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. Design and development of new packaging fitting environmental sustainability have nowadays become almost compulsory. 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.

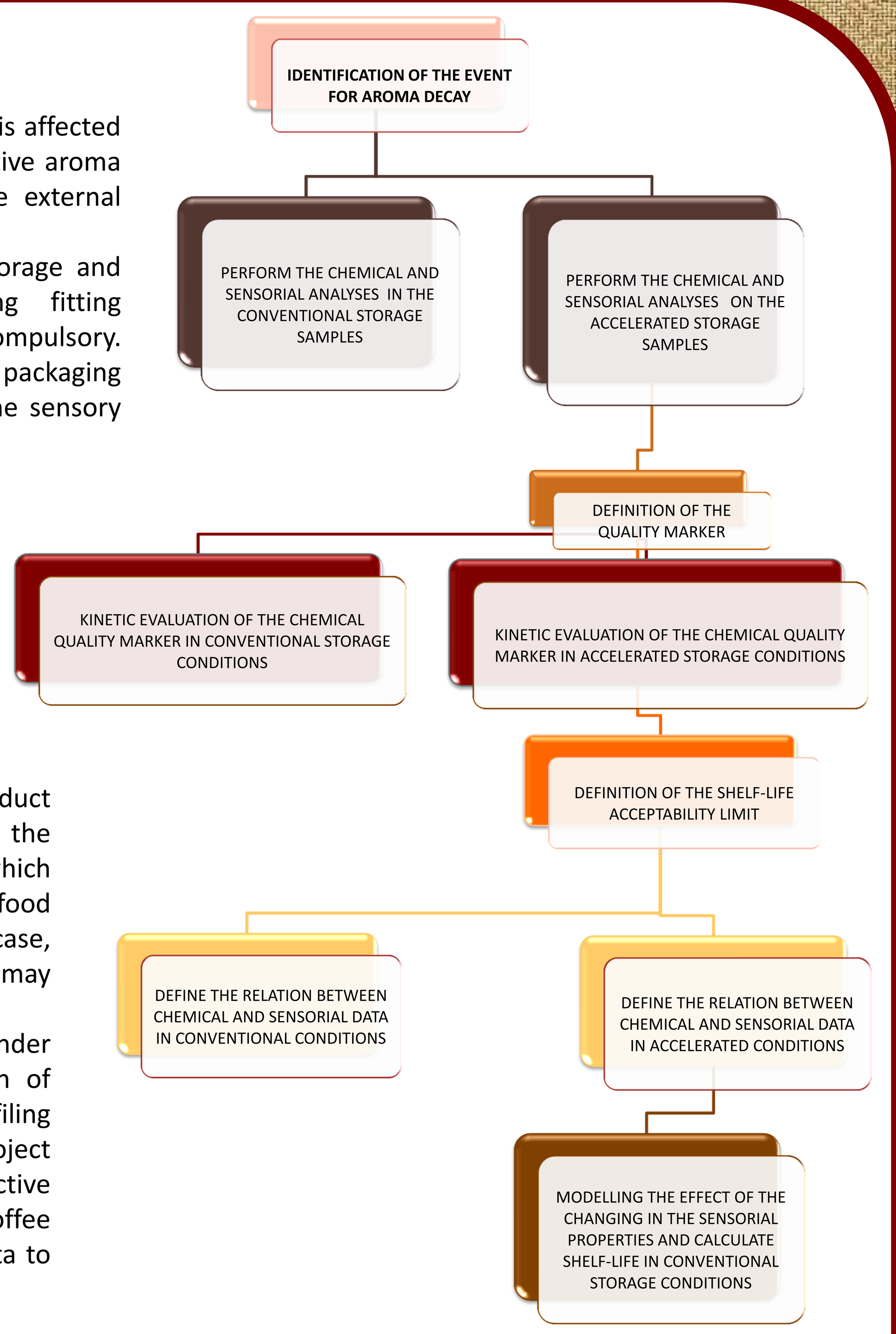


Figure 1

This methodology 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 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.

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 and stored with four types of packaging (A, B_{eco}, C_{eco}, D_{eco}) were analyzed in two replicates over a period of 180 days. A total of 195 samples have been analyzed over this period.

After roasting samples were immediately packed in the investigated packaging materials 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 SPME data Sheet from Supelco 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 used was a SGE SolGelwax (100% polyethylene glycol) 30 m L x 0.25 mm dc x 0.25 µm *df* (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 suitable for SPME analyses and was set 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]. After ISTD loading, the fibre was exposed to the matrix headspace at 50 °C for a further 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

Aroma fingerprinting exploration of the different packaging and storage conditions over time through PCA elaboration shows a clear relationships between storage conditions and the sample distribution indicating a modification in the volatile fraction composition. In particular, under the conventional storage condition, the time effect over the 180 days considered is evident and linear regardless of the type of packaging (Fig 2a). On the other hand, under stressed conditions, samples are unevenly scattered on the plan highlighting a packaging-related aging that affect the aroma quality of the coffee (Fig. 2b).

The relationships between the variation of the aroma fingerprinting over time have to be monitored in order to define a kinetic model. This evaluation has been done through a PLS algorithm following the scheme 1.

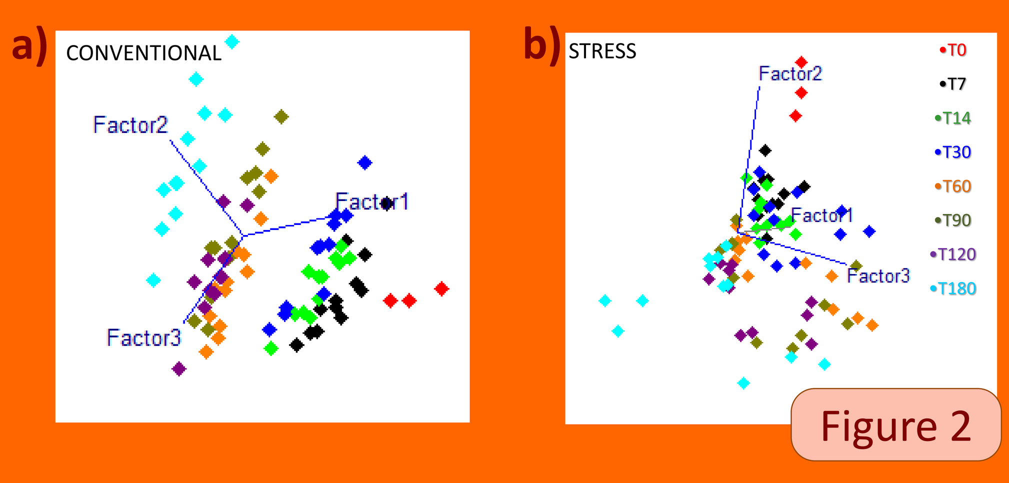
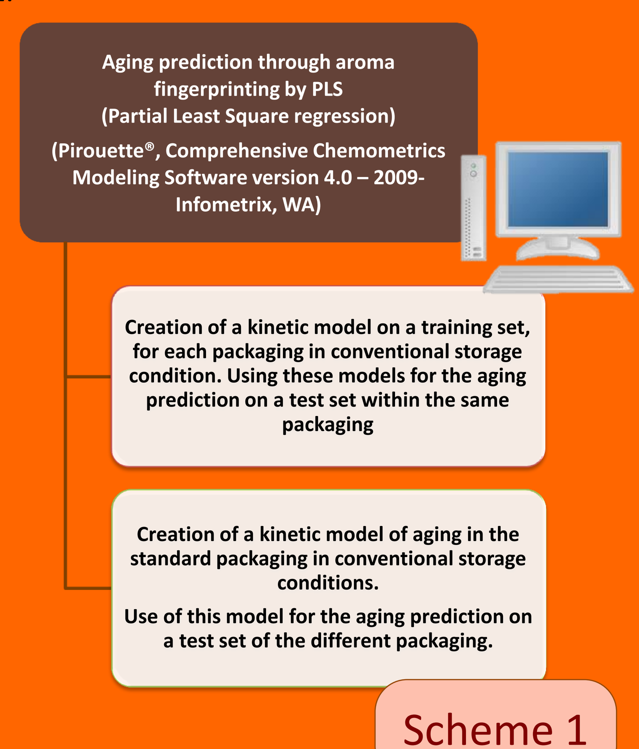


Figure 2

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 carried out 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 within each packaging. PLS results shows a good fitting between aroma changes and time with standard packaging A even with 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} (and to a lesser extent in C_{eco} and D_{eco}) under stressed conditions (Fig 3b). Under these conditions a predicted time at least equal to or greater than the real one (180 days) was expected because of their aging of a further factor of "x" due to the stressed conditions. As expected the impact of packaging on the coffee aroma is more evident under stressed conditions and it is justified by the different permeability (in & out). The visualization of the kinetic evolution of the coffee aroma in the different packaging explains the breakdown of the chemiometric models (Fig 4). Although this approach is rather fast, automatic and easy to export, it has proven to be effective only within the same packaging 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
L1T90BC	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.

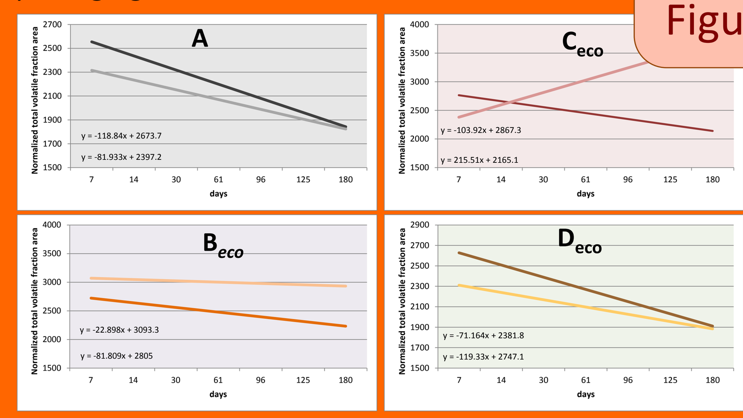


Figure 4

Figure 4 Time evolution comparison of the coffee aroma fingerprinting in conventional and stressed storage conditions in different packaging.

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

The different permeability of packaging 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 in terms of 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

Compounds	A	B_{eco}	C_{eco}	D_{eco}
Methanethiol	-0.2	-0.56	-0.18	-
Acetaldehyde	-0.87	-0.71	-0.62	-0.73
Furan	0.82	0.92	0.98	0.48
Acetone	-0.16	0.32	0.95	-0.44
Methyl acetate	0.89	0.95	0.99	0.71
Furan, 2-methyl-	0.89	0.84	0.94	0.39
2-Butanone	0.89	0.99	0.99	0.88
Butanal, 2-methyl-	0.7	0.63	0.92	-0.17
Butanal, 3-methyl-	0.49	0.49	0.58	-0.22
Furan, 2,5-dimethyl-	0.65	-0.09	0.88	0.19
2,3-Butanedione	-0.6	-0.65	-0.59	-0.87
2,3-Pentanedione	-0.4	-0.34	-0.75	-0.87
2-Vinylfuran	-0.26	-0.31	0.09	-0.72
Hexanal	0.85	0.58	0.31	0.93
2,3-Hexanedione	-0.87	-0.86	-0.9	-0.94
1H-Pyrrole, 1-methyl-	0.93	0.91	0.68	0.19
2-Vinyl-5-methylfuran	0.24	-0.25	-0.21	-0.35
Pyridine	0.89	0.95	0.95	0.91
Pyrazine	0.93	0.96	0.98	0.86
Pyrazine, methyl-	-0.84	-0.55	0.96	-0.71
2-Butanone, 3-hydroxy-	0.18	0.69	0.92	-0.16
2-Propanone, 1-hydroxy-	0.91	0.98	0.95	0.87
Pyrazine, 2,5-dimethyl-	-0.28	0.71	0.96	0.1
Pyrazine, 2,6-dimethyl-	-0.44	0.68	0.96	0.08
Pyrazine, ethyl-	-0.25	0.49	0.95	0.05
Pyrazine, 2,3-dimethyl-	-0.1	0.36	0.88	0.11
1-Hydroxy-2-butanone	0.65	0.77	0.85	-0.12
Pyridine, 3-ethyl-	-0.4	0.22	0.21	-0.45
Pyrazine, 2-ethyl-6-methyl-	0.83	0.92	0.98	0.91
Pyrazine, 2-ethyl-5-methyl-	0.82	0.9	0.97	0.9
Pyrazine, 2-ethyl-3-methyl- + Pyrazyne, trimethyl	0.8	0.9	0.97	0.89
2-N-PROPYLPYRAZINE	-0.46	-0.17	0.72	-0.27
2-Furanmethanethiol	-0.43	-0.68	-0.4	-
2-Ethyl-3,6-dimethylpyrazine	-0.53	0.16	-0.21	-0.56
Acetic acid	0.85	0.95	0.97	0.82
Furfural	-0.49	-0.21	-0.9	0.66
Acetoxyacetone	-0.93	-0.91	-0.78	-0.9
Acetylfuran	-0.87	-0.78	0.98	-0.86
Furfuryl acetate	0.78	0.88	0.98	0.87
5 METHYL FURFURAL	-0.33	0.47	0.87	-0.05
1H-Pyrrole-2-carboxaldehyde, 1-methyl-	-0.64	-0.53	0.84	-0.59
Furfuryl alcohol	-0.72	-0.08	0.94	-0.85
furfuryl pyrrole	0.69	0.88	0.96	0.75
Guaiacol	0.06	0.45	0.93	0.37
2-Acetylpyrrole	-0.93	-0.76	0.93	-0.71
1H-Pyrrole-2-carboxaldehyde	-0.43	-0.36	0.94	-0.18
Guaiacol <4-ethyl->	-0.56	-0.11	0.57	-0.61
Guaiacol <4-vinyl->	-0.94	-0.81	-0.96	-0.94

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

Table 1 shows the variables better correlated to time under stressed storage conditions with the different packaging. The variables which increase 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 highlights different behaviors of some compounds depending on packaging, e.g. acetic acid, 4-vinyl guaiacol or furfurylpirrole that have a reverse trend with packaging C_{eco} when compared to the others (Fig 5).

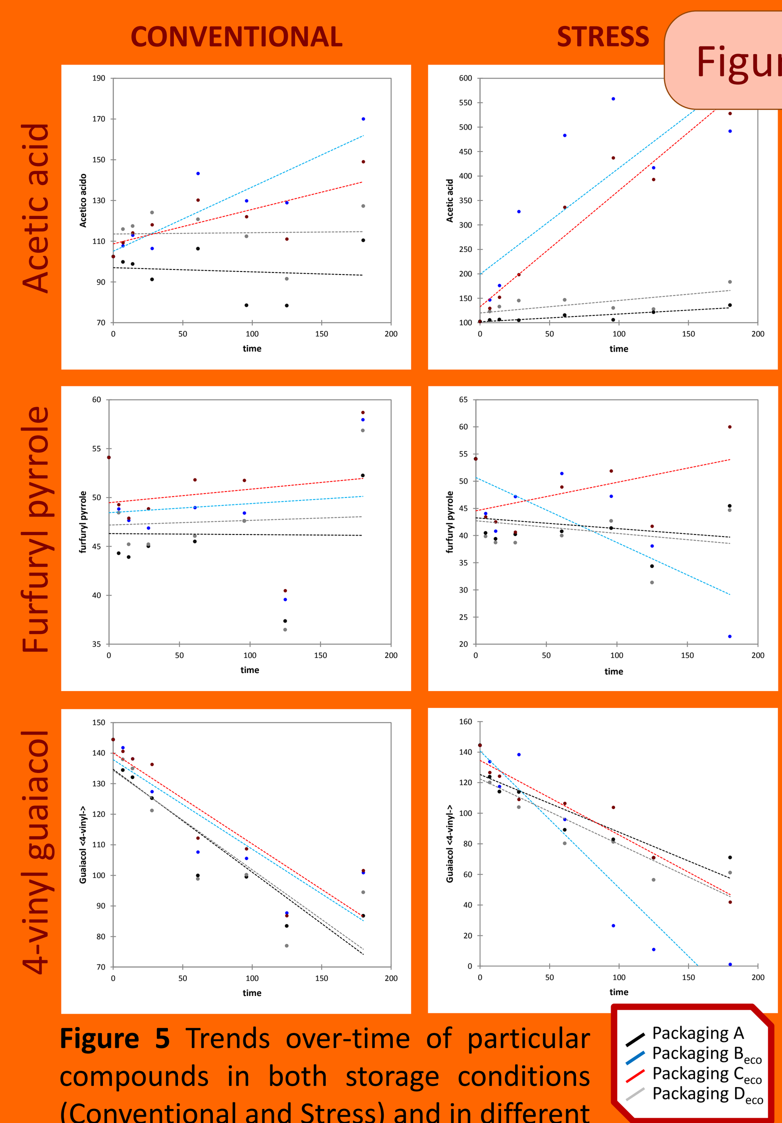


Figure 5

Figure 5 Trends over-time of particular compounds in both storage conditions (Conventional and Stress) and in different packaging (A, B_{eco}, C_{eco}, D_{eco}).

Packaging B_{eco} shows larger amounts of acetic acid and 2-butanone while furfural, furfuryl alcohol, furfuryl pyrrole, and 4-vinyl guaiacol are less abundant than in all other packaging. Packaging D_{eco} is characterized by higher amount of hexanal (Table 2). This behavior can be symptomatic of oxidative and hydrolytic phenomena occurring with B-packaged coffee while a more distinct oxidative aging characterizes the D_{eco}-packaged coffee (Table 2).

Table 2

	D_{eco}		A_{eco}		B_{eco}		C_{eco}	
compounds	C	S	C	S	C	S	C	S
Methanethiol	-100	-100	-100	-100	-100	-100	-100	-100
Acetaldehyde	-68	-85	-71	-79	-70	-89	-66	-81
Furan	-1	-26	2	10	-15	3	2	89
Acetone	-16	-20	-16	-10	-7	46	2	193
Methyl acetate	37	10	35	44	26	-10	45	342
Furan, 2-methyl-	6	-24	38	44	0	17	19	90
2-Butanone	48	34	42	57	45	422	56	383
Butanal, 2-methyl-	-14	-41	21	3	0	45	3	52
Butanal, 3-methyl-	1	-35	15	-2	2	12	10	14
Furan, 2,5-dimethyl-	-44	-49	-15	-20	-41	19	-39	-8
2,3-Butanedione	-66	-90	-45	-52	-45	-46	-40	-56
2,3-Pentanedione	-70	-96	-40	-51	-44	-88	-44	-65
2-Vinylfuran	-45	-67	-26	-39	-42	-74	-39	-35
Hexanal	2192	4877	1036	1423	1010	740	864	780
2,3-Hexanedione	-72	-96	-43	-57	-48	-88	-47	-62
1H-Pyrrole, 1-methyl-	-10	-41	13	-1	1	-97	6	-1
2-Vinyl-5-methylfuran	-40	-57	-25	-37	-37	-89	-34	-47
Pyridine	-2	-18	0	-9	20	-33	13	83
Pyrazine	-2	-14	-5	-8	18	41	13	143
Pyrazine, methyl-	-38	-48	-40	-47	-31	-21	-33	8
2-Butanone, 3-hydroxy-	-42	-49	-41	-42	-17	-61	-24	97
2-Propanone, 1-hydroxy-	22	6	13	23	81	-95	58	235
Pyrazine, 2,5-dimethyl-	-17	-33	-22	-33	-15	-18	-15	-1
Pyrazine, 2,6-dimethyl-	-18	-35	-22	-34	-17	-23	-16	-6
Pyrazine, ethyl-	-22	-36	-25	-34	-19	-6	-20	2
Pyrazine, 2,3-dimethyl-	-7	-27	-12	-27	-5	-15	-4	-2
1-Hydroxy-2-butanone	-41	-46	-40	-32	-12	-86	-29	62
Pyridine, 3-ethyl-	-15	-37	-22	-35	-14	-65	-14	-25
Pyrazine, 2-ethyl-6-methyl-	4	-17	-2	-17	3	1	5	3
Pyrazine, 2-ethyl-5-methyl-	-1	-19	-7	-19	-2	1	1	1
Pyrazine, 2-ethyl-3-methyl- + Pyrazyne, trimethyl	12	-14	4	-14	11	-12	13	-3
2-N-PROPYLPYRAZINE	-26	-39	-28	-39	-25	-23	-25	-22
2-Furanmethanethiol	-100	-100	-100	-100	-100	-100	-100	-100
2-Ethyl-3,6-dimethylpyrazine	-13	-36	-21	-37	-13	-31	-11	-31
Acetic acid	24	79	8	32	66	380	45	415
Furfural	-27	-15	-51	-50	-28	-79	-36	-55
Acetoxyacetone	-51	-54	-55	-56	-40	-73	-46	-22
Acetylfuran	-43	-47	-47	-49	-34	0	-38	14
Furfuryl acetate	2	-10	-6	-14	1	27	2	35
5 METHYL FURFURAL	-27	-35	-39	-42	-20	-55	-24	1
1H-Pyrrole-2-carboxaldehyde, 1-methyl-	-32	-42	-37	-44	-29	-6	-29	-1
Furfuryl alcohol	-47	-47	-53	-48	-27	-52	-36	27
furfuryl pyrrole	5	-17	-3	-16	7	-60	8	11
Guaiacol	-15	-27	-24	-31	-11	15	-12	17
2-Acetylpyrrole	-39	-42	-46	-46	-31	-16	-35	9
1H-Pyrrole-2-carboxaldehyde	-47	-38	-53	-47	-31	-5	-39	46
Guaiacol <4-ethyl->	-21	-37	-29	-39	-19	-9	-20	-11
Guaiacol <4-vinyl->	-35	-58	-40	-51	-30	-99	-30	-71

Table 2 Variation coefficients between T180 vs T0 in conventional (C) and stressed conditions (S) in the 4 packaging considered. In green: decrease more than 20% and in red: increase more than 20%.

Conclusions

Although other authors have already worked on aging markers of coffee, their studies have mostly defined markers of freshness because they considered a too short time delay for a product with such a long shelf-life [6-8]. Moreover, it has to be noted that the already reported results do not involve shelf-life data but an in depth investigation of food kinetics deterioration. Shelf-life assessment requires the definition of a criterion for the end of a packaging life that involves not only the product but also its packaging . These preliminary results show us that the evolution of the aroma compounds during the storage of the roasted coffee powder are very different and mostly related to the packaging considered.

These complex phenomena are difficult to be correctly described through a fingerprinting approach but require in depth specific marker studies in order to define a kinetic model suitable to describe the aging of coffee under conventional storage conditions, in particular when new packaging are considered. In order to obtain the shelf-life of the roasted coffee powder, these results must then be correlated to the sensory evaluation data whose define the product acceptability limit.

References

[1] I. Flament. Coffee flavour chemistry. (2002) John Wiley & Sons Ltd, West Sussex, England
[2] D. Kilcast and P. Subramaniam.. (2011). Woodhead Publishing Ed, Cambridge UK
[3] UNI 10534 – (December 1995)
[4] M.C.Nicoli, S.Calligaris, L.Manzocco. Food Eng. Rev. (2009) 1:159-168.
[5] Y. Wang, , J. O'Reilly, ,. Chen, Y, & J Pawliszyn, . (2005) J.Chromatogr. A, 1072, 13–17.
[6] K. Marin, T. Pozrl, E. Zlatic and A. Plestenjak. (2008) Food Technol. Biotechnol. 46 (4) 442–447.
[7] M. Bröhan, T. Huybrighs, C. Wouters, B. Van der Bruggen (2009), 116 480-483.
[8] A.N.Gloss, B. Schonbachler, M. Rast, L. Deuber, C. Yeretzian.(2014) CHIMIA International Journal for Chemistry, 68(3):179-82.