Modeling the Secondary Shelf Life of Ground Roasted Coffee

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This work was addressed to study the secondary shelf life of ground roasted coffee. To this purpose, fresh dark-roasted ground coffee samples were equilibrated at increasing water activity (a_w) values up to 0.44 and stored at 30 °C for up to 1 month. To simulate home storage conditions, the headspace atmosphere was periodically perturbed by opening for a short time and then closing the packaging. The changes of some chemical and physicochemical indexes of coffee staling were studied, and sensory analysis was carried out to determine the end point of coffee acceptability. The results showed that the volatile compounds in the headspace are representative indexes of the quality depletion of roasted ground coffee during home usage. The sensory and instrumental results were used to develop a mathematical model allowing to simply and quickly calculate the secondary shelf life of coffee on the basis of its a_w value at a given temperature.

KEYWORDS: Coffee; storage; consumer acceptability; modeling

INTRODUCTION

As known, roasted coffee is a shelf-stable product toward enzymatic and microbial spoilage. In fact, because of the high temperature attained in the roasting process, coffee is characterized by a very low water activity (a_w) as well as by the presence of Maillard reaction products with antimicrobial properties (*1, 2*). However, during storage, coffee may undergo important chemical and physical changes, responsible for coffee staling, which affects the quality and acceptability of the brew (*3*). 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 (*4*). Temperature, oxygen concentration, and relative humidity are the major factors that affect the shelf life of roasted coffee. Nowadays, optimization of processing and packaging technologies allows processors to greatly slow these alterative phenomena, so that it is possible to attribute to coffee a long shelf life, generally of the order of 1−2 years (*5*).

The rate of coffee degradation reactions, however, may suddenly increase after the packaging has been opened by the consumer, thus determining the so-called secondary shelf life (*6*). Secondary shelf life represents the length of time after packaging opening during which a food product does maintain acceptable igienic, nutritional, and sensory properties. It is a matter of fact that during home or catering usage, coffee is almost never consumed immediately after the opening of the packaging. More often, its usage lasts a few days or weeks. As a consequence, during the consumption time, degradation reactions may proceed with higher rates due to the changed storage conditions. The evaluation of the secondary shelf life may therefore represent a tool in order to improve product

management during consumption and to maximize its shelf life during storage. It must be pointed out that although many authors reported studies on the shelf life of foods, including roasted coffee, most of them are actually relevant to the stability of these products during storage, as they do not identify the end point of product acceptability (*6−8*). By contrast, only a few studies deal with the shelf life prediction of coffee as a function of processing and environmental variables (*9, 10*), while to our knowledge, no studies have been carried out on the evaluation of the secondary shelf life of this product.

Therefore, the aim of this study was to investigate the secondary shelf life of roasted ground coffee under home storage simulation conditions, i.e., storage of the product, preliminarily equilibrated at different a_w values, at 30 °C for approximately 1 month in packages that were periodically opened for a short time and subsequently closed. The evaluation of the secondary shelf life of roasted coffee was carried out by means of sensory analysis as well as by investigation of the changes of some chemical and physicochemical indexes of coffee staling. The objective was to find a proper indicator responsible for coffee staling in order to identify suitable, fast analytical tools to predict consumer acceptability and hence the secondary shelf life of coffee.

MATERIALS AND METHODS

Sample Preparation. Aliquots of 10 g of fresh dark-roasted ground coffee (cv. Arabica) from an Italian industrial production were taken from hermetically sealed packages and placed in Petri plates (120 mm diameter). These were then introduced in a 5 L capacity hydration cell containing 500 mL of water and left to equilibrate up to a_w values of 0.17, 0.23, 0.36, and 0.44. Preliminary trials were carried out in order to determine the lengths of time necessary to hydrate samples at the desired a_w values, the results of which were less than 2 h. Coffee directly taken from the hermetically sealed package, having an a_w of 0.09 ± 0.01, which corresponded to a moisture content of 0.75% on a dry

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basis, was also used. To keep the relative humidity constant during the experiment, 250 g of the coffee samples equilibrated at the different a_w values were then transferred into 500 mL capacity screw-capped glass bottles and placed in jars containing saturated salt solutions with a_w values close to those of the coffee samples. Jars containing the coffees were subsequently transferred into a thermostat at 30 °C. To simulate home storage conditions, every day, the bottles containing the coffee samples were opened, held for 1 min inside the jars, and then closed again.

Total Solid Content. The total solid content was determined according to AOAC methods (*11*).

Water Activity. The water activity (a_w) was determined by means of a dew point measuring instrument (AQUA LAB, Decagon, Pullman, WA) at 25 °C.

Sorption Isotherms. Sorption isotherms were measured by accurately weighing samples in vacuum desiccators containing saturated salt solutions with constant water vapor pressure, until constant weight (*12*). Measurements were carried out at 25 °C. Saturated salt solutions with relative humidities between 11 and 91% were used.

Best-fitting statistical analysis of the experimental data of the sorption isotherm was performed by using the Guggenheim–Andersson–deBoer (GAB) model (*13*) (eq 1)

$$m = \frac{m_0 c a_w}{(1 - k a_w)(1 - k a_w + c k a_w)} \quad (1)$$

where a_w is the water activity, m is the moisture content (g water/g solids), m_0 is the moisture monolayer value (g water/g solids), and c and k are constants.

Peroxide Value Analysis. The peroxide values of coffee oil were determined according to an AOAC method. Coffee oil was obtained by solid–liquid extraction using chloroform–methanol (Carlo Erba, Italy) mixtures (2:1 v/v) by stirring at room temperature for 3 h. The ratio between the ground coffee and the solvent mixture was 1:6 w/v. After filtration through filter paper (Whatman #1), the oil was separated from the solvent by evaporation (Heidolf Instruments, model 4001, Germany).

Headspace Gas Chromatographic Analysis. Analyses were performed by using a Fisons gas chromatograph (HRGC MEGA 2 series, Fisons Instruments, Milano, Italy) equipped with an automatic sampler and a flame ionization detector (Carlo Erba HS 250, Carlo Erba Strumentazioni, Milano, Italy). A 2 mm × 2 mm i.d. glass packed column filled with Carbowapack 20 M 80/100 mesh (Waters Ass., Framingham, MA) was used. The operating conditions were as follows: column temperature, 80 °C; detector oven temperature, 200 °C; injector temperature, 200 °C; carrier gas, nitrogen; and flow rate, 35 mL/min. Aliquots of about 1.5 g of coffee were introduced in 10 mL capacity vials, which were hermetically closed with butyl septa and metallic caps. Before analysis, samples were conditioned at 40 °C in a temperature-controlled water bath. The sample headspace volume injected was 0.5 mL using a precision sampling syringe (Dynatech Precision Sampling, Baton Rouge, LA), provided with a pressure lock and a gas volume capacity of 0–0.5 mL.

Before analysis, samples were stored at 40 °C for 24 h in a temperature-controled bath to reach equilibrium conditions. The chromatograms were analyzed using a ChromCard for Windows software (Ver. 1.18, 1996, Carlo Erba Instruments).

Sensory Analysis. The end of secondary shelf life of ground roasted coffee stored at 30 °C was determined through sensory analysis by applying the survival analysis (*14, 15*). This method was developed to evaluate times until an event of interest, often called survival time, taking into account the presence of censored data (*14*). A staggered sampling design based on the evaluation of increasing number of samples as storage time progressed from time 0 to about 30 days, i.e., approaching the end of shelf life, was used (*16*). Three panelists were used at the beginning of the test. Their numbers were increased by one at each sampling time, until half of the tasters judged the samples unacceptable. After that, the number of panelists was increased by U + 1, where U is the number of unacceptable responses for the previous test time. Panelists were screened according to the criterion that they consumed at least one cup of coffee every day. Aliquots of 3 g of

ground roasted coffee were placed into 30 mL capacity plastic containers and sealed with a pressure cap. Before the sensory test, samples were left to equilibrate at room temperature for 1 h. Panelists were asked to sniff the samples and report whether the coffee was acceptable or unacceptable. A response of acceptability implied that the tester would be using that coffee powder to prepare the beverage. The CensorReg procedures from S-PLUS (Insightful Corporation, Seattle, WA, version 7) were used according to Hough et al. (*15*). Censoring was defined as follows. At a given storage time *t*, two possible answers could be given by the panelists: (i) The sample was perceived as acceptable, indicating that it would be rejected beyond time *t*; thus, the data were right censored. (ii) The sample was perceived as unacceptable, indicating that the panelist would start rejecting the product before time *t*; thus, the data were left censored. Data were fitted by the logistic distribution parameters and the storage time corresponding to 50% of consumers rejecting the product [$F(t) = 50\%$ quantile] and were estimated by maximizing the likelihood function. This is a mathematical expression, which describes the joint probability of obtaining the data actually observed on the subjects on the study as a function of the unknown parameters of the model being considered. The 50% consumers rejecting the product was considered because it is a well-accepted limit in shelf life studies (*9*).

Data Analysis. The results reported in this work are the average of at least three determinations and the coefficients of variation, calculated as the percentage ratio between the standard deviation and the mean value, and were less than 15% for gas chromatographic analyses and less than 5% for a_w, total solid content, and peroxide value determinations.

The significance of the differences among means was determined using the Tukey–Krammer test (JMP, version 3.2.5, SAS Institute, Cary, NC). Means were considered to be significantly different at $p <$ 0.05.

Best-fitting analysis by least squares regression was performed by Table Curve 2D software (version 5.01, SPSS Inc., Chicago, IL), and the goodness of fit was evaluated on the basis of statistical parameters of fitting [R^2, p, and standard error (SE)]. Fitting by maximizing the likelihood function was performrd by S-PLUS (Insightful Corp., version 7).

RESULTS AND DISCUSSION

As already mentioned, the secondary shelf life of roasted coffee was evaluated by means of instrumental and sensory analyses. In particular, the former were used to study the changes of selected indexes, which are supposed to describe coffee staling, i.e., oxidation reactions and release of volatile compounds; the latter were performed by using survival analysis to assess consumer acceptance limits.

Instrumental Analyses. To study the changes of the oxidative state of coffee lipid fractions, the samples equilibrated at a_w values ranging between 0.09 and 0.44 were analyzed for their peroxide value during 1 month of storage at 30 °C. All samples showed a peroxide value below 2 mequiv O_2/kg_{fat} during the entire storage time (data not shown). This result did not surprise us very much, despite the very high temperatures reached during the roasting process. In fact, the high oxidative stability of the coffee lipid fraction is attributable to the presence of naturally occurring polyphenols and Maillard reaction products with high antioxidant properties, which are formed during the heating process (*17*). Besides, although the sample's packaging was opened every day for 1 min, it is likely that the small amounts of oxygen, eventually migrating from the atmosphere to the headspace of the coffee-containing bottles, were immediately consumed by the Maillard reaction products possessing oxygen scavenging properties (*18*). These results are in agreement with those by Cardelli and Labuza (*9*), who found that the concentration of available oxygen for oxidative reaction is the limiting factor of the degradation reaction rate.
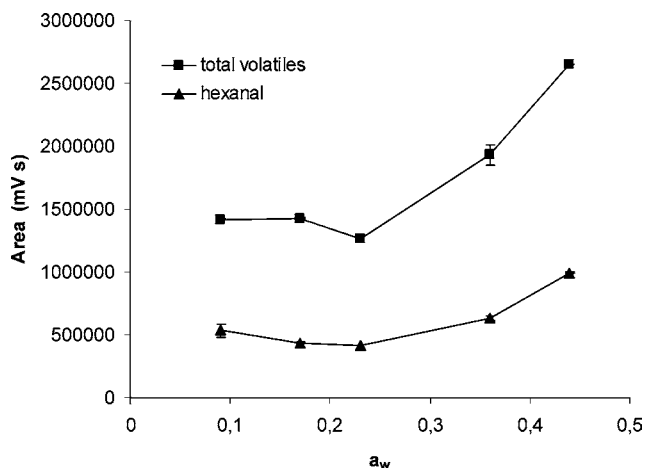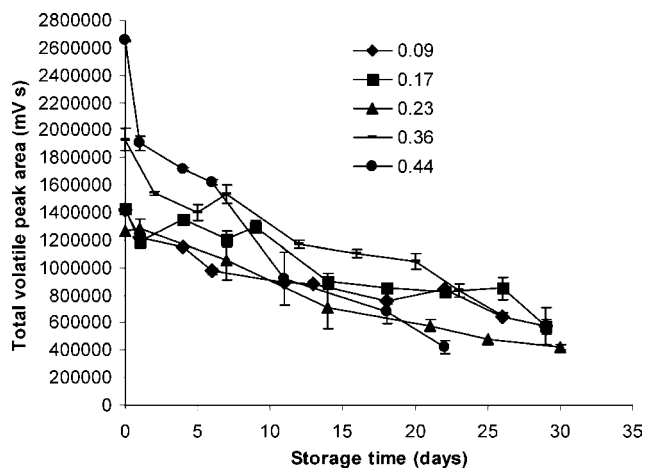
Figure 1. Changes in the peak area of total volatile compounds and hexanal in the headspace of roasted ground coffee at zero storage time as a function of a_w.
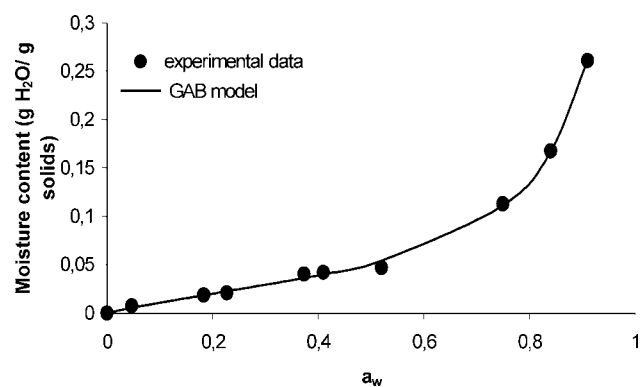
Figure 2. Moisture sorption isotherm for fresh-roasted ground coffee at 30 °C.

Figure 3. Changes in the peak area of total volatile compounds in the headspace of roasted ground coffee equilibrated at different a_w values as a function of storage time.

Figure 1 shows the changes of the peak area of total volatile compounds and hexanal in the headspace of coffee samples equilibrated at different a_w values at zero storage time. Up to a_w of 0.23, no significant changes in volatile area were observed, while a further increase of a_w was associated with a strong increase in volatile area. The a_w associated with the increase of volatile compounds in the headspace was close to the a_w at the moisture monolayer, which was calculated from the experimental data of the moisture sorption isotherm at 30 °C of the coffee samples (**Figure 2**) by using the GAB equation ($R^2 = 0.99$, $p < 10^{-6}$, SE = 0.0034). In particular, the calculated moisture monolayer value was 0.035 g water/g solids, which corresponded to an a_w of 0.33. These results compare well to the published data (*10, 19−21*).

As known, in low moisture foods, such as roasted coffee, the majority of volatile compounds is still present in the food matrix, even if it is more volatile than water (*22*). The partitioning phenomena are controlled by interactions between volatile molecules and nonvolatile substances (*23*). From a physical−chemical standpoint, the main mechanisms for retention of volatile compounds in dehydrated foods, as in the roasted coffee, are represented by solubilization in the oil and water fractions and/or adsorption to polar and nonpolar sites (*10, 22, 24−26*). Although low molecular weight volatile substances can migrate in a vitreous matrix, as in the roasted coffee (*27*), their partition kinetics increase by exposing the food system to progressively increasing relative moisture values. It must be pointed out that many literature reports relevant to the mechanisms of volatile retention associate the release of these

molecules from dehydrated matrixes during moistening to structural collapse of the matrix itself (*28−31*). As reported by Cardelli-Freire (*32*), the T_g value of roasted coffee may vary from 170 to 130 °C as the water content is increased from 0 to 13% dry basis. According to the GAB model applied to the above shown sorption isotherm, a moisture content of 13% corresponds to an a_w of about 0.80. That means that in our experimental conditions, the structure of the roasted coffee would be well below the glass transition temperature in the a_w range between 0 and 0.44. This was also confirmed by the fact that the coffee structure in all of the considered a_w ranges was that of a free-flowing powder (data not shown). Therefore, it is likely that the release of volatile compounds in the headspace depends on thermodynamic rather than kinetic mechanisms; therefore, its occurrence can be predicted with reference to a_w changes rather than the glass transition and molecular mobility theory (*24, 33*). In particular, on the basis of our results, the increase in volatiles occurred once a critical water content, i.e., the moisture monolayer value, was attained (*22, 24*). Therefore, at a_w values lower than 0.3, the main amount of volatile compounds would be partially solubilized in the coffee oil and in the low water content, partially physically held in the glassy matrix. At moisture contents above that of the monolayer, water competes for hydroxyl groups, and hydrogen bonds between carbohydrate molecules are disrupted, leading to a great volatile loss (*22*). Besides, the increased competition with water for the polar sites of the coffee matrix would be responsible for an enrichment of the vapor phase of polar volatile compounds (*34, 35*).

Figures 3 and **4** show the changes of the peak area of total volatile compounds and hexanal in the headspace of coffee samples equilibrated at different a_w values and stored at 30 °C for up to 1 month. Because samples were found to reach equilibrium a_w values in less than 2 h, equilibration time was considered to be negligible as compared to storage time. As expected, the headspace volatile compounds progressively decreased with the increase of storage time, although the dependence of volatiles from storage time was affected by the initial a_w. Because of the different hydration of the samples, the higher the a_w, the greater the volatile loss during storage time is. It must be pointed out that although similar values were reached after 1 month of storage, samples cannot be considered to have similar "richness" in flavor. In fact, the sample with an initial a_w value of 0.44 has suffered a considerable loss of volatiles during equilibration and a further depletion during
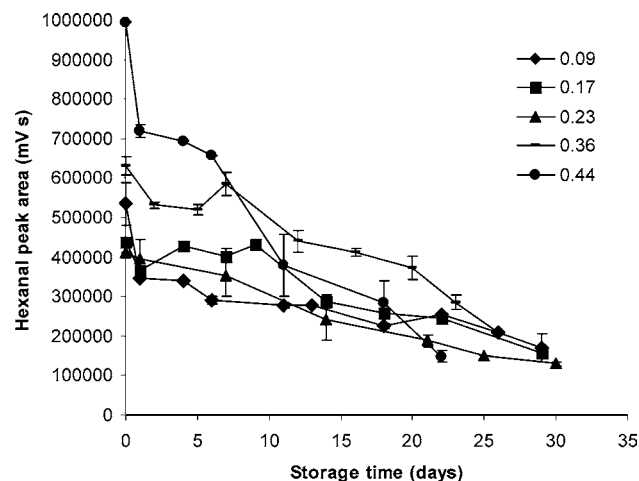
Figure 4. Changes in the peak area of hexanal in the headspace of roasted ground coffee equilibrated at different a_w values as a function of storage time.

Table 1. Regression Parameters and Correspondent SE and p Values of Eq 2 Obtained by Best-Fitting of Total Volatile and Hexanal Areas as a Function of Storage Time and a_w

dependent variable (mV s)	parameter	value	SE	p
total volatile area	a	842818	66157	$<10^{-6}$
	b	2599890	267715	$<10^{-6}$
	c	−143046	10766	$<10^{-6}$
hexanal area	a	227710	24919	$<10^{-6}$
	b	1182844	100838	$<10^{-6}$
	c	−54950	4055	$<10^{-6}$

storage; on the contrary, the sample with an initial a_w value of 0.09 at the end of storage time still contained a great amount of volatile compounds entrapped in the coffee matrix (*31*).

The changes of the peak area of total volatile compounds and hexanal as a function of storage time were found to follow a pseudo-zero-order kinetics. The individual and combined effects of storage time (t) and a_w on volatile loss were studied by the application of the response surface methodology. Although best-fitting was performed in order to study the main, interactive, and quadratic effects of storage time and a_w on the changes in volatile compounds, only the influence of a_w and of the interaction between storage time and a_w were found to be significant. Because no quadratic effect of the variable "time" was found as significant, a pseudo-zero-order kinetics of the volatile compounds was confirmed. The general best-fit equation for total volatile and hexanal peak areas (A) resulted as follows:

$$A = a + b \cdot a_w + c \cdot t \cdot a_w \qquad (2)$$

Table 1 shows the values of the regression parameters and the correspondent SE and p of eq 2.

The coefficient of determination (R^2) and the SE of the best-fitting equations of total volatile and hexanal areas as a function of storage time and a_w were 0.810 and 206200 and 0.820 and 77676, respectively.

Sensory Analysis. To coincide with the instrumental analyses, coffee samples equilibrated at different a_w values were analyzed for sensory acceptability during storage at 30 °C. As already mentioned, for this purpose, the survival analysis was used. Because no statistical tests are available to compare the goodness of fit of different models for censored data, as indicated by Hough et al. (*15*), visual assessment of estimation was performed

Table 2. Secondary Shelf Life of Ground Roasted Coffee, Defined as Storage Time Corresponding to 50% of Consumers Rejecting the Sample, as a Function of a_w

	50% quantile		
a_w	95% lower limit	estimated quantile	95% upper limit
0.09	17	20	23
0.17	19	23	26
0.23	16	22	28
0.36	11	17	23
0.44	10	13	16

Table 3. Area of Total Volatile Compounds in the Headspace Corresponding to the End of Sensory Shelf Life

		total volatile area (mV s) at shelf life		
a_w	secondary shelf life (days)	95% lower limit	estimated	95% upper limit
0.09	20	857948	819325	780702
0.17	23	822760	725489	652536
0.23	22	914383	716979	519576
0.36	17	1212316	903336	594357
0.44	13	1357367	1168546	979725

to select the best model among the six standard distributions (smallest extreme value, Weibul; normal, log-normal, logistic, and loglogistic). The logistic distribution was finally chosen because of its simplicity and good fit to the data. The maximum likelihood estimates the parameters of the logistic distribution, allowing us to calculate the storage time corresponding to 50% of consumers rejecting the coffee (**Table 2**).

The end of secondary shelf life was almost constant around 20 days at a_w values lower than 0.36. At higher a_w values, the secondary shelf life greatly decreased to about 13 days in correspondence to the a_w of 0.44. These results are in agreement with the high loss of volatile compounds of samples equilibrated at the highest a_w value (**Figures 3** and **4**). In fact, it can be suggested that the accelerated release of volatile compounds from the coffee samples equilibrated at a_w higher than 0.3 is responsible for the earliest unacceptability response expressed by the panelists.

From the data reported in **Figure 3**, it was possible to determine, for the coffee samples equilibrated at the different a_w values, the area of total volatile compounds in the headspace in correspondence of the end of sensory shelf life (**Table 3**). Statistical analysis demonstrated that these values were not significantly different ($p > 0.5$). Therefore, a mean value was calculated, which resulted in 866735 mV s, corresponding to an area of about 60% with respect to that of the sample before equilibration, i.e., the coffee at the moment of opening the packaging. This means that independently from the hydration degree of the coffee samples, the end of shelf life was reached when the same volatile vapor pressure was measured in the headspace.

Relation between Sensorial and Instrumental Indexes. Because the volatile compounds were found to follow a pseudo-zero-order kinetics (eq 2), the secondary shelf life of coffee can be predicted according to the following equation:

$$SL = \frac{A_f - A_{eq}}{k}$$

where SL is the secondary shelf life, expressed as days; A_f is the area of volatile compounds corresponding to the limit of

Secondary Shelf Life of Coffee

J. Agric. Food Chem., Vol. 54, No. 15, 2006   **5575**
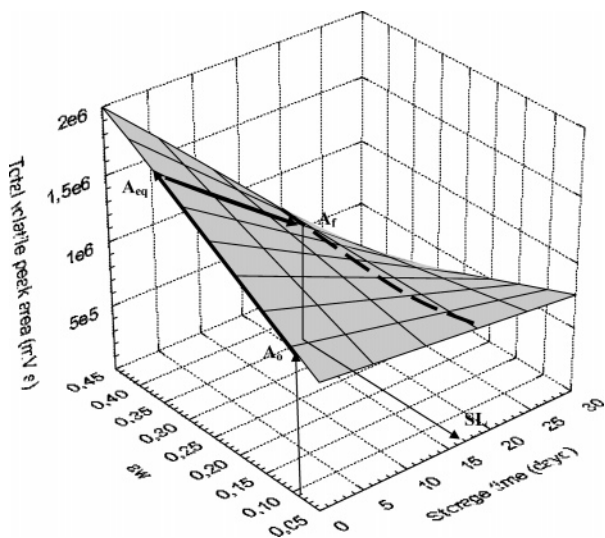
Figure 5. Surface plot of the changes of total volatile area as a function of a_w and storage time according to eq 2. Dotted line, curve of total volatile area corresponding to the sensory acceptability limit; A_o, total volatile area of coffee at $a_w = 0.09$; A_{eq}, total volatile area of coffee equilibrated at $a_w = 0.36$; and A_f, total volatile area of coffee equilibrated at $a_w = 0.36$ at the end of shelf life.

coffee sensory acceptability; A_{eq} is the area of volatile compounds at zero storage time after equilibration; and k represents the changes of the area of the volatile compounds in the headspace. In our experimental conditions, the changes in the area of volatile compounds as a function of storage time t and a_w are described by eq 2. On the basis of this result, A_{eq} and k can be easily calculated. In fact, A_{eq} can be calculated by attributing a zero value to storage time in eq 2:

$$A_{eq} = a + b \cdot a_w \qquad (4)$$

The rate of changes of total volatile, k, at a constant a_w can be calculated as the first derivative of eq 2 (dA/dt):

$$k = \frac{dA}{dt} = c \cdot a_w \qquad (5)$$

It can be observed that both A_{eq} and k do not assume constant values but are actually linear functions of a_w.

By substituting A_f, A_{eq}, and k in eq 3, secondary shelf life can be written as follows:

$$SL = \frac{A_f - (a + b \cdot a_w)}{c \cdot a_w} \qquad (6)$$

In our experimental conditions, A_f of total volatile compounds was demonstrated to be equal to 866735 mV s, corresponding to 60% of A_o, while a, b, and c values are reported in **Table 1**. Hence, eq 6 can be written as follows:

$$SL = \frac{866735 - (842818 + 2599890 \cdot a_w)}{-143046 \cdot a_w} \qquad (7)$$

Equation 6 represents a simple and rapid mathematical instrument that allows us to calculate the secondary shelf life of coffee on the basis of its a_w.

Figure 5 graphically shows the use of eq 6 in predicting the secondary shelf life of ground roasted coffee. In particular, the surface plot of the changes of total volatile area is represented as a function of a_w and storage time. The dotted line represents the curve of total volatile area corresponding to the sensory acceptability limit (A_f curve). As an example, the prediction of secondary shelf life of a sample with an initial a_w of 0.09 stored at 0.36 a_w was considered. In particular, the volatile area increases from 0.09 to 0.36 a_w in negligible time. During storage, the total volatile peak area decreases with a rate described by eq 5 till the A_f curve is reached. The time corresponding to the secondary shelf life can thus be calculated accordingly.

In general terms, the shelf life assessment of foods represents a challenge for food scientists and producers. In fact, the evaluation and the prediction of the shelf life of a food under different environmental conditions allow us to steer out proper processing and storage strategies as well as home and catering handling. Although nowadays methodologies and predictive mathematical modeling are available to determine the shelf life of foods, very often the main problems are represented by (i) the identification of an index representative of the quality decay, which could be measured in economically acceptable lengths of time; (ii) the difficulty to identify the limit value reached by the selected index in correspondence of the end of sensory acceptability; and (iii) the presence of environmental factors (a_w, temperature, pressure, oxygen concentration, etc.), which can strongly affect shelf life, but whose effect is difficult to account for in predictive models due to the complexity of calculations.

The results obtained in this work suggest that the volatile compounds in the headspace are representative indexes of the quality depletion of roasted ground coffee during home use. The changes of volatile compounds were found to be dependent on coffee a_w values. However, the end of the sensory acceptability of coffee during usage was clearly independent from coffee a_w and corresponded to a loss of volatile substances of about 60%. Therefore, the cheaper and faster instrumental analysis of the loss of volatile compounds can be performed instead of the sensory test in order to follow quality depletion. The sensory and instrumental results were used to develop a mathematical model allowing us to simply and quickly calculate the secondary shelf life of coffee on the basis of its a_w value at 30 °C.

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5576 *J. Agric. Food Chem.,* Vol. 54, No. 15, 2006

Anese et al.

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