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Preliminary study of flavor compounds as oxidation markers in bottled white wines of Greek origin

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ABSTRACT

Aim: The aim of this project was to identify the characteristic flavor and off-flavor compounds that could be used as potential oxidation markers to establish the quality of the stored wines and to predict the wines' shelf life employing a mathematical model.

Materials and methods: Six mono-varietal Greek white wines (produced by three varieties) were bottled using two types of corks having different oxygen permeability properties. Volatile compounds, resistance to oxidative degradation and total and free-sulfur dioxide content were recorded in all samples. Results were processed using the root cause analysis versus packaging and storage conditions. Additionally, a predictive model has been constructed to estimate the shelf life of the bottled wine.

Results: Physicochemical analysis indicated the absence of significant oxidative degradations during the first 7 months. Furthermore, 12-month stored samples showed a significant alteration in their flavor profile. Based on the concentration of the selected oxidation marker (isoamyl-alcohol), the possibility of the bottled product not reaching the end of its shelf life, has been used to quantify the product's quality. A very successful fit was achieved between mathematical and experimentally obtained data concerning shelf life predictions.

Significance and impact of the study: The modeling of the results indicated the importance of cork selection due to the Oxygen Transmission Rate (OTR) values that potentially impact the quality of the wines in time, according to the evolution of the isoamyl-alcohol concentration. For the wine industry, the selection of the appropriate cork according to the wine type is an important consideration.

KEYWORDS

packaging, flavor compounds, cork oxygen permeability, mathematical models

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INTRODUCTION

Key physicochemical properties that enable the packaging to achieve its protection functions are its barrier properties to oxygen, carbon dioxide, moisture, light and aroma compounds. Its inertness, with respect to the migration of low molecular weight compounds from the package to the product and/or flavour scalping (sorption of volatile aroma compounds of the product by the packaging material) is also highly significant (Revi *et al.*, 2014). Cylindrical cork stoppers are the classic closure used in the wine industry. The impermeability of cork to liquids and gases and its high compressibility and flexibility, make it ideal for sealing bottles. However, it is well known that in bottled wines sealed with cork several problems may occur; these include cork taint, mainly due to 2,4,6-trichloroanisole (TCA), resulting in the rejection of wine by consumers; variability in transmission (i.e. diffusion and permeation) of gases that can contribute to post-bottling oxidation of wine (Giunchi *et al.*, 2008).

In general, bottle storage contributes to the improvement of red wine quality. By contrast for white wine, it can lead to organoleptical defects such as color alteration (browning) and eventually deterioration of the overall quality and marketability. However, some white wines may derive short-term benefits from the development of a characteristic bottle bouquet (Kallithraka *et al.*, 2009).

During storage, the oxidation of both white and red wines is characterized by the transformation of aroma compounds, leading to a loss of characteristic varietal and secondary aromas of wines, and subsequently to the formation of new aromas characteristic of older oxidized wines or atypical aromas associated with wine deterioration. Several wine compounds, such as esters and terpenes, are transformed during wine storage, and eventually some loss of wine aroma may occur (Roussis and Sergianitis, 2008). Indeed, such an oxidative ageing first gives rise to typical flavors, which are generally described as “rancio” in sweet fortified wines and as non-desirable flavors of “honey-like,” “cooked vegetable,” “farm-feed,” “hay,” and “woody-like” in dry white wines (Karbowiak *et al.*, 2010).

In a study aiming in correlating the oxidative alterations of wine compounds to the oxygen availability through permeation, Garde-Cerdán and Ancín-Azpilicueta (2007) demonstrated that wine stored for 6 months in bottle with SO_2, showed a higher concentration of the majority of the flavor compounds studied, in comparison to wines aged in bottle without SO_2. Also, the color development after bottling depends on the contact of wine with oxygen throughout storage, (Ghidossi *et al.*, 2012). Traditionally, acetaldehyde is considered to have an offensive odor and taste, which brings bitterness and oxidized flavor to wine, and if its level exceeds 50 mg/L in a table wine, it means that the wine has been oxidized (Zhai *et al.*, 2001). However, acetaldehyde appears to be the typical substance of the ripe nut flavor in some dry sherry wines subjected to biological or oxidative ageing (Ferreira *et al.*, 1997).

Hydrolysis of acetates and esters with storage time, is another important factor resulting in the loss of the fruity character of young white wines, an effect accelerated by high temperature and low pH, (Perez-Coello *et al.*, 2003). Approximately 50% of the volatile compounds, (excluding ethanol) have a negative impact on the aroma and flavor of wine (Jackson *et al.*, 2000). The most significant mono-alcohols are propanol, 2-methyl propanol (isobutanol), the amyl alcohols (3-methyl-2-methyl- butanol) and 2-phenylethanol. Most researchers believe that these compounds contribute more to the intensity of the flavor of the wine than the quality, which is significantly reduced if in concentrations more than 400 mg / L (Ribéreau-Gayon *et al.*, 2006). On the other hand, 2-phenylethanol concentration in wines has a positive impact on wine quality (Ribéreau-Gayon *et al.*, 2006).

Alcohols are mainly of must alcoholic fermentation origin, while only hexanol, the hex-3-enol and octanol are present in grapes (Gurbuz *et al.*, 2006). An acetic acid concentration of at least 0.90 g/l (a volatile acidity of 0.95 g/l expressed in H_2SO_4) is required to produce a noticeable bitter, sour aftertaste. Even at these high levels however, it does not have a strong odor, whereas ethyl acetate is perceptible at much lower concentrations (Ribéreau-Gayon *et al.*, 2006).

It is relatively common for the aromas of white wines aged in bottle to develop defects. Changes in the oxidation marker concentrations during ageing are the phenylacetaldehyde (Ferreira *et al.*, 2002), the methional (Escudero *et al.*, 2000), and the sotolon (Escudero *et al.*, 2000; Ferreira

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et al., 2002) all of which are well known to be associated with the oxidative evolution of dry white wines stored under oxygen. Since the above researchers demonstrated that the choice of packaging can influence the dissolved oxygen level in the bottle and consequently the redox potential of the wine, they have suggested monitoring changes in these compounds during the experimentation.

Accordingly, the variability of this aromatic deterioration is due to considerable differences in permeability to oxygen among cork stoppers (Skouroumounis *et al.*, 2005). Their results demonstrated that the choice of the packaging, as the choice of the closure if uncontrolled, could promote the formation of oxidation flavors in dry white wines during a short period of ageing. Specifically, wines sealed with the synthetic closure were relatively oxidised in aroma, brown in colour, and low in sulfur dioxide compared to wines held under the other closures. A struck flint/rubber (reduced) aroma was discernible in the wines sealed under the screw caps or in glass ampoules. Wines sealed under natural bark corks in this study showed negligibly reduced characters (Skouroumounis *et al.*, 2005) .

While detrimental effects of excessive exposure to oxygen are well established, little is known about the exact impact on wine quality of low levels of oxygen exposure. Research on wine oxidation has been approached broadly. From a macroscopic point of view, modifications of sensory perceptions are considered, while work on the microscopic scale attempts to delineate the step-by-step mechanisms involved in oxidation (Karbowiak *et al.*, 2010).

Therefore, this work aimed at studying the oxidation evolution for white Greek wines, as impacted by oxygen transmission rates of the corks, by assessing the ingress of oxygen into the bottles, through the identification of specific quality indicators. Attent ion was directed towards the flavor compounds that evolve during the storage of the wines over a 12 month period. An additional goal was therefore set, for establishing the relationships among these indicators and a model-based shelf life prediction.

MATERIALS AND METHODS

1. Bottled wine samples

Three different white varieties grown in Greece (Assyrtiko, Malagouzia and Sauvignon blanc) were used in the production of six monovarietal wines. Wine samples were provided from Alpha Estate, Estate Argyros, Domaine Biblia Chora, Domaine Costa Lazaridi, Domaine Porto Karras and Papargyriou Estate. All samples were bottled in 750-ml glass bottles. The bottles were sealed using two agglomerated type corks: DIAM P015= 0.0008 cm^3/day, DIAM P035 = 0.0015 cm^3/day, (www.diam-closures.com) and stored under dark conditions at 20°C. After 0, 90, 210 and 360 days of storage, 2 bottles were removed and each one was analyzed in two replicates.

2. SO_2 analysis

Immediately after opening the bottle, free and bound sulfur dioxide contents were determined according to the OIV (1990) iodometric titrating method.

3. GC Analysis

- SPME extraction set-up

The SPME holder and the fiber 50/30-μm divinylbenzene – carboxen on poly(dimethylsiloxane) (DVB–CAR–PDMS) used in the analyses were purchased from Supelco (Aldrich, Bornem, Belgium). SPME fiber was preconditioned for 5 min at 220°C in the GC injector. For the following analyses, 5 min of desorption after each extraction was used as conditioning time. An aliquot of 7 ml of wine, 3 ml distilled water, 3g/10 ml for saturation NaCl and 10μl 3-octanol as internal standard were transferred into a screwcap glass vial with a Teflon rubber septum, in a thermostated bath 35°C and stirred for 10 min at 400 rpm before the fiber was exposed to the headspace for 30min under the same conditions.

- GC-MS analysis

Analysis of volatile compounds was performed using an Agilent 7890A GC, equipped with an Agilent 5873C MS detector. The column used was an HP-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and the gas carrier was helium with a flow rate of 1 mL/min. The injector and MS-transfer line were maintained at 250 ºC and 260 ºC, respectively. Oven temperature was held at 30 ºC for 5 min and raised to 160 ºC at 4 ºC/min and then to 240 ºC at 20 ºC/min. The samples were measured using synchronous full scan and selected ion monitoring (SIM mode). The scan parameters

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ran from 35 m/z to 400 m/z, and both full scan and SIM acquisitions were performed with an EMV Gain Factor of 7. All analyses were carried out in duplicate.

- Statistical analysis

All determinations were run in duplicate and values were averaged. Correlations between P0.15 and P0.35 closures were established using one-way analysis and comparisons for each pair using Student's t. Also, comparisons for all pairs using Tukey – Kramer HSD. All statistical analyses were performed by JMP (10.0.0).

RESULTS AND DISCUSSION

1. Corks

Given the permeability of the two cork types, as provided by the producer, (DIAM P015= 0.0008 cm^3/day, DIAM P035 = 0.0015 cm^3/day), we may comment that the amount of oxygen entering the bottles over a 12 month time period is respectively 0.168 cm^3 and 0.315 cm^3 per 750 ml of wine, or 0.224 cm^3 and 0.420 cm^3 per liter of wine, corresponding to 0.32 and 0.6 mg, respectively.

Accordingly, every alteration of the oxidation indicators (increase or decrease in mg/L), may correspond to the respective increase of the oxygen in the wine mass. Hence, for the same amount of oxygen present in the wine mass, there are certain alterations in the wine chemical, physical and sensorial properties. The rate of oxygen increase, for the 360 days of storage inside the wine mass for the P0.15 and P0.30 corks were 0.024 and 0.045, respectively, in accordance to the two corks' differences in OTR values provided.

We observed lower concentrations of free sulfur dioxide at 20^{o}C, with a statistically significant difference between the 0 and 3rd month in respect of Alpha samples but not in the case of Papargyriou samples. Between the two types of cork, P0.15 and P0.35, there is no significant statistical differences, except for the Papargyriou samples at 3 months of storage in which P0.35 cork maintained higher amounts of free SO_2, but this trend was not consistent after 12 months of storage.

If the free SO_2 content drops below 10 mgL^{-1}, white wine will experience increasing oxidation (Li *et al.*, 2008). The values determined for free SO_2 in the various packaging materials were low, potentially as a result of sulphites acting reductively by producing oxidation products (combined SO_2). In fact, sulphur dioxide is the most important and widely used chemical to prevent wine from browning. Besides antioxidant, SO_2 also has antimicrobial properties and other important functions. However, its excessive use can drastically compromise the quality of wine and excessive quantities of SO_2 can impair the wine's flavors and aromas or may promote cloudiness in the wine during storage (Li *et al.*, 2008). The decrease of the SO_2 content in a very short period confirmed the higher oxygen transfer rate. As expected, a decrease in SO_2 occurred in all the packaging configurations, independent of the permeability of the cork. (Figure 1).

The final SO_2 content was below 20 mgL^{-1}, which is considered a rather low-level value after 12 months of storage. Apparently, oxygen that diffuses in the wine results in a similar SO_2 depletion in all the wine samples. Therefore, the insignificant detected differences for each wine in time, were most likely due to the fact that within the 12 months-time period, the P0.35 corks did not result in excess permeation of oxygen and, as a consequence, a similar SO_2 oxidation occurred in the packed wine of either cork (Mentana *et al.*, 2009).

According to Godden *et al.* (2001) the loss of SO_2 was in general highly correlated with an increase in wine browning (OD_{420}) and the concentration of SO_2 in the wine at six months was a strong predictor of future browning in the wine, particularly after eighteen months. Neither the concentration of dissolved oxygen at bottling (0.6–3.1 mg/L), nor the physical closure measures were predictors of future browning. For several closures, upright storage tended to accelerate loss of SO_2 from the wine, but in many cases this effect was marginal.

However, the direct reaction of sulphur dioxide with oxygen under wine conditions is very slow and essentially irrelevant. Thus, the sulfur dioxide potentially reacted with hydrogen peroxide, aldehydes and ketones (Lopes *et al.*, 2009).

A decrease in SO_2 was shown to accelerate the oxidation of wine and the change of hue, therefore color development after bottling depends on the contact of wine with oxygen throughout storage. Furthermore, the chromatic

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changes during wine browning were well documented regarding the aromatic deterioration occurring prior to the color change (Escudero *et al.*, 2002; Silva-Ferreira *et al.*, 2002). At the same time, attention has focused on flavor degradation during wine browning and on the relationship between the changes in flavor and color of the wine (Ferreira *et al.*, 1997; Ferreira *et al.*, 2002). Timberlake and Bridle (1976) first proposed one of the mechanisms by which acetaldehyde could contribute to the formation of dimer and trimer between flavanols (tannins), later it was confirmed by other researchers (Es-Safi *et al.*, 1999; Fulcrand *et al.*, 1996; Saucier *et al.*, 1997). These reactions increase the color of the yellow spectral region and likewise the condensation degree (Lopez-Toledano *et al.*, 2004).

In the current tudy the following esters were determined: ethyl butanoate (EB), ethyl hexanoate (EH), ethyl octanoate (EO), ethyl decanoate (ED) and ethyl dodecanoate (EDD) (the ethyl ethers of straight-chain fatty acids), ethyl 2-methylbutanoate (E2mB) and ethyl 2-methylpropanoate (E2mP) (the ethyl esters of branched acids), isoamyl acetate (IA), 2-phenylethyl acetate (PA) and hexyl acetate (HA) (the acetates) and the higher alcohols, isoamyl alcohol (ISA) and phenethyl alcohol (PEA). In addition, EB and EH were reported to enrich the wine with strawberry-like aromas, EO with odors of ripe fruit, ED and EDD with waxy and fruity flavors, E2mB by strawberry, apple and anise odors, E2mP by pineapple, mango and cherry notes while IA and PA are described by banana and rose notes respectively (Sumby *et al.*, 2010). PEA is characterized by rose, pungent, honey and floral while ISA by banana and fusel alcoholic odors (Gurbuz *et al.*, 2006).

Distinct differences in the flavors present after 12 months of storage between the two corks for the Assyrtiko were recorded for the ethyl isobutyrate, ethyl 2-methyl butyrate, ethyl caprylate, ethyl decanoate and isoamly alcohol. The first three esters and isoamyl alcohol showed an increase in the wines sealed with the cork P0.15 and a decrease in the wines sealed with the cork P0.53 whereas the opposite was observed for ethyl decanoate. For the Malagouzia wines, the compounds that showed differences between the samples were ethyl caproate, ethyl dodecanoate and isoamyl alcohol. Ethyl caproate and isoamyl alcohol contents increased only in the wines sealed ith P0.15 while the ethyl dodecanoate content increased only in the samples that were sealed with the P0.35 corks. For the Sauvignon blanc wines, the compounds that differ among the samples depending on the type of cork were ethyl 2-methyl butyrate, ethyl caproate, ethyl dodecanoate, hexyl acetate, 2-phenylethyl acetate and isoamyl alcohol. Isoamyl alcohol, ethyl decanoate, 2-phenylethyl acetate and hexyl acetate contents increased in the wines closed with P0.35 whereas the opposite was observed for the remaining compounds, their values only increasing in the samples closed with P0.15. The concentration of specific ethyl esters, such as ethyl isobutyrate, ethyl dodecanoate, ethyl caproate and ethyl butyrate, increased at 12 months, while the concentrations of the rest of the esters (ethyl decanoate, ethyl-2-methyl butyrate) did not change significantly compared with their initial concentrations. In general, shorter chain ethyl esters (such as ethyl-2-methyl butyrate an ethyl caprylate and caproate) seem to be more susceptible to oxidation as their concentrations decrease in the samples with higher oxygen exposure during storage. In contrast, the concentration of longer chain esters (such as ethyl decanoate and dodecanoate) might

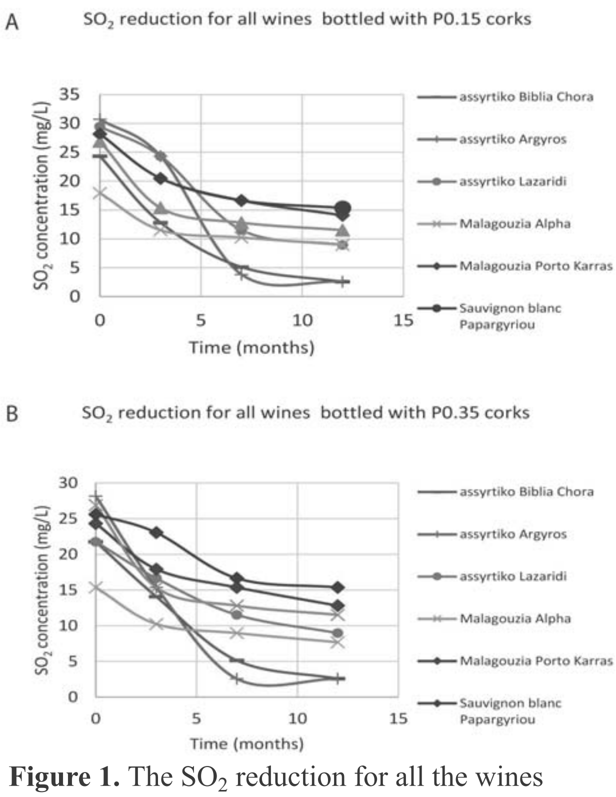

Figure 1. The SO_2 reduction for all the wines bottled at A) P0.15 and B) P0.35 corks, stored at 20 °C for 12 months.

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TABLE 1. Volatile compounds identified in the three varieties stored at 20 °C at the 360th day of storage, with either the P0.15 or the P0.30 type of cork.

Volatile compounds	Assyrtiko		Malagouzia		Sauvignon blanc	
	P0.15	P0.35	P0.15	P0.35	P0.15	P0.35
Ethyl butyrate	ND*	ND	+	+	+	+
*Ethyl-2-methyl butyrate	+	-	ND	ND	+	-
*Ethyl isobutyrate	+	-	+	+	+	+
*Ethyl caprylate	+	-	+	+	+	+
*Ethyl caproate	ND	ND	+	-	+	-
*Ethyl decanoate	-	+	+	+	-	+
*Ethyl dodecanoate	+	+	-	+	+	+
Isoamyl acetate	ND	ND	ND	ND	+	+
Phenylethyl alcohol	+	+	+	+	+	+
*2-Phenylethyl acetate	ND	ND	ND	ND	-	+
*Hexyl acetate	ND	ND	ND	ND	-	+
*Isoamyl alcohol	+	-	+	-	-	+

Compounds marked with * indicate differences in their presence between the two corks at the time of sampling (12 months of storage). (+) indicates an increase and (-) indicates a decrease in their presence, all compared to time 0.

be increased with the exposure of the wines to higher oxygen contents.

Regarding the concentration of the remaining compounds, phenethyl alcohol, increased during storage in all samples studied whereas, isoamyl acetate content increased in Sauvignon blanc wines and ethyl butyrate in Malagouzia and Sauvignon blanc wines.

As previously reported by Makhotkina and Kilmartin (2012), wines lose their fresh, fruity characters over time in the bottle. Such changes have been associated with oxidation reactions occurring in white wines. The concentration of volatile acetate esters, including isoamyl acetate, hexyl acetate and 2-phenyl ethyl acetate were found to decrease with time. The temperature at which the wines were stored significantly influenced the rate of acetate ester degradation: the higher the temperature the faster the rate of degradation, due to hydrolysis of the ester to acetic acid and an alcohol.

Furthermore, the wine hydrolysis products such as those deriving from the hydrolysis of acetate esters are the acetic acid and the respective higher alcohols, confirmed via the monitoring of the alcohols in all the wines. An increase in the concentrations of the phenethyl alcohol and isoamyl alcohol were observed. In similar studies, an increase in the concentrations of higher alcohols in different wines was reported (Garde-Cerdán *et al.*, 2008) while in other studies the concentration remained unchanged during storage under various conditions (Roussis *et al.*, 2005). Garde-Cerdán and Ancín-Azpilicueta (2007) concluded that the SO_2 concentration has an influence on the evolution of the alcohols and the esters in wine and, to a lesser extent, on the evolution of the acids during bottle ageing.

Through the analysis of the results in Table 1, we may now determine those compounds that could adequately distinguish the alterations within each of the wines studied in this work. From this, we may propose certain oxidation indicative markers as shown in Table 2.

Interestingly, certain compounds were found to be affected by the cork in two wines; ethyl decanoate and ethyl 2-methyl butyrate for the Assyrtiko and Sauvignon blanc varieties; ethyl caproate for the Malagouzia and Sauvignon blanc varieties. Isoamyl alcohol was the only compound whose presence was dependent on the type of cork in all samples studied and for this reason it was selected for the construction of the mathematical models. By contrast, the remaining compounds were exclusively present in significantly different amounts only in one of each of the studied wines.

In general, since esters are produced in excess by the end of fermentation, they gradually hydrolyze during storage until equilibrium with their corresponding acids and alcohols is

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TABLE 2. A summary of the indicative ester and higher alcohol markers for the oxidative alterations occurring within the wines according to variety.

Assyrtiko	Malagouzia	Sauvignon blanc
Ethyl isobutyrate	Ethyl caproate	Ethyl 2-methyl butyrate
Ethyl 2-methyl butyrate	Isoamyl alcohol	Isoamyl alcohol
Ethyl caprylate	Ethyl dodecanoate	Ethyl caproate
Ehyl decanoate		Ethyl decanoate
Isoamyl alcohol		2-Phenylethyl acetate
		Hexyl acetate

achieved (Gonzalez-Centero *et al.*, 2016). Accordingly, the results of this study could be explained by the specific hydrolysis – esterification equilibrium involved. As reported by Makhotkina and Kilmartin (2012) the rate of esterification reactions depends on the initial concentration of the branched acid from which the ester is formed i.e. the more of the acid a wine contains the higher the esterification rate. These changes in the composition of the individual ester content of the wines are dependent on wine chemical composition and primarily on pH, ethanol content and storage temperature (Garde-Cerdan *et al.*, 2004). However, González-Centeno *et al.* (2016) reported a considerable increase (up to 3.7 folds) for ethyl ester and higher alcohol acetate concentration with barrel ageing. A similar increase in the concentration of ethyl butyrate, ethyl hexanoate and isoamyl acetate with ageing has been reported by Garde-Cerdan *et al.* (2002) and Jimenez Moreno and Ancin-Azpilicueta (2006). According to Jackson (2014) a slow synthesis of these compounds may be expected during ageing since their concentration in wine is commonly below the equilibrium level at the end of fermentation. Moreover, release into the wine may occur during yeast cellular lysis (Jimenez Moreno and Ancin-Azpilicueta, 2006).

2. Modeling of the wine flavor compounds as potential oxidation markers

Significant differences in the slopes of the evolution of isoamyl-alcohol during the 12 months of storage between the two corks were identified. This particular compound decreased when the P0.35 cork was used for the Assyrtiko and Malagouzia variety wines. In contrast, Sauvignon blanc wines indicated a higher presence of isoamyl-alcohol, when the P0.35 corks were used.

In order to estimate the time needed for the bottled wine to overpass an arbitrarily defined, acceptable quality threshold, it is necessary to translate the microscopic-level measured values of $C_{\text{isoamyl alcohol}}$ into a macroscopic quality index. This could be proposed as the probability of the wine not to reach the end of its shelf life during a defined time period, customarily positioned at 12 months. This probability has been shown by Coutelieris and Kanavouras (2006) and Kanavouras and Coutelieris (2006) to be analogous to the fraction of the area between the concentration over time curve and above the arbitrarily defined acceptable quality threshold over the overall area of the concentration curve. By expressing areas integrals, the probability, P_{safe}, for the wine not to reach the end of its shelf life during the predefined time period, can be obtained:

$$P_{safe} = 1 - \frac{\int_{time\_critical}^{end\_of\_period} C_{isoamyl\_alcohol}(t)dt}{\int_{0}^{end\_of\_period} C_{isoamyl\_alcohol}(t)dt} \quad (1)$$

By defining the end_of_period at 12 months and by denoting time_critical as t_{cr}, the above eq. (1) becomes:

$$P_{safe} = 1 - \frac{\int_{t_{cr}}^{12} C_{isoamyl\_alcohol}(t)dt}{\int_{0}^{12} C_{isoamyl\_alcohol}(t)dt} \quad (2)$$

Subsequently, the process for calculating the t_{cr} is as follows. First, we have to find out the point where the threshold line intersects with the concentration curve. The perpendicular coordinate value represents the critical time while the vertical coordinate identifies the limit above which the P_{safe} has also to be calculated. Clearly, different thresholds correspond to different t_{cr} and consequently to different P_{safe} values. A graphical representation of the above is given in the next Figure 2.

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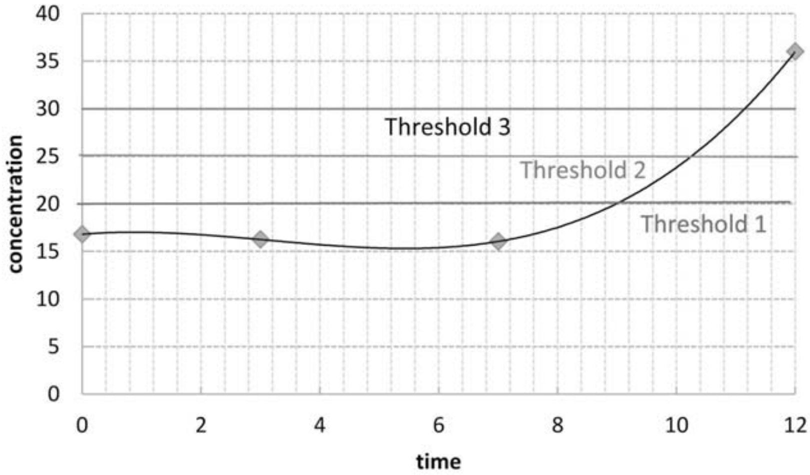

FIGURE 2. Graphical representation of the identification of critical time in equation (2).

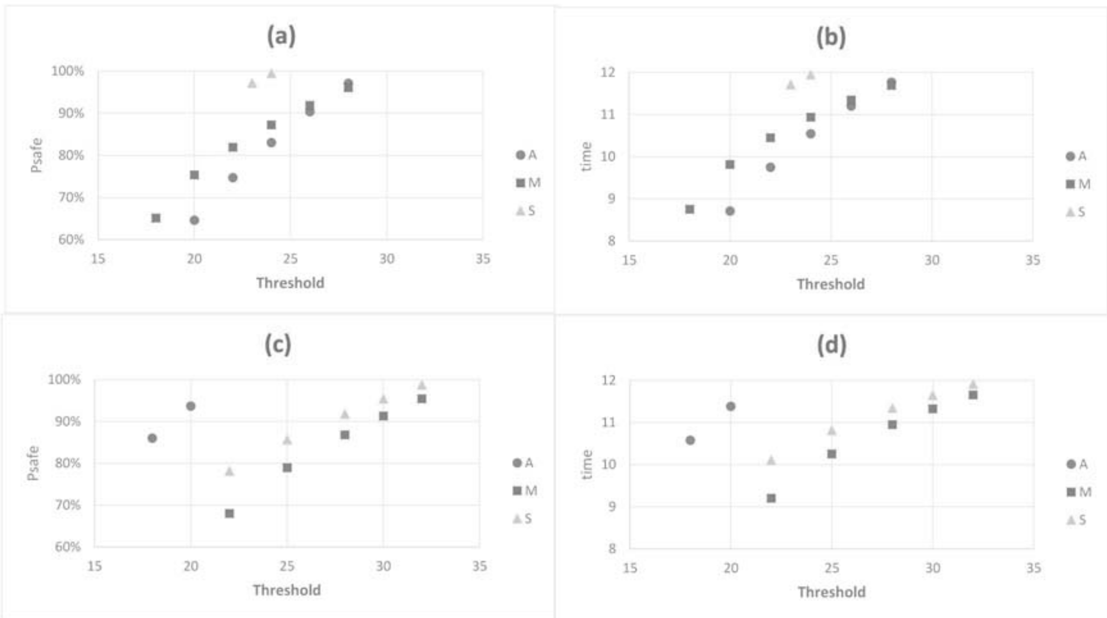

FIGURE 3. Effect of threshold value on P_{safe} and t_{cr} for P0.15 cork (a, b), and P0.35 (c, d), and the three wine varieties (A-Assyrtiko, M-Malagouzia, S-Sauvignon blanc).

Based on the above, we may now plot the impact of the threshold selection on the possibility of each bottled wine not reaching the end of its shelf life during a defined time period, as well as the consequent critical time at which this is expected to occur. The abscissa of the point that the curve in Figure 2 cuts the threshold line, represents the shelf-life of the product. For instance, the shelf-life is approx. 9.2 when Threshold 1 is selected. Obviously, shelf live value is strongly dependent on threshold selection.

As shown in Figure 3, the comparison between (a) and (c) indicates a significant effect of the cork OTR on the P_{safe}; though, different wines responded differently to the oxygen transmitted through the cork and reaction outcome of the oxidation phenomena as reported by the evolution of the selected marker of isoamyl alcohol. For wines bottled with cork P0.15, the Sauvignon blanc showed higher concentrations of isoamyl alcohol compared to Assyrtiko variety. The Managouzia wines showed similar trends to Assyrtiko, but with slight deviations at low quality thresholds. It is important to note, that the same behavior has been observed when t_{cr} was considered. Actually, the impact of the threshold level on the critical time could be of a completely different mode compared to that of the P_{safe} value. That depends on the shape of the indicator's concentration curve in time. In this case, this curve approximates a straight line within the region of interest (i.e. within the domain of the arbitrarily given specific hreshold values). Therefore, the relationship between critical time and possibility (P_{safe}), should be quasi-linear.

CONCLUSIONS

In this study, the investigation of the impact of oxygen permeating through the corks on the oxidation markers for various Greek white wines was performed. A series of three characteristic varieties, cultivated in Greece and bottled at different wineries, were used in order to extend the understanding of the oxidative alterations. Evidently, a rather distinct preservation methodology is followed by each winery since characteristic differences were reported for the initially added SO_2 concentrations in the wines.

Regarding the impact of the two corks it was notable that significant differences could be determined between the two corks for wines stored at 20°C. Whether the rates among the various reactions in the wines would be similarly affected by elevated or lower temperatures in time, still requires further investigation.

Based on the analytical results of the flavor compounds evolution, this study could conclude that the two corks studied in this work supported a limited oxidation acceleration with indistinctive differences at the early storage times and no significant impact could have been reported on the majority of the flavor compounds of the wines. Contrary to the analytical results, the mathematical treatment of the collected data as performed herein, did reveal particular variations in the oxidation level between the wines bottled with different corks.

In addition, the mathematical treatment of the results, indicated that a high consideration should be placed regarding the selection of the packaging materials, in relation to the quality threshold we wish to set for the products in question. Specifically, the lower the quality threshold, the higher the probability of the wine not reaching the end of the shelf life during the 12 months of storage. When the baseline was tested for a 5% step-wise increment, the probability raise was rather low. The modeling of the results indicated the importance of cork selection due to the OTR values that may impact on the quality of the wines in time, according to the evolution of the isoamyl-alcohol concentration. In practice, the outcome of the mathematical treatment supported the position that P0.15 has a better performance and a positive effect on the quality of the three wines.

Consequently, we may conclude that properties of the packaging may facilitate a limited modification of the added chemicals and preservatives in the wine. When engineered within technological boundaries, the holistic approach of matching appropriate packaging with the edible product contributes to the production of high-quality consumables. Factors to be considered when implementing this approach include; initial quality of the wine; the target markets; cost of the packaging; wine making technology adopted. Packaging materials and storage conditions play a significant role in the fine-tuning of the quality of the product. Packaging is therefore an important consideration when seeking to maximize customer satisfaction and securing the position of the product in a highly competitive modern market.

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