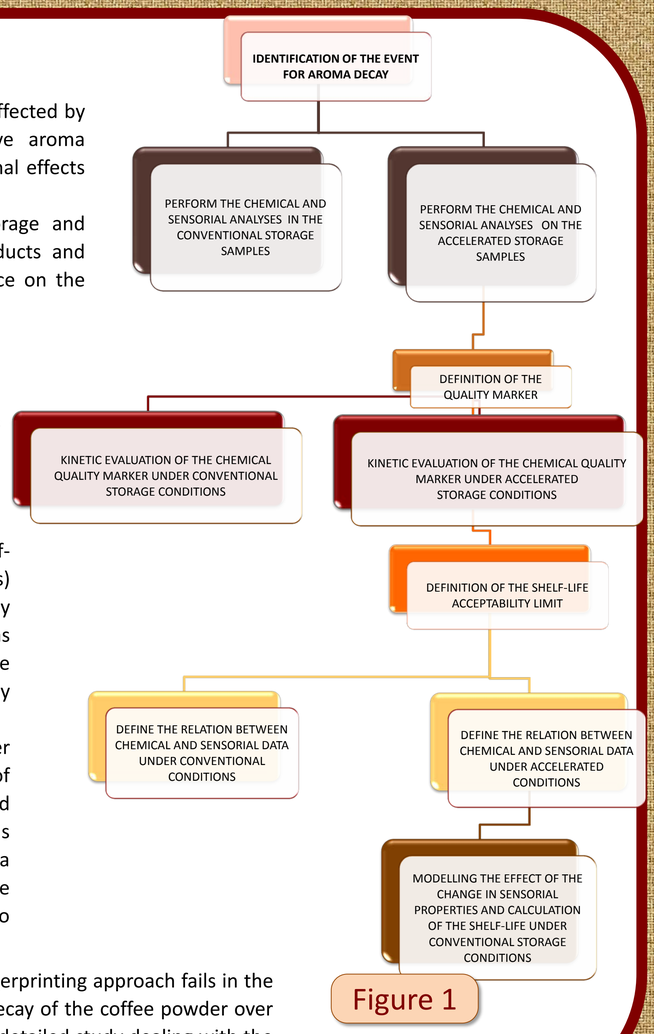


Figure 1

Preliminary analytical results show that the untargeted fingerprinting approach fails in the definition of a kinetic model that correctly describes the decay of the coffee powder over time due to the complexity of the coffee aroma and that a detailed study dealing with the changing of the aroma profile must be done.

Materials & Methods

Coffee Samples

Roasted coffee samples (50/50 Arabica-Robusta) from three different production batches were stored in two different types of packaging (A, B*eco)*. Samples were analyzed in two replicates over a period of 180 days. A total of 100 samples has been analyzed over this period.

After roasting samples were immediately ground, packed and stored at room temperature (conventional storage conditions Temp.: 25°C) and under stress storage conditions (Temp.: 40°C, 90% of relative humidity); analyses were carried out after 0, 7, 14, 30, 60, 120 and 180 days of storage.

SPME devices and GC-MS conditions

SPME fibres coated with 65-µm thick polydimethylsiloxane/divinylbenzene (PDMS/DVB) were purchased from Supelco (Bellefonte U.S.A). Fibres were conditioned according to Supelco instruction in the GC Injection port.

Analyses were run on a GCMS-QP2010 system (Shimadzu - Milano, Italia) equipped with an autosampler combi-PAL AOC 5000 Autoinjector (Shimadzu - Milano, Italia).

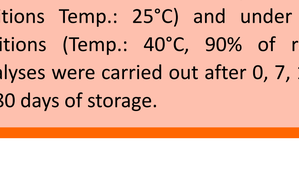
The separation column was a SGE SolGelwax (100% polyethylene glycol) 30 m L x 0.25 mm d*c* x 0.25 µm d*f* (SGE- Melbourne, Australia). Helium (2mL/min) was used as carrier gas. The oven temperature was programmed as follow: 40°C (1 min.) - 3°C/min. - 200°C -10°C/min. – 250°C (5 min.). The injector was fitted with a liner for SPME analyses at 230°C in split mode (split ratio: 5/1).

The MS spectrometer was set as follow: ionization mode: electron impact, ionization energy: 70eV, m/z interval 35-350 m/z, transfer line temperature: 250°C, ion source temperature: 200°C.

SPME procedure for sampling and injection

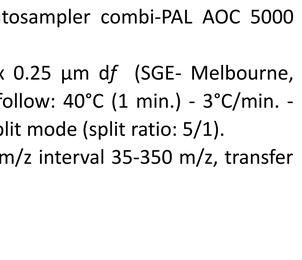
1.5g of roasted coffee powder was transferred to a septum-sealed glass vial (20mL). The Internal Standard loading procedure onto the SPME fibre was as follows: the SPME device was exposed to 5 ul of ISTD (C13) standard solution (1.0 g/L) in dibutyl phthalate placed in a 20 mL sealed vial at 50 °C for 20 min [5]. The fibre was then exposed to the matrix headspace at 50 °C for another 40 min. After sampling, the SPME device was directly introduced into the GC injector to recover analytes by thermal desorption for 10 min at 230 °C.

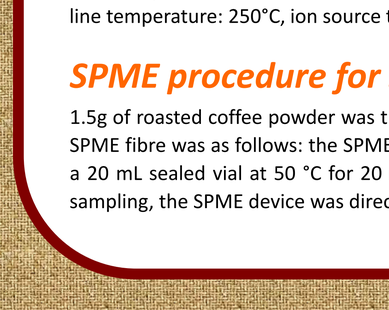
Results and Discussion



Coffee aroma evolution over time to predict the coffee shelf-life was first studied by applying a metabolomics approach. Metabolomics is a comprehensive analytical approach to identify and quantify coffee aroma components. In metabolomics different analytical strategies are used to determine the chemical composition of a given matrix. In this case we used an "*untargeted fingerprinting*" and a "*targeted metabolite profiling*" strategies.

Untargeted fingerprinting is useful for a high-throughput analysis in which extensive metabolite identification and quantitation are generally not used. Appropriate statistical data processing is mandatory to highlight differences between samples by comparing patterns (or "*fingerprints*").



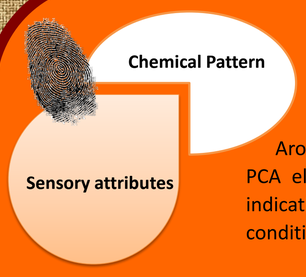


Targeted metabolite profiling compares samples on the basis of the quali-quantitative distribution of a selected number of known metabolites.

In this work an untargeted fingerprinting approach was first applied to define a robust statistical model to describe the kinetic evolution of the coffee aroma under stressed condition in different packaging to define the shelf-life of coffee in conventional storage condition. This strategy has proven to be successful within samples belonging the same packaging but not when used for different packaging.

Due to the complexity of the coffee aroma and the failure of the untargeted fingerprinting approach, a detailed study of the aroma evolution over time was then carried out looking for specific components related to time as quality markers of coffee aging through a metabolite profiling strategy. Details are given in the dedicated section.

Untargeted fingerprinting strategy



Aroma fingerprinting investigation of different packaging and storage conditions over time run by PCA elaboration shows a clear relationships between storage conditions and sample distribution indicating a change of the volatile fraction composition. In particular, under conventional storage conditions, the time effect over 180 days is evident and linear regardless of the packaging (Fig 2a).

On the other hand, under stressed conditions, samples are unevenly scattered on the plane highlighting a packaging-related aging that affects the aroma quality of the coffee (Fig. 2b). The relationships between the variation of the aroma fingerprinting over time have to be monitored to define a kinetic model. This evaluation has been done by applying a PLS algorithm in agreement with scheme 1.

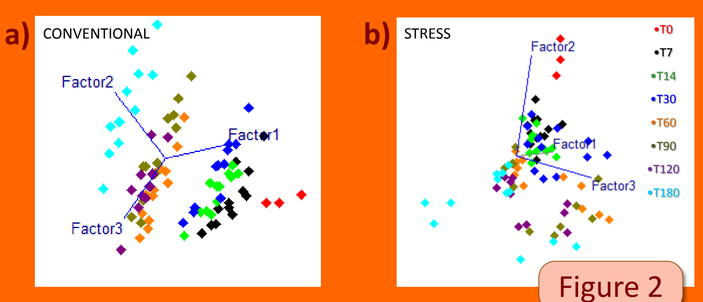
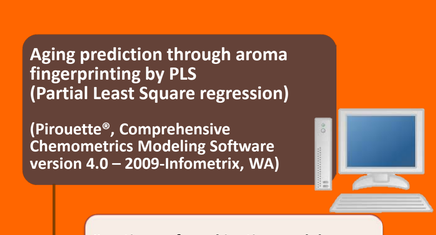


Figure 2

Figure 2 *a) PCA Scores in conventional and b) under stressed storage conditions of the roasted coffee aroma fingerprinting analyzed over 180 days. Categorical variable: time. Pre-process: autoscale, 3PCs explained variance: 84.8% a), 79.2% b). Legend: Red: T0, black: T7, light green: T14, blue: T30, orange: T60, dark green: T90, purple: T120, heavenly: T180.*



Scheme 1

A kinetic modeling has first been developed on a training set of samples and its ability to predict correctly the aging of the samples has been checked through a test set of samples. PLS applied to standard packaging A resulted in a good correlation between aroma changes and time under conventional or stressed storage conditions (Fig 3a), although the kinetic model fails with the prediction of coffee aging in particular when applied with packaging B_{eco} under stressed conditions (Fig 3b). Under the latter conditions, a time prediction longer than the real one (180 days) was expected because aging was affected of a further factor "x" due to stress. As expected, the impact of packaging on coffee aroma is more evident under stress because of the different packaging material permeability (in & out). Although this approach is rather fast, automatic and easy to extend, it has been effective only within the same packaging (especially in conventional conditions) and cannot be extended to all packaging.

Figure 3

a)

CONV.

AC test set

	Meas Y	Predi Y
L2T0	1	-7
L1T7AC	7	-5
L3T7AC	7	13
L3T14AC	14	19
L1T30AC	28	32
L2T60AC	61	58
L1T90AC	96	97
L3T120AC	125	115
L2T180AC	180	187

STRESS.

AS

	Meas Y	Predi Y
L1T7AS	7	1
L3T14AS	14	14
L1T30AS	28	35
L2T60AS	61	65
L1T90AS	96	98
L3T120AS	125	110
L2T180AS	180	178

b)

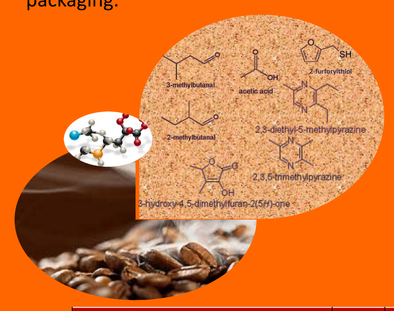
B_{eco}C

	Meas Y	Predi Y
L2T7BC	7	-10
L1T14BC	14	-10
L3T30BC	28	-18
L2T60BC	61	-10
L3T90BC	96	61
L3T120BC	125	75
L2T180BC	180	197

B_{eco}S

	Meas Y	Predi Y
L2T7BS	7	-57
L2T14BS	14	-56
L3T30BS	28	-90
L2T60BS	61	-25
L3T60BS	61	-1
L3T90BS	96	-159
L2T120BS	125	-129
L2T180BS	180	-399

Figure 3 *Prediction of coffee aging on a test set of packaging A and B_{eco} under conventional and stressed storage conditions. A & B_{eco}: packaging, C: Conventional, S: stress.*



Targeted metabolites profiling strategy

Table 1

Compounds	A	B_{eco}
Methanethiol	-0.2	-0.56
Acetaldehyde	-0.87	-0.71
Furan	0.82	0.92
Acetone	-0.16	0.32
Methyl acetate	0.89	0.95
Furan, 2-methyl-	0.89	0.84
2-Butanone	0.89	0.99
Butanal, 2-methyl-	0.7	0.63
Butanal, 3-methyl-	0.49	0.49
Furan, 2,5-dimethyl-	0.65	-0.09
2,3-Butanedione	-0.6	-0.65
2,3-Pentanedione	-0.4	-0.34
2-Vinylfuran	-0.26	-0.31
Hexanal	0.85	0.58
2,3-Hexanedione	-0.87	-0.86
1H-Pyrrole, 1-methyl-	0.93	0.91
2-Vinyl-5-methylfuran	0.24	-0.25
Pyridine	0.89	0.95
Pyrazine	0.93	0.96
Pyrazine, methyl-	-0.84	-0.55
2-Butanone, 3-hydroxy-	0.18	0.69
2-Propanone, 1-hydroxy-	0.91	0.98
Pyrazine, 2,5-dimethyl-	-0.28	0.71
Pyrazine, 2,6-dimethyl-	-0.44	0.68
Pyrazine, ethyl-	-0.25	0.49
Pyrazine, 2,3-dimethyl-	-0.1	0.36
1-Hydroxy-2-butanone	0.65	0.77
Pyridine, 3-ethyl-	-0.4	0.22
Pyrazine, 2-ethyl-6-methyl-	0.83	0.92
Pyrazine, 2-ethyl-5-methyl-	0.82	0.9
Pyrazine, 2-ethyl-3-methyl- +Pyrazyne, trimethyl	0.8	0.9
2-N-PROPYLPYRAZINE	-0.46	-0.17
2-Furanmethanethiol	-0.43	-0.68
2-Ethyl-3,6-dimethylpyrazine	-0.53	0.16
Acetic acid	0.85	0.95
Furfural	-0.49	-0.21
Acetoxyacetone	-0.93	-0.91
Acetylfuran	-0.87	-0.78
Furfuryl acetate	0.78	0.88
5 METHYL FURFURAL	-0.33	0.47
1H-Pyrrole-2-carboxaldehyde, 1-methyl-	-0.64	-0.53
Furfuryl alcohol	-0.72	-0.08
furfuryl pyrrole	0.69	0.88
Guaiacol	0.06	0.45
2-Acetylpyrrole	-0.93	-0.76
1H-Pyrrole-2-carboxaldehyde	-0.43	-0.36
Guaiacol <4-ethyl->	-0.56	-0.11
Guaiacol <4-vinyl->	-0.94	-0.81

The aroma profiling approach allows us to follow the kinetics of several markers over time.

The different permeability of packaging under stressed condition influences the composition of coffee aroma over time and, as a consequence, it's aging. Partial Least Squares-Discriminant Analysis (PLS-DA) has here afforded to create a classification model within a defined category (packaging) on the basis of the aroma compounds. This model has made possible to assess whether the samples were classified in function of aging within each package and to determine which compounds better characterized the packaging in terms of aging.

Table 1 shows the variables better time-correlated under stressed storage conditions with different packaging. The variables increasing linearly as a function of time are in red, and in green those that decrease. As can be noted compounds such as 2-butanone, hexanal, pyridine are always positively connected to time, albeit to a different extent depending on packaging, the same is true for acetoxyacetone or 2,3-hexanedione. These results highlight different behaviors of some compounds depending on packaging, e.g. 2,5 and 2,6-dimethylpyrizines, 5-methylfurfural.

Stress conditions do not form new compounds related to the aging of coffee but rather strengthen their change in comparison to the conventional storage conditions.

Table 1 *PLS-DA correlation coefficients related to the aging stressed storage conditions as a function of the type of packaging.*

Conclusions

Aging markers of coffee have already been investigated, but above all defining markers of freshness because the time delay considered was too short for a product with such a long shelf-life [6-8]. Moreover, these studies mainly reported results not involving shelf-life data and investigated food kinetics deterioration. Shelf life assessment requires the definition of a criterion to establish the end of the life of a product, which involves not only the product but also its packaging. These preliminary results show that the evolution of aroma compounds during storage of the roasted coffee powder is different and highly related to the packaging considered.

The complex phenomena involved are difficult to be correctly described through a fingerprinting approach, but they require in depth studies on specific marker(s) in order to define a kinetic model describing coffee aging under conventional storage conditions, in particular when different packaging are considered. The shelf-life of the roasted coffee powder can be defined by correlating these results to the sensory evaluation data to define comparative product acceptability limit.

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