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Modeling of Greek coffee aroma loss during storage at different temperatures and water activities

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Abstract

Greek coffee is a traditional product of superior aroma and flavor. Changes of aroma volatile compounds of ground roasted coffee can occur during storage, leading to “coffee staling” which affects the quality and acceptability of the brew. Temperature and water activity effect quality especially during home storage, after opening of the vacuum pack (secondary shelf-life). The objective was to define volatile indices of greek coffee quality and model their change as a function of temperature and water activity during storage. Greek coffee samples were equilibrated at constant water activities a_w (0.15, 0.22, 0.33, 0.52) and stored at constant temperatures (25, 35, 45°C). The profile of volatile compounds was obtained directly from ground coffee samples using purge and trap-gas chromatography-mass spectrometry methodology. Furfural was considered to be a good aroma marker of greek coffee staling during storage; furfural changes (expressed by coffee aroma loss rate constants, k_{vol}) were well correlated to storage temperature T and a_w. Increase of water activity (for a_w values above 0.33) and increase of storage temperature (from 25 to 45°C) caused decrease of shelf life estimated based on aroma indices for greek coffee. The shelf life for coffee samples of a_w 0.52 stored at temperatures 25 and 45°C was found to be 82-92 and 20-23 days, respectively. At 45°C, a_w decrease from 0.52 to 0.33 led to shelf life increase from 20-23 to 36-41 days. Additionally, coffee aroma loss was expressed based on sensory evaluation (scores for aroma intensity and overall impression, 1-9). Rate constants for coffee aroma loss based on sensory scoring of coffee brews were calculated (k_{sens}). A comprehensive mathematical model of 3 parameters that describes the effects of storage temperature and water activity on k_{vol} and k_{sens} was developed allowing the calculation of shelf life (SL) for greek coffee during (home) storage.

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Keywords: Coffee; Staling; Temperature; Water activity; Aroma; Sensory

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1. Introduction

Ground roasted coffee is a shelf-stable product with regards enzymatic and microbial spoilage. Due to the high temperature attained in the roasting process, coffee is characterized by a very low water activity (a_w) as well as the presence of Maillard reaction products with antimicrobial properties [1]. However, during storage, coffee may undergo important chemical and physical changes, responsible for coffee “staling”, which affects the quality and acceptability [2]. The main causes of coffee staling are attributable to losses of volatile compounds, in particular, of key sulfur-containing odorants and oxidation reactions, the latter being responsible for off-flavor formation [3].

Temperature, oxygen concentration and relative humidity/water activity are the major factors that affect the shelf life of roasted coffee. The rate of coffee degradation reactions, may significantly increase after the packaging has been opened by the consumer, thus determining the so-called “secondary shelf life”. It is a matter of fact that during home usage, coffee is almost never consumed immediately after the opening of the packaging. More often, its usage lasts a few days or weeks [3]. The evaluation of the secondary shelf life may therefore represent a tool in order to improve product management up to consumption and to maximize its shelf life during storage [4].

Coffee aroma, which involves more than 800 volatile compounds, is one of the most contributory factors for the high acceptability of coffee by consumers [5]. In fact, in the coffee industry, sensory profiling is still the most widespread technique employed to evaluate the final quality of both raw material and finished products. Several research groups have tried to associate coffee staling with chemical changes in roasted coffee, obtaining the ratios between certain pairs of volatile compounds, called aroma indices, which have been used as indicators of coffee storage time [3].

The objective of this study was to determine and characterize changes in the composition of the volatile fraction of greek coffee as a function of temperature and water activity during storage.

2. Materials & Methods

2.1. Sample preparation

Greek coffee (ground, roasted, blend of Arabica and Robusta coffee varieties) samples equilibrated at a_w values, 0.15, 0.22, 0.33, 0.52, were stored at temperatures T, 25, 35, 45°C. To maintain the water activity values, coffee samples were placed in jars over saturated salt solutions (no salt -initial a_w value-, CH_3COOK, $MgCl_2$, $Mg(NO_3)_2$*$6H_20$, respectively). Water activity was measured with a Rotronic A6 AM3t-AwVD (Basserdorf, Switzerland) a_w-meter. To simulate home storage conditions, coffee samples were not hermetically packaged.

2.2. Analysis of ground coffee aroma compounds & identification of greek coffee volatile profile

The profile of volatile compounds was obtained directly from ground coffee samples using purge & trap(OI Analytical 4660, USA)-gas chromatography (Triple-Axis Detector model EI and Agilent 1909/S capillary column 30x0.25 mm i.d., coating thickness 0.25 μm)-mass spectrometry methodology (Agilent Technologies 5975 C, mass spectrometer detector MSD, EI 70 eV).

The ground coffee samples were analyzed in the purge-and-trap concentrator under working conditions: gas flow 40mL/min, purge time 20 min, purge temperature 80°C, system pressure 22,8 psi, trap temperature (purge) 30°C, trap temperature (desorption) 190°C, desorption time 1,5 min, 6-port-valve temperature 155°C, transfer line temperature 150°C, bake temperature 210°C, water management temperature 130°C, and septum purge flow 3 mL/min. Analyses in the GC-MS were performed afterwards: injector temperature 180°C, carrier gas nitrogen, flow rate 1 mL/min, split ratio 10:1, oven temperature programmed from 50°C (0.5 min at constant temperature) to 70°C at 5°C/min and then to 160°C at 10°C/min, and post run temperature 240°C (5 min). Each sample was analyzed in duplicate.

The storage temperature T and water activity a_w effect on volatile compounds was studied. Coffee aroma loss (coffee aroma loss rate, k_{vol}) was determined, and kinetically modeled.

2.3. Sensory evaluation of coffee brew

Sensory evaluation by eight trained panelists (1-9 hedonic scale, selected sensory attributes: aroma intensity, aftertaste, off-taste, overall impression, and sample acceptability compared to the fresh sample) was conducted to determine the effect of storage temperature and water activity on coffee aroma (coffee aroma loss rate based on sensory evaluation, k_{sens}). The aim was to correlate instrumental and sensorial results for aroma loss during coffee staling.

Greek coffee is a strong brew, served with foam on top and the grounds in the bottom of the cup. It is usually made in the traditional small pot which allows the proper amount of foam, which adds to the unique taste. For the preparation of geek coffee samples, the brew was removed from heat and served when the foam started rising to the top of the pot. Coffee brew samples were prepared fresh and the temperature was kept constant until the sensory evaluation. The time between the samples preparation and sensory testing was very short, less than 15 minutes, to minimize aroma loss. The panellists rinsed their mouth with water and waited for 2 min between samples.

3. Results & Discussion

3.1. Analysis of greek coffee aroma, fresh and stale

Volatile compounds identified and quantified throughout days of storage at temperatures studied were as follows: hexanal, n-decanal, n-heptanal, nonanal, 3-methyl butanal, 2-methyl butanal, trans-2-octenal (aldehydes), methyl-acetate (ester), 2-amylfuran, 2-methyltetrahydrofuran, furfural, furfuryl acetate, furfuryl alcohol, 5-methyl furfural, furfural formate (furans), 2,3 pentanedione, 1-hydroxy-2-propanone, 3-hydroxy-2-butanone (ketons), 1-H-pyrrole (pyrrole), 2-methyl pyrazine, 2-ethyl-3-methyl pyrazine, 2-ethyl-5-methylpyrazine, 2-ethyl-6-methyl pyrazine, 2,3-dimethyl pyrazine, 2,5-dimethyl pyrazine (pyrazines), 2-ethyl-1-hexanol (alcohol).

Pyrazines and furans seem to compose the aromatic mixture of greek coffee. They both represent important classes of compounds of fresh roasted coffee aromas [3]. Pyrazines (2-methylpyrazine and 2-5-dimethylpyrazine), furans (2-furfurylalcohol and 2-furfurylacetate) and lactones (γ-butyrolactone) have been used as the three classes of compounds present in roasted coffee and black instant coffee beverages [5, 6, 7]. Pyrazines are related to roasty and earthy/musty flavors in ground roasted coffee and coffee brews [8, 9]. As far as furans are concerned, they have been proposed as responsible for the burnt sugar, burnt and caramel aromas in roasted coffee [10] and also for the caramel flavor in coffee brew [11]. Among detected furans, furfural that is the oxidative product of furfuryl alcohol showed an exponential increase with storage that could be described mathematically. Furfural was selected as Greek coffee staling index.

Among aldehydes detected, hexanal, n-decanal, n-heptanal and nonanal (malty flavor) were the most abundant. The formation of hexanal (rancid flavor), due to the oxidation of polyunsaturated fatty acids such as linoleic acid, seems to have a certain influence on the staling of the coffee brew [3]. In the present study, hexanal exhibited a stationary phase and then a rapid increase during storage; however it could not be considered as a good marker for Greek coffee staling.

3.2. Changes of coffee aroma compounds during storage

The response for furfural of each sample stored at different temperature and water activity conditions was calculated to the response of fresh coffee sample (F). Peak areas were measured by calculation of total area based on integration of the basic ion (m/z of the most intense ions 100%). In Fig. 1, the change of furfural for coffee samples stored at different temperatures T 25, 35, 45°C for water activity a_w 052 was representatively shown.

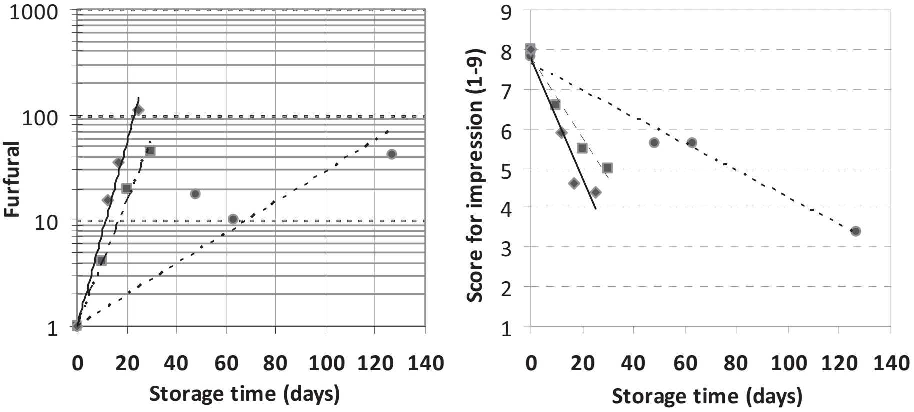

Fig. 1. (α) Changes in furfural (expressed as Furfural response of the sample/Furfural response of reference sample, fresh, at 0 day) of Greek coffee brews and (b) Scores for overall impression of greek coffee brews (storage conditions: water activity a_w 0.52, temperature T 25, 35, 45°C)

The best-fit equation for furfural resulted as follows:

$$F= \exp(k_{vol}*t) \tag{1}$$

where t is the storage time (days) and k_{vol} is the coffee aroma loss rate (1/days). According to k_{vol} results, increase of water activity (for a_w values above 0.33) and increase of storage temperature (from 25 to 45 °C) caused decrease of shelf life estimated based on selected aroma index for Greek coffee. Aroma loss rates k_{sens} were also calculated according to Eq. (2) and results obtained during sensory evaluation.

$$S= S_o+(k_{sens}*t) \tag{2}$$

where S and S_o is the scores for aroma intensity and/or overall impression during sensory evaluation at storage time t (days) and t_o (day 0), and k_{sens} is the coffee aroma loss rate based on sensory evaluation (1/days). k_{vol} values were in good correspondence with the values calculated for quality deterioration rates k_{sens} based on sensory acceptance of coffee samples (R^2=0.900-0.999).

3.3. Sensory evaluation of coffee brew during storage

The score for the most significant sensory attributes (aroma intensity and overall impression) of coffee samples was correlated to furfural changes of the respective samples (Figures 2a, 2b) in Eq.3.

$$S=[C_1 * \ln(F)] + C_2 \tag{3}$$

where S is the score for aroma intensity and overall impression during sensory evaluation. The equation constants C_1 and C_2 for aroma intensity and overall impression attributes were calculated as -0.836 and 7.69 (R^2= 0.898), -0.858 and 7.88 (R^2= 0.895), respectively. The score 5, chosen as the acceptability level for coffee brew samples on the basis of the percentage of consumer rejection, was found to correlate to 30 times increase of furfural response.

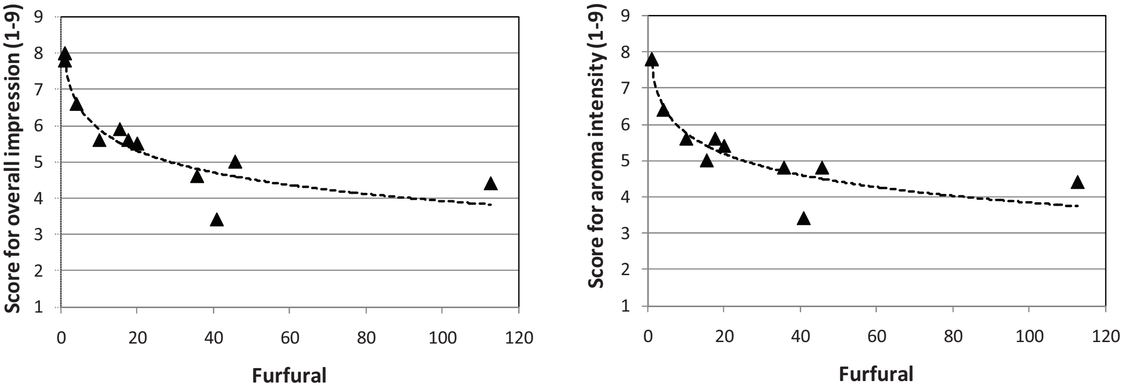

Fig. 2. Score for (a) aroma intensity and (b) overall acceptance vs furfural responses of coffee brews (storage conditions: water activity a_w 0.52, temperature T 25, 35, 45°C)

3.4. Effect of storage temperature and water activity

Temperature dependence of the rates of coffee aroma loss was adequately described by Arrhenius kinetics in the whole temperature range studied (Activation energy E_a= 66.9 kJ/mol for storage conditions: a_w 0.52, T 25, 35, 45°C). The water activity effect on coffee aroma loss rates was found to follow an exponential-type equation. A comprehensive mathematical model that describes the above mentioned effects of storage temperature and water activity was developed. The model can be used for the prediction of aroma loss rates as function of temperature and water activity (Eq. 4).

$$\ln k_{vol/sens} = C_1 + C_2 * \left(\exp(a_w - a_{wref})\right) + C_3 * ((1/T_{ref}) - (1/T)) \tag{4}$$

where k_{vol} or k_{sens}, coffee aroma loss rate based on furfural response or coffee quality loss rate based on sensory evaluation (1/days), C_1, C_2, C_3 constants of the Equation, T_{ref} (=298K) and $a_{w\ ref}$ (=0.15, fresh, ground coffee water activity) the reference temperature and water activity values, respectively. C_1, C_2, C_3 were calculated as -6.15, -2.32, 4141, respectively (R^2= 0.997).

Since the sensory analysis testing scores follow pseudo zero order kinetic, and the furfural response first order, the shelf life (SL) of the coffee brew can be finally predicted accordingly (Eq. 5):

$$SL = \frac{S - S_0}{k_{sens}} = \frac{\ln F}{k_{vol}} \tag{5}$$

In Table 2 calculated shelf-life values for greek coffee samples stored at different temperature and water activity conditions are presented. Eq. (4) is a simple mathematical tool allowing calculation the shelf life of greek coffee brews accounting for the attitude of consumers as well as the instrumental measurement for aroma.

Table 2. Shelf-life values calculated based on aroma retention for coffee samples stored at different temperatures (25-45°C) and a_w (0.15-0.52)

Storage temperature, °C	Water activity, a_w	Shelf life, days calculated based on sensory analysis results	Shelf time days calculated based on coffee aroma analysis results
45	0.52	20	23
45	0.33	36	41
45	0.15	57	65
35	0.52	31	35
35	0.33	55	63
35	0.15	87	99
25	0.52	82	92
25	0.33	87	98
25	0.15	137	156

4. Conclusions

Taking into account the limited knowledge of the behavior of the volatile compounds of Greek coffee initially and during storage, this study was conducted to monitor and characterize changes in the composition of the volatile fraction of Greek coffee stored at room temperatures by means of purge & trap GC-MS. Moreover the behavior was examined to find some aroma indices that could be good indicators of coffee staling. The results of the study would give an idea about the possibility of the control of its quality by measuring only a few volatile compounds. Furthermore, they can be used to define tolerance on home storage conditions of Greek coffee.

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