



Corso di dottorato di ricerca in:

“Alimenti e Salute Umana”

Ciclo 36°

Titolo della tesi

**Novel approaches for the evaluation of white wine aging in bottle
and application of innovative technologies for the management of
dissolved oxygen**

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Riassunto

L'evoluzione dei vini bianchi risulta essere una tematica di forte interesse, sia dal punto di vista della ricerca, che produttivo. Tra i parametri cruciali per valutare le potenzialità legate all'evoluzione di un vino bianco, vi sono l'analisi della concentrazione dell'anidride solforosa e la valutazione colore, mediante assorbanza a 420 nm, i quali tuttavia, non restituiscono un quadro esaustivo. Grazie al concomitante avanzamento tecnologico ed all'incremento delle conoscenze in enologia, nuove metodiche permettono oggi di meglio valutare lo stato evolutivo del vino. Tra queste metodiche troviamo la gas-cromatografia per la valutazione della componente volatile e la voltammetria ciclica, quest'ultima risulta essere un'analisi di forte interesse, soprattutto in seguito allo sviluppo di potenziostati portatili e degli elettrodi screen-printed, permettendo un'ulteriore semplificazione della tecnica d'analisi. Data la natura e la complessità della matrice vino, la voltammetria ciclica necessita di conoscenze approfondite per l'interpretazione dei risultati, in quanto dal voltammogramma ottenuto, non risulta possibile differenziare i differenti processi registrati.

Nella presente tesi di dottorato, differenti tipologie di analisi sono state impiegate al fine di valutare l'evoluzione di trentasei vini bianchi monovarietali, prodotti nel nord-est Italia. Sia i parametri classici impiegati per la valutazione dell'evoluzione, quali contenuto di anidride solforosa, assorbanza a 420 nm, sia la valutazione dei composti carbonilici e la voltammetria ciclica sono risultati efficaci e significativi al fine di valutare l'evoluzione dei campioni, seppur quest'ultima in modo minore.

I dati ottenuti dalla voltammetria ciclica, così come gli spettri relativi al campo del UV e del visibile, sono stati impiegati con successo al fine di predire alcune variabili analizzate nel progetto di dottorato, mediante l'applicazione della regressione dei minimi quadrati parziali (PLS).

Inoltre, i dati relativi alla voltammetria ciclica sono stati correlati alle distanze sul piano fattoriale basato sull'analisi delle componenti principali (PCA) di diversi parametri al fine di valutarne la relazione. Tale elaborazione sarà utile per lo sviluppo futuro di un modello previsionale in grado di stimare i cambiamenti legati all'evoluzione.

Contestualmente, è stato sviluppato un ulteriore progetto al fine di determinare gli effetti sull'evoluzione del vino legati sia alla gestione dei gas disciolti, mediante applicazione della membrana contactor, sia dall'uso di diverse tipologie di chiusure. Nel dettaglio, sono state testate tre diverse chiusure a vite, ciascuna con caratteristiche differenti, insieme a un tappo in sughero agglomerato.

I risultati ottenuti hanno evidenziato che la gestione dei gas disciolti durante la fase di imbottigliamento ha comportato una significativa riduzione della concentrazione di ossigeno disciolto, soprattutto in combinazione con l'utilizzo di chiusure a vite.

L'utilizzo della membrana contactor ha inoltre dimostrato di avere un impatto positivo sull'evoluzione. In particolare, l'analisi dei parametri chimici ha rivelato una minore propensione all'evoluzione in combinazione con tappo in sughero agglomerato e nel liner Saranex. Per quanto riguarda la presenza dei composti carbonilici, i liner 'M' e Saranex hanno mostrato una minore concentrazione rispetto alle altre chiusure impiegate, suggerendo una minore evoluzione nel tempo.

Quindi, l'utilizzo della membrana contattore si conferma efficace nel preservare il vino bianco imbottigliato sia nel breve che nel lungo periodo.

Parole chiave: evoluzione, vino bianco, voltammetria ciclica, chiusura, membrana *contactor*, ossigeno disciolto.

Abstract

Evolution in white wines is a topic of considerable interest from both research and production perspectives. Analytically, the concentration of sulfur dioxide and color evaluation, measured by absorbance at 420 nm, are crucial parameters for assessing the potential evolution of a sample. However, these parameters do not provide an exhaustive vision and, in this regard, technological progress and increased knowledge in enology have allowed the development of methodologies to obtain more detailed parameters to assess the evolution state of a wine, such as the use of gas chromatography to evaluate the volatile component. Cyclic voltammetry is an interesting analysis, especially after the development of portable potentiostats and disposable screen-printed electrodes, which have allowed a further simplification of this method of analysis. However, interpreting the results of cyclic voltammetry requires a detailed understanding of the analysis and the matrix. Due to the complexity of the wine matrix, the resulting voltammogram may not allow the discrimination of the different processes.

In this work, different typologies of analysis have been used to evaluate the evolution of thirty-six monovarietal white wines, produced in the north-east of Italy. The parameters commonly used to evaluate the evolution of the samples, such as sulfur dioxide content and absorbance at 420 nm, were found to be effective, as well as, the evaluation of carbonyl compounds. Furthermore, cyclic voltammetry was found to be effective, for this purpose, but in a lower order.

Additionally, data acquired from cyclic voltammetry, as well as spectra obtained in the UV and visible spectra, were used to predict some variables analyzed in the dissertation, with good results, through the application of Partial Least Squares (PLS).

Moreover, data related to cyclic voltammetry were correlated to distances on a factorial plane based on PCA of different parameters to assess the relationship. This will be useful for the future development of a forecast model that can estimate evolution-related changes.

Finally, a second project was developed to evaluate the effect of managing dissolved gases, specifically oxygen, using a contactor membrane. The project also examined the effect of different

closures, including an agglomerated cork closure and three different screw caps with different liners and different characteristics, the most important of which, from an enological point of view, is the oxygen transfer rate (OTR).

Gas management during bottling resulted in a significant decrease in dissolved oxygen concentration, particularly when combined with screw caps.

The use of the contactor membrane resulted in a lower tendency of evolution, as determined by chemical parameters and the assessment of the carbonyl compounds contained in the wine. The analysis reveals a tendency towards lower evolution of agglomerated cork closures and the use of Saranex liner by the assessment of chemical parameters, while with regard to the presence of carbonyl compounds, some of the tested liners differed from the rest by a lower presence, thus a lower evolution. Therefore, the use of contactor membrane is an effective method for preserving bottled white wine in the short- and long-term.

Keyword: evolution, white wine, cyclic voltammetry, closure, contactor membrane, oxygen dissolved

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Introduction

1. Wine modifications

The evolution of wine is a topic of considerable discussion in enological research, affecting the perception of quality, mainly through two main pathways: oxidative and reductive (Gabrielli et al., 2021).

The International Organization for Standardization (ISO) 9001:2008 (2008) defines quality as the product characteristics that meet customer requirements. This definition highlights two key factors: the product intrinsic properties, including chemical composition, taste, and color, and its extrinsic properties, such as packaging and marketing information. Additionally, it is essential to consider the link of product with customer satisfaction (Charters & Pettigrew, 2007).

Customer satisfaction is a crucial aspect to investigate, particularly in the context of a complex matrix such as wine. In the case of wine, it is necessary to have the absence of production and aging defects, as well as the identification of customers based on price and distribution channel (Franco-Luesma et al., 2019).

The sensory aspect of wine is a critical factor (Charters and Pettigrew, 2007), but it is often impossible to assess it before purchase (Gambetta et al., 2017). One approach, based on the perception of a panel, is to assign a score to help the consumer evaluating the quality of the wine (Gawel & Godden, 2008). Hopper *et al.* (2015) found a significant correlation between chemical parameters of wine and sensory analysis. However, this study is a preliminary investigation, and additional studies will follow. Nonetheless, this approach can serve as a viable technique for quickly establishing wine quality perception and assessing how it relates to wine evolution.

The International Organization of Vine and Wine (OIV) defines wine as “a beverage resulting exclusively from the partial or complete alcoholic fermentation of fresh grapes, whether crushed or not, or grape must” (OIV, 2022). As wine is classified as a beverage, i.e. a "food", it is necessary to link the concept of evolution with that of shelf-life. Shelf-life could be defined as the period of time

during which foods can satisfy the primary needs of consumers and exhibit limited changes in sensory quality (Kilcast & Subramaniam, 2000).

Wine can be described as a complex system in continuous change, which undergoes modifications during the storage phases (Recamales et al., 2006). Dubourdieu (1992) has summarized this phenomenon by proposing an aging curve for bottled red wine, which could also be applied to white wines, taking into account some precautions related to the different timing of the evolution, depending on the composition. The curve can be divided into three phases: maturation, maturity, and decline. Each phase is distinguished by distinct sensory and chemical characteristics.

The duration of each phase, and more generally the evolution of a white wine, is determined by many factors, from the grape production to the storage conditions of the bottled wine, taking in consideration each single step (Kallithraka et al., 2009; Salacha et al., 2008; Silva Ferreira et al., 2003). In particular, for bottle storage, it is essential to take into account the packaging, in terms of the closure (Castellanos et al., 2021; Dimkou et al., 2011; Furtado, Lopes, et al., 2021; Skouroumounis et al., 2005), but it is also necessary to consider the characteristics of the glass bottle (Arapitsas et al., 2020).

Moreover, it is also necessary to evaluate some environmental factors, mainly temperature and light (Bekbölet, 1990; Dias et al., 2012; Fracassetti et al., 2017; Grant-Preece et al., 2017; Ough, 1985).

Different studies have analyzed the potential and current state of wine evolution through various analyses and evolution markers. However, the extended waiting times required to study wine evolution are one of the main difficulties. Accelerated tests are frequently used to overcome this problem, although they are very effective from the point of view of time, but they often do not respect the timing of the kinetics that take place in the bottle, in fact this type of kinetics exploits the use of temperature, this leads to a modification of the Arrhenius equation to speed up the chemical reactions, and it has been seen that does not reflect a real behavior of evolution (Cejudo-Bastante et al., 2013; Kallithraka et al., 2009; Ma et al., 2022; Ough, 1985).

Possible modifications of wine during bottle storage

The evolution of wine is primarily attributed to non-enzymatic processes, in which oxygen plays a crucial role (Danilewicz, 2003; Ugliano, 2013). Oxygen is responsible, either directly or indirectly, of many reactions in wine, causing changes that could lead to oxidized characteristics. Conversely, the absence of oxygen can result in reductive faults (Ugliano, 2013).

Oxygen is involved in many pathways, oxidizing various chemical components of wine, including polyphenols, volatile compounds and antioxidants (Bueno et al., 2010; Danilewicz, 2003; Waterhouse et al., 2016). These reactions exhibit non-selective behavior and can occur without discrimination. Oxygen is more reactive as a hydroxyl radical produced through the Fenton reaction, which requires the presence of iron and copper (Figure 1) (Li et al., 2008).

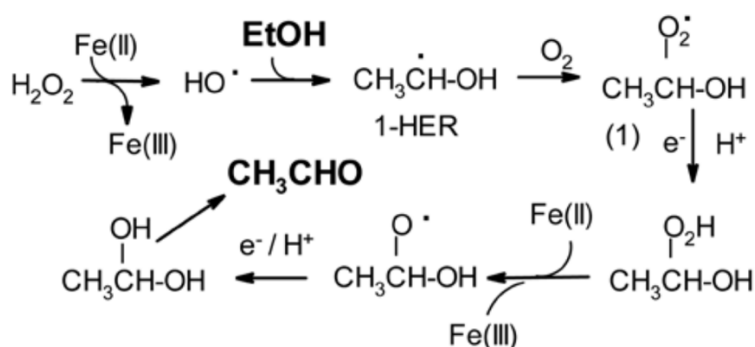


Figure 1 Proposed mechanism by Danilewicz (2021), based on the Fenton reaction, the production of acetaldehyde.

The order of reaction for the different species depends on their concentration, but also on their structure. This process has been comprehensively investigated by Danilewicz (2003, 2016). Oxidation products result in the formation of quinones, depending on the pathway of oxidizing phenolic compounds (0.2-0.5 g/L in white wines) (Gutiérrez-Escobar et al., 2021). Additionally, oxidative reactions can impact the volatile composition of white wines, with a particular effect on aldehyde concentration (Culleré, et al., 2007; Marrufo-Curtido et al., 2021). The most significant aldehydes from a sensory perspective are acetaldehyde, phenylacetaldehyde, and methional, causing an overall decrease in the concentration of fruity aroma compounds. Studies demonstrate the potential of limiting the amount of aldehydes by using different types of resins (Marrufo-Curtido et al., 2021).

Oxidation

Evolution in wine is predominantly associated to oxidative phenomena and, as previously mentioned, this phenomenon turns out to be at the expense of different molecules present in wine. The impact of oxidation on the phenolic component has been extensively studied. Danilewicz (2021) observed a reduction over time of more reactive polyphenols when wine is exposed to oxygen. Figure 2 depicts an oxidation pathway involving different steps for the catechol functional group and in a similar way for pyrogallol species, highlighting in particular the importance related to the presence of iron for the formation of hydroperoxyl radical (Figure 2 step 1), which reacts with catechol functional groups (Figure 2 step 2), leading to the formation of semiquinone radical and by effect of further oxidation to quinone (Figure 2 step 3). In step 2, hydrogen peroxide is produced, which reacts with ferrous iron (as shown in Figure 2, step 4), resulting in the production of hydroxyl radical. This unstable molecule oxidizes different classes of compounds (as shown in Figure 2, step 5), including alcohols and organic acids, leading to the formation of aldehydes and keto acids, respectively (Waterhouse & Laurie, 2006).

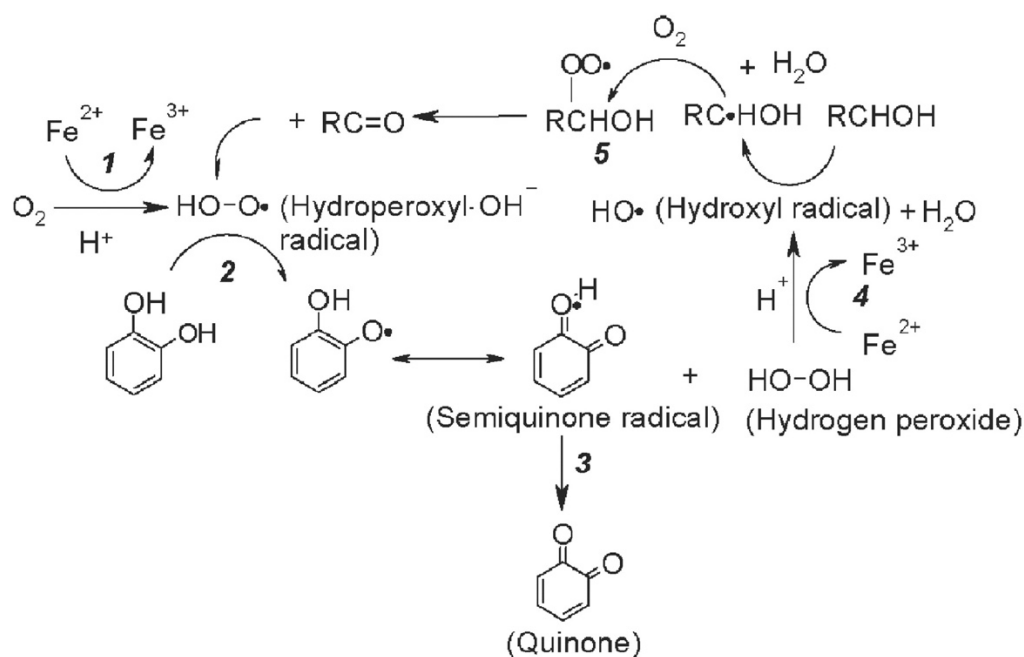


Figure 2 The pattern of the phenolic component on the primary reaction (Waterhouse & Laurie, 2006).

The described process turns out to be one of the effects related to the presence of oxidative phenomena, which can occur during wine production in the winery or in the bottle. For this reason, it is important

to minimize exposure to oxygen during the process to avoid spoiling the quality of the wine. Certain winemaking techniques executed at winery level may cause an increase in dissolved oxygen. Research suggests that cold tartaric stabilization, filtration using rotary vacuum filters, and bottling procedures are the most effective practices (Table 1) (Catarino et al., 2014).

Table 1 Increase of dissolved oxygen during enological treatment for white wines, mean and standard deviation (Catarino et al., 2014).

Oenological treatment	Oxygen increase (mg/L)
Protein stabilization	0.13 ± 0.05
Cold tartaric stabilization	2.29 ± 1.78
Filtration (membrane cartridges)	0.51 ± 0.18
Bottling (glass bottles)	1.11 ± 0.47
Packaging (bag-in-box)	2.22 ± 0.77

The use of inert gases and technological advancements has markedly reduced the amount of dissolved gas during transfer stages. Studies indicate that an inert gas mixture of CO₂ and Ar (20:80) is the most effective. However, this application is economically expensive, consequently, from an economic point of view, CO₂ remains the most recommended option (Del Barrio-Galán et al., 2023).

It is possible to regulate the concentration of gases, particularly oxygen and carbon dioxide, by utilizing a membrane contactor (Figure 3) during or prior to bottling that complies with Resolution OIV-OENO 499-2013 (OIV, 2013). Vidal et al. (2010) obtained a strong reduction of dissolved oxygen through the application of a contactor membrane, bringing the final oxygen concentration at 0.2 mg/L for white wines and 0.14 mg/L for red wines. Membranes can be characterized by different materials, coating and pore sizes, and different membranes can give different results (Breniaux et al., 2019). Reducing dissolved oxygen concentration could be a useful treatment to decrease the use of antioxidants, such as sulfur dioxide, from harvest to bottling (Schonenberger et al., 2014). This technique does not affect a wine volatile composition but can preserve aroma compounds reducing oxygen and limiting oxidative phenomena and aldehyde formation (Errichiello et al., 2021; J. C. Vidal et al., 2010).

After bottling, it is more difficult to intervene. The primary factor that affects the dissolved oxygen in bottled wine is the characteristics of the closure, which are influenced by the storage conditions.

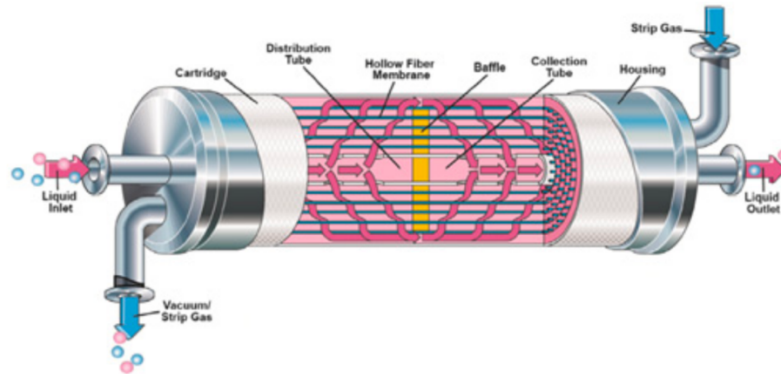


Figure 3 Section and working diagram of a contactor membrane (Schonenberger et al., 2019).

Reductive fault

Reductive defects are defined by the presence of volatile sulfur compounds (VSCs). VSCs have low odor thresholds and high volatility, as hydrogen sulfide, ethanethiol, and methanethiol. These compounds are recognized by an odor reminiscent of "rotten egg", "rotten cabbage", or "onion" which reduces the perception of wine aroma (Franco-Luesma et al., 2016; Waterhouse et al., 2016). These compounds are principally associated with yeast metabolism, which is influenced by numerous factors, including the presence of sulfur dioxide, low concentrations of assimilable nitrogen, peptides, and amino acids. Figure 4 illustrates a summary diagram of the metabolism that occurs within the yeast cell related to the production of VSCs (Dzialo et al., 2017).

Light-struck defect

The light-struck off-flavor could be another fault that may occur in bottled wine. Riboflavin (vitamin B2) plays a crucial role in this pathway, as it is produced by yeast metabolism during fermentation (Di Canito et al., 2023; Fracassetti et al., 2017, 2020; Grant-Preece et al., 2017). The onset of the fault also requires sulfur amino acids, specifically methionine. The exposure to light, characterized by a wavelength between 370 and 450 nm, triggers a reaction that leads to the formation of methanethiol and dimethyl disulfide, which are characterized by the odors of onion and cooked cabbage (Fracassetti, Di Canito, et al., 2021; Mislata et al., 2022).

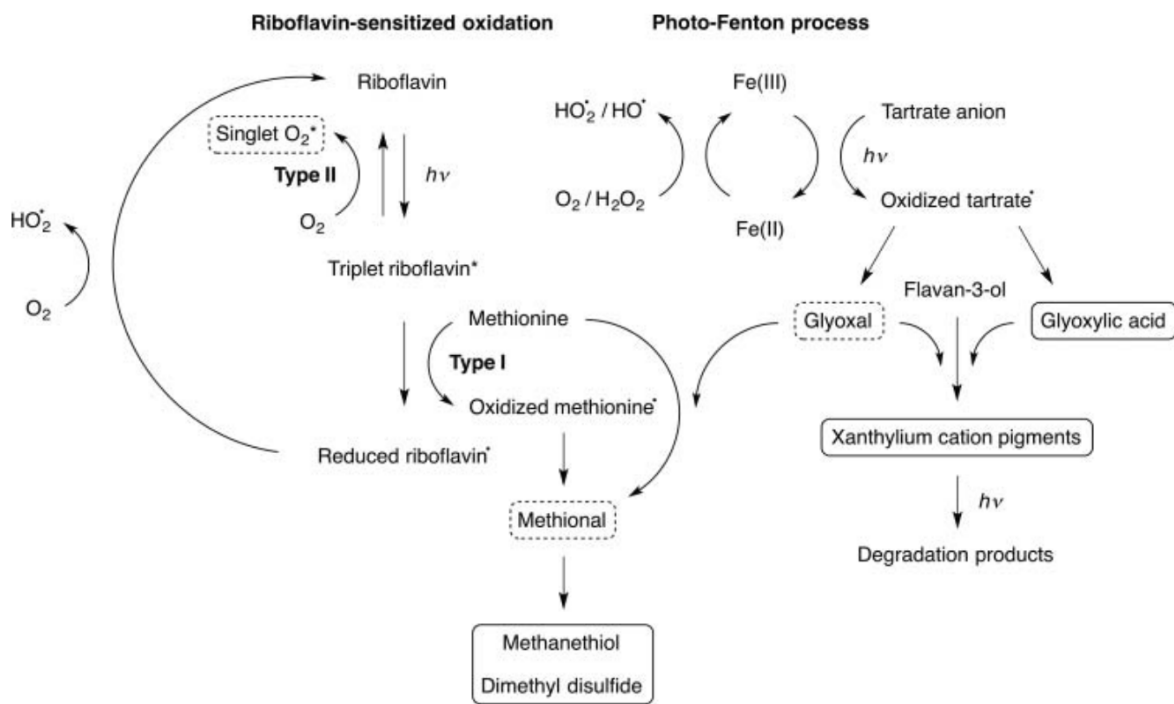


Figure 5 The oxidation of wine components, sensitized by riboflavin, and the photo-Fenton process in bottled white wine exposed to light, lead to the formation of sulfured volatile compounds that are indicators of light-struck defect (Grant-Preece et al., 2017).

To prevent this defect, several enological treatments are available. For instance, zeolites, charcoal, or bentonites can partially remove riboflavin (Fracassetti, Limbo, et al., 2021; Noviello et al., 2021; Vendramin et al., 2021); while sulfur dioxide, glutathione, and tannins can limit the formation of volatile sulfur compounds (Fracassetti et al., 2019, 2020, 2023; Fracassetti, Limbo, et al., 2021).

Atypical aging

Another defect, known as atypical aging, has been discussed controversially in recent years.

The fault originates from indolyl-3-acetic acid, a plant hormone that may decrease during bottle aging and results in the formation of 2-aminoacetophenone, which is the principal cause of this defect (Alpeza et al., 2021; Nardin et al., 2022). This compound is characterized by a low odor threshold, which has been described as smelling like naphthalene. Since it has a distinctive aroma, it may be confused with 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) (Alpeza et al., 2021). Appropriate amounts of sulfur dioxide are effective in preventing this pathway, and also ascorbic acid has been confirmed to be a potential preventive agent (Nardin et al., 2022). Additionally, tannins can limit the concentration of 2-aminoacetophenone during the process. It is worth noting that red wines are less susceptible to this particular fault (Nardin et al., 2022).

Other studies have identified sotolon (4-hydroxy-2,3-dimethyl-2H-furan-5-one) and aldehydes, as responsible for atypical aging. It is a defect that could be present during barrel aging (Lavigne et al., 2008). It has been identified as a curry smell, and it may determine a significantly reduction of the fruity aroma of wines (Lavigne et al., 2008). Sulfur dioxide has been demonstrated to inhibit the formation of sotolon, but storage conditions, and mostly the presence of dissolved oxygen, can influence the concentration sotolon, leading to higher values than odor threshold. The temperature acts as a trigger, affecting the rate of reactions and, as a result, the production of sotolon (Cutzach et al., 1999; Gabrielli et al., 2015, 2021). In both pathways, oxygen has been identified as a crucial factor.

Pinking

Pinking is a wine fault that causes a change in color from white to salmon red. This alteration is caused by the presence of malvidin-3-O-glucoside. According to Cosme et al. (2019), this phenomenon can occur even at low concentrations of malvidin-3-O-glucoside, approximately 0.3 mg/L, which can be found in the concentration of white wine.

The exact mechanism behind pinking is unclear, although the role of oxygen is believed to be significant. Although polymerization of anthocyanins is thought to be the cause, pinking has also been observed under reducing conditions (Andrea-Silva et al., 2014; Cojocaru & Antoce, 2019; Gonçalves et al., 2022).

Pinking can be prevented or minimized by adding tannins, polyvinylpolypyrrolidone (PVPP), ascorbic acid, and sulfur dioxide (Cojocaru & Antoce, 2019; Lamuela-Raventó et al., 2001).

Formation of ethyl carbamate

From a safety point of view, it is necessary to consider the formation of ethyl carbamate (EtCAR). This compound has been classified in Group 2A by the International Agency for Research on Cancer (IARC) in 2007 as probably carcinogenic to humans (Fu et al., 2016; Kodama et al., 1994). It is present in fermented foods and beverages (Kodama et al., 1994). A concentration limit is established for EtCAR, depending on the country of production, and the OIV has released the method OIV-MA-BS-25, and subsequent updates, for its quantification by gas chromatography-mass spectrometry (GC-MS) (OIV, 2009).

The formation of ethyl carbamate is linked to the presence of three precursors, urea, arginine and citrulline, which operate in independent pathways (Fu et al., 2016). Therefore, the precursors are divided into different pathways, which are separate and have independent formation rates (Figure 6), but it was found that they have a comparable activation energy (Hasnip et al., 2004). Urea concentration correlates with alcoholic fermentation, while citrulline content relates to malolactic fermentation. Consequently, this makes red wines, which commonly undergo malolactic fermentation, more affected by this problem (Larcher et al., 2013). Furthermore, in the alcoholic fermentation, nitrogen catabolite repression (NCR) does not allow the utilization of arginine for urea production, thus limiting ethyl carbamate formation (Fu et al., 2016).

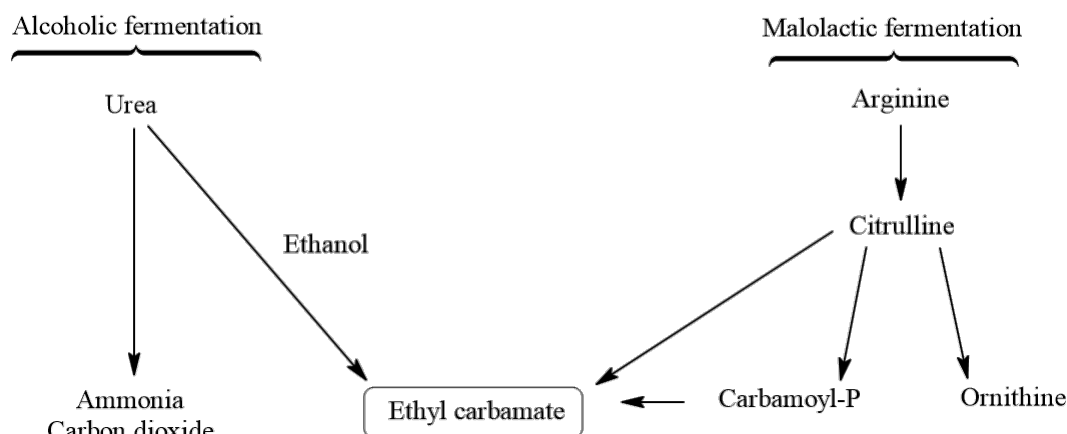


Figure 6 Formation of ethyl carbamate (EC) in alcoholic and malolactic fermentation (Fu et al., 2016).

The strains of yeast and malolactic bacteria could be selected to reduce their concentration and the relative susceptibility of the wine to ethyl carbamate formation (Larcher et al., 2013).

Temperature plays a key role in the formation of ethyl carbamate in bottled wines, with a positive correlation and significant effect. Hasnip et al. (2004) found a relationship between temperature and ethyl carbamate formation, as well as a correlation between time and temperature. This data could be used to develop a tool for determining the formation of ethyl carbamate. It is important to highlight the potential positive impact of high alcohol content and low pH values on the acceleration of ethyl carbamate formation (Kodama et al., 1994).

1. Effect of wine composition and production technology

Production process

The composition of wine is crucial in determining its quality and its potential for evolution. Starting from the vineyard, several aspects can affect the grape composition and the relative wine production, such as variety and viticultural approach (Panagiotakopoulou & Morris, 1991). Similarly, different winemaking approaches can be employed at winery scale (Alti-Palacios et al., 2023; Ju et al., 2023; Lukić et al., 2015; Radeka et al., 2023). Basically, there are two different approaches to winemaking, the first is to use technologies and oenological treatments to correct the wine parameters, and the

second is to minimize the inputs during the process to obtain a more natural and specific product. Skin maceration is one of the most important treatments affecting wine composition (Lukić et al., 2015). This is typically employed for red wines, but it is increasingly used for white and orange wines to produce more complex and structured flavors. The process of maceration has an impact on color, phenolic, and volatile composition. When used for longer periods, greater amounts of volatile compounds (e.g. monoterpenes) can be extracted. As a result, the produced wine exhibits a more structured, fruity, and fresh aroma, along with higher levels of phenols, could lead in elevated bitterness, astringency, and antioxidant activity (Alti-Palacios et al., 2023; Lukić et al., 2015; Petropulos et al., 2014; Radeka et al., 2023). This may also contribute to a lower level of antioxidant addition, and a more saturated and intense color as a result of a higher extraction of phenolic compounds. The temperature during maceration has a significant impact on the concentration of volatile compounds. Lower temperatures tend to lead to better preserve floral and fruity aromas, however, a decrease in temperature may also result in lower extraction from the marc and longer skin contact times. This technique is commonly applied in prefermentation for white wines, but extending it over fermentation can further enhance the composition of the wine (Alti-Palacios et al., 2023). Other techniques can also affect the chemical composition and the potential evolution of the wine. One of the main aspects to consider is the use of wood chips or barrel aging. It is necessary to take into account the wood species, degree of toasting, volatile compounds, and phenolic composition (Correia et al., 2023; Delia et al., 2017; Herrero et al., 2016).

Use of antioxidants

Various antioxidants can be used to limit oxidative pathways and preserve wine during the aging process.

Sulfur dioxide

Sulfur dioxide (SO₂) is commonly used in winemaking due to its properties of antioxidant, antioxidasic and antiseptic agent. At wine pH, it is present in various forms, including molecular SO₂, bisulfite and sulfite ion (free SO₂); moreover, bisulfite ion (which in wine is the most representative component of free SO₂) can bind other molecules giving bound SO₂ (Boulton et al., 1999; Scrimgeour et al., 2015). The molecular form constitutes the minor fraction, but provides the most effective microbiological protection. Bisulfite ion comprises the primary free form component. The balance between the molecular form and bisulfite ion is pH and temperature-dependent, and both are necessary for wine protection. Bisulfite ion can react with numerous molecules, including carbonyl compounds, tannins, and sugars. The most active SO₂-binding compound is acetaldehyde, which irreversibly binds bisulfite ion, making it ineffective for wine preservation. Sulfur dioxide can indirectly react with oxygen scavenging hydrogen peroxide, limiting aldehyde formation and polymerization of phenolic compounds. This prevents oxidation and the development of off-flavors (Comuzzo & Zironi, 2013; Danilewicz, 2012; Elias & Waterhouse, 2010; Fracassetti, Limbo, et al., 2021; Li et al., 2008; Panero et al., 2015; Sacks et al., 2020; Ugliano, 2013). Moreover, sulfur dioxide can reduce quinones, retarding browning and preventing Fenton reaction.

Panagiotakopoulou & Morris (1991) found that for wines with low phenolic content, it is possible to reduce the sulfur dioxide content, this behavior is mainly related to the variety, related to their less susceptibility to oxidative phenomena.

It is essential to underline that sulfur dioxide is an allergen, being potentially harmful for human health. Several methods have been suggested to decrease the presence of sulfur dioxide in wine.

Ascorbic acid

Ascorbic acid has been studied as an alternative to sulfur dioxide in winemaking and it was one of the first options considered (Panagiotakopoulou & Morris, 1991). Ascorbic acid has a strong ability to scavenge oxygen and reduce quinones, as well as in scavenging hydrogen peroxide and free radicals. However, when ascorbic acid is oxidized, it produces dehydroascorbic acid. This molecule has pro-oxidant activity in wine, which is the reason why ascorbic acid requires sulfur dioxide to limit further oxidative pathways (Figure 7). It is important to limit reactions that lead to the production of xanthylium cation, in part responsible for the increase in values related to color (Barril et al., 2009; Bradshaw et al., 2011; Comuzzo et al., 2015, 2017; Comuzzo & Zironi, 2013; Danilewicz, 2016; Skouroumounis et al., 2005).

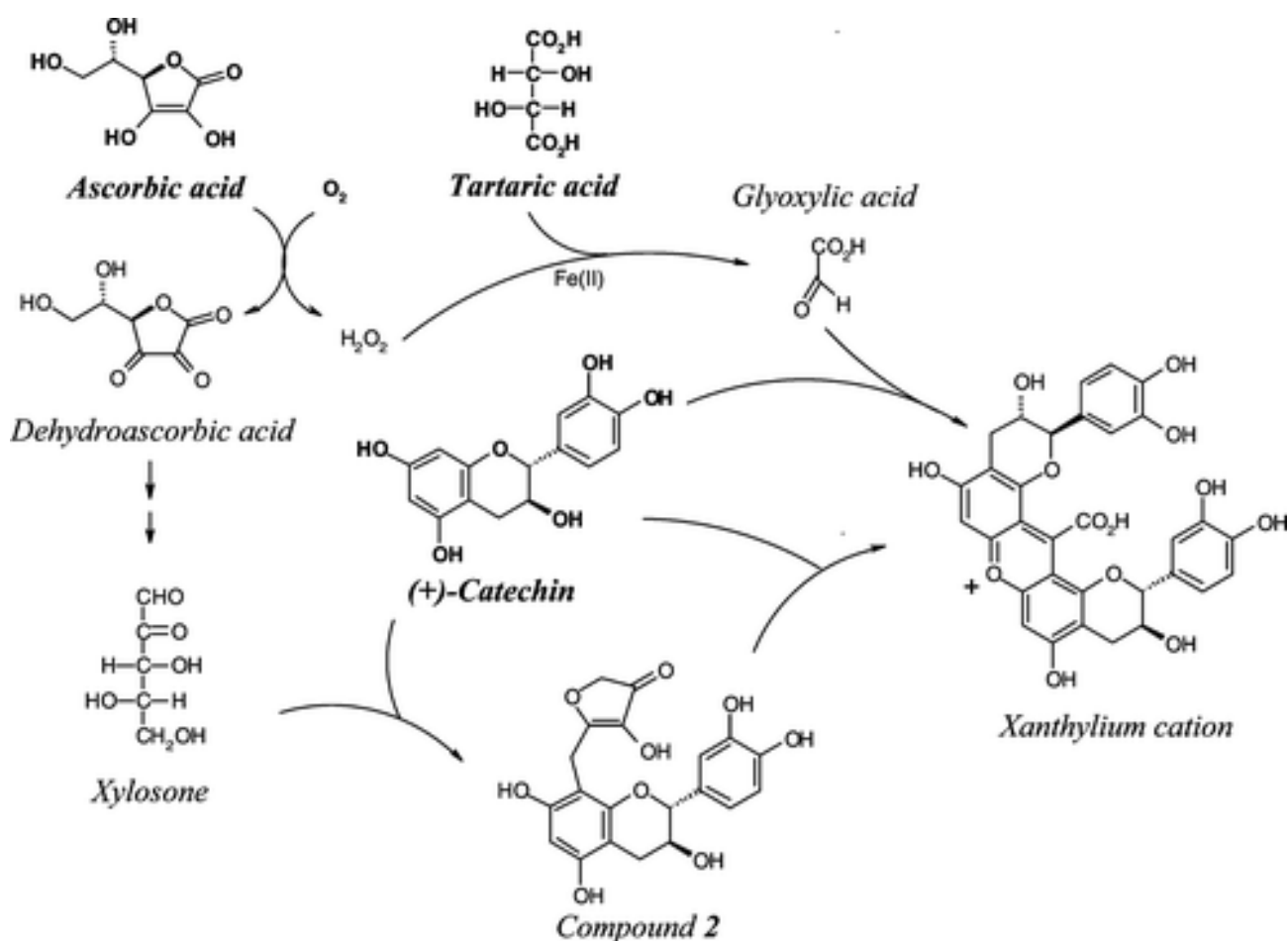


Figure 7 This may also contribute to a lower level of antioxidant addition, and a more saturated and intense color (Barril et al., 2009).

Tannins

The application of tannins is widely used in oenology for their antioxidant and antiradical activity, leading to a higher evolution potential (Strati et al., 2021; Tourtoglou et al., 2014). However, the application of tannins can induce changes in color and volatile composition, this aspect depends on the dose and represents a negative effect (Strati et al., 2021). Tannin properties are determined by their botanical origin (raw material), with hydrolysable tannins being mostly produced from oak and chestnut (Jordão & Cosme, 2022; Tourtoglou et al., 2014; Waterhouse et al., 2016). Tannins can increase the rate of oxygen consumption and redox potential, also demonstrating antiradical properties. The use of tannins may represent a strategy to reduce the amount of sulfur dioxide used (Panero et al., 2015; Strati et al., 2021; Tourtoglou et al., 2014).

The tannin family includes condensed tannins formed by flavanol units, extracted from various botanical species, e.g. tara, tea and lemon. These class of tannins are commonly associated with protein stability applications, although they also possess radical scavenging, but less pronounced than hydrolysable tannins (Paissoni et al., 2022; Sarni-Manchado et al., 1999).

Paissoni et al. (2022) found a correlation between the addition of enological tannins and the antioxidant properties during a short period of storage. However, it is important to consider the sensory changes in the wine.

Bioprotection

Bioprotection has been developed to minimize the addition of antioxidant molecules, mainly sulfur dioxide. These strategies additionally facilitate the production of wine with increased acidity, decreased pH, and enhanced aromatic composition (Morata et al., 2021; Nardi, 2020; Naselli et al., 2023; Rubio-Bretón et al., 2018). Furthermore, this strategy allows obtaining more natural wines. Bioprotection can be classified into two strategies: the inoculation of living organisms or the addition of metabolites. The strategies for action may include competition for nutrients, space and oxygen, as well as the production of peptides and proteins with antimicrobial properties (Di Gianvito et al., 2022).

Notably, glutathione and melatonin are the molecules produced by yeast that are most interesting from an antioxidant perspective for the wine matrix and can be exploited for bioprotection. However, further studies are necessary to better understand the conditions that stimulate this production (Lebleux et al., 2023).

Escott et al. (2024) tested the application of various yeast strains and found that *Lachancea thermotolerans* can reduce pH, leading to an increase in total acidity. This suggests that managing pH through non-*Saccharomyces* yeast could be a strategy to control must fermentation from the wild microbiome of grapes, inactivate enzymes and limit the amount of sulfur dioxide.

Yeast derivatives

Yeast derivatives (YD) can be considered as a substitute of aging on yeast lees. Less is defined in the *Regulation (EU) No 1308/2013* (2013) as the residue of wine or must related to fermentation, storage, and authorized treatment, obtained from filtering or centrifuging of both matrices. Yeast cells are identified as the most advantageous component from an aging perspective, as they can cause various reactions such as oxygen consumption and release of amino acids (Comuzzo et al., 2017; Salmon et al., 2002; Stamenković Stojanović et al., 2023; Voce et al., 2021). Nevertheless, they have also negative aspects such as the adsorption of polyphenols, but the capacity of YD to adsorb polyphenols can also reduce browning, which may be related to its insoluble fraction consisting of cell wall residues (Comuzzo et al., 2015; Salmon et al., 2002). YDs can be chosen based on their composition and production method. Usually, *Saccharomyces cerevisiae* yeasts are subjected to enzymatic/thermal treatments to produce yeast derivatives (Comuzzo & Zironi, 2013; Voce et al., 2021). However, researchers are currently investigating the use of other technologies, such as ultrasounds, pulsed electric field (PEF) or high-pressure homogenization to accelerate cell breakdown and autolysis (Feng et al., 2022; Voce et al., 2021). Furthermore, the production of yeast autolysates from non-*Saccharomyces* strains is also being studied (Voce et al., 2022). Selecting the appropriate formulation is critical to achieving the desired result, because various oenological stages and

techniques result in different product characteristics and applications. Yeast byproducts are mainly composed of cell walls and soluble components, such as polysaccharides, proteins, peptide, amino acids, glutathione and other compounds. The aroma can be modified and volatile molecules can be preserved during aging (Stamenković Stojanović et al., 2023). Commercial formulations can be enriched for specific applications in the winemaking process (Comuzzo & Zironi, 2013).

Glutathione

Glutathione (GSH) has low oxygen scavenging activity, but its use limits the polymerization of phenolic compounds and the relative production of browning (Comuzzo et al., 2015; El Hosry et al., 2009). Furthermore, GSH has the potential to reduce the quinone, thereby increasing the concentration of phenolic content. Moreover, the application of GSH can limit the reduction of aroma molecules, especially terpenes and esters (Panero et al., 2015; Stamenković Stojanović et al., 2023). In comparison to ascorbic acid and tannins, glutathione does not influence sulfur dioxide consumption. Therefore, it can be used in combination with sulfur dioxide, allowing the reduction of SO₂ levels (Comuzzo et al., 2015, 2017; Comuzzo & Zironi, 2013; El Hosry et al., 2009; Panero et al., 2015; Stamenković Stojanović et al., 2023; Ugliano et al., 2020).

El Hosry et al. (2009) reported that glutathione may be useful in preventing atypical aging.

2. Environmental factors

Temperature

Temperature is a crucial factor that affects the reaction rate by influencing the Arrhenius activation energy and the Arrhenius equation (Ma et al., 2022). It should be noted that higher temperature does not always result in a faster reaction (Scrimgeour et al., 2015). Instead, its effect depends on whether the reaction is endothermic or exothermic. The exposure to high temperatures and temperature fluctuations are typically associated with the transportation of goods in non-refrigerated containers

and trucks (Butzke et al., 2012). Lower temperatures reduce the evolution pathways and preserve the bottled wine during storage (Castellanos et al., 2021).

As mentioned before, there is a relationship found by Hasnip et al. (2004) between temperature and ethyl carbamate production.

Various investigations using data loggers have demonstrated that temperature may exceed 40°C during transport, along with a temperature variation of more than 25°C between night and day (Butzke et al., 2012; Ough, 1985). Temperature fluctuations may impact on the volume of bottled wine and subsequently the headspace volume, resulting in an increased possibility of oxygen transfer through the closures (Butzke et al., 2012; Dimkou et al., 2011; Morozova et al., 2015). Several studies indicate that the volatile composition of wine varies, with an increase in the concentration of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), dioxanes, and dioxolanes, while the concentration of alcohols, terpenes, esters, and acetates decreases. These variations appear to result from hydrolysis and esterification reactions, leading to a reduction in fruit flavor and freshness (Benucci, 2020; Betnga et al., 2021; Cejudo-Bastante et al., 2013; Culleré, et al., 2007; Hopfer et al., 2015; Scrimgeour et al., 2015).

Furthermore, temperature can affect even non-volatile compounds. Elevated temperatures can enhance the oxidative reactions that affect polyphenols, such as catechin, caffeic acid and gallic acid, resulting in the formation of quinones and browning (Betnga et al., 2021; Singleton, 1976).

Furthermore, Ough (1985) reported on the impact of temperature on the volatile component, resulting in a decrease of acetic esters, as well as on the color, which exhibited increased browning.

As discussed above, antioxidants, such as sulfur dioxide or ascorbic acid, can improve wine preservation during transport especially if used in combination with refrigerated vehicles (Ough, 1985; Scrimgeour et al., 2015).

Light

As previously explained, light exposure is also a factor to consider as it can lead to light-struck defect, in the presence of riboflavin and sulfur-containing amino acids, mainly methionine. The high light transmission capacity of flint glass compared to green or dark glasses is largely associated with this defect (Arapitsas et al., 2020; Dias et al., 2012; Grant-Preece et al., 2017). In colored glass bottles, the light transmission is dependent on the weight and thickness of the bottle (Dias et al., 2012; Grant-Preece et al., 2017). Exposure to light can negatively affect volatile compounds, acetates, alcohols, and fatty acids. The undesirable ‘light-struck’ flavor, caused by riboflavin, generates an irreversible defect by increasing VSCs, particularly methanethiol and dimethyl disulfide (Fracassetti, Di Canito, et al., 2021). Fracassetti et al. (2019) found that the risk of developing of light struck fault is lower when the riboflavin level is less than 50 µg/L.

To inhibit light-induced transformations, it is necessary to use clarifying agents that reduce riboflavin, such as bentonite, zeolite, charcoal, and colored bottles with higher weight (Fracassetti, Limbo, et al., 2021; Grant-Preece et al., 2017; Noviello et al., 2021; Vendramin et al., 2021). The use of antioxidants, specifically sulfur dioxide or tannins, is recommended. Additionally, it is possible to decrease emissions between wavelengths of 370 and 450 nm by choosing LED lights based on their emitted wavelengths (Mislata et al., 2022).

3. Role of packaging and closures

The choice of closure is a crucial factor in wine evolution, as it impacts headspace volume (Table 2). However, the use of screw caps leads to an increase in headspace volume, ultimately reducing the initial sulfur dioxide concentration. This correlation is founded upon the relationship between the volume of headspace and the oxygen concentration in the wine, which is gradually depleted over time (Brajkovich et al., 2005; Dimkou et al., 2011; Morozova et al., 2015). It is crucial to account for temperature-induced volume alterations, particularly those linked with transportation, as they could result in potential leakage (Godden et al., 2001).

Table 2 Headspace height (cm) for different typologies of closures (Cantu et al., 2022).

Closure typology	Headspace height (cm)
Natural Cork	1.3 ± 0.1
Synthetic Cork	1.5 ± 0.2
Screw Cap	4.8 ± 0.1

Finally, the surface treatment of the closure plays a crucial role in proper insertion and adhesion to the bottleneck, in avoiding gas transfer through the space between the closure and the glass, and in facilitating uncorking (Chanut et al., 2021; Lopes et al., 2007).

The aging process of bottled wine must consider not only the closure used but also the storage conditions. Specifically, horizontal storage is generally linked to slower evolution, as evidenced by acetaldehyde levels and absorbance at 420 nm (Mas et al., 2002). The positioning of a bottle plays a crucial role, particularly for cork, because it influences the hydration of the closure. As this hydration is important for the mechanical properties of the closure, in particular the Young's modulus. These factors also have an impact on synthetic closures, albeit to a lesser degree due to their lower tendency to absorb moisture (Lagorce-Tachon, Karbowiak, Champion, et al., 2015; Lagorce-Tachon et al., 2016).

Role of the container

Glass bottle is the principal packaging container for wine and a necessary requirement for adhering to many geographical indication production guidelines. The design of the bottle can vary, but color, weight and shape of the neck are essential factors from an enological point of view. Weight affects both thickness and resistance, while darker hues significantly reduce UV-visible transmission, especially if bottles are heavier. It is important to note that darker bottles attain higher temperatures when stored outdoor, thereby accelerating oxidative processes (Dias et al., 2012; Maury et al., 2010).

As well as the characteristics of the bottle and the environmental factors to which it is exposed, it is necessary to consider the characteristics of the closure used, among which permeability turns out to be one of the main factors.

Role of the closure

Desorption

Desorption is a mechanism that allows the closure to release compounds into the wine. The investigation of this phenomenon aims to minimize the occurrence of off-flavors in wine. The main desorption phenomenon involves the release of 2,4,6-trichloroanisole (TCA). Analytical methods have been developed to detect TCA and can also be used for in-line cork selection. Corks can release various compounds, including TCA, 2,4,6-tribromoanisole and geosmin, into wine (Coquet et al., 2008; Moreira et al., 2016; Pinto et al., 2019). Additionally, synthetic closures can release chemicals depending on the presence of additives and materials used (Furtado, Lopes, et al., 2021).

Scavenging

Conversely, scavenging refers to the ability to absorb substances from the wine, and this mechanism is related to the characteristics of the material. Some mechanisms such as TCA scavenging are currently being studied. Closures, specifically, can adsorb non-polar compounds from contaminated wines. This adsorption might be related to the paraffins applied on the cork surface or the synthetic material used for the closures (Capone et al., 1999).

Furthermore, sulfides can be scavenged by closures, specifically hydrogen sulfide which can react with cork components, but this effect is not strictly related to sulfur compounds, related to off-flavors, but in a more general way, also to other classes of molecules, e.g. esters. Synthetic closures are not as efficient and have a lower effect on, for example, dimethyl sulfide (Silva et al., 2012).

Bioactive function

The closure can be characterized by various bioactive functions, mainly related to cork closures, specifically related to phenolic compounds. The phenolic composition of cork is primarily associated with gallic acid, known for its antioxidant activity. Additionally, vanillins are abundant in this material and known for their antioxidant properties, but the transfer of such compounds from the cork to the wine during bottle aging has not been studied (Crouvisier-Urien et al., 2019; Fernandes et al., 2009; Mislata et al., 2020).

Cork closures

Nonetheless, the choice of wine closures is an essential factor in modulating wine evolution. Among the various closures available, cork is the prevalent material and the most traditionally associated with wine. Cork is an organic material derived from *Quercus suber* L., a tree which grows in the Western Mediterranean area (Furtado, Lopes, et al., 2021). Cork can be subjected to structural imperfections that result in reduced yield during the manufacturing process. Additionally, the quality of cork closures can be greatly affected by discrepancies in the raw material, which may fluctuate significantly within production batches (Karbowiak et al., 2019).

Nowadays, the aforementioned issues have been mitigated thanks to the careful selection of raw materials and various analyses used to classify the production.

The internal structure of cork plays a significant role in classifying the material prior to the production of closures. Various methods, such as X-ray, optical imaging, scanning electron microscopy, and Fourier transform infrared spectroscopy (FTIR), can be used to analyze the internal structure and porosity (Crouvisier-Urien et al., 2019; Oliveira et al., 2015). Understanding the static and dynamic behavior and composition of closures can aid in comprehending their mechanical properties, which are linked to other key parameters (Furtado, Oliveira, et al., 2021; Suffo et al., 2022).

The study of internal structure is an important part of understanding closure properties after the bottling stage. When inserted into the bottleneck, the closure undergoes compression, which can alter its mechanical properties (Lopes et al., 2007).

It is also necessary to consider eventual defects related to the internal structure of the closure, as well as those related to the surface (Anjos et al., 2008; Lagorce-Tachon, Karbowiak, Loupiac, et al., 2015). Specifically, mold growth on the cork surface prior to production can result in the well-known issue of ‘cork smell’, which is primarily caused by the presence of 2,4,6-trichloroanisole (TCA) but can also be linked to the release of other molecules from the closures into the wine (Furtado, Oliveira, et al., 2021; Silva et al., 2011).

Cork closures are classified into two categories: natural and technical. Natural cork consists of a single piece, cut from a cork plank. This operation (die-cutting) leads to a higher production of waste; this extra material can be reused in other industries, such as construction or can be ground to produce technical closures. Cork granules and glue are the primary components of technical closures (Crouvisier-Urien et al., 2018b). The range of cork granule sizes available for selection is between 0.9 and 14.3 mm. Technical cork may also include cork disks positioned at the top and bottom, with a variable number (Crouvisier-Urien et al., 2018b; Mislata et al., 2020).

Synthetic closures

Synthetic closures have been developed to address the issue of TCA presence. These closures provide cost savings, improved microbiological safety, and less variability within batches compared to natural cork closures. Injection, extrusion, and co-extrusion techniques can be used in manufacturing synthetic closures. More homogeneous oxygen transmission rate, as well as adhesion to the bottle neck, can be achieved by using co-extrusion with two different materials (Giunchi et al., 2008).

Screw caps

Screw caps are now increasingly used as wine closures. These closures consist of an aluminum capsule and a plastic liner that controls the permeability, with a significant reduction of oxygen transfer rate (OTR) achieved by applying an aluminum layer. The advantages of this closure type are

its ease of use for consumers and the high level of production uniformity (Crouvisier-Union et al., 2018a).

The use of synthetic closures and screw caps results in a lower OTR. This effect is predominantly observed in the initial period subsequent to bottling while it might deteriorate over time due to the crystallization of plastic material, leading to the loss of its mechanical properties (Brajkovich et al., 2005; Castellanos et al., 2021; Mas et al., 2002).

Wine closures and OTR

As described previously, selecting the ideal closure is a challenging task, as multiple parameters must be evaluated, with OTR being a critical factor to consider. Numerous studies have analyzed and compared OTR levels and generally found that screwcaps have the lowest permeability, followed by technical cork, natural cork, and synthetic materials, considering long evolution times.

However, the magnitude of OTR levels may vary depending on specific material characteristics and other influencing factors, primarily related to the properties of the materials. Consequently, OTR can vary in a rather wide range and, in addition, OTR, can be measured using different methods whose results are frequently not comparable one each other, as shown in Table 3 (Crouvisier-Union et al., 2018a; A. S. Oliveira et al., 2020; Ugliano, 2013).

Table 3 Overview of oxygen transfer rate obtained from the literature.

Method	Unit	Natural cork	Technical cork	Syntethic	Screw cap	Ref
Luminescence	mg/L/year	4.56	4.07		0.61	(Castellanos et al., 2021)
Luminescence	mg/day				0.0016	(Vidal et al., 2014)
Coulometric	mg/day	0.0016				(Poças et al., 2010)
Coulometric	mg/day		0.005	0.047	0.005 - 0.067	(Vidal et al., 2017)
Luminescence	mg/day			0.014		(Vidal et al., 2017)
Colorimetric	mg/day		0.005			(Vidal et al., 2017)
Colorimetric	mg/L/month	2.3 - 3.8*	1.4 - 2.8*	3.6 - 4.3*		(Lopes et al., 2005)

*data related to the first month of storage period

The initial approach suggested was based on free sulfur dioxide consumption; it was analyzed by titration which is affected by various reactions with other wine compounds and also requires a long time for the analysis (Boulton et al., 1999; Brajkovich et al., 2005).

The previous method is invasive, thus a colorimetric approach has been proposed to address this issue. The technique utilized indigo carmine, which changes color from yellow to indigo following oxidation, although it takes time to measure through CIE Lab (Brotto et al., 2010; Lopes et al., 2005). Oxygen determination can be achieved through oxygen titration by the Winkler reaction, as well as through the use of manganese hydroxide solution, but this is not commonly used (Kontoudakis et al., 2008; Winkler, 1888).

The chemiluminescence method is commonly utilized due to its non-invasive nature and capability to closely simulate real conditions. It is also a rapid and easy to evaluate method with a wide range of applications from the winery to the bottling aging. Although evaluating the OTR of packaging can be time-consuming, this method has proven to be effective (Diéval et al., 2011; Morozova et al., 2015; Ugliano et al., 2020; Vidal et al., 2011).

Another method is a manometric method, based on the change in pressure between two compartments separated by the closure, the change is measured with a manometer. Subsequently, an equation must be applied to obtain the value of OTR, considering various parameters involved in the analysis (Lagorce-Tachon et al., 2014; Lequin et al., 2012).

Finally, it seems very valuable to study the OTR using the Mocon[®] equipment (Mocon Inc., Minneapolis, MN, USA), which is a globally accepted standard method used to determine packaging permeability by using a patented coulometric sensor to detect oxygen. However, this instrument requires a dry environment and a flow of nitrogen for the measurement, so in the absence of wine, in fact a bottle neck is used in which is inserted the cork. It requires long times to obtain the measurement, especially for large size closures, in particular regarding the length (Mayer & Toumela, 2008; Poças et al., 2010).

As previously discussed, multiple techniques have been devised to estimate OTR. However, its analysis is challenging.

4. Assessment of wine aging potential

The assessment of the aging potential of a bottled wine is a complex issue, and to understand it, different analyses could be performed (Karbowski et al., 2010). Researchers have been developing and refining various techniques that can be considered as possible approaches to the analysis of wine, in order to obtain useful indicators of the evolution potential and, moreover, to give the possibility to improve it. Furthermore, researchers are also looking at obtaining this information in a shorter period of time, making enological treatments more effective and reducing the risks of occurrence of instability and off-flavors.

Potential wine evolution markers

The measurement of sulfur dioxide is a fundamental parameter, in particular the free form; it was used in various projects as an indication of evolution, highlighting a negative correlation between free sulfur dioxide content and wine evolution (Brajkovich et al., 2005; Cantu et al., 2022). Furthermore, the reduction in SO₂ levels correlates with a higher absorbance at 420 nm, i.e. a more intense browning (Brajkovich et al., 2005; Kanavouras et al., 2020). The use of CIELab parameters as a basic parameter is becoming more common; it requires the acquisition of spectra in transmittance mode, from which the wavelengths are sampled to obtain the L*, a* and b* parameters. This type of analysis improves the comprehension of color changes beyond just those associated with browning (Castellanos et al., 2021; Ling et al., 2019).

To assess wine oxidizability, accelerated browning tests like the POM test can be employed. This test applies oxidative and thermal stress to samples in order to simulate their evolution over time (Müller-Späth, 1992; Singleton, 1976).

The quantification of phenolic composition, particularly flavanol content, can be used as an index of evolution, since flavanols are some of the most oxidizable polyphenols and contribute to browning. Their quantification makes possible to understand if the wine is susceptible to oxidation and, at the same time, for example, colorimetric quantification of catechin content based on derivatization with 4-(dimethylamino)-cinnamaldehyde (DAC) (Zironi et al., 1992).

Additionally, the antioxidant capacity and oxidative stability of wine can be analyzed using the DPPH or FRAP method. The former uses 2,2-diphenyl-1-picrylhydrazyl free radical, the latter utilizes Fe(III) to oxidize polyphenols and provides an indication related to the antioxidant potential. It is important to note that not all molecules that react with the molecules used in the analysis can act as antioxidants in wine, or only at low levels (Danilewicz, 2015; Romanet et al., 2019).

High-performance liquid chromatography (HPLC) is an analytical method used to fractionate and quantify wine components. Several methods have been developed, such as riboflavin concentration and the relative risk of susceptibility to 'light-struck' defect (Fracassetti et al., 2017), determination of sotolon content related to atypical aging (Gabrielli et al., 2015), and characterization of phenolic content (Ju et al., 2023).

Near-infrared spectroscopy is an analytical technique that operates in the range of 800-2500 nm. It is fast, easy to perform, and applicable in various fields. Its applications include quality control of cork (Mellado-Carretero et al., 2021), discrimination of wine aging in different wood species (Martelo-Vidal & Vázquez, 2014; Nardi et al., 2020), and quantification of polyphenol concentration in wine, with related difficulties associated with the analysis technique that is not specific to the particular molecule or class of compounds of interest.

Additionally, it can predict other parameters such as volatile compounds through the application of statistical methods (Smyth et al., 2008).

Through the application of various methods of gas chromatography-mass spectrometry, it is possible to measure the concentration of volatile compounds in wine, to evaluate changes or to study the occurrence of defects or the possible susceptibility of a wine to their appearance. In particular, the

concentration of sotolon in relation to atypical aging (ATA) can be analyzed (Lavigne et al., 2008). Additionally, sulfur compounds, including methional, hydrogen sulfide, and dimethyl disulfide, are linked to reductive faults and ‘light-struck’ taste. Finally, volatile compounds like 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), diethyl succinate, ethyl 9-decenoate, and carbonyl compounds such as phenylacetaldehyde and acetaldehyde may be responsible for oxidative reactions typically linked to aging (Gambetta et al., 2017; Moreira et al., 2019b; Recamales et al., 2006).

Sensory analysis

Sensory analysis represents the first tool used by the winemaker to understand changes related to the enological treatment, to understand the perception of evolution in the winery. This approach requires a high degree of experience and training. Additionally, it can be utilized to evaluate and score the wine in competitions based on its quality. Sensory analysis serves as a marketing tool for communicating the wine characteristics and obtaining an objective evaluation of its quality (Charters & Pettigrew, 2007; Gawel & Godden, 2008).

Sensory analysis is a crucial tool for applied research, providing a means to assess changes related to aging (Bueno et al., 2010; Saltman et al., 2020), as well as to gauge the impact of the treatments and techniques employed (Gambetta et al., 2017; Ju et al., 2023). Additionally, it is possible to correlate sensory data with analytical variables (Araujo et al., 2021).

Cyclic voltammetry

Cyclic voltammetry is becoming increasingly relevant in academic research. This technique allows to register the flow of electrons to study oxidation and reduction processes, by the use of three different electrodes (working, counter and reference). Quantitative information related to compound parameters can be obtained from this analysis, but obtaining this information for wine, which is a complex matrix, can be challenging. Statistical methods may aid in overcoming this difficulty by establishing correlations with other parameters (Kilmartin et al., 2002; Martins et al., 2008; Zhang et

al., 2017). Voltammetry applied to wine provides insights into antioxidant molecules, added substances, and phenolic compounds. This analysis is useful for distinguishing wines of different varieties as well as different treatments if they affected the phenolic composition (Geană et al., 2020; Thomaz et al., 2022).

This analysis can be conducted using various approaches to enhance the confirmation and investigation of the phenomena. Nonetheless, the procedure is straightforward and takes only several minutes to perform. The utilization of disposable screen-printed electrodes has further facilitated the analysis by removing the necessity for cleaning the working electrode. Screen-printed electrodes are composed of a substrate, typically ceramic, on which the three different electrodes are printed, and they can be made in different material. In the oenological field, carbon is often used for the working electrode and auxiliary electrode, and silver or silver/silver chloride for the reference electrode. Enzymes can be utilized to modify screen-printed electrodes, enabling the detection and quantification of particular compounds like glucose, malic acid, and sulfite (Lupu et al., 2004; Molinero-Abad et al., 2014). In addition, portable devices have been developed to enable direct measurements in the winery (Barragan & Kubota, 2020; Siegl et al., 2018).

Other innovative analysis methods

Radical species can be detected and measured through the application of electron paramagnetic resonance spectroscopy. This analytical technique offers insights into the resistance of wines to oxidation (Nikolantonaki et al., 2019).

The demand for more rapid tests is leading to the development of systems based on different sensors, such as microwaves, for the determination of markers such as those related to oxidative processes, in particular phenylacetaldehyde and 1-octen-3-one (Rossignol et al., 2021).

Evaluation of white wine evolution by conventional and innovative approaches

The evolution of bottled white wine is a complex field with high academic and technological interest. Evolution is characterized by several reactions that can involve different substrates and modify the matrix through different pathways, affecting the most important factor for wine consumers, the sensory perception. Different analysis can be done to evaluate evolution of white wines, in particular various chemical and spectrophotometric parameters have been used in the past to evaluate wine evolution, mainly the concentration of free and combined sulfur dioxide and absorbance at 420 nm for color assessment. Different factors can have a key role on evolution, as mentioned before, but at the moment, no tool has been identified to predict an accurate evolution time of a wine before bottling, in order to provide more precise indications for the implementation of this time interval.

1. Aim of the project

This part of the PhD project aims to investigate different approaches for the evaluation of white wine evolution. In particular: i) to study how different conventional (e.g. wine color, free and bound sulfur dioxide, browning test) and non-conventional indicators (e.g. carbonyl compounds, cyclic voltammetry) can describe wine modifications over time; ii) to assess if fast analytical methods such as cyclic voltammetry can predict the values of some analytical parameters connected to wine aging; iii) to evaluate if the indicators examined, in particular cyclic voltammetry can predict in certain extent white wine aging potential.

Thirty-six commercial wines from the 2020 vintage were collected and analyzed during bottle evolution in controlled conditions. Evaluations were carried out every four months, starting from two months after the collection. Analyses were conducted at two, six, ten, and twelve months from the start of the project to assess different parameters related to evolution. Samples were collected from wineries located in the northeast of Italy. Different varieties of grapes were used for the production of samples, including Bianchetto, Chardonnay, Friulano, Pinot Blanc, Pinot Gris, Sauvignon and Malvasia.

Statistical methods (such as PCA and Anova) were used to describe the modifications of the different samples during bottle aging and to assess eventual role of the variety or the effect of the closure. Correlations between the different analytical techniques used and the corresponding data were evaluated. These correlations were most closely studied by using Partial Least Squares (PLS) to evaluate predictive models aimed at determining, from cyclic voltammetry, values of some relevant enological parameters related to wine evolution and assessing wine aging potential.

2. Materials and Methods

Samples

Thirty-six single-variety commercial wines from the 2020 vintage were collected from the northeast area of Italy. Samples were stored at the temperature of 20 ± 5 °C and relative humidity 70 ± 10 %. The varieties considered were Bianchetto, Chardonnay, Friulano, Pinot Blanc, Pinot Gris, Sauvignon and Malvasia. The collected wines were produced according to the wine project of the individual wineries, without any constraints related to the production process or packaging (bottle and closure). Various closures were used, such as natural and technical cork, injected and co-extruded synthetics closures, screw caps and, finally, alternative synthetic closures recently introduced in the oenological field. Samples were collected within sixty days after bottling.

Reagents

HPLC grade (+)-catechin hydrate (≥ 98 %), 4-(dimethylamino)-cinnamaldehyde (DAC) (≥ 98 %), 4,4'-dithiodipyridine (DTDP) (98 %), ethyl heptanoate (99 %), ethylenediaminetetraacetic acid (EDTA) (ACS reagent, 99 %), hydrochloric acid (37 % v/v), hydrogen peroxide (stabilized for synthesis, 30 % v/v), L-glutathione reduced (≥ 98 %), HPLC grade methanol, methyl red (ACS reagent), methylene blue (ACS reagent), *n*-alkanes mixture (C₇-C₃₀), *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) (LiChropur™, ≥ 99 %), *p*-fluorobenzaldehyde (98 %), 85 % phosphoric acid (ACS reagent), sodium acetate (ACS reagent, ≥ 99 %), were purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany). Sodium chloride (ACS reagent) was purchased from Fluka (Honeywell, Charlotte, NC, USA). MilliQ water was produced by a MilliQ Plus apparatus (Merck Millipore, Billerica, MA, USA).

Spectrophotometric measurements

All spectrophotometric determinations were carried out using a V-530 UV/Vis spectrophotometer (Jasco Co. Ltd., Tokyo, Japan) with poly(methyl methacrylate) (PMMA) and polystyrene (PS) 10 mm cuvettes (Kartell Spa, Labware Division, Noviglio, Italy) for UV and visible wavelengths, respectively.

Wine color

Wine color was analyzed by measuring the absorbance at 420 nm against Milli Q grade water, using 10 mm optical path length disposable PMMA cuvettes.

Moreover, CIELAB parameters (L^* , a^* , b^*) were also evaluated according to the procedure described by Pérez-Magariño & González-San José (2001); transmittance spectra were acquired in the wavelength range 380-780 nm (with 0.5 nm intervals), reading against Milli Q water. CIELAB parameters were calculated for the CIE illuminant D_{65} and 10° standard observer conditions.

Total phenolic index (TPI)

TPI was calculated by measuring the absorbance at 280 nm against Milli Q water and multiplying the data by the dilution factor (10 dilutions).

Browning assay

The browning assay used in the present study was the POM-test, evaluated as proposed by Müller-Späth (1992). Five mL of wine were spiked with 25 μ L of 3% H_2O_2 solution and heated at 65 $^\circ$ C for 1 hour. Then, absorbance at 420nm was measured and the POM-test was calculated by the following equation:

$$POM - test = \frac{Abs\ 420_{H_2O_2} - Abs\ 420_{wine}}{Abs\ 420_{wine}} \times 100$$

Flavanols

Flavanols were analyzed using the procedure proposed by Zironi et al. (1992). The method involves the derivatization of flavanol molecules with a solution of 4-(dimethylamino)cinnamaldehyde (DAC). A DAC reagent solution was prepared by dissolving 1g of DAC in 250 mL of hydrochloric acid (37% v/v) and then adding 750 mL of methanol. For the analysis, 2.5 mL of DAC solution was mixed with 0.5 mL of wine in a disposable PMMA cuvette. After 5 minutes, the absorbance was measured at 640 nm against a blank in which the wine was replaced with a hydroalcoholic solution (ethanol 10% v/v). Quantitative analysis was carried out according to a calibration curve prepared with (+)-catechin in a range of 0-25 mg/L.

Total thiols

Total thiols content was determined using the method proposed by Gallardo-Chacón et al. (2010) with some modifications. The method is based on derivatization with 4,4'-dithiodipyridine (DTDP). For the analysis, 2.7 mL of acetate buffer (0.1 N, pH 4.5) containing ethylenediaminetetraacetic acid (EDTA) (0.2 mM) was mixed with 0.3 mL of wine in a PS cuvette and 0.125 mL of DTDP reagent (4 mM DTDP in 12mM HCl) was used. After 5 minutes the absorbance was read at 324 nm against a blank in which the sample was replaced with milliQ water. A calibration curve was prepared using glutathione to calculate the concentration of total thiols within a range of 0-200 mg/L.

Sulfur dioxide

The methods proposed by OIV (2019) were used to measure the free and total sulfur dioxide. These methods are classified respectively by code OIV-MA-AS323-04A1 and OIV-MA-AS323-04A2.

Analysis of volatile compounds

Volatile compounds were analysed by HS-SPME-GC-MS, using a GC2030 Nexis gas chromatograph (Shimadzu, Kyoto, Japan) coupled with a QP2020NX mass spectrometer and an HT2800T

autosampler (HTA S.r.l., Brescia, Italy). A divinylbenzene/carboxen/polydimethylsiloxane (DVB-CAR-PDMS, 50/30 μm x 2 cm) fiber (Supelco, Bellefonte, PA, USA) was used for SPME. Column was a 30 m x 0.25 mm i.d. x 0.25 μm DB-Wax (Agilent Technologies, Santa Clara, CA, USA) and the carrier gas was helium at a flow rate of 35 cm/s.

Ten millilitres of samples were added to 3 g of NaCl in 20 mL glass vials and immediately sealed. Ethyl heptanoate was used as internal standard at 2.17 mg/L. The analysis was carried out setting the following conditions: incubation for 15 minutes at 40 °C under stirring (500 rpm, 5 seconds on and 2 seconds off), microextraction for 15 minutes, injection and desorption for 5 minutes of the fiber into the injector. Injection was carried out in splitless mode. The initial oven temperature was 40 °C held for 5 minutes; then it was ramped at 4 °C/min up to 240 °C, held for 15 minutes. For the qualitative analysis, mass spectra were acquired at 70 eV and compared with those reported in the NIST 20 mass spectrum library. Moreover, linear retention indices were calculated, using *n*-alkanes (C₇-C₃₀), and compared with those found in literature. Finally, for some of the detected compounds identification was confirmed by comparison with commercial standards. Semi-quantitative analysis was carried out by the internal standard method.

Table 4 Qualitative table related to the analysis of volatile compounds, with the indication of the classification group of the compounds detected. Abbreviation RI: retention index; EE: ethyl ester; AE: acetic esters; OE: other ester; AM: aging marker; AL: alcohol; OA: short and medium chain fatty acid; O: other.

Compound	Group	Calculated RI	Reported RI	CAS	Rif.
ethyl acetate	O	880	884	141-78-6	Tatsuka et al. (1990)
2-methyl-1-propanol	AL	1109	1094	78-83-1	Tatsuka et al. (1990)
3-methyl-1-butanol acetate	AE	1119	1126	123-92-2	Tatsuka et al. (1990)
3-methyl-1-butanol	AL	1219	1211	123-51-3	Tatsuka et al. (1990)
ethyl hexanoate	EE	1237	1241	123-66-0	Umano et al. (1986)
hexyl acetate	AE	1272	1276	142-92-7	Tatsuka et al. (1990)
1-hexanol	AL	1360	1359	111-27-3	Tatsuka et al. (1990)
methyl octanoate	OE	1388	1390	111-11-5	Tressl et al. (1978)
ethyl octanoate	EE	1447	1441	106-32-1	Umano et al. (1986)
3-methylbutyl hexanoate	OE	1462	1453	2198-61-0	Tressl et al. (1978)
(2R,3R)-butane-2,3-diol	O	1542	1544	24347-58-8	Tanaka et al. (2003)
1-octanol	AL	1562	1561	111-87-5	Umano et al. (1994)
2-methyl-propanoic acid	OA	1567	1574	79-31-2	Umano et al. (1986)
3-methylbutyl 2-hydroxypropanoate	AM	1570	1570	19329-89-6	Ledauphin et al. (2004)
(2S,3S)-butane-2,3-diol	O	1578	1581	19132-06-0	Tanaka et al. (2003)
butanoic acid	OA	1626	1628	107-92-6	Rezende & Fraga (2003)
ethyl decanoate	EE	1646	1643	110-38-3	Umano et al. (1986)
3-methylbutyl octanoate	OE	1661	1658	2035-99-6	Tressl et al. (1978)
diethyl succinate	AM	1676	1679	123-25-1	Brander et al. (1980)
ethyl 9-decenoate	AM	1691	1703	67233-91-4	Gürbüz et al. (2006)
1,1,6-trimethyl-1,2-dihydronaphthalene (TDN)	AM	1737	1712	30364-38-6	Winterhalter (1991)
ethyl 2-phenylacetate	EE	1809	1822	101-97-3	Tatsuka et al. (1990)
ethyl dodecanoate	EE	1844	1847	106-33-2	Umano et al. (1986)
hexanoic acid	OA	1844	1849	142-62-1	Rezende & Fraga (2003)
2-phenylethanol	AL	1905	1912	60-12-8	Nagarajan et al. (2001)
diethyl malate	AM	2039	2041	7554-12-	Selli et al. (2006)
ethyl tetradecanoate	EE	2050	2043	124-06-1	Umano et al. (1986)
octanoic acid	OA	2058	2070	124-07-2	Tatsuka et al. (1990)
ethyl hexadecanoate	EE	2257	2243	628-97-7	Umano et al. (1986)
decanoic acid	OA	2272	2279	334-48-5	Rezende & Fraga (2003)

Carbonyl compounds

For carbonyl compounds, the method proposed by Moreira et al. (2019), based on *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) derivatisation, was used with some modifications. Internal standard was *p*-fluorobenzaldehyde at 0.64 mg/L in wine. Chromatographic conditions were as above, while microextraction was held for 45 min.

Cyclic voltammetry

Cyclic voltammetry was performed using the setup proposed by Comuzzo et al. (2017), with some modifications. The analysis was performed using the potentiostat PGSTAT 30 controlled by the software Ecochemie GPES 3.2 (Ecochemie, Utrecht, The Netherlands), on 10 mL of samples using a screen-printed Metrohm 110 (Metrohm Italiana Srl, Origgio, Italy). The screen-printed Metrohm 110 consists in a ceramic substrate on which the three different electrodes are printed. These are the working and auxiliary carbon electrodes and the reference electrode made of silver. It is worth noting that each electrode was used only once.

Sensory analysis

The samples were analyzed by quantitative descriptive analysis for the evaluation of different parameters by olfactory and retro-nasal perception. Each sample was identified by a three-digit number and served in a randomized order. The samples were evaluated by a panel of twelve judges, 8 male and 4 female, between 25 and 60 years of age. The judges scored the intensity of each parameter on a scale of zero to ten, low to high. The sensory test was carried out at the Laboratory of Sensory Analysis (LABAS) of the University of Udine (Italy).

The obtained data were normalized to reduce the subjective component of evaluation and enable comparison of results among different judges. Finally, judges were selected using SensTools 2.3.20 software (OP&P Products Research B.V., Utrecht, The Netherlands).

Statistical analysis

One-way ANOVA, Factorial ANOVA and Tukey HSD test were carried out on analytical and sensory data using the software Statistica 8 (Statsoft Inc., Tulsa, OK, USA). Differences were considered significant at $p < 0.05$. Principal Component Analysis (PCA) and Partial Least Square (PLS) performed using R, version 4.2.1 (R Development Core Team). In particular, PLS in cross-validation was performed by classification and regression training (abbr. caret) package version 6.0-94, available at <https://CRAN.R-project.org/package=caret>. This statistical method of analysis provided as results the value related to the intercept with the y-axis, the value of R^2 and the value of Root Mean Squared Error (RMSE); the latter defines the measure of absolute error between the predicted and observed values.

3. Results and discussion

Description of wine evolution by chemical analysis

As discussed in several publications, evolution impacts on phenolic composition of white wines, leading to oxidation and browning. Spectrophotometric analysis can be utilized to evaluate this effect by the measurement of the absorbance at 420 nm. This value tends to increase over time, as observed in the present study, as a result of different evolutionary pathways.

However, the CIE Lab method is increasingly being used for color assessment, providing more comprehensive information, by three different parameters that define the coordinates to obtain the full gamut of human color perception: the lightness of the color (L^*), the position between red and green (a^*), and the position between yellow and blue (b^*).

Sulfur dioxide content can provide a good indicator of wine evolution and it could define oxidability risk. For this reason, it is essential to evaluate the content of sulfur dioxide, both free and combined, as it is currently the most used antioxidant in several foods, including wine. The free fraction is the most effective against oxidative processes, mitigating them and protecting the wine during its evolution in the bottle until consumption.

Other parameter can be used, in order to assess the oxidability potential of the sample, it is possible to carry out assays in order to evaluate the difference before and after the treatment with oxidizing compounds, thus obtaining an index of oxidative potential, such as POM test. The POM test is related in particular to the phenolic composition and to the oxygen content, providing a parameter related to the wine analyzed, difficult to compare between different samples.

Among the different parameters analyzed, was also evaluated the content of total thiol compounds by derivatization with DTDP.

Basing on factor analysis, Principal Component Analysis (PCA) was performed, with a coefficient of 0.70 as the selection limit. Moreover, in the data obtained, the parameter b^* is particularly significant and shows a strong correlation with the absorbance at 420 nm, as demonstrated in Figure 8. The

parameters b^* related to the CIE Lab were not used for principal component analysis because it is redundant compared to the abs 420 nm parameter.

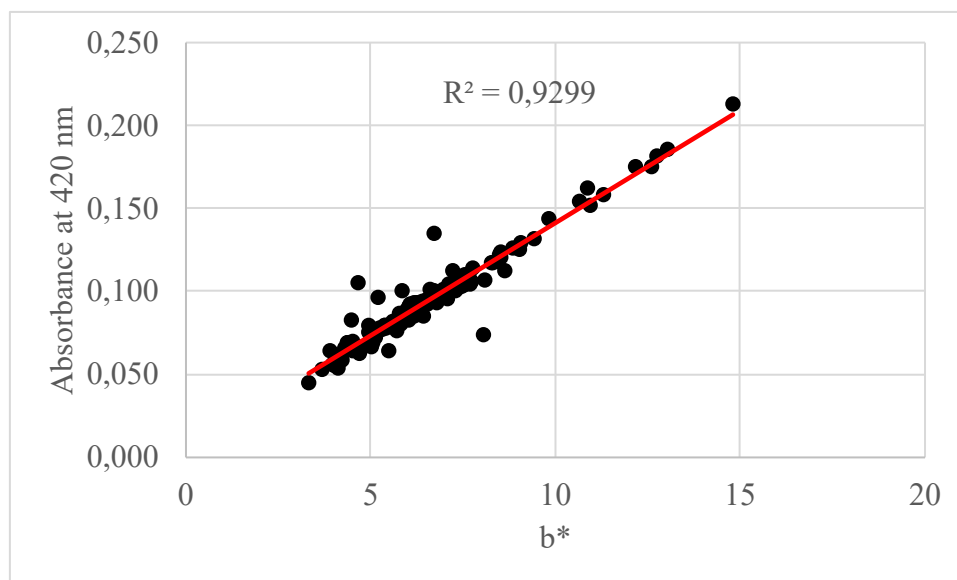


Figure 8 Correlation between the absorbance at 420 nm and the parameter b^* of CIE Lab.

During the experiment, the samples showed a significant decrease in free SO_2 concentration between the first and second sampling point (two and six months from the start of the project, respectively), as can be seen in Figure 9 and Figure 10. There is also a tendency for the absorbance at 420 nm, an indicator of browning, to increase, which appears to be slightly more evident at the final sampling point, fourteen months after the start of the experiment. These results are in agreement with theoretical knowledge and also with various published works, in particular with Benucci (2020) for the variation of the SO_2 content and with Castellanos et al. (2021) and Kanavouras et al. (2020) for the variation of the absorbance at 420 nm. Variations in this parameter seem to be limited, which could be due to the use of techniques that have allowed the production of highly stable wines over time.

As shown, the experimentation resulted in a lower graphic dispersion of the samples over time, indicating fewer differences between samples.

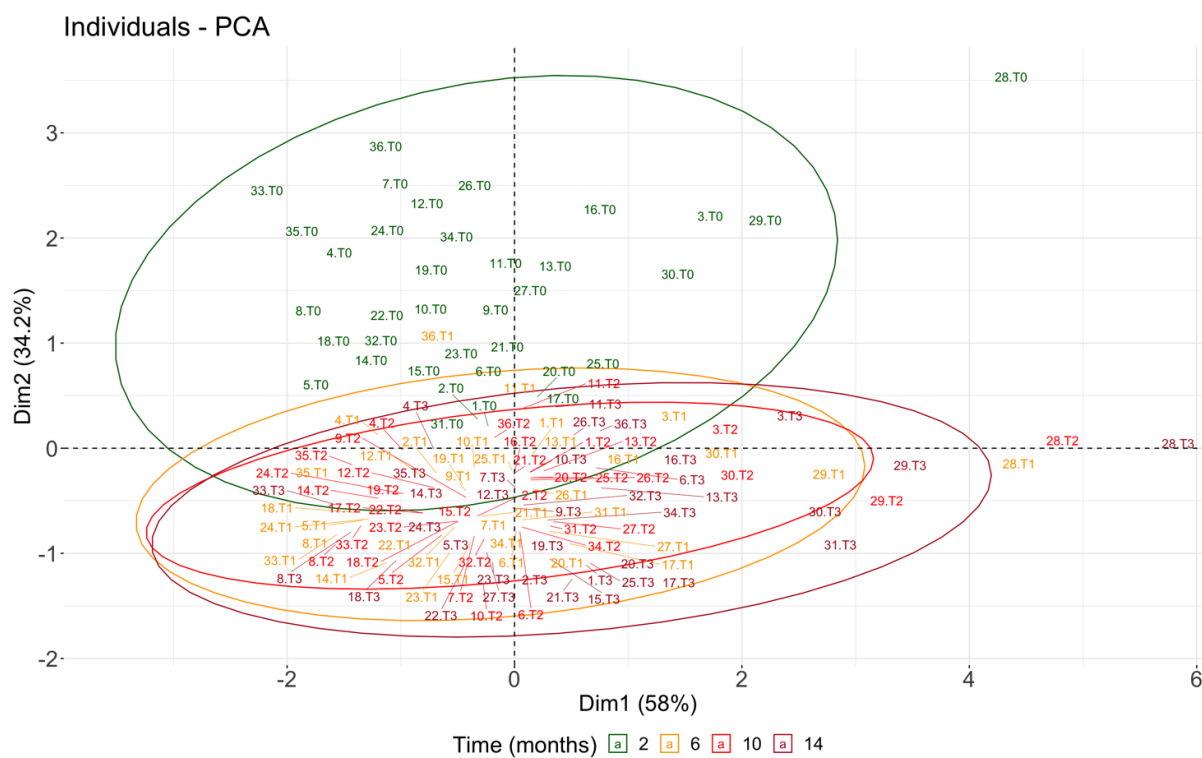


Figure 9 Score plot based on the chemical parameters. The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.

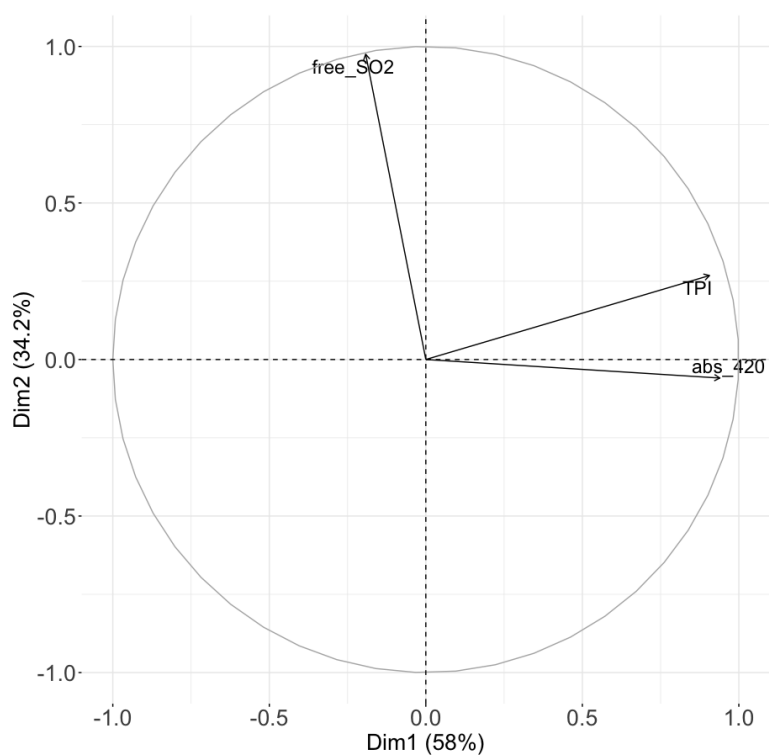


Figure 10 Loading plot of the chemical parameters.

Absorbance at 420 nm, showed a significant increase between the different samplings, as shown in Table 5. However, significant differences were recorded between the different varieties used to produce the samples, with higher values reported for the Chardonnay variety, followed by Sauvignon and Friulano, and finally Pinot Gris (Table 7). This trend may be related to enological treatment during winemaking production aimed at achieving oxidative stabilization.

The remaining parameters related to the CIE Lab analysis, did not lead to significant differences, according to ANOVA analysis (Table 5), for the L* parameter, while regarding a*, a decrease in the values obtained was observed between 2 (T0) and 10 months (T2), with the greatest decrease between 6 and 10 months.

The concentration of sulfur dioxide showed a significant decrease in the free fraction between the T0 and T1 samplings and then it is stabilized during the whole project. Contrary, the combined fraction showed an initial increase, which could be related to the decrease of free sulfur dioxide.

No significant variation was identified in the flavanols content, attributed to the high heterogeneity among samples.

Finally, the POM test was used to assess oxidability potential, which involves applying oxidative and thermal stress in combination. Overall, the POM test showed a decrease in this value from the second to the third sampling point, indicating a possible oxidation at the expense of the phenolic component, although the values for the total polyphenol index remained stable.

The application of different closures resulted in a significant differentiation of the samples based on chemical parameters (

Table 6). The use of synthetic closures and screwcaps resulted in higher levels of free sulfur dioxide, indicating better preservation of samples against oxidative processes. Additionally, analyzing the data related to absorbance at 420 nm for these closures confirmed this behavior, although no significant differences were found among the samples for this parameter, except for the alternative caps, which recorded higher values than the other closures.

Table 5 Effects of the evolution on the analyzed chemical parameters. Data are means and standard deviations of the sample set. Differences in the effect of time were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Variable	Time (months)								p-value
	2		6		10		14		
Total thiols (mg/L)	383.5 ± 276.1	b	263.3 ± 146.9	ab	247.8 ± 133.8	a	154.5 ± 96.7	a	***
Flavanols (mg/L)	11.8 ± 10.1	a	12.9 ± 10.7		10.9 ± 10.0		13.7 ± 19.3		ns
Free SO ₂ (mg/L)	27.6 ± 7.0	b	8.9 ± 4.7	ab	8.6 ± 3.2	a	7.3 ± 4.2	a	***
Combined SO ₂ (mg/L)	70.8 ± 20.5	a	87.4 ± 23.0	b	83.8 ± 22.4	ab	76.7 ± 21.0	ab	*
POM test (%)	35 ± 28	c	30 ± 15	bc	13 ± 17	a	16 ± 20	ab	***
L*	98.7 ± 0.63		98.7 ± 0.62		98.31 ± 0.6		98.30 ± 0.58		ns
a*	-0.71 ± 0.40	c	-0.84 ± 0.35	bc	-1.24 ± 0.61	a	-1.03 ± 0.35	ab	***
b*	6.14 ± 1.96		6.53 ± 1.99		6.53 ± 1.91		7.47 ± 2.31		ns
TPI	8.0 ± 2.5		7.5 ± 2.4		7.5 ± 2.5		7.8 ± 2.6		ns
Abs 420 nm	0,087 ± 0,027 a	a	0,091 ± 0,027 ab	ab	0,095 ± 0,026 ab	ab	0,109 ± 0,032 b	b	*

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

Table 6 Effects of the evolution on the analyzed chemical parameters. Data are means and standard deviations of the sample set. Differences in the effect of closure typology were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Variable	Closure											p-value	
	Technical		Screwcap		Natural		Alternative		Co-extruded		Syntetic		
Total thiols (mg/L)	173.0 ± 102.6	a	360.1 ± 121.3	bc	264.7 ± 108.4	b	480.9 ± 284.6	c	418.5 ± 238.5	c	466.2 ± 297.3	c	***
Flavanols (mg/L)	15.1 ± 16.1		13.0 ± 4.9		11.1 ± 5.1		7.9 ± 8.0		4.5 ± 1.4		6.6 ± 1.7		ns
Free SO ₂ (mg/L)	12.0 ± 8.5	a	17.0 ± 11.8	bc	12.2 ± 9.8	ab	12.1 ± 10.6	ab	13.2 ± 12.1	ab	20.8 ± 11.3	c	***
Combined SO ₂ (mg/L)	75.8 ± 24.4	a	71.8 ± 13.1	ab	78.1 ± 18.7	ab	85.4 ± 7.1	ab	98.3 ± 20.3	b	90.7 ± 13.9	ab	**
POM test (%)	28 ± 20	b	25 ± 28	b	17 ± 17.9	ab	0 ± 9.3	a	33 ± 20	b	12.9 ± 25.8	ab	***
L*	98.48 ± 0.64	b	98.59 ± 0.32	b	98.61 ± 0.48	b	97.35 ± 2.63	a	98.93 ± 0.38	b	98.88 ± 0.75	b	**
a*	-0.89 ± 0.41	b	-0.59 ± 0.28	b	-0.99 ± 0.44	b	-1.89 ± 0.46	a	-0.95 ± 0.31	b	-0.9 ± 0.43	b	***
b*	6.83 ± 2.09	a	6.26 ± 0.56	a	6.02 ± 1.35	a	10.38 ± 1.42	b	5.67 ± 1.01	a	4.85 ± 1.16	a	***
TPI	7.5 ± 2.8	a	7.9 ± 0.5	a	7.4 ± 1.3	a	11.6 ± 0.7	b	6.6 ± 1.3	a	6.5 ± 0.5	a	***
Abs 420 nm	0.097 ± 0.029	a	0.089 ± 0.008	a	0.089 ± 0.017	a	0.147 ± 0.021	b	0.080 ± 0.016	a	0.078 ± 0.028	a	***

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

Table 7 Effects of the evolution on the analyzed chemical parameters. Data are means and standard deviations of the sample set. Differences in the effect of variety were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Variable	Variety				p-value	
	Sauvignon	Pinot gris	Chardonnay	Friulano		
Total thiols (mg/L)	261.8 ± 201.2	266.8 ± 160.1	253.2 ± 162.8	266.2 ± 251.84	ns	
Flavanols (mg/L)	18.6 ± 15.3 b	8.2 ± 4.5 a	14.2 ± 19.33 ab	9.6 ± 6.2 a	**	
Free SO ₂ (mg/L)	14.5 ± 10.4	14.0 ± 9.0	11.7 ± 9.7	11.9 ± 10.1	ns	
Combined SO ₂ (mg/L)	74.8 ± 17.1	81.8 ± 16.7	87.4 ± 29.7	74.1 ± 23.6	ns	
POM test (%)	30 ± 25	17 ± 18	26 ± 22	23 ± 25	ns	
L*	98.67 ± 0.47	96.15 ± 14.91	98.27 ± 0.87	98.38 ± 1.52	ns	
a*	-0.99 ± 0.3 b	-0.59 ± 0.33 c	-1.26 ± 0.48 a	-1.09 ± 0.5 ab	***	
b*	6.55 ± 1.44 ab	5.85 ± 1.18 a	7.85 ± 2.66 b	6.66 ± 2.39 ab	*	
TPI	8.0 ± 1.9 ab	7.0 ± 1.6 a	8.7 ± 3.6 b	7.1 ± 2.3 ab	*	
Abs 420 nm	0.094 ± 0.020 ab	0.084 ± 0.016 a	0.112 ± 0.038 b	0.096 ± 0.033 ab	**	

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

In the correlation matrix, it can be observed that exists a notable correlation in the experimental data obtained between the flavanols content and the total polyphenols index (IPT) (Figure 11). Additionally, their concentration also correlates with color measurements, both absorbance at 420 nm and the b* parameter associated with the CIE Lab color space. Lastly, the observed negative correlation between the browning index, as evaluated by the POM test, and absorbance at 420 nm is interesting, albeit not strictly significant.

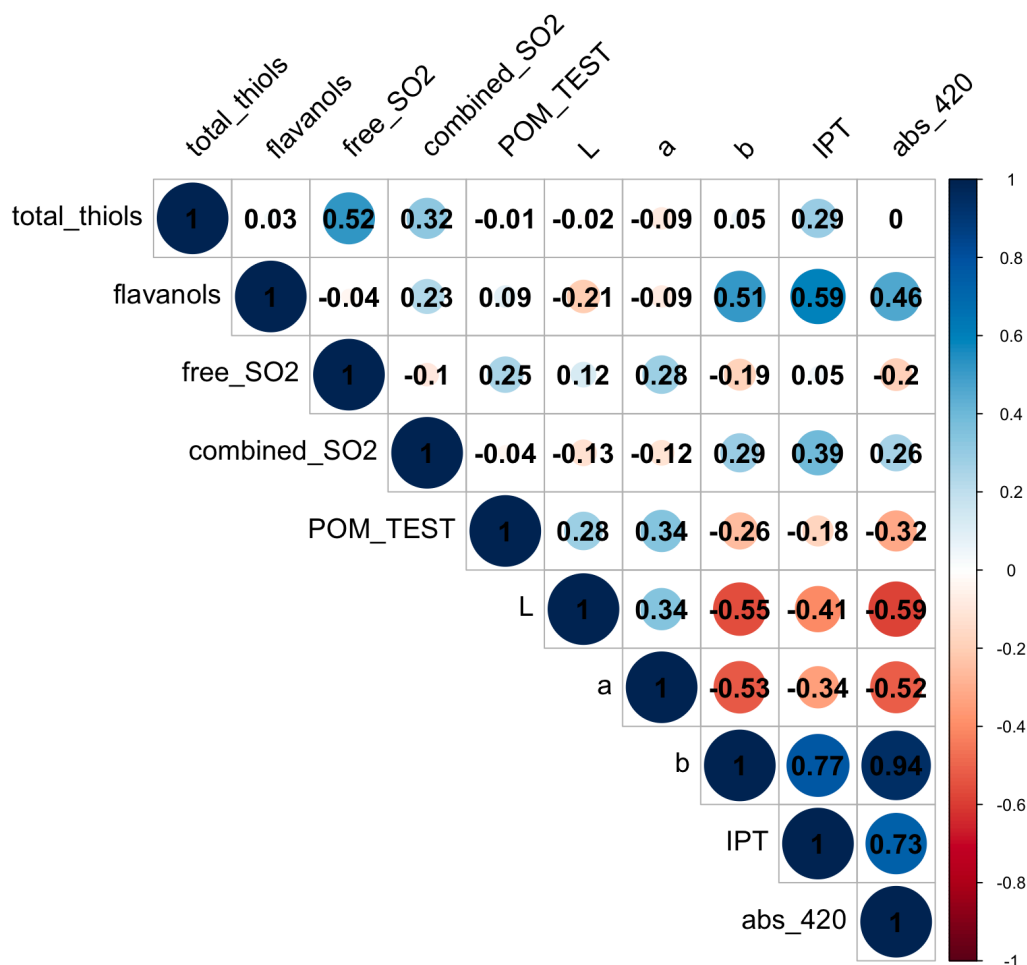


Figure 11 Correlation matrix of chemical parameters analyzed.

The use of different chemical and spectrophotometric parameters, as described above, can be very useful to study the evolution of a wine, even if they may lead to obtaining values relative to the sample analyzed and which are hardly comparable between different wines.

Furthermore, these determinations have the advantage of being relatively easy to carry out and of the presence of a wide range of studies that allow a simpler interpretation of the data.

Volatile composition for describing wine evolution

The study of volatile compounds is a relevant subject, albeit frequently deviating from strict alignment with sensory attributes, as the latter appear to be related to the involvement of perception and recognition thresholds. Additionally, this parameter is significantly influenced by factors such as

grape variety, use of technology during production, the packaging used, and various environmental factors imposed on the packaging. This aspect has sparked considerable debate, as over time, wine tends to undergo a gradual diminution of its volatile components, resulting in a diminished aromatic bouquet and sometimes the development of defects. Furthermore, sensory deviations can be caused by oxidation or reduction mechanisms.

The volatile composition, analyzed by gas chromatography, is used to evaluate the concentrations of different groups of compounds and their changes over time.

Specifically, in the present study different compounds were identified and divided into six different families: ethyl esters, acetic esters, other esters, aging markers, higher alcohols, and short and medium chain fatty acids. The volatile compounds were categorized according to Table 4.

Principal component analysis (PCA) was performed on the obtained data. Based on the explained variance, factor analysis was not performed to select the most representative variables.

PCA suggests that the samples presented a decrease (Figure 12 and Figure 13), not linear, in the concentration of the volatile compounds of the different classes over the experimental period. The difference became more pronounced between the second and third sampling points, in particular, the volatile compounds associated with fermentation, such as ethyl esters. The results obtained appear to be quite in agreement with those obtained by Vázquez-Pateiro et al. (2020), with an overall reduction over time.

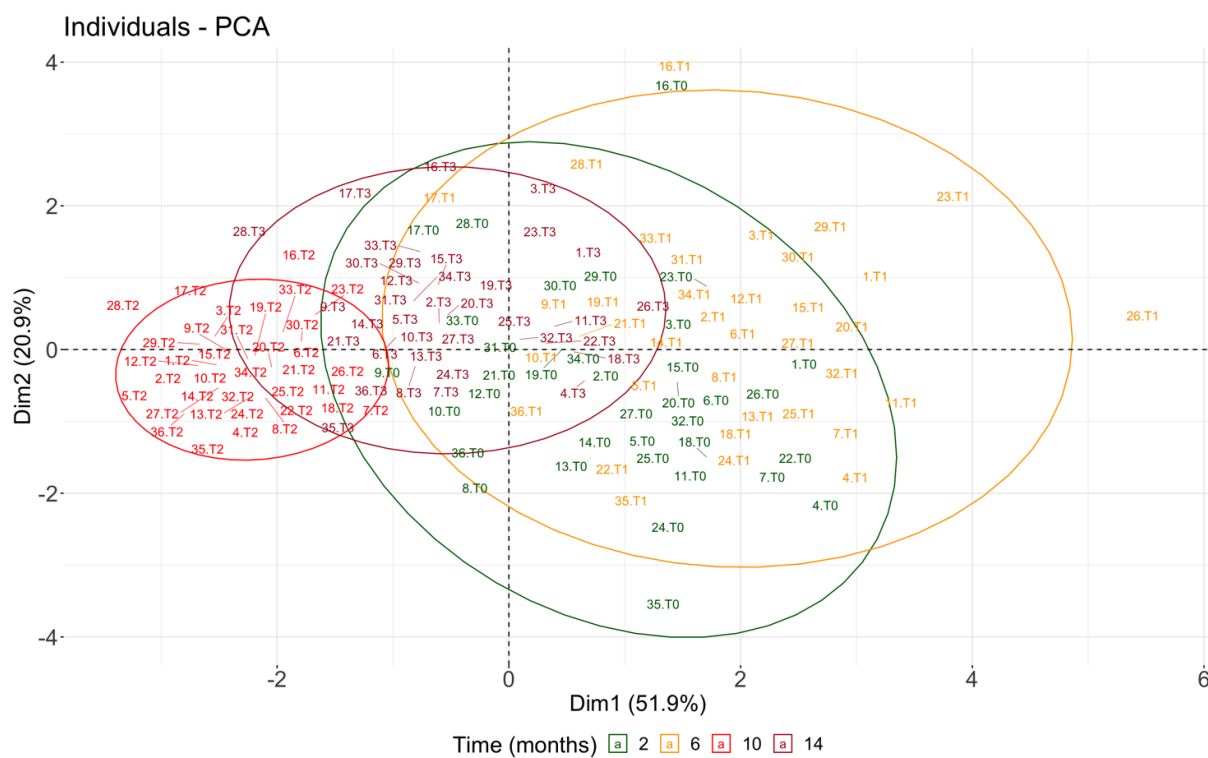


Figure 12 Score plot based on the classification of volatile compound groups concentration ($\mu\text{g/L}$). The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.

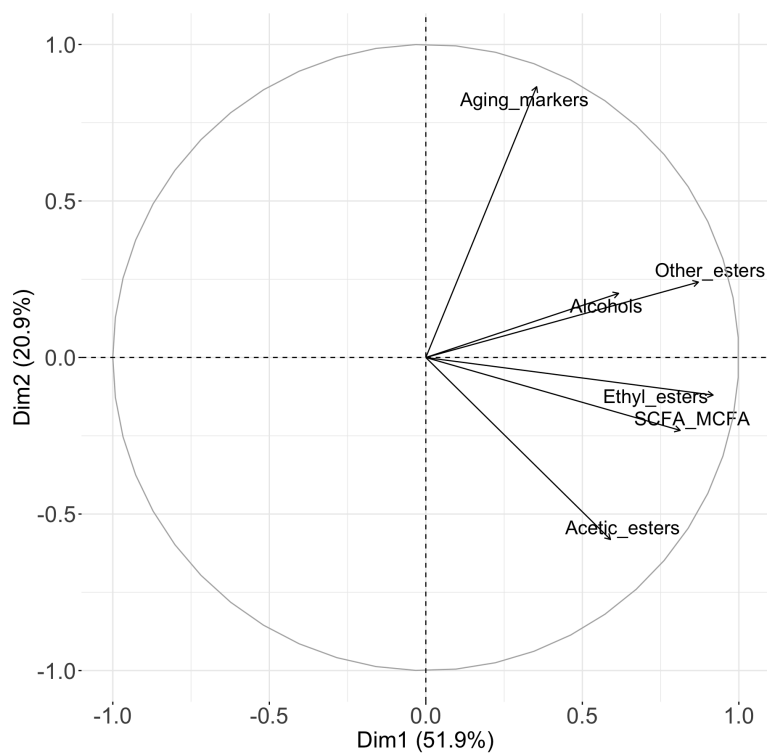


Figure 13 Loading plot of the concentration ($\mu\text{g/L}$) of volatile composition based on the volatile group classification. Abbreviation SCFA_MCFA: Short and Medium Chain Fatty Acids.

Regarding ethyl esters, a variation in their content was observed during the experiment, but the difference in mean concentration between the initial sampling point and the final one does not seem to be statistically different. From the point of view of the varieties, Pinot Gris was the one with the highest endowment, followed by Sauvignon, then Chardonnay and Friulano, with no significant difference between the last two (Table 10).

The compound most present within the family of ethyl esters seemed ethyl octanoate, which did not show significant differences between the two extreme sampling points, but with fluctuations in concentration at intermediate points; ethyl hexanoate, which underwent a significant reduction in concentration over the course of the experiment, this trend was found also for ethyl decanoate, but with a less significant reduction.

There was a reduction in the content also for acetic esters throughout the experiment, with the greatest reduction being recorded at the sampling points of six and ten months after the start of the project.

Also for this class of volatile compounds, Pinot Gris was found to have a higher mean concentration, followed by Sauvignon and finally Chardonnay and Friulano.

The compounds present within this class are 3-methyl-1-butanol acetate and hexyl acetate; both underwent a reduction over the course of the study, marked by a decline between six and ten months, and then recorded stability in concentration.

The category other esters, constituted as in Table 8, showed no significant differences between the first and the last sampling points, but with significant changes in the intermediate sampling point.

No significant differences were found between the different varieties.

The most prevalent compounds within the category were 3-methylbutyl hexanoate and 3-methylbutyl octanoate, which varied in concentration over the course of the experiment, but not significantly when comparing the first and last sampling points.

Aging-related compounds are compounds that have been reported in studies to be associated with development. This group shows an increase over the course of the experiment, with some fluctuation, as reported by Dombre et al. (2015).

The most abundant compounds within the family are diethyl succinate and ethyl 9-decenoate, respectively, with the former showing a significant increase over the course of the experiment and the latter showing no significant variation. Diethyl succinate in particular has been described as a marker of evolution, as it tends to increase in concentration, especially in the early stages of storage, and then tends to decrease, in both red and white wines (Câmara et al., 2006).

From the point of view of the varieties, the richest in these compounds was the Friulano variety, followed by Chardonnay, and finally Pinot gris and Sauvignon, even if with no significant differences between them (Table 9).

A decrease in the concentration of higher alcohols was observed over the course of the study, particularly during the period between six and ten months following the commencement of the project. The compounds mostly present within the family were 3-methyl-1-butanol, 2-phenylethanol and 1-octanol, which underwent a significant reduction, most pronounced between six and ten months after the start of the experiment. Hexanol also showed a significant and gradual decrease, 2-methyl-1-propanol decreased between the start and the end of the experiment, but mainly between two and six months.

The samples obtained from the Friulano variety were found to have a higher endowment of higher alcohols, followed by Chardonnay, Sauvignon and finally Pinot Gris.

Finally, short and medium chain fatty acids (SCFA_MCFA), showed a decrease over the course of the experiment, but not significant between the first and last sampling points, with significant variations at intermediate sampling points.

The most abundant compounds within the family were octanoic acid, which showed a decrease in concentration mainly between six and ten months after the start of the project, followed by hexanoic acid and decanoic acid, which, however, did not show significant changes considering the extreme sampling points.

No significant differences were found between the different varieties.

No relationship was found between volatile compounds analyzed in this research project and the closure used, with the exception of the variation of acetic ester; the highest content is related to the use of extruded synthetic corks and the lowest value for agglomerated corks.

The analysis of volatile compounds is a detailed examination of a wide range of compounds that are subjected to various processes that may affect their concentrations and, in this regard, would not be optimal markers for estimating the evolution state and potential of the sample analyzed, as also described in this study. Furthermore, this analysis requires advanced instrumentation that can be difficult to manage in a production environment, and the analysis of the data is time consuming.

Table 8 Effects of the evolution on the concentration ($\mu\text{g/L}$) of volatile composition based on the volatile group classification. Data are means and standard deviations of the sample set. Differences in the effect of time were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Compound	Time (months)								p-value
	2		6		10		14		
Ethyl esters	2308.1 ± 554.7	b	2645.8 ± 577.0	c	1231.1 ± 268.2	a	1997.0 ± 458.1	b	***
ethyl hexanoate	475.2 ± 105.9	c	537.2 ± 123.6	d	162.4 ± 30.8	a	323.5 ± 62.9	b	***
ethyl octanoate	1372.7 ± 330.5	bc	1548.3 ± 326.1	c	812.4 ± 222.6	a	1277.1 ± 290.2	bc	***
ethyl decanoate	444.0 ± 165.7	bc	532.37 ± 179.3	c	244.6 ± 91.9	a	383.2 ± 141.0	b	***
ethyl 2-phenylacetate	6.9 ± 3.4	b	5.6 ± 2.4	b	1.8 ± 0.9	a	1.6 ± 0.8	a	***
ethyl dodecanoate	8.2 ± 6.5	a	18.1 ± 12.7	b	7.9 ± 4.5	a	9.9 ± 6.1	a	***
ethyl tetradecanoate	0.4 ± 0.2	a	1.2 ± 0.5	b	0.4 ± 0.2	a	0.3 ± 0.2	a	***
ethyl hexadecanoate	0.8 ± 0.5	a	3.0 ± 1.6	b	1.5 ± 0.9	a	1.3 ± 0.9	a	***
Acetic esters	254.1 ± 149.8	c	187.1 ± 99.1	b	51.8 ± 27.6	a	60.6 ± 35.9	a	***
3-methylbutyl acetate	202.6 ± 130.6	c	145.8 ± 82.8	b	38.0 ± 21.7	a	47.4 ± 30.6	a	***
hexyl acetate	51.5 ± 30.0	b	41.3 ± 22.8	b	13.7 ± 7.7	a	13.2 ± 7.5	a	***
Other esters	13.8 ± 3.0	b	20.6 ± 5.1	c	7.4 ± 1.8	a	14.1 ± 2.9	b	***
methyl octanoate	3.2 ± 1.0	b	3.4 ± 1.5	b	1.3 ± 0.5	a	3.3 ± 0.9	b	***
3-methylbutyl hexanoate	5.1 ± 1.3	b	8.1 ± 2.5	c	2.8 ± 0.7	a	4.4 ± 0.9	b	***
3-methylbutyl octanoate	5.5 ± 1.9	b	9.0 ± 2.7	c	3.3 ± 1.0	a	6.4 ± 1.7	b	***
Aging markers	35.9 ± 15.7	a	51.1 ± 21.3	b	26.8 ± 8.7	a	48.5 ± 16.2	b	***
3-methylbutyl 2-hydroxypropanoate	0.5 ± 0.8		0.7 ± 0.8		0.3 ± 0.5		0.5 ± 0.9		ns
diethyl butanedioate	23.8 ± 14.7	a	34.8 ± 19.1	b	19.5 ± 8.5	a	36.5 ± 15.0	b	***
ethyl dec-9-enoate	9.6 ± 9.7	ab	12.7 ± 12.3	b	5.5 ± 5.7	a	8.0 ± 7.8	ab	*
1,1,6-trimethyl-2H-naphthalene (TDN)	1.6 ± 1.1	a	2.0 ± 1.5	ab	1.1 ± 0.7	a	2.6 ± 2.2	b	***
diethyl 2-hydroxybutanedioate	0.3 ± 0.3	a	0.9 ± 0.3	b	0.4 ± 0.4	a	0.8 ± 0.4	b	***

continue

Alcohols	665.7 ± 236.5	c	573.4 ± 156.9	b	238.1 ± 56.7	a	308.4 ± 70.4	a	***
2-methylpropan-1-ol	26.3 ± 18.1	b	9.9 ± 5.7	a	5.0 ± 2.5	a	10.9 ± 5.3	a	***
3-methylbutan-1-ol	562.4 ± 199.7	b	493.4 ± 139.1	b	190.2 ± 46.1	a	244.4 ± 53.5	a	***
hexan-1-ol	30.2 ± 11.4	b	27.4 ± 9.8	b	16.6 ± 5.9	a	21.1 ± 8.1	a	***
octan-1-ol	1.7 ± 0.6	b	2.1 ± 0.7	b	0.7 ± 0.3	a	1.0 ± 0.4	a	***
2-phenylethanol	45.1 ± 19.2	b	40.7 ± 15.8	b	25.4 ± 7.6	a	31.1 ± 11.9	a	***
SCFA_MCFA	109.9 ± 45.8	b	135.6 ± 38.0	c	65.4 ± 19.8	a	88.6 ± 25.8	b	***
2-methylpropanoic acid	1.3 ± 0.5	c	1.4 ± 0.5	c	0.4 ± 0.2	a	0.8 ± 0.3	b	***
butanoic acid	0.9 ± 0.2	b	1.2 ± 0.2	c	0.7 ± 0.2	a	0.7 ± 0.2	a	***
hexanoic acid	22.4 ± 6.3	b	28.4 ± 7.1	c	13.2 ± 3.8	a	19.3 ± 5.0	b	***
octanoic acid	69.7 ± 29.7	b	80.7 ± 23.4	b	39.3 ± 11.8	a	53.5 ± 15.9	a	***
decanoic acid	15.6 ± 11.3	a	23.8 ± 9.6	b	11.8 ± 5.5	a	14.2 ± 6.4	a	***

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Table 9 Effects of the evolution on the concentration ($\mu\text{g/L}$) of volatile composition based on the volatile group classification. Data are means and standard deviations of the sample set. Differences in the effect of closure typology were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Compound	Closure											p-value
	Technical		Screwcap		Natural		Alternative		Co-extruded		Syntetic	
Ethyl esters	2050.6 $\pm$ 727.5	a	2569.0 $\pm$ 812.1	b	2301.8 $\pm$ 808.0	ab	1821.6 $\pm$ 619.0	a	1888.7 $\pm$ 512.0	a	1631.2 $\pm$ 440.0	**
ethyl hexanoate	367.6 $\pm$ 166.4		413.5 $\pm$ 179.3		426.8 $\pm$ 216.6		321.1 $\pm$ 135.6		345.1 $\pm$ 159.1		373.8 $\pm$ 152.9	ns
ethyl octanoate	1243.2 $\pm$ 410.7	b	1548.9 $\pm$ 455.7	c	1358.8 $\pm$ 412.4	bc	1153.5 $\pm$ 386.8	abc	1004.2 $\pm$ 221.9	a	1198.4 $\pm$ 274.1	abc
ethyl decanoate	421.1 $\pm$ 181.1	a	584.4 $\pm$ 193.9	b	395.0 $\pm$ 176.3	a	333.4 $\pm$ 144.1	a	268.8 $\pm$ 94.8	a	306.3 $\pm$ 117.3	***
ethyl 2-phenylacetate	3.6 $\pm$ 2.9	abc	5.6 $\pm$ 4.3	bc	5.4 $\pm$ 3.6	b	2.3 $\pm$ 1.7	a	4.4 $\pm$ 3.6	abc	3.7 $\pm$ 2.8	abc
ethyl dodecanoate	12.4 $\pm$ 10.3		13.9 $\pm$ 9.1		10.5 $\pm$ 6.6		9.9 $\pm$ 7.9		7.4 $\pm$ 3.8		5.3 $\pm$ 2.8	ns
ethyl tetradecanoate	0.6 $\pm$ 0.5	b	0.6 $\pm$ 0.4	ab	0.6 $\pm$ 0.6	ab	0.5 $\pm$ 0.5	ab	0.3 $\pm$ 0.3	ab	0.3 $\pm$ 0.2	*
ethyl hexadecanoate	2.0 $\pm$ 1.5	b	2.0 $\pm$ 1.3	ab	1.7 $\pm$ 1.2	ab	0.9 $\pm$ 0.6	a	0.9 $\pm$ 0.5	a	0.8 $\pm$ 0.4	***
Acetic esters	112.4 $\pm$ 89.3	a	229.4 $\pm$ 157.1	bc	162.4 $\pm$ 120.0	ab	86.1 $\pm$ 59.4	a	146.1 $\pm$ 118.1	c	263.3 $\pm$ 262.0	b
3-methylbutyl acetate	86.5 $\pm$ 70.2	a	176.7 $\pm$ 123.5	bc	126.8 $\pm$ 101.0	ab	71.8 $\pm$ 51.7	a	215.2 $\pm$ 243.3	c	116.2 $\pm$ 95.8	ab
hexyl acetate	25.9 $\pm$ 22.3	a	52.7 $\pm$ 38.8	b	34.5 $\pm$ 29.3	ab	14.3 $\pm$ 7.8	a	48.0 $\pm$ 27.8	b	29.9 $\pm$ 22.7	ab
Other esters	13.5 $\pm$ 5.6	ab	16.5 $\pm$ 6	bc	16.3 $\pm$ 8.6	ab	18.6 $\pm$ 8.1	c	14.0 $\pm$ 5.3	a	10.5 $\pm$ 4.1	ab
methyl octanoate	2.9 $\pm$ 1.5		3.0 $\pm$ 1.5		2.6 $\pm$ 1.0		2.9 $\pm$ 0.7		1.9 $\pm$ 0.9		3.1 $\pm$ 1.2	ns
3-methylbutyl hexanoate	5.0 $\pm$ 2.4	ab	6.0 $\pm$ 2.6	bc	4.8 $\pm$ 2.2	ab	6.7 $\pm$ 3.1	c	3.6 $\pm$ 1.5	a	5.4 $\pm$ 2.5	abc
3-methylbutyl octanoate	5.6 $\pm$ 2.5	ab	7.4 $\pm$ 2.3	bc	6.6 $\pm$ 2.9	ab	9.0 $\pm$ 4.5	c	4.9 $\pm$ 2.4	a	5.5 $\pm$ 2.2	ab
Aging markers	42.5 $\pm$ 20.3	b	36.6 $\pm$ 8.8	ab	36.4 $\pm$ 13.0	b	47.0 $\pm$ 13.7	b	50.4 $\pm$ 14.0	a	16.4 $\pm$ 6.6	b
3-methylbutyl 2-hydroxypropanoate	0.5 $\pm$ 0.8		0.3 $\pm$ 0.3		0.3 $\pm$ 0.3		0.5 $\pm$ 0.3		0.1 $\pm$ 0.1		0.9 $\pm$ 1.1	ns
diethyl butanedioate	32.6 $\pm$ 17.5	b	16.4 $\pm$ 6.7	a	27.4 $\pm$ 12.0	ab	41.1 $\pm$ 10.9	b	11.8 $\pm$ 5.4	a	18.9 $\pm$ 7.6	a
ethyl dec-9-enoate	6.5 $\pm$ 5.9	a	17.4 $\pm$ 5.0	b	6.5 $\pm$ 6.3	a	2.5 $\pm$ 1.7	a	3.1 $\pm$ 2.1	a	29.1 $\pm$ 9.1	c
1.1.6-trimethyl-2H-naphthalene (TDN)	2.1 $\pm$ 1.9		1.8 $\pm$ 1.0		1.4 $\pm$ 1.1		2.3 $\pm$ 1.1		0.9 $\pm$ 0.4		1.1 $\pm$ 0.5	ns
diethyl 2-hydroxybutanedioate	0.7 $\pm$ 0.4	a	0.6 $\pm$ 0.3	a	0.4 $\pm$ 0.3	a	0.63 $\pm$ 0.3	a	0.3 $\pm$ 0.2	a	0.4 $\pm$ 0.4	abc

continue

Alcohols	434.8 ± 219.6	a	384.3 ± 152.4	a	459.5 ± 249.0	a	652.66 ± 348.7	b	447.1 ± 231.0	ab	447.3 ± 234.4	a	**
2-methylpropan-1-ol	12.6 ± 12.5	a	8.6 ± 6.0	a	12.3 ± 11.0	a	24.72 ± 20.7	b	9.8 ± 9.0	a	13.3 ± 11.9	ab	**
3-methylbutan-1-ol	359.3 ± 189.3	a	329.0 ± 138.5	a	356.0 ± 203.1	a	544.18 ± 309.0	b	385.2 ± 219.4	ab	376.3 ± 200.7	a	**
hexan-1-ol	23.4 ± 9.2	ab	21.1 ± 6.5	ab	16.7 ± 8.2	a	38.33 ± 9.9	c	30.4 ± 13.4	bc	23.4 ± 9.7	ab	***
octan-1-ol	1.2 ± 0.6	a	1.2 ± 0.8	a	1.19 ± 0.6	a	2.13 ± 1.0	b	1.1 ± 0.8	a	2.2 ± 0.9	b	***
2-phenylethanol	38.2 ± 16.6	b	24.4 ± 7.2	ab	36.4 ± 16.3	ab	43.27 ± 15.5	b	20.8 ± 6.9	a	31.9 ± 14.3	ab	**
SCFA_MCFA	103.5 ± 46.4	b	119.3 ± 28.0	b	107.4 ± 37.5	ab	66.01 ± 23.0	a	99.8 ± 35.8	ab	73.9 ± 31.0	ab	**
2-methylpropanoic acid	0.9 ± 0.5	ab	0.7 ± 0.4	a	1.2 ± 0.6	bc	1.74 ± 0.7	c	0.8 ± 0.3	ab	0.9 ± 0.4	ab	***
butanoic acid	0.8 ± 0.3	a	1.1 ± 0.4	c	1.0 ± 0.3	abc	0.82 ± 0.3	ab	0.9 ± 0.3	abc	1.0 ± 0.3	bc	***
hexanoic acid	20.3 ± 8.1	ab	22.3 ± 6.5	ab	22.6 ± 7.9	ab	16.11 ± 5.5	a	19.0 ± 7.2	ab	24.7 ± 8.3	b	*
octanoic acid	62.9 ± 28.8	b	71.8 ± 16.8	b	65.4 ± 24.3	ab	39.74 ± 13.8	a	44.0 ± 18.7	ab	60.6 ± 21.7	ab	**
decanoic acid	18.5 ± 10.4	b	23.3 ± 5.6	b	14.6 ± 7.4	ab	7.59 ± 3.7	a	9.3 ± 5.9	a	12.5 ± 5.9	ab	***

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Table 10 Effects of the evolution on the concentration ($\mu\text{g/L}$) of volatile composition based on the volatile group classification. Data are means and standard deviations of the sample set. Differences in the effect of variety were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Compound	Variety								p-value
	Sauvignon		Pinot gris		Chardonnay		Friulano		
Ethyl esters	2089.9 ± 693.3	ab	2196.7 ± 751.1	b	1993.9 ± 700.0	a	1858.4 ± 658.6	a	*
ethyl hexanoate	400.9 ± 158.3	b	388.9 ± 182.3	b	374.3 ± 179.5	ab	330.0 ± 154.5	a	*
ethyl octanoate	1286.6 ± 391.9		1333.4 ± 413.3		1234.8 ± 411.8		1132.5 ± 366.9		ns
ethyl decanoate	384.9 ± 193.4		455.2 ± 189.8		370.0 ± 159.5		378.5 ± 167.2		ns
ethyl 2-phenylacetate	4.5 ± 3.5		4.3 ± 3.3		3.6 ± 3.1		3.4 ± 2.7		ns
ethyl dodecanoate	10.1 ± 7.6		12.3 ± 9.8		9.5 ± 7.7		11.8 ± 10.4		ns
ethyl tetradecanoate	0.7 ± 0.4		0.6 ± 0.5		0.5 ± 0.4		0.5 ± 0.6		ns
ethyl hexadecanoate	2.3 ± 1.6	b	1.7 ± 1.3	ab	1.2 ± 0.9	a	1.4 ± 1.3	a	**
Acetic esters	140.3 ± 119.7	ab	185.9 ± 165.0	b	117.7 ± 96.5	a	96.0 ± 71.8	a	***
3-methylbutyl acetate	101.0 ± 89.1	a	152.4 ± 144.1	b	96.2 ± 78.5	a	71.7 ± 55.3	a	***
hexyl acetate	39.3 ± 32.5	b	33.6 ± 24.4	ab	21.5 ± 19.9	a	24.3 ± 21.8	a	**
Other esters	14.6 ± 5.9		13.2 ± 5.5		14.1 ± 6.4		14.3 ± 5.5		ns
methyl octanoate	3.2 ± 1.3	b	2.5 ± 1.3	a	2.7 ± 1.3	ab	2.9 ± 1.4	ab	*
3-methylbutyl hexanoate	5.2 ± 2.5		4.8 ± 2.3		5.3 ± 2.7		5.3 ± 2.2		ns
3-methylbutyl octanoate	6.2 ± 2.7		5.9 ± 2.4		6.1 ± 3.3		6.0 ± 3.0		ns
Aging markers	37.5 ± 19.9	a	34.6 ± 13.8	a	42.0 ± 16.0	ab	49.9 ± 22.1	b	**
3-methylbutyl 2-hydroxypropanoate	0.3 ± 0.2	a	0.2 ± 0.1	a	0.5 ± 0.5	a	1.1 ± 1.3	b	***
diethyl butanedioate	27.4 ± 16.0	a	20.9 ± 9.2	a	29.4 ± 12.2	a	39.1 ± 21.4	b	***
ethyl dec-9-enoate	6.3 ± 7.0		11.3 ± 9.9		10.2 ± 11.3		7.4 ± 8.4		ns
1.1.6-trimethyl-2H-naphthalene (TDN)	2.9 ± 2.5	b	1.5 ± 1.0	a	1.3 ± 0.9	a	1.7 ± 0.9	a	***
diethyl 2-hydroxybutanedioate	0.6 ± 0.3		0.6 ± 0.4		0.6 ± 0.5		0.5 ± 0.3		ns

continue

Alcohols	432.5 ± 174.5	ab	364.1 ± 178.8	a	468.9 ± 271.1	bc	543.6 ± 266.6	c	***
2-methylpropan-1-ol	11.2 ± 7.6	a	8.8 ± 7.2	a	14.8 ± 17.8	ab	18.4 ± 14.4	b	***
3-methylbutan-1-ol	355.0 ± 152.5	ab	309.9 ± 165.2	a	393.6 ± 232.7	bc	449.9 ± 235.4	c	***
hexan-1-ol	28.3 ± 12.4	b	18.1 ± 5.2	a	22.8 ± 10.6	ab	27.7 ± 9.7	b	***
octan-1-ol	1.4 ± 0.7	ab	1.2 ± 0.7	a	1.3 ± 0.7	ab	1.6 ± 0.9	b	*
2-phenylethanol	36.5 ± 14.1	b	26.2 ± 7.7	a	36.3 ± 19.9	b	46.0 ± 15.5	c	***
SCFA_MCFA	103.9 ± 37.6		109.3 ± 40.9		91.4 ± 43.4		92.3 ± 46.8		ns
2-methylpropanoic acid	1.0 ± 0.4	ab	0.8 ± 0.4	a	1.0 ± 0.6	b	1.3 ± 0.6	c	***
butanoic acid	0.9 ± 0.2		0.8 ± 0.3		0.9 ± 0.4		0.8 ± 0.3		ns
hexanoic acid	22.0 ± 7.2		21.8 ± 7.3		20.8 ± 9.2		18.4 ± 7.6		ns
octanoic acid	64.3 ± 24.1		66.7 ± 25.5		55.0 ± 26.2		55.5 ± 28.9		ns
decanoic acid	15.6 ± 8.8		19.1 ± 9.1		13.6 ± 8.8		16.4 ± 11.0		ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Description of wine evolution by sensory analysis

Sensory analysis is a key approach within the evaluation of the evolution of wines, since it gives the possibility to evaluate parameters that the final consumer will also evaluate.

The evolution of white wines can result in various changes, including visual changes that cause browning, olfactory and retro nasal changes, which are very difficult to be evaluated because they are linked to perception and identification thresholds. Olfactory and retro nasal variations can be related to the appearance of reductive notes, characterized by the formation of sulfur off-flavors, which have a low perception threshold, leading to a suppression of the aromatic composition, as well as to the appearance of oxidative notes related to the formation of aldehydes and moreover, the modification of the phenolic content can affect the gustatory perception of the wine, making it softer.

Sensory analysis was not conducted at the initial sampling point due to Covid-19 pandemic restrictions. This resulted in a critical loss of information from an experimental perspective, unable to examine overall sample trends over the course of the experiment.

Throughout the experiment, a gradual and significant decrease in perceived quality was observed from both the olfactory and retro-olfactory perspectives. No significant differences were found between the different sampling points regarding the presence of reduced olfactory notes. However, from the retro nasal point of view, this characteristic increased, particularly between the third and fourth sampling points, at ten and fourteen months after the start of the trial, respectively.

The sensory analysis evaluated the presence of oxidative notes. A decrease in this parameter was observed between the second and third sampling points, which occurred six and ten months after the start of the project, respectively. The decrease was more significant in the olfactory than in the retro-olfactory profile. There was a subsequent increase in the last sampling point Figure 14 and Figure 15. The values obtained for the characters of ‘oxidized’ and ‘reduced’ were significant; however, the differences between the samples remain minimal, analyzing the PCA. Therefore, the wines were not found to be significantly affected by these perceptions in terms of quality as perceived by the panel test.

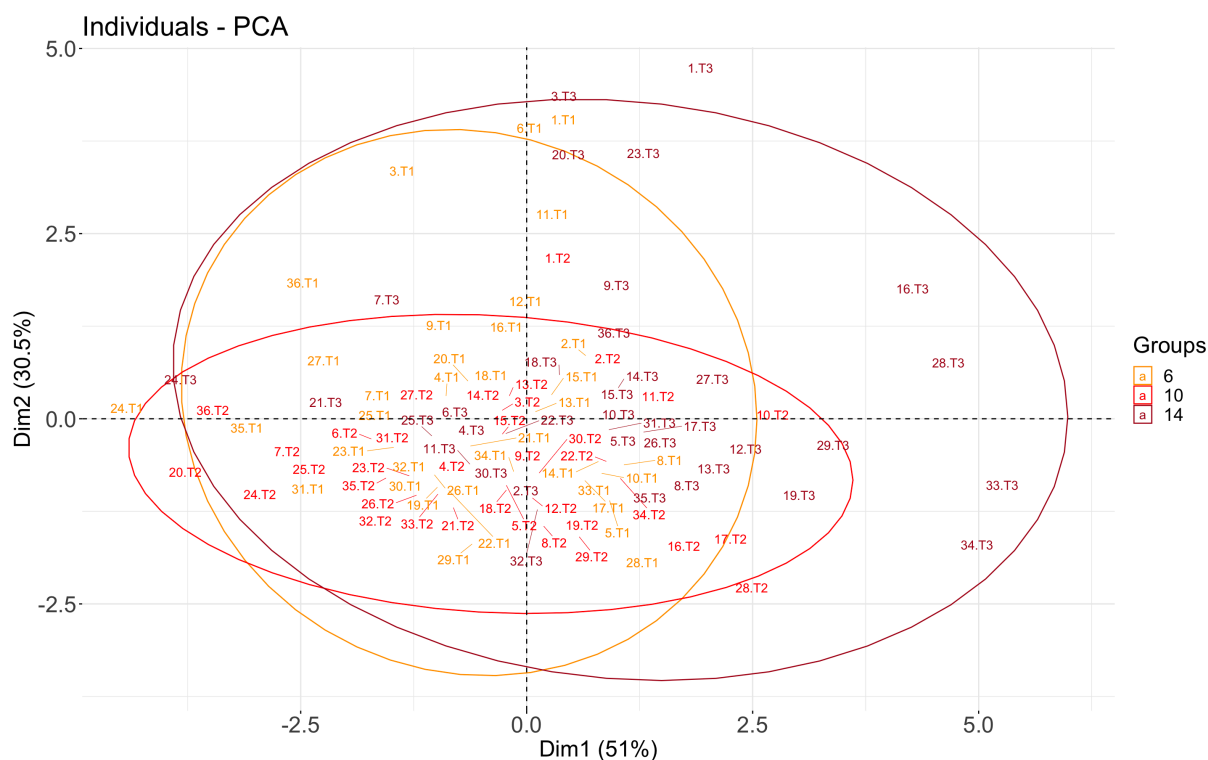


Figure 14 Score plot based on the sensory analysis. The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.

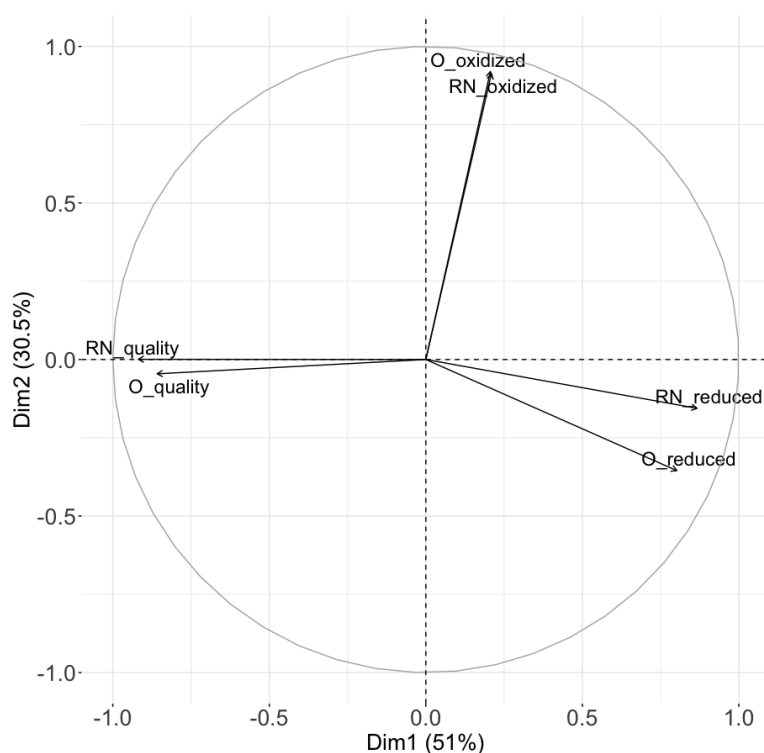


Figure 15 Loading plot of the sensory analysis. Abbreviation O_quality: Olfactory perceived quality; O_reduced: Olfactory reduced aroma; O_oxidized: Olfactory oxidized aroma; RN_quality: Retro nasal perceived quality; RN_reduced: Retro nasal reduced aroma; RN_oxidized: Retro nasal oxidized aroma.

Table 11 Effects of the evolution on the sensory analysis. Data are means and standard deviations of the sample set. Differences in the effect of time were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Variable	Time (months)						p-value
	6		10		14		
Olfactory perceived quality	4.50 ± 0.99	b	4.04 ± 1.09	ab	3.70 ± 0.97	a	**
Olfactory reduced aroma	1.64 ± 1.07		1.67 ± 0.91		1.70 ± 1.14		ns
Olfactory oxidized aroma	1.30 ± 0.95	b	0.70 ± 0.51	a	1.44 ± 0.85	b	***
Retro nasal perceived quality	4.28 ± 0.83	b	4.02 ± 0.97	ab	3.52 ± 1.07	a	**
Retro nasal reduced aroma	1.27 ± 0.79	a	1.50 ± 0.77	a	2.36 ± 1.64	b	***
Retro nasal oxidized aroma	0.89 ± 0.67	ab	0.59 ± 0.44	a	1.13 ± 0.88	b	***

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

Table 12 Effects of the evolution on the sensory analysis. Data are means and standard deviations of the sample set. Differences in the effect of closure typology were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Variable	Closure												p-value
	Technical		Screwcap		Natural		Alternative		Co-extruded		Syntetic		
Olfactory perceived quality	3.84 ± 0.88	a	4.56 ± 1.33	a	4.72 ± 1.22	a	4.08 ± 1	a	3.66 ± 1.17	a	4.93 ± 0.99	a	**
Olfactory reduced aroma	1.91 ± 0.96	a	1.7 ± 0.94	a	1.4 ± 1.14	a	2.58 ± 0.91	a	2.16 ± 1.38	a	0.91 ± 1.07	a	*
Olfactory oxidized aroma	1.28 ± 0.95		1.51 ± 0.9		1 ± 0.55		0.68 ± 0.61		0.61 ± 0.42		1.2 ± 0.65		ns
Retro nasal perceived quality	3.73 ± 0.73	ab	4.77 ± 1	bc	4.74 ± 1.29	c	3.85 ± 0.55	abc	3.21 ± 1.07	a	4.55 ± 1.23	bc	***
Retro nasal reduced aroma	1.81 ± 0.85	ab	1.25 ± 0.52	ab	1.03 ± 1.34	a	1.9 ± 1.3	ab	2.57 ± 2.21	b	1.26 ± 1.58	ab	**
Retro nasal oxidized aroma	1.04 ± 0.83	a	1.13 ± 0.45	a	0.55 ± 0.36	a	0.45 ± 0.27	a	0.48 ± 0.24	a	0.79 ± 0.63	a	**

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

Table 13 Effects of the evolution on the sensory analysis. Data are means and standard deviations of the sample set. Differences in the effect of variety were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Variable	Variety								p-value
	Sauvignon		Pinot gris		Chardonnay		Friulano		
Olfactory perceived quality	4.76 ± 1.03	b	3.94 ± 0.84	a	4.07 ± 0.94	ab	3.58 ± 1.14	a	**
Olfactory reduced aroma	1.03 ± 1.08	a	2.04 ± 1.14	b	1.92 ± 0.89	b	2.28 ± 0.78	b	***
Olfactory oxidized aroma	1.9 ± 0.59	b	0.98 ± 0.57	a	0.83 ± 0.59	a	0.93 ± 1.13	a	***
Retro nasal perceived quality	4.61 ± 0.89	b	3.93 ± 0.84	ab	3.7 ± 0.84	a	3.54 ± 1.17	a	**
Retro nasal reduced aroma	1.12 ± 1.05		1.78 ± 1.22		1.92 ± 1.2		2.01 ± 1.29		ns
Retro nasal oxidized aroma	1.46 ± 0.43	b	0.74 ± 0.73	a	0.72 ± 0.38	a	0.61 ± 0.94	a	***

ns: 'not significant'; $p < 0.05$: '**'; $p < 0.01$: '***'; $p < 0.001$: '****'

Performing the ANOVA analysis on the obtained data, it is possible to see that as a result of the evolution there was a reduction in the perceived quality, while from the olfactory point of view no differences were found for both reduced and oxidized aroma. In contrast, based on the retro nasal perception, these parameters showed a tendency to increase (Table 11).

Additionally, significant differences were observed among the different varieties. The study found that the Sauvignon variety had statistically higher values in terms of perceived qualities and the oxidized descriptors, both from the olfactory and retro nasal point of view, compared to the other varieties (Chardonnay, Pinot gris, and Friulano) (Table 13). However, Sauvignon obtained smaller values for the oxidized character, which were statistically different from the other varieties.

The study found that natural cork was perceived to have higher quality scores, while co-extruded synthetic closures were perceived to have lower scores for the same parameter (Table 12).

Perceived quality and reduction character are strictly related parameters. Reduction characters can often lead to a suppression of the wine aroma, which in turn reduces its olfactory and retro nasal perception, negatively impacting its sensory aspect. This is evident from the correlation matrix between the different parameters analyzed by the sensory analysis in Figure 16.

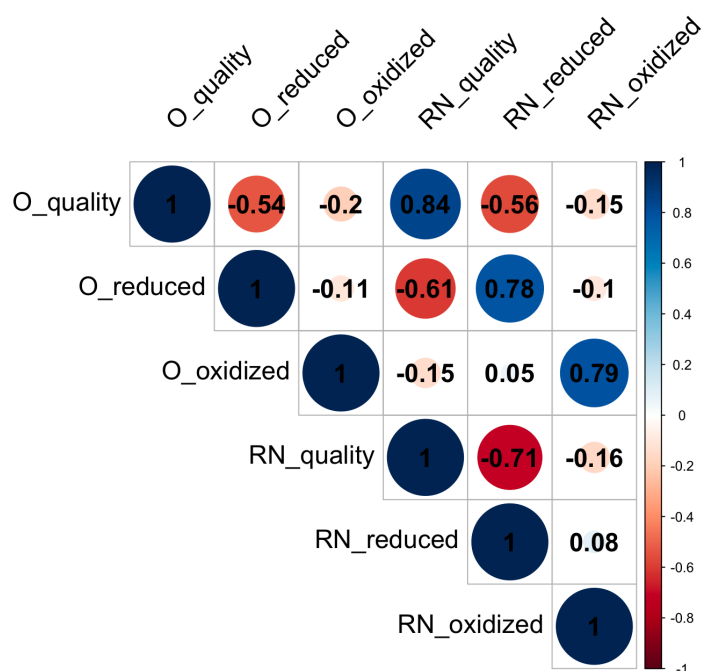


Figure 16 Correlation matrix based on sensory parameters analyzed. Abbreviation O_quality: Olfactory perceived quality; O_reduced: Olfactory reduced aroma; O_oxidized: Olfactory oxidized aroma; RN_quality: Retro nasal perceived quality; RN_reduced: Retro nasal reduced aroma; RN_oxidized: Retro nasal oxidized aroma.

Due to the Covid-19 pandemic and related restrictions, information linked to the first sampling point was lost, making it impossible to fully evaluate the potential of sensory analysis in this study.

The data collected suggests that sensory analysis is a complex parameter for evaluating ageing potential, especially for very stable wines, such as those analyzed, which showed minimal differences in the parameters evaluated from the second sampling point onwards.

Trained operators must also be recruited to carry out a panel test.

Carbonyl compound analysis to describe wine evolution

Carbonyl compounds are a group of compounds associated with evolution. They can be generated by three different pathways, as described by Ugliano (2013). Which may involve the Strecker degradation of amino acids and quinones or the oxidation of alcohols. This formation is characterized by different starting substrates, leading to a broad spectrum of molecules.

During our investigation, fifteen distinct carbonyl molecules were identified. Factor analysis was performed on the data obtained, and variables with a coefficient above 0.7 were used to generate the PCA, as shown in Figure 17 and Figure 18. Throughout the experiment, there was a general gradual increase in the absolute areas related to the different carbonyl compounds analyzed. However, at the last sampling point, which occurred fourteen months after the start of the experiment, there was a general tendency for a decrease in carbonyl compounds. The analyzed samples showed a differentiation that could be related to a variation in the glycolaldehyde content.

The concentration of aldehydes can be affected in relation to their reactivity by a wide spectrum of molecules. In particular, pyranoanthocyanin and catechin polymers can be generated directly or indirectly via aldehydes, resulting in a development of an orange color in red wines. However, this process can also occur in white wines (Rivas-Gonzalo et al., 1995).

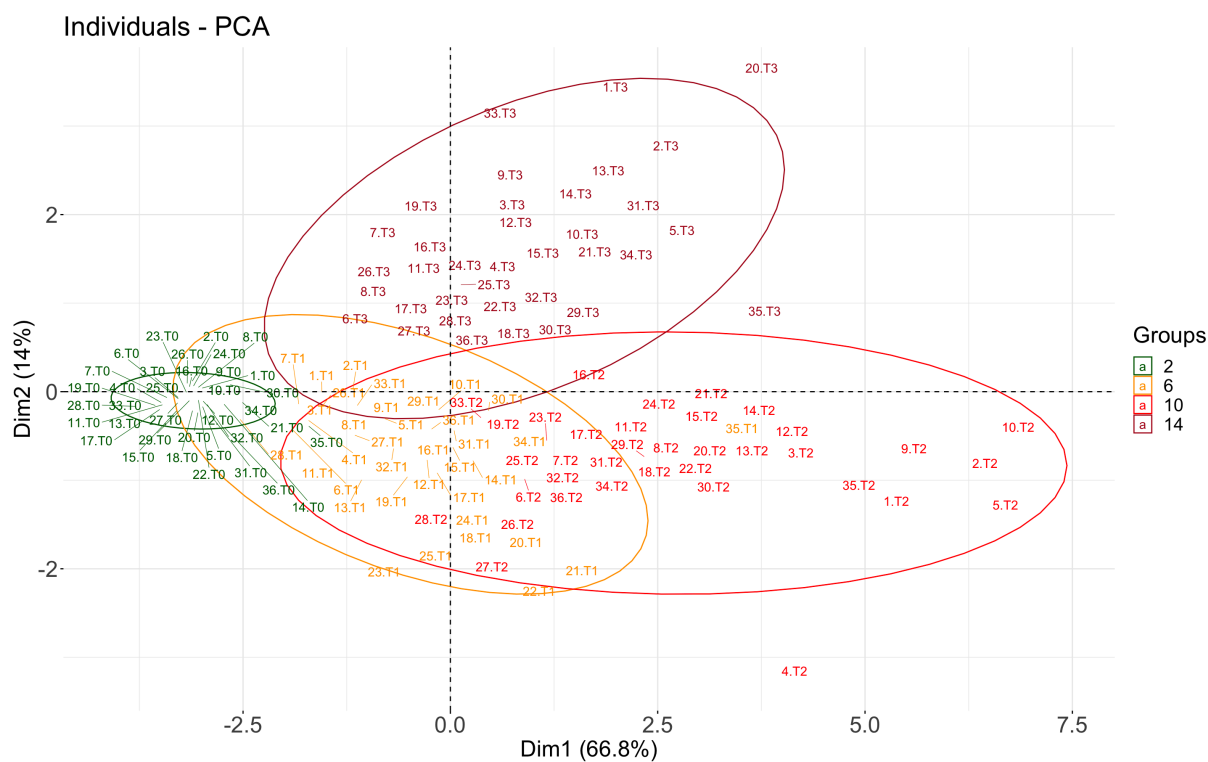


Figure 17 Score plot based on the absolute area of carbonyl compounds. The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.

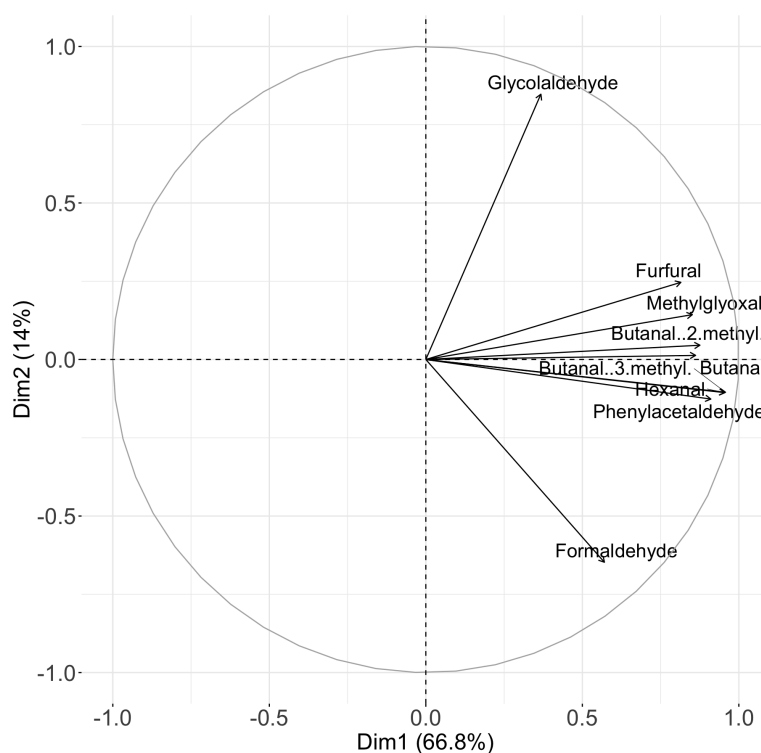


Figure 18 Loading plot of the absolute area of carbonyl compounds.

According to the bibliography, acetaldehyde is the most represented aldehyde; it has been noted that it can represent up to 90% of the total aldehydes in wine, being formed by the metabolism of microorganisms, but also during the evolution of the finished wine as a result of ethanol oxidation. Acetaldehyde was excluded from PCA due to being slightly below the imposed threshold. In addition, since it is present in larger quantities compared to the other carbonyl compounds, it was more appropriate to treat it separately. The experiment recorded an increase in acetaldehyde content mainly between two and six months, followed by stability between ten and fourteen months. Similarly to the PCA, the ANOVA analysis showed a tendency to increase the absolute areas, and consequently the percentage change, associated with carbonyl compounds (Table 14).

Table 14 Effects of the evolution on the absolute area of carbonyl compounds content. Data are the percentage variation related to absolute area of the sample set. Differences in the effect of time were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$. Also reported are p-values for differences between samples based on variety and closure.

Compound	Time (months)								Time	Variety	Closure
	2		6		10		14				
Formaldehyde	100	a	520	b	695	c	199	a	***	ns	ns
Acetaldehyde	100	a	153	b	182	c	177	c	***	***	**
Acetone	100	a	202	bc	231	c	173	b	***	***	ns
n-Butanal	100	a	278	b	448	c	355	bc	***	ns	***
2-Butanone	100	a	252	ab	416	b	303	ab	*	*	**
3-Pentanone	100	a	343	b	660	c	511	bc	***	ns	***
2-methylbutanal	100	a	299	b	509	d	412	c	***	ns	***
3-Methylbutanal	100	a	343	b	648	d	414	c	***	*	*
n-Hexanal	100	a	350	b	719	d	441	c	***	*	*
Glycolaldehyde	100	a	307	ab	445	b	2140	c	***	ns	*
2-Furaldehyde	100	a	134	a	594	b	499	b	***	ns	**
Benzaldehyde	100	a	220	ab	340	b	182	a	***	*	ns
Phenylacetaldehyde	100	a	472	b	1271	c	583	b	***	*	*
Methylglyoxal	100	a	302	b	407	c	386	c	***	ns	ns

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

No general and significant relationship was found between the concentration of carbonyl compounds and the varieties used in the production of the respective wines, but in particular for 3-methylbutanal and phenylacetaldehyde, the concentration seems to be higher for samples obtained from Pinot gris, followed by Sauvignon and Chardonnay, and finally samples obtained from Friulano.

The analysis of carbonyl compounds, as well as the analysis related to the volatile component, also appears to be difficult to perform due to the fact it requires specific instruments that could be problematic to manage in the winery, even if skilled personnel are required. Aldehydes related to Strecker reactions, in particular, tends to increase with wine evolution due to oxidative pathways. Therefore, this class of compounds could be used as a marker to understand the evolution state of a wine.

Description of wine evolution by cyclic voltammetry

Cyclic voltammetry (CV) is an electrochemical analytical technique that utilizes three electrodes: a reference electrode, a counter electrode, and a working electrode. In this project, screen-printed electrodes were used; the different electrodes are printed on a ceramic substrate. Despite wine is a complex matrix composed of various oxidizable substrates, making it difficult to identify the different molecules involved in the redox processes during analysis, CV can be useful in understanding the reductive-oxidative potential of wine.

In the present work, CV data elaboration was primarily focused on the variations of the anodic trace. The data obtained were used to calculate the integral of the anodic curve, dividing it into 100 mV intervals. Figure 19 and Figure 20 displays the results of principal components analysis (PCA) carried out after these calculations. The most significant variation was observed between the first (two months after the start of the experiment) and the subsequent sampling points.

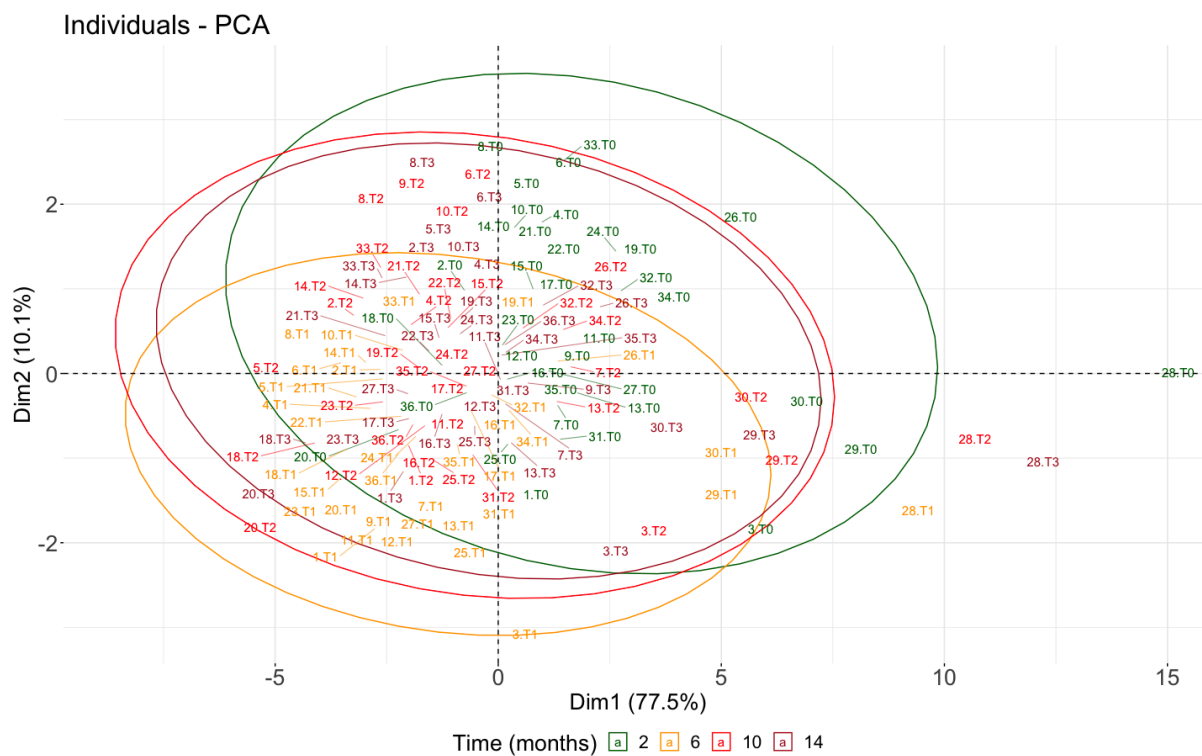


Figure 19 Score plot based on the cyclic voltammetry. The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.

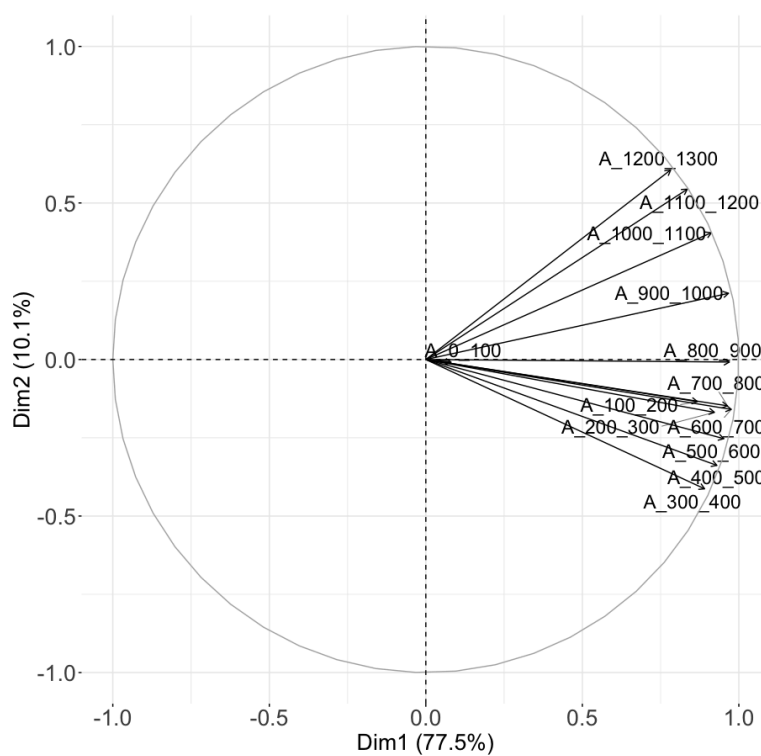


Figure 20 Loading plot based on the cyclic voltammetry, trough integral every 100 mV.

ANOVA carried out on the integral of the different portions of the anodic plot allowed to find out statistical differences among the wines from the different sampling points (Table 15). In particular, the most relevant changes were found for the anodic regions between 0 and 100 mV and from 800 mV to the end of the plot (1300 mV). Currently, there are no studies investigating the processes recorded in the terminal part of the anodic trace, this could be related to processes established as a result of the application of the potential, but it is necessary to investigate in order to better interpret the data obtained. In the opposite way the initial part of the anodic curve is crucial for evaluating the effectiveness of different antioxidants used in enology, in particular ascorbic acids as founds by Kilmartin et al. (2002). Additionally, the central part of the curve (from 300 to 600 mV) appears to be correlated with the phenolic composition of the wine, as found by Kilmartin et al. (2002). However, in this range, no significant differences were found between the different sampling points in the present study.

Table 15 Effects of the evolution on the cyclic voltammetry. Data are means and standard deviations of the sample set. Differences in the effect of time were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Integral range (mV)	Time (months)								p-value
	2		6		10		14		
Anodic trace	67177 ± 8505	b	56059 ± 8169	a	59930 ± 8502	a	60473 ± 7852	a	**
0 - 100	163 ± 28	b	149 ± 23	b	117 ± 29	a	151 ± 26	b	***
100 - 200	338 ± 93		296 ± 64		281 ± 96		316 ± 114		ns
200 - 300	967 ± 450		870 ± 422		855 ± 415		896 ± 388		ns
300 - 400	1539 ± 580		1356 ± 526		1313 ± 555		1317 ± 498		ns
400 - 500	1935 ± 633		1637 ± 549		1630 ± 599		1631 ± 548		ns
500 - 600	2467 ± 685		2092 ± 617		2070 ± 665		2077 ± 625		ns
600 - 700	3214 ± 680		2765 ± 639		2868 ± 666		2885 ± 601		ns
700 - 800	4169 ± 642		3554 ± 603		3665 ± 655		3679 ± 590		ns
800 - 900	5183 ± 644	b	4369 ± 611	a	4545 ± 672	a	4590 ± 606	a	**
900 - 1000	6697 ± 777	b	5583 ± 733	a	5910 ± 788	a	6012 ± 731	a	**
1000 - 1100	9075 ± 1012	c	7510 ± 950	a	8128 ± 997	ab	8265 ± 936	b	***
1100 - 1200	12887 ± 1420	c	10605 ± 1319	a	11697 ± 1375	b	11801 ± 1286	b	***
1200 - 1300	18537 ± 1898	c	15268 ± 1808	a	16844 ± 1836	b	16848 ± 1714	b	***

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

Table 16 Effects of the evolution on the cyclic voltammetry. Data are means and standard deviations of the sample set. Differences in the effect of closure typology were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Integral range (mV)	Closure											p-value	
	Technical		Screwcap		Natural		Alternative		Co-extruded		Syntetic		
Anodic trace	59898 ± 9992	a	59703 ± 5683	a	59144 ± 5506	a	75363 ± 4204	b	57707 ± 3545	a	62299 ± 5611	a	***
0 - 100	143 ± 34		134 ± 26		149 ± 29		152 ± 13		159 ± 26		143 ± 33		ns
100 - 200	294 ± 111	a	299 ± 31	a	293 ± 49	a	437 ± 47	b	325 ± 40	ab	316 ± 49	ab	**
200 - 300	806 ± 410	a	902 ± 166	a	841 ± 133	a	1839 ± 162	b	779 ± 186	a	934 ± 248	a	***
300 - 400	1279 ± 561	a	1463 ± 109	a	1355 ± 155	a	2538 ± 228	b	1222 ± 133	a	1275 ± 319	a	***
400 - 500	1617 ± 645	a	1789 ± 165	a	1661 ± 171	a	2842 ± 262	b	1569 ± 115	a	1573 ± 321	a	***
500 - 600	2104 ± 767	a	2256 ± 243	a	2109 ± 222	a	3228 ± 287	b	2012 ± 132	a	2034 ± 318	a	***
600 - 700	2851 ± 769	a	3006 ± 290	a	2854 ± 230	a	3954 ± 269	b	2792 ± 154	a	2868 ± 336	a	***
700 - 800	3680 ± 773	a	3849 ± 290	ab	3677 ± 305	a	4658 ± 277	b	3763 ± 170	ab	3733 ± 417	a	**
800 - 900	4583 ± 809	a	4665 ± 350	ab	4565 ± 389	a	5586 ± 315	b	4630 ± 225	a	4740 ± 458	a	**
900 - 1000	5961 ± 963	a	5884 ± 488	a	5881 ± 546	a	7221 ± 384	b	5805 ± 287	a	6273 ± 539	ab	***
1000 - 1100	8152 ± 1223	a	7918 ± 765	a	7996 ± 819	a	9751 ± 499	b	7758 ± 465	a	8638 ± 709	ab	***
1100 - 1200	11648 ± 1700	a	11256 ± 1223	a	11388 ± 1256	a	13705 ± 684	b	10995 ± 801	a	12313 ± 992	ab	***
1200 - 1300	16775 ± 2322	a	16275 ± 1800	a	16367 ± 1805	a	19446 ± 941	b	15891 ± 1190	a	17452 ± 1397	ab	***

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

Table 17 Effects of the evolution on the cyclic voltammetry. Data are means and standard deviations of the sample set. Differences in the effect of variety were identified by different letters within the same row, as determined by ANOVA and Tukey HSD test at a significance level of $p < 0.05$.

Integral range (mV)	Variety								p-value
	Sauvignon		Pinot gris		Chardonnay		Friulano		
Anodic trace	59524 ± 6109	ab	59001 ± 5425	a	65037 ± 13589	b	60622 ± 8918	ab	*
0 - 100	155 ± 33	b	143 ± 31	ab	133 ± 24	a	149 ± 33	ab	*
100 - 200	312 ± 48		278 ± 61		335 ± 151		315 ± 87		ns
200 - 300	813 ± 234	a	770 ± 193	a	1110 ± 617	b	932 ± 452	ab	**
300 - 400	1380 ± 437		1251 ± 323		1615 ± 728		1316 ± 595		ns
400 - 500	1699 ± 422	ab	1565 ± 334	a	1983 ± 857	b	1628 ± 607	ab	*
500 - 600	2158 ± 405	ab	2002 ± 333	a	2506 ± 1050	b	2091 ± 601	ab	*
600 - 700	2937 ± 430	ab	2744 ± 340	a	3249 ± 1041	b	2856 ± 592	ab	*
700 - 800	3862 ± 539	ab	3606 ± 394	a	4031 ± 979	b	3614 ± 572	ab	*
800 - 900	4744 ± 569		4512 ± 435		4926 ± 1034		4550 ± 619		ns
900 - 1000	6010 ± 624		5847 ± 538		6365 ± 1278		6037 ± 800		ns
1000 - 1100	8041 ± 851	ab	8014 ± 786	a	8681 ± 1581	b	8308 ± 1059	ab	*
1100 - 1200	11292 ± 1350	a	11535 ± 1200	ab	12370 ± 2056	b	11853 ± 1463	ab	*
1200 - 1300	16117 ± 1989	a	16727 ± 1703	ab	17727 ± 2626	b	16967 ± 2024	ab	**

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

Significant differences were also observed in the area subtended by the anodic trace depending on the wine typology. Indeed, Chardonnay had the widest area, followed by Sauvignon, Friulano, and finally Pinot gris (Table 17).

Significant differences were finally found among the different closures, with a tendency for higher integral values for samples with alternative closures (ArdeaSeal®) over the entire anodic trace, in particular those made of plastic material and an internal core (Table 16).

Cyclic voltammetry is easier to perform compared to volatile and carbonyl analysis. It requires specific instrumentation as well, but it is easier to manage, to perform, and less expensive. Technological development has significantly improved the potential of this analysis, leading to the development of portable devices and also the development of disposable screen-printed electrodes that do not require cleaning, which may be difficult and affect the result. The data obtained through cyclic voltammetry can be complex to interpret, but the aim of this study and future work is to develop statistical models to make it easier to understand the data obtained and, at the same time, to supply parameters that may be easier for the operator to interpret.

Despite the fact that the temporal differences obtained in the present study are not highly significant, the potential of this analysis could be considerable, and this is the reason why many research groups, even those not related to the wine sector, are focusing their attention on cyclic voltammetry.

Investigation of correlations between sulfur dioxide content and color with other parameters analyzed

As previously mentioned, the basic parameters to evaluate the evolutionary potential of a wine are mainly related to the sulfur dioxide content, particularly the free fraction, which provides protection against both microbiological and oxidative faults. In addition, the absorbance at 420 nm is another key parameter for the evaluation of the evolution state, in particular concerning browning. Both of these parameters are influenced by the enological practices and the chemical composition of the wines, but they are crucial for the evaluation of the potential of evolution from a technical and enological point of view. To assess the effectiveness of these parameters, sulfur dioxide content and color, traditionally used to analyze the evolution of white wines, the correlations and their significance with the different parameters analyzed were determined, in order to assess whether they can indirectly provide insight into evolution-related effects. This could provide further support for the evaluation of the evolutionary potential.

Investigation of correlations between sulfur dioxide content and color with chemical parameters analyzed

In this part of the project, they have been used to evaluate the correlations with the other chemical parameters measured during the experiment. Results are reported in Table 18.

The correlation between wine color (Abs 420 nm) and various parameters such as the content of flavanols, which directly influence the absorbance measured, appears to be in line with the expected results, and since this class of compounds is also evaluated by the total polyphenols index (TPI), there is a positive correlation also between TPI and Abs 420 nm.

Additionally, high color values should potentially be the result of evolution processes that have already taken place, leading to an increase in browning; resulting wine should be more stable towards oxidation and, therefore, the POM test value should be lower.

Table 18 Correlation index and significance between the typical parameters used to establish the protection to evolution and other chemical parameters analyzed.

	Free SO ₂		Combined SO ₂		Total SO ₂		Abs 420 nm	
Total thiols	0.36	ns	0.67	*	0.9	***	0.27	ns
Flavanols	-0.65	*	0.57	ns	0.36	ns	0.88	***
POM test	0.61	*	-0.66	*	-0.43	ns	-0.9	***
L*	0.69	*	-0.61	*	-0.37	ns	-1	***
a*	0.68	*	-0.65	*	-0.4	ns	-0.95	***
b*	-0.68	*	0.62	*	0.38	ns	0.99	***
TPI	-0.59	ns	0.66	*	0.45	ns	0.96	***

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Investigation of correlations between sulfur dioxide content and color with volatile composition

Correlations were evaluated also with the volatile compounds analyzed during the experiment, as shown in Table 19.

The data showed a reduction in the concentration of free sulfur dioxide, which is an important factor in the preservation of the volatile fraction of the wine; in particular, the correlation with the amount of acetic acid esters and higher alcohols was significant. In contrast, the group called evolution markers and free sulfur dioxide amount shows a negative correlation.

There is a negative correlation also between total and combined SO₂ and the content of ethyl esters, acetic esters and fatty acids.

Finally, wine color tends to increase over time due to oxidative processes. It appears to be negatively correlated with most of the volatile compounds, excluding aging markers. However, there are significant correlations with ethyl esters, acetic esters and fatty acids. As a result, the overall concentration of the volatile compounds is suppressed during evolution.

Table 19 Correlation index and significance between the typical parameters used to establish the protection to evolution and the groups of volatile compounds analyzed

	Free SO ₂		Combined SO ₂		Total SO ₂		Abs 420 nm	
Ethyl esters	0.28	ns	-0.81	**	-0.7	*	-0.78	*
Acetic esters	0.89	***	-0.65	*	-0.02	ns	-0.87	**
Other esters	-0.21	ns	-0.46	ns	-0.76	*	-0.35	ns
Aging markers	-0.73	*	0.13	ns	-0.54	ns	0.49	ns
Alcohols	0.66	*	-0.35	ns	0.04	ns	-0.36	ns
SCFA MCFA	0.27	ns	-0.82	**	-0.71	*	-0.8	*

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Investigation of correlations between sulfur dioxide content and color with carbonyl compounds

Evolution does not only reduce the volatile fraction, but it also leads to the formation of carbonyl compounds generated both by oxidative pathways and Maillard reaction (Culleré, et al., 2007).

The concentration of free sulfur dioxide is crucial for the limitation and reduction of these products.

The study found a strong negative correlation between the content of sulfur dioxide, which decreases over time, and the content of carbonyl compounds, which increases.

Although there is no significant correlation related to combined sulfur dioxide content and absorbance at 420 nm, significant negative correlations appear to be present with total sulfur dioxide content (Table 20).

It is important to note that the carbonyl compounds principally affect the aromatic fraction, so this parameter does not appear to be correlated. Further studies and approaches could lead to correlations, providing an additional tool for analysis.

Table 20 Correlation index and significance between the typical parameters used to establish the protection to evolution and the carbonyl compounds.

	Free SO ₂		Combined SO ₂		Total SO ₂		Abs 420 nm	
Formaldehyde	-0.67	**	0.06	ns	-0.28	ns	-0.35	ns
Acetaldehyde	-0.96	***	0.04	ns	-0.41	ns	0.09	ns
Acetone	-0.74	***	-0.27	ns	-0.63	**	-0.34	ns
Butanal	-0.82	***	-0.23	ns	-0.65	**	-0.16	ns
Propionaldehyde	-0.59	*	-0.11	ns	-0.37	ns	-0.23	ns
Butanone	-0.69	**	-0.36	ns	-0.62	**	-0.04	ns
Pentanone	-0.84	***	-0.07	ns	-0.45	ns	0.07	ns
2-Methylbutanal	-0.83	***	-0.2	ns	-0.63	**	-0.08	ns
3-Methylbutanal	-0.9	***	0.05	ns	-0.36	ns	-0.05	ns
Hexanal	-0.9	***	0.05	ns	-0.36	ns	-0.07	ns
Glycolaldehyde	-0.73	***	-0.07	ns	-0.54	*	0.4	ns
Furfural	-0.81	***	-0.18	ns	-0.56	*	0.09	ns
Benzaldehyde	-0.58	*	-0.03	ns	-0.35	ns	-0.2	ns
Phenylacetaldehyde	-0.76	***	-0.06	ns	-0.43	ns	-0.16	ns
Methylglyoxal	-0.95	***	0.02	ns	-0.49	*	0.06	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Investigation of correlations between sulfur dioxide content and color with parameters related to sensory analysis

Finally, regarding the aromatic component, a sensory analysis was carried out and the data were correlated with the evolution markers commonly used in oenology, i.e. sulfur dioxide content and wine color.

In particular, the correlation between the sensory parameters analyzed and the free sulfur dioxide content was found to be significant (Table 21). A negative correlation was observed between free sulfur dioxide and reduced aroma. However, this does not appear to be directly linked to the effect of sulfur dioxide on the compounds responsible for the reduction (which should be more noticeable at higher SO₂ levels); instead, this effect could plausibly be linked to the suppression of the fermentative aromatic fraction that occurred with the evolution and the disappearance of the free fraction of the sulfur dioxide.

Furthermore, a significant negative correlation exists between the sulfur dioxide content and the retro-nasal perception of oxidation, which could be related to the presence and the increased content of carbonyl compounds linked to the reduction of SO₂.

Lastly, the evolution process affects the perceived quality; the latter it is negatively and significantly correlated with color, as assessed by absorbance at 420 nm. This parameter also appears to be positively correlated with reduced character.

Table 21 Correlation index and significance between the typical parameters used to establish the protection to evolution and the parameters analyzed by sensory analysis.

	Free SO ₂		Combined SO ₂		Total SO ₂		Abs 420 nm	
Olfactory perceived quality	0.6	ns	-0.18	ns	0.04	ns	-0.77	*
Olfactory reduced aroma	-0.68	*	0.6	ns	0.37	ns	0.93	***
Olfactory oxidized aroma	-0.01	ns	-0.47	ns	-0.37	ns	0.14	ns
Retro nasal perceived quality	0.72	*	-0.23	ns	0	ns	-0.89	***
Retro nasal reduced aroma	-0.67	*	0.62	ns	0.39	ns	0.94	***
Retro nasal oxidized aroma	-0.27	ns	-0.62	ns	-0.63	*	0.25	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Investigation of correlations between sulfur dioxide content and color with cyclic voltammetry

As previously mentioned, the last analysis we considered is cyclic voltammetry and the study focused on the anodic curve (Table 22).

Positive correlations were found between the integral of the anodic curve and the sulfur dioxide content. Significance increased when considering bound and total SO₂.

Positive correlations were also found between the integrals of the different regions of the anodic curve and the absorbance at 420 nm, in particular for the middle part, between 100 and 900 mV. This could be related to the phenolic content, since, as seen above, positive correlations were found between color, TPI and flavanols.

Table 22 Correlation index and significance between the typical parameters used to establish the protection to evolution and the parameters analyzed by cyclic voltammetry.

	Free SO ₂		Combined SO ₂		Total SO ₂		Abs 420 nm	
CV_A	0.43	*	0.54	*	0.65	***	0.46	*
A_0_100	0.43	*	-0.5	*	-0.33	ns	-0.43	*
A_100_200	0.06	ns	0.62	***	0.5	*	0.72	***
A_200_300	0.01	ns	0.72	***	0.52	*	0.75	***
A_300_400	-0.07	ns	0.66	***	0.45	*	0.84	***
A_400_500	-0.03	ns	0.69	***	0.5	*	0.83	***
A_500_600	0.02	ns	0.72	***	0.56	**	0.81	***
A_600_700	0.1	ns	0.72	***	0.6	**	0.76	***
A_700_800	0.18	ns	0.67	***	0.62	***	0.73	***
A_800_900	0.32	ns	0.62	***	0.65	***	0.63	***
A_900_1000	0.46	*	0.54	*	0.66	***	0.47	*
A_1000_1100	0.43	*	0.49	*	0.6	**	0.43	*
A_1100_1200	0.48	*	0.47	*	0.6	**	0.37	ns
A_1200_1300	0.5	*	0.47	*	0.6	**	0.34	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Investigation of correlations between cyclic voltammetry and other parameters analyzed

As discussed sulfur dioxide and absorbance at 420 nm are useful indicators to assess the evolution potential of white wine. The analysis of color, in particular, is very simple and fast, but it requires a spectrophotometer, an instrument that is easy to use, but many wineries, especially the small ones, do not own it as analytical instrument, due to space and cost reasons.

One of the goals of this study is to evaluate potential alternative markers for the evaluation of wine components and to estimate wine evolutionary potential, with low-cost instruments and also with instruments that could be portable while maintaining ease of use. Cyclic voltammetry is an analysis that has recently found application in the enological field and potentially has suitable characteristics for this goal.

In order to study the potential of voltammetry based on the data obtained, the correlations existing between the anodic trace related to cyclic voltammetry and the different parameters analyzed were evaluated.

Investigation of correlations between cyclic voltammetry and chemical parameters analyzed

As previously described, CV, specifically the integral of the anodic plot, shows a significant positive correlation with sulfur dioxide content (Table 23). In the analysis, the concentration of total sulfur dioxide is significantly correlated with the final part of the anodic curve, but when the sulfur dioxide fractions are analyzed separately, the fraction of free sulfur dioxide is significantly correlated with the extremes of the curve (0-100 and 900-1300 mV), while the fraction of combined sulfur dioxide shows a significant correlation throughout the entire anodic trace, with the most significant correlation occurring in the middle part of the curve, between 100 and 900 mV.

Table 23 Correlation index and significance between parameters obtained by cyclic voltammetry and the chemical parameters analyzed.

	CV_A	A_0_100	A_100_200	A_200_300	A_300_400	A_400_500	A_500_600	A_600_700	A_700_800	A_800_900	A_900_1000	A_1000_1100	A_1100_1200	A_1200_1300
Total thiols	0.41 *	-0.04 ns	0.45 *	0.52 *	0.51 *	0.53 *	0.53 *	0.53 *	0.55 **	0.56 **	0.46 *	0.37 ns	0.39 ns	0.4 *
Flavanols	0.31 ns	-0.48 *	0.61 **	0.59 **	0.75 ***	0.73 ***	0.72 ***	0.68 ***	0.66 ***	0.56 **	0.34 ns	0.26 ns	0.21 ns	0.16 ns
Free SO ₂	0.43 *	0.43 *	0.06 ns	0.01 ns	-0.07 ns	-0.03 ns	0.02 ns	0.1 ns	0.18 ns	0.32 ns	0.46 *	0.43 *	0.48 *	0.5 *
Combined SO ₂	0.54 *	-0.5 *	0.62 ***	0.72 ***	0.66 ***	0.69 ***	0.72 ***	0.72 ***	0.67 ***	0.62 ***	0.54 *	0.49 *	0.47 *	0.47 *
Total SO ₂	0.65 ***	-0.33 ns	0.5 *	0.52 *	0.45 *	0.5 *	0.56 **	0.6 **	0.62 ***	0.65 ***	0.66 ***	0.6 **	0.6 **	0.6 **
POM test	-0.33 ns	0.47 *	-0.59 **	-0.68 ***	-0.74 ***	-0.72 ***	-0.68 ***	-0.63 ***	-0.58 **	-0.48 *	-0.33 ns	-0.3 ns	-0.25 ns	-0.23 ns
L	-0.47 *	0.42 *	-0.71 ***	-0.76 ***	-0.85 ***	-0.84 ***	-0.8 ***	-0.75 ***	-0.71 ***	-0.63 ***	-0.48 *	-0.44 *	-0.39 ns	-0.36 ns
a	-0.47 *	0.35 ns	-0.73 ***	-0.77 ***	-0.83 ***	-0.81 ***	-0.77 ***	-0.72 ***	-0.69 ***	-0.61 **	-0.48 *	-0.45 *	-0.4 *	-0.37 ns
b	0.46 *	-0.44 *	0.71 ***	0.74 ***	0.85 ***	0.83 ***	0.81 ***	0.77 ***	0.73 ***	0.64 ***	0.47 *	0.42 *	0.36 ns	0.33 ns
IPT	0.53 *	-0.31 ns	0.81 ***	0.86 ***	0.96 ***	0.95 ***	0.93 ***	0.89 ***	0.86 ***	0.76 ***	0.56 **	0.49 *	0.44 *	0.41 *
Abs 420 nm	0.46 *	-0.43 *	0.72 ***	0.75 ***	0.84 ***	0.83 ***	0.81 ***	0.76 ***	0.73 ***	0.63 ***	0.47 *	0.43 *	0.37 ns	0.34 ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Investigation of correlations between cyclic voltammetry and volatile composition

The experiment found also significant correlations between cyclic voltammetry and volatile composition (Table 24). However, due to the fluctuations in concentration of the different classes, as described above, voltammetry does not show a good correlation with this parameter, except for aging markers.

Many of the analyzed aromatic compounds are related to the variety or the production process.

Further evaluations are necessary to better interpret and analyze the correlations between the different classes of compounds and the integral related to the anodic trace of the cyclic voltammetry.

Table 24 Correlation index and significativity between parameters obtained by cyclic voltammetry and the groups of volatile compounds analyzed.

	CV_A		A_0_100		A_100_200		A_200_300		A_300_400		A_400_500		A_500_600		A_600_700		A_700_800		A_800_900		A_900_1000		A_1000_1100		A_1100_1200		A_1200_1300	
Ethyl esters	-0.91	***	0.73	***	-0.59	*	-0.56	*	-0.49	*	-0.5	*	-0.53	*	-0.55	*	-0.57	*	-0.64	**	-0.87	***	-0.96	***	-0.97	***	-0.98	***
Acetic esters	-0.4	ns	0.77	***	-0.52	*	-0.72	***	-0.68	**	-0.67	**	-0.63	**	-0.6	**	-0.51	*	-0.45	*	-0.37	ns	-0.41	ns	-0.41	ns	-0.41	ns
Other esters	-0.93	***	0.66	**	-0.56	*	-0.47	*	-0.45	*	-0.46	*	-0.51	*	-0.54	*	-0.59	*	-0.68	**	-0.9	***	-0.97	***	-0.98	***	-0.98	***
Aging markers	-0.54	*	0.24	ns	-0.11	ns	0.02	ns	0.08	ns	0.05	ns	0.01	ns	-0.01	ns	-0.07	ns	-0.17	ns	-0.48	*	-0.6	*	-0.62	**	-0.63	**
Alcohols	0.18	ns	0.01	ns	0.4	ns	0.33	ns	0.39	ns	0.41	ns	0.45	*	0.45	*	0.48	*	0.46	*	0.24	ns	0.06	ns	0.01	ns	0	ns
SCFA_MCFA	-0.83	***	0.84	***	-0.71	***	-0.79	***	-0.7	***	-0.72	***	-0.74	***	-0.76	***	-0.71	***	-0.72	***	-0.8	***	-0.84	***	-0.82	***	-0.82	***

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Investigation of correlations between cyclic voltammetry and carbonyl compounds

There is a strong negative correlation between the integral of the anodic trace and carbonyl compounds analyzed (Table 25). As expected, due to evolution, a reduction in the anodic plot related to voltammetry and simultaneous increase in the content of carbonyl compounds was observed.

Table 25 Correlation index and significativity between parameters obtained by cyclic voltammetry and carbonyl compounds analyzed.

	CV_A	A_0_100	A_100_200	A_200_300	A_300_400	A_400_500	A_500_600	A_600_700	A_700_800	A_800_900	A_900_1000	A_1000_1100	A_1100_1200	A_1200_1300
Formaldehyde	-0.88 ***	-0.85 ***	-0.73 ***	-0.66 ***	-0.67 ***	-0.7 ***	-0.72 ***	-0.75 ***	-0.8 ***	-0.84 ***	-0.9 ***	-0.89 ***	-0.89 ***	-0.89 ***
Acetaldehyde	-0.81 ***	-0.9 ***	-0.77 ***	-0.64 ***	-0.68 ***	-0.71 ***	-0.74 ***	-0.75 ***	-0.81 ***	-0.85 ***	-0.85 ***	-0.8 ***	-0.77 ***	-0.77 ***
Acetone	-0.93 ***	-0.79 ***	-0.78 ***	-0.73 ***	-0.73 ***	-0.77 ***	-0.81 ***	-0.83 ***	-0.86 ***	-0.91 ***	-0.95 ***	-0.94 ***	-0.92 ***	-0.91 ***
Butanal	-0.9 ***	-0.8 ***	-0.77 ***	-0.7 ***	-0.74 ***	-0.78 ***	-0.83 ***	-0.84 ***	-0.89 ***	-0.92 ***	-0.93 ***	-0.89 ***	-0.86 ***	-0.85 ***
Propionaldehyde	-0.7 ***	-0.91 ***	-0.8 ***	-0.67 ***	-0.67 ***	-0.7 ***	-0.73 ***	-0.74 ***	-0.77 ***	-0.79 ***	-0.74 ***	-0.69 ***	-0.67 ***	-0.66 ***
Butanone	-0.78 ***	-0.83 ***	-0.91 ***	-0.77 ***	-0.76 ***	-0.79 ***	-0.82 ***	-0.81 ***	-0.83 ***	-0.85 ***	-0.81 ***	-0.76 ***	-0.73 ***	-0.72 ***
Pentanone	-0.78 ***	-0.89 ***	-0.75 ***	-0.59 ***	-0.62 ***	-0.65 ***	-0.7 ***	-0.71 ***	-0.77 ***	-0.8 ***	-0.81 ***	-0.77 ***	-0.75 ***	-0.74 ***
2-methylbutanal	-0.89 ***	-0.8 ***	-0.74 ***	-0.64 ***	-0.67 ***	-0.72 ***	-0.77 ***	-0.77 ***	-0.82 ***	-0.87 ***	-0.91 ***	-0.89 ***	-0.87 ***	-0.86 ***
3-methylbutanal	-0.81 ***	-0.92 ***	-0.77 ***	-0.64 ***	-0.67 ***	-0.71 ***	-0.74 ***	-0.75 ***	-0.81 ***	-0.85 ***	-0.85 ***	-0.81 ***	-0.78 ***	-0.78 ***
Hexanal	-0.81 ***	-0.92 ***	-0.78 ***	-0.64 ***	-0.67 ***	-0.71 ***	-0.74 ***	-0.75 ***	-0.81 ***	-0.85 ***	-0.85 ***	-0.81 ***	-0.78 ***	-0.78 ***
Glycolaldehyde	-0.69 ***	-0.6 ***	-0.67 ***	-0.65 ***	-0.75 ***	-0.77 ***	-0.79 ***	-0.77 ***	-0.8 ***	-0.8 ***	-0.72 ***	-0.65 ***	-0.61 ***	-0.62 ***
Furfural	-0.7 ***	-0.89 ***	-0.82 ***	-0.69 ***	-0.73 ***	-0.76 ***	-0.79 ***	-0.78 ***	-0.81 ***	-0.82 ***	-0.75 ***	-0.69 ***	-0.66 ***	-0.65 ***
Benzaldehyde	-0.85 ***	-0.81 ***	-0.71 ***	-0.71 ***	-0.75 ***	-0.75 ***	-0.74 ***	-0.76 ***	-0.78 ***	-0.81 ***	-0.86 ***	-0.85 ***	-0.84 ***	-0.86 ***
Phenylacetaldehyde	-0.8 ***	-0.92 ***	-0.78 ***	-0.66 ***	-0.69 ***	-0.72 ***	-0.74 ***	-0.76 ***	-0.8 ***	-0.84 ***	-0.83 ***	-0.79 ***	-0.76 ***	-0.76 ***
Methylglyoxal	-0.81 ***	-0.84 ***	-0.75 ***	-0.67 ***	-0.74 ***	-0.78 ***	-0.81 ***	-0.82 ***	-0.88 ***	-0.89 ***	-0.85 ***	-0.78 ***	-0.75 ***	-0.76 ***

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Investigation of correlations between cyclic voltammetry and parameters related to sensory analysis

Finally, the evaluation of the existing a weak correlation between the anodic trace of cyclic voltammetry and the sensory data (Table 26). The results showed significant positive correlations, particularly in the range of 0-100 and 900-1300 mV, between the integral of the anodic trace and the presence of the reductive character, both from the olfactory and retro-olfactory point of view, although they often turn out to have low significance. The presence of this character may be more pronounced in young wines, which are more protected by the antioxidant added. However, the perception of reduction is related to the general reduction of the volatile component, further investigations will be carried out to better understand the relationship between the two variables.

Finally, there is a significant negative correlation between the anodic trace and the oxidation character perceived by sensory analysis.

Table 26 Correlation index and significativity between parameters obtained by cyclic voltammetry and the parameters analyzed by sensory analysis.

	CV_A		A_0_100		A_100_200		A_200_300		A_300_400		A_400_500		A_500_600		A_600_700		A_700_800		A_800_900		A_900_1000		A_1000_1100		A_1100_1200		A_1200_1300	
Olfactory perceived quality	-0.2	ns	0.56	*	0.11	ns	0.26	ns	0.23	ns	0.23	ns	0.18	ns	0.17	ns	0.1	ns	0.03	ns	-0.16	ns	-0.28	ns	-0.25	ns	-0.24	ns
Olfactory reduced aroma	0.61	**	-0.91	***	0.26	ns	0.29	ns	0.24	ns	0.24	ns	0.27	ns	0.28	ns	0.27	ns	0.33	ns	0.56	*	0.66	**	0.66	**	0.65	**
Olfactory oxidized aroma	-0.58	*	0.67	**	-0.05	ns	-0.21	ns	-0.08	ns	-0.08	ns	-0.08	ns	-0.11	ns	-0.04	ns	-0.13	ns	-0.49	*	-0.64	**	-0.7	***	-0.72	***
Retro nasal perceived quality	-0.44	ns	0.73	***	-0.06	ns	0.08	ns	0.08	ns	0.08	ns	0.04	ns	0	ns	-0.05	ns	-0.15	ns	-0.4	ns	-0.51	*	-0.49	*	-0.47	*
Retro nasal reduced aroma	0.63	**	-0.83	***	0.3	ns	0.22	ns	0.19	ns	0.2	ns	0.23	ns	0.26	ns	0.29	ns	0.37	ns	0.59	*	0.67	**	0.66	**	0.64	**
Retro nasal oxidized aroma	-0.62	**	0.69	***	-0.09	ns	-0.26	ns	-0.12	ns	-0.12	ns	-0.11	ns	-0.13	ns	-0.07	ns	-0.16	ns	-0.52	*	-0.67	**	-0.73	***	-0.75	***

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Application of partial least squares (PLS) to forecast oenological parameters

Cyclic voltammetry is mainly applied for the evaluation of the phenolic content and the antioxidant properties of wine (Kilmartin et al., 2002), but as highlighted in the present work, the data obtained in the course of the experiment also show significant correlations with the presence of carbonyl compounds, generally produced from oxidative processes, as well as with the volatile fraction. Considering such correlations between CV and the other analytical parameters analyzed, implementing the present study could lead to the development of a predictive system for evaluating individual parameters and the evolutionary potential of the analyzed wine.

In this specific part of the PhD project, Partial Least Square (PLS) analysis was performed to suggest a possible predictive model, based on the use of CV, full, and anodic traces to forecast other analytical parameters. The potential advantage is linked to the availability of a fast and relatively cheap analytical tool able to deliver results without the need of sample preparation procedures and trained personnel.

The same approach was also carried out on the UV and visible spectra, to evaluate the potential predictive capacity of such analytical outputs. These analyses are also easy to perform, but in the case of the UV spectrum, it is necessary to perform a 1:10 dilution of the sample in the case of white wines. PLS was performed both processing original data (as acquired, without any data pretreatment) and after pretreatment by the first derivative.

This analytical technique was used in cross-validation to evaluate the practicability of one of the aims of the PhD project.

Application of partial least squares (PLS) to forecast chemical parameters analyzed

In particular,

Table 27 shows the results for the PLS in relation to the chemical parameter analyzed.

For total thiol compounds, good results were obtained by using CV data, especially pre-processing data by first derivative, which allowed to obtain lower intercept values and, at the same time, a greater R^2 , Figure 21.

However, the model depicted in Figure 21 exhibits a high degree of sample scatter when plotted based on the measured and predicted values. This phenomenon can be mitigated through the application of additional analytical techniques and the development of two different models based on the concentration of total thiol compounds. These approaches could enhance the overall prediction of their content.

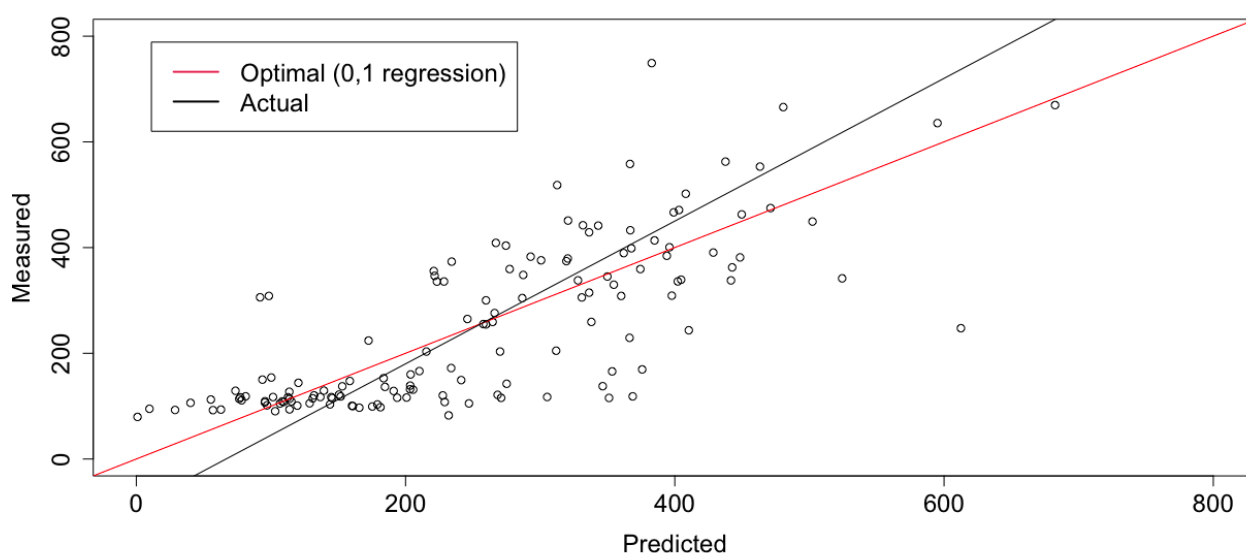


Figure 21 Plot of measured versus predicted values for total thiol compounds by applying PLS to cyclic voltammetry data pre-processed by first derivative. Intercept: -81.99; R^2 : 0.68; RMSE: 102.46.

In terms of phenolic content, particularly flavanols and TPI, both parameters showed very good results, with low intercept and high R^2 values using cyclic voltammetry, especially in both cases the best result was obtained using the data related to the whole plot, combined with the pre-treatment of the data by the application of the first derivative, Figure 22. In these cases, good values were also obtained for the UV (Figure 23) and visible spectra, especially for the TPI.

Furthermore, the generated models exhibit a satisfactory distribution of samples, resulting in predicted values that are highly concordant with the measured value, as can be demonstrated by the RMSE value. It may be necessary to implement the model by including additional samples with a high total polyphenol index, which could lead to a reduction in the overestimation beyond the value of seven of the illustrated parameter, thus further reducing the error and making the regression more robust.

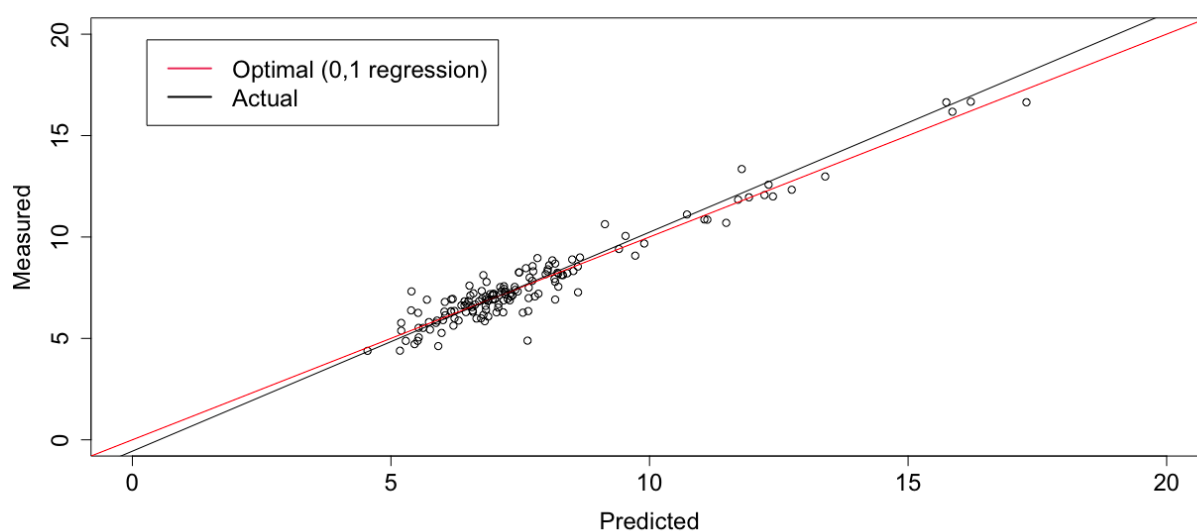


Figure 22 Plot of measured versus predicted values for total polyphenol index (TPI) by applying PLS to cyclic voltammetry data pre-processed by first derivative. Intercept: -0.56; R^2 : 0.92; RMSE: 0.62.

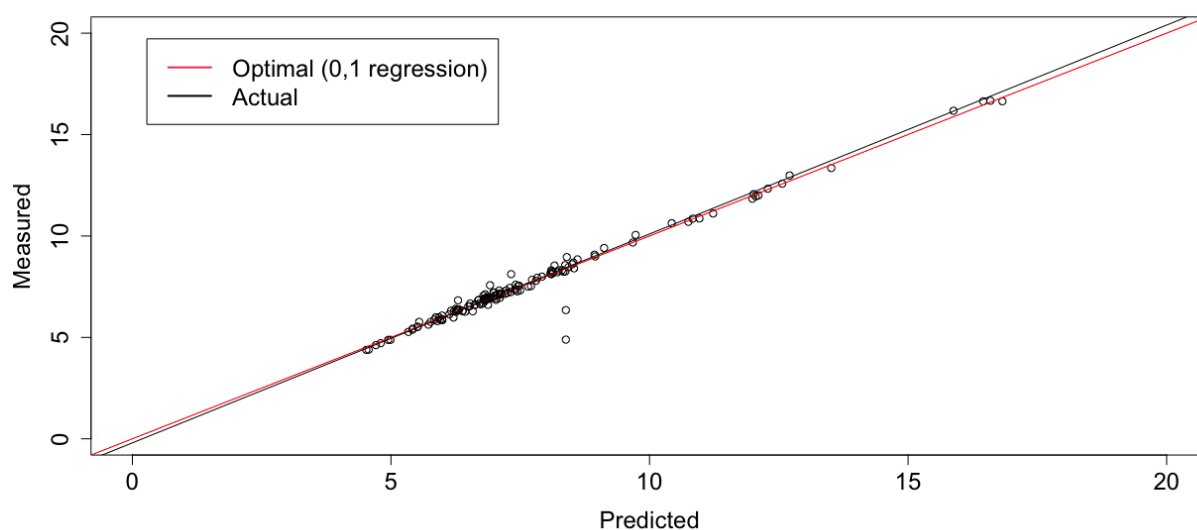


Figure 23 Plot of measured versus predicted values for total polyphenol index (TPI) by applying PLS to UV spectra data pre-processed by first derivative. Intercept: -0.20; R^2 : 0.97; RMSE: 0.38.

In order to analyze the prediction of the sulfur dioxide content, both free and combined, the best prediction values were obtained by using the data of the whole curve obtained by cyclic voltammetry, especially regarding the free fraction of sulfur dioxide, Figure 24, which is often of greater enological interest, more particularly at bottling time, in order to be able to guarantee a better oxidative stability to the bottled wine.

The model obtained for the free sulfur dioxide concentration is deemed satisfactory based on the metrics employed, with a value for both the intercept and RMSE within acceptable values. This is related to a fair dispersion of the samples, as shown in Figure 24.

In order to obtain more accurate predicted values, implementation of additional samples may be necessary in order to make the distribution more homogeneous; furthermore the application of

additional statistical techniques to the data obtained from cyclic voltammetry may be necessary.

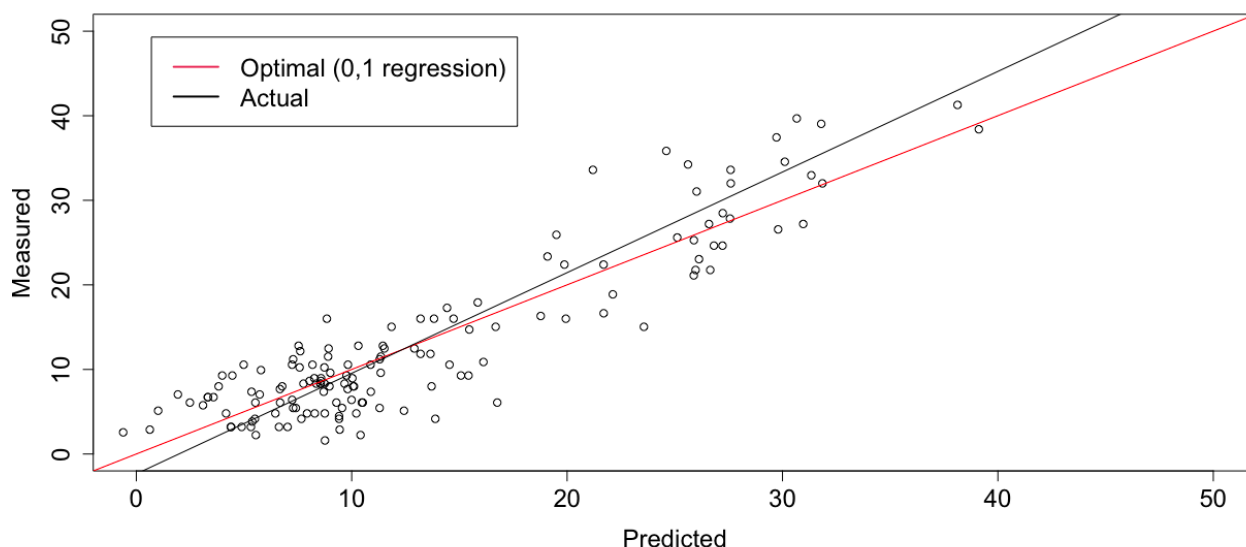


Figure 24 Plot of measured versus predicted values for free sulfur dioxide content (mg/L) by applying PLS to cyclic voltammetry data pre-processed by first derivative. Intercept: -2.35; R^2 : 0.81; RMSE: 4.15.

With regard to the oxidation potential evaluated by the POM test, the results cannot be considered good, due to a high intercept value and also a low R^2 , Figure 25. This is related to the high dispersion of samples. A statistical analysis of the dataset and the application of additional statistical techniques could potentially lead to improved results in order to obtain a predictive model.

The employed analysis is one of the potential analytical techniques that could be applied to the assessment of wine oxidability potential, which is influenced by different factors. In this regard, an alternative approach could be the use of alternative methodologies.

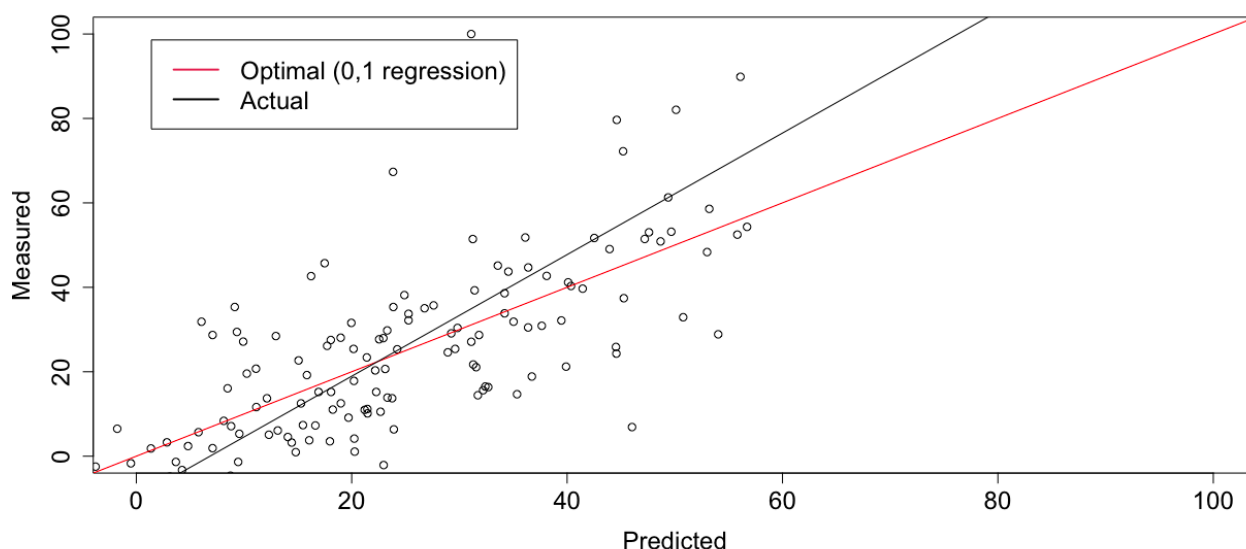


Figure 25 Plot of measured versus predicted values for POM test by applying PLS to cyclic voltammetry data pre-processed by first derivative. Intercept: -9.80; R^2 : 0.56; RMSE: 14.42.

Finally, the color was evaluated both by measuring the absorbance at 420 nm and by the CIE Lab method, to determine the L^* , a^* and b^* parameters. With regard to the L^* and a^* parameters, the results obtained do not seem acceptable, but at least at present they do not seem to be considered parameters of fundamental importance in the enological field with regard to white wines, where L^* defines the color space between black and white, while a^* defines the space between red and green. On the other hand, the parameter b^* (which defines the color space between yellow and blue) turns out to be a variable comparable to the absorbance reading at 420 nm, which turns out to be structured for the purpose of evaluating color. Both parameters, absorbance at 420 nm (Figure 26) and b^* (Figure 27), obtained a good fitting by using CV data, but especially b^* obtained a significant improvement using the visible spectrum, both without preprocessing the data and by using the first derivative, Figure 28.

In particular, the model developed with the measurement of absorbance at 420 nm revealed minimal differences between the samples, which led to the clustering. This may compromise the robustness of the model. Consequently, the implementation of the dataset could potentially enhance the outcome.

Conversely, the evaluation by the b^* parameter yielded a more uniform distribution, resulting in satisfactory results when applying partial least squares (PLS) to cyclic voltammetry data that had been pre-processed by a first derivative. The predicted results exhibited minimal deviation from the measured values. Moreover, the model developed on visible spectrum data demonstrated excellent performance, which resulted in minimal differences between predicted and measured values.

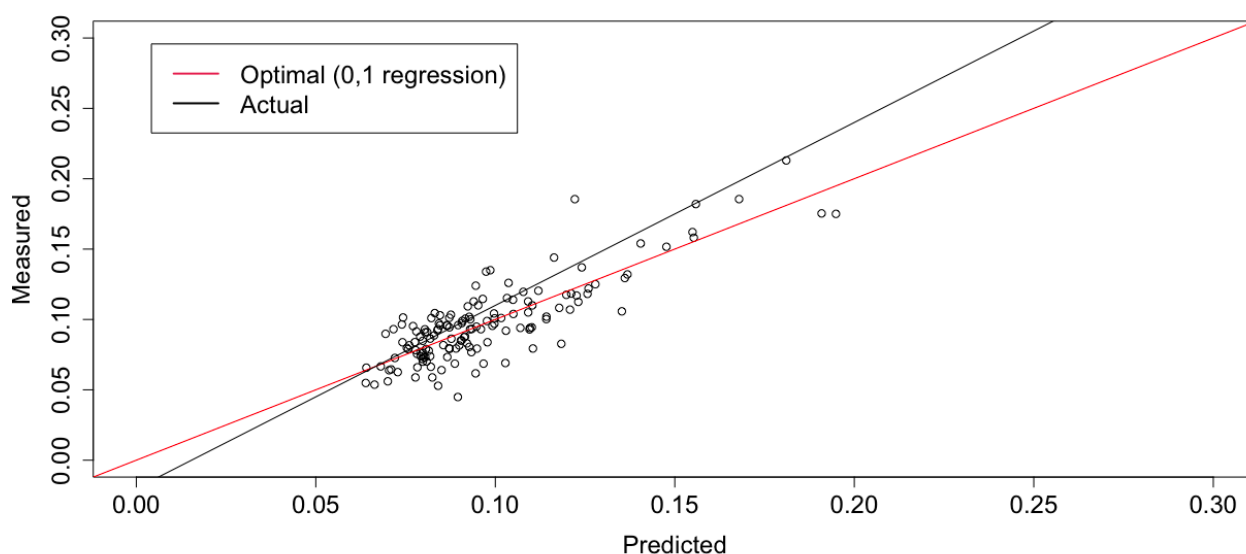


Figure 26 Plot of measured versus predicted values for absorbance at 420 nm by applying PLS to cyclic voltammetry data. Intercept: -0.02; R^2 : 0.70; RMSE: 0.01.

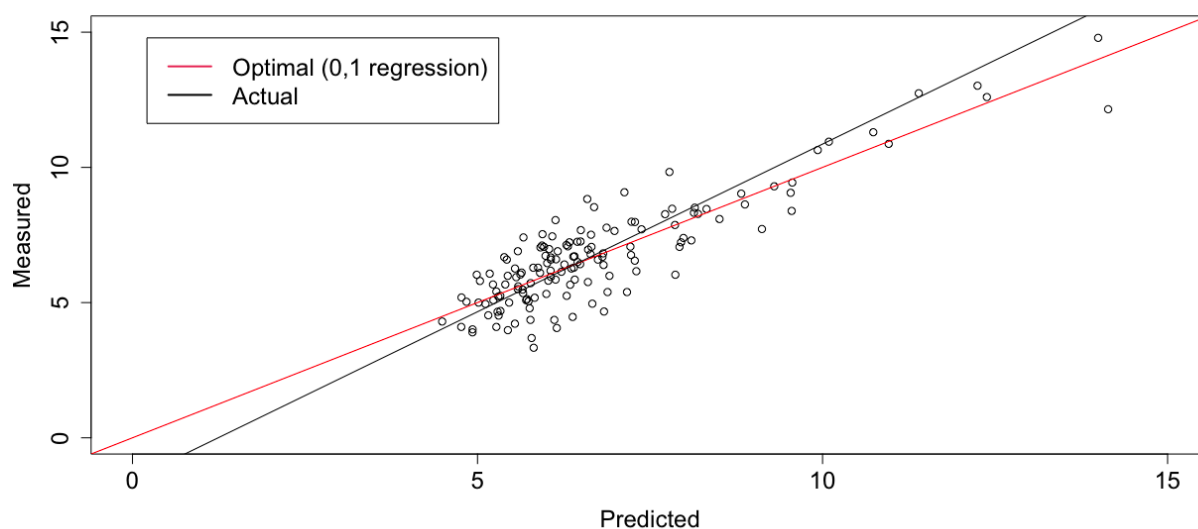


Figure 27 Plot of measured versus predicted values for parameter b^* relative to CIE Lab by applying PLS to cyclic voltammetry data pre-processed by first derivative. Intercept: -1.54; R^2 : 0.76; RMSE: 0.93.

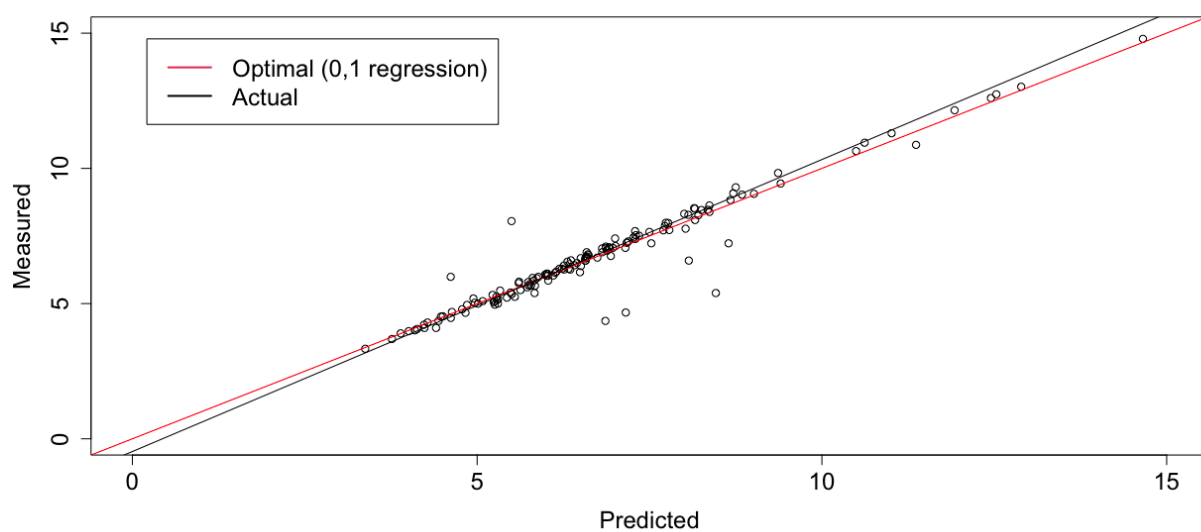


Figure 28 Plot of measured versus predicted values for parameter b^* relative to CIE Lab by applying PLS to visible spectra data. Intercept: -0.47; R^2 : 0.92; RMSE: 0.52.

Table 27 Results of PLS analysis related to chemical and spectrophotometrical parameters analyzed by the use of raw data and by the application of the first derivative ($f(x)$) of cyclic voltammetry, UV and visible spectra.

		Cyclic voltammetry data	Cyclic voltammetry data, first derivative	Anodic trace data	Anodic trace data, first derivative	UV spectra	UV spectra, first derivative	Visible spectra	Visible spectra, first derivative
Total thiol content	Intercept	-116.93	-81.99	-126.31	-116.52	-214.49	-234.32	-238.51	-226.70
	R ²	0.55	0.68	0.51	0.55	0.19	0.12	0.08	0.13
	RMSE	122.37	102.46	127.18	122.15	164.89	172.34	174.76	170.38
Catechin	Intercept	-3.10	-2.79	-6.22	-3.24	-2.72	-2.73	-7.23	-8.39
	R ²	0.74	0.77	0.49	0.73	0.78	0.78	0.41	0.32
	RMSE	6.10	5.73	8.54	6.16	5.64	5.65	9.21	9.92
Free sulfur dioxide	Intercept	-2.61	-2.35	-3.13	-4.46	-6.90	-6.84	-12.66	-12.09
	R ²	0.79	0.81	0.75	0.65	0.47	0.48	0.02	0.07
	RMSE	4.37	4.15	4.78	5.71	7.15	7.12	9.62	9.40
Combine sulfur dioxide	Intercept	-30.89	-21.65	-42.93	-52.43	-53.97	-53.72	-74.45	-69.53
	R ²	0.60	0.72	0.45	0.33	0.30	0.30	0.08	0.11
	RMSE	13.58	11.37	16.01	17.70	17.93	17.89	20.66	20.38
POM test	Intercept	-12.05	-9.80	-12.63	-13.53	-17.23	-18.91	-18.74	-20.70
	R ²	0.46	0.56	0.44	0.40	0.24	0.16	0.17	0.08
	RMSE	15.97	14.42	16.35	16.92	19.15	20.06	19.90	20.92
L*	Intercept	-97.43	-97.12	-97.51	-96.66	-84.04	-74.24	-88.73	-96.74
	R ²	0.00	0.00	0.00	0.01	0.14	0.24	0.09	0.01
	RMSE	7.45	7.44	7.45	7.42	0.81	0.76	7.11	7.42
a*	Intercept	0.42	0.38	0.50	0.55	0.42	0.63	0.80	0.60
	R ²	0.57	0.60	0.49	0.49	0.56	0.35	0.18	0.31
	RMSE	0.30	0.29	0.33	0.34	0.31	0.37	0.41	0.38
b*	Intercept	-1.72	-1.54	-0.92	-1.74	-1.90	-1.98	-0.47	-0.49
	R ²	0.74	0.76	0.71	0.74	0.71	0.70	0.92	0.92
	RMSE	0.99	0.93	1.04	0.99	1.05	1.07	0.52	0.52
IPT	Intercept	-0.74	-0.56	-0.98	-0.86	-0.28	-0.20	-1.88	-1.43
	R ²	0.90	0.92	0.87	0.88	0.96	0.97	0.75	0.81
	RMSE	0.71	0.62	0.82	0.77	0.44	0.38	1.13	0.99
ABS 420 nm	Intercept	-0.02	-11.25	-12.91	-11.81	-17.30	-18.91	-17.81	-20.70
	R ²	0.70	0.50	0.42	0.47	0.23	0.16	0.21	0.08
	RMSE	0.01	15.43	16.52	15.81	19.19	20.06	19.41	20.92

Application of partial least squares (PLS) to forecast volatile composition.

The application of PLS to the volatile component, as shown in Table 28, based on the UV and visible data, does not lead to the creation of a predictive model. However, using cyclic voltammetry, especially with the entire voltammetric trace, leads to good results, particularly for the classes containing ethyl esters and alcohols, as shown in Figure 29 and Figure 30.

The models yielded concentration values that were not particularly accurate. Both models underestimated the predicted values below 2000 $\mu\text{g/L}$ for ethyl esters, and 400 $\mu\text{g/L}$ for alcohols. Conversely, the prediction was overestimated above these concentrations.

In particular, the graph obtained by comparing the measured values with the predicted values in the model developed for ethyl esters exhibited a high degree of sample scattering.

A further evaluation of the metrics employed reveals the necessity for the implementation of additional statistical techniques and dataset analysis in order to reduce the error in the estimation of concentration values. This will lead to a reduction in the root mean square error (RMSE) value.

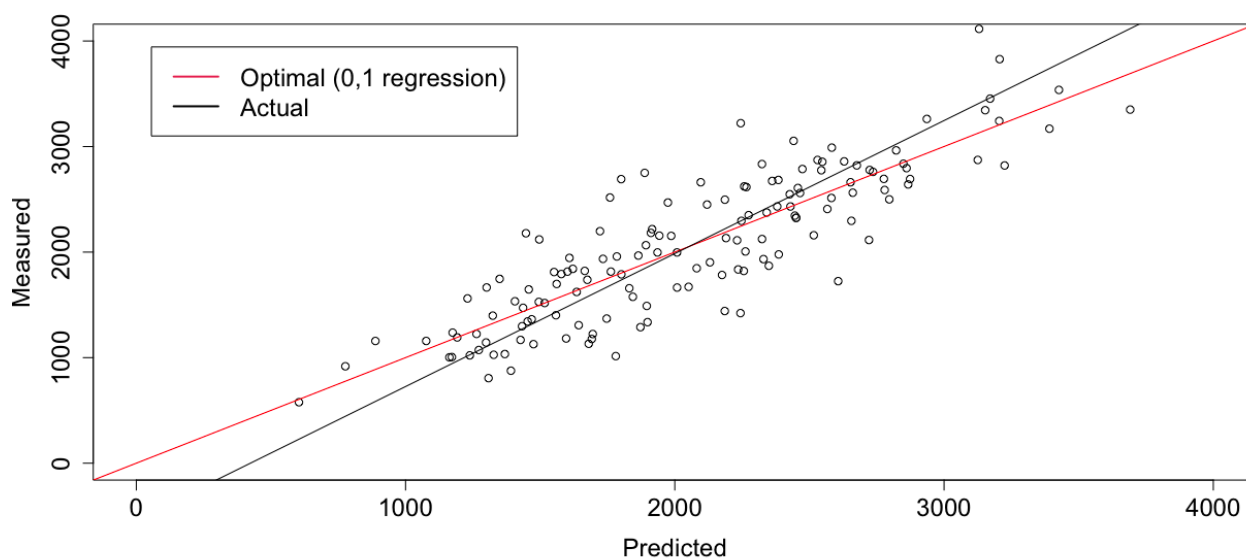


Figure 29 Plot of measured versus predicted values for ethyl esters content ($\mu\text{g/L}$) by applying PLS to cyclic voltammetry data. Intercept: -503; R^2 : 0.75; RMSE: 346.

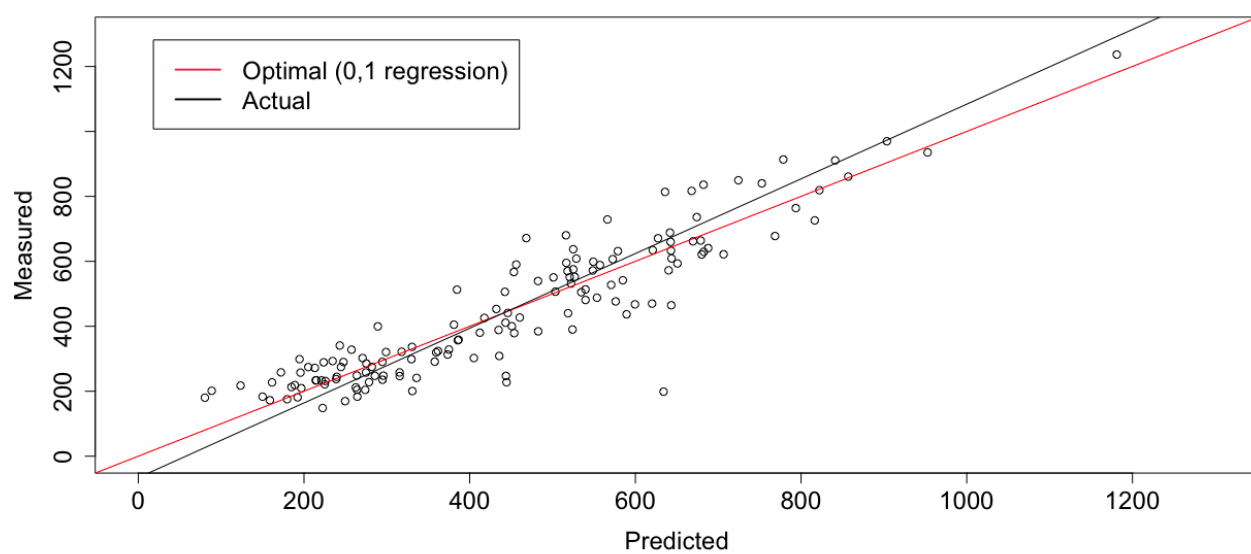


Figure 30 Plot of measured versus predicted values for alcohols content ($\mu\text{g/L}$) by applying PLS to cyclic voltammetry data. Intercept: -66; R^2 : 0.85; RMSE: 87.

Table 28 Results of PLS analysis related to the groups of volatile compounds analyzed, by the use of untreated data and by the application of first derivative ($f(x)$) of cyclic voltammetry, UV and visible spectra.

		Cyclic voltammetry data	Cyclic voltammetry data, first derivative	Anodic trace data	Anodic trace data, first derivative	UV spectra	UV spectra, first derivative	Visible spectra	Visible spectra, first derivative
Ethyl esters	Intercept	-503	-682	-854	-821	-1884	-1.830	-1854	-1943
	R ²	0.75	0.66	0.58	0.60	0.09	0.12	0.10	0.05
	RMSE	346	404	452	443	677	667	665	681
Acetic esters	Intercept	-51	-47	-62	-52	-94	-92	-111	-96
	R ²	0.61	0.63	0.52	0.60	0.29	0.30	0.15	0.26
	RMSE	74	72	82	75	101	100	109	102
Other esters	Intercept	-6	-5	-6	-7	-14	-14	-13	-14
	R ²	0.58	0.62	0.57	0.48	0.00	0.01	0.06	0.01
	RMSE	4	4	4	5	6	6	6	6
Aging markers	Intercept	-9	-7	-17	-12	-34	-38	-37	-35
	R ²	0.78	0.84	0.59	0.71	0.21	0.10	0.13	0.18
	RMSE	10	8	14	12	19	21	20	20
Alcohols	Intercept	-66	-98	-134	-178	-226	-412	-426	-429
	R ²	0.85	0.78	0.70	0.60	0.50	0.10	0.05	0.05
	RMSE	87	106	124	143	162	218	221	222
SCFA_MCFA	Intercept	-24	-21	-34	-33	-85	-86	-83	-85
	R ²	0.76	0.79	0.66	0.67	0.16	0.15	0.17	0.14
	RMSE	21	19	25	24	39	39	39	39

Application of partial least squares (PLS) to forecast parameters related to sensory analysis.

Cyclic voltammetry is not a robust forecaster of sensory analysis data, except for a few parameters, e.g. retro nasal perceived quality based on first derivative pre-treated cyclic voltammetry data (Table 29). Therefore, the use of UV and visible spectra did not provide good values for the development of a model at this stage, but the use of voltammetry data allowed an improvement, although the values were still not acceptable. This phenomenon is more pronounced in sensory analysis compared to other parameters and it is related to the low heterogeneity of the wines analyzed, as shown in Figure 31, for the application of PLS on data related to olfactory perception of oxidized aroma, for which the results show a small dispersion of the samples, though they tend to have values between zero and three on a scale of zero to ten.

It is evident that the application of additional statistical techniques is necessary to develop an effective model for estimating values related to sensory analysis.

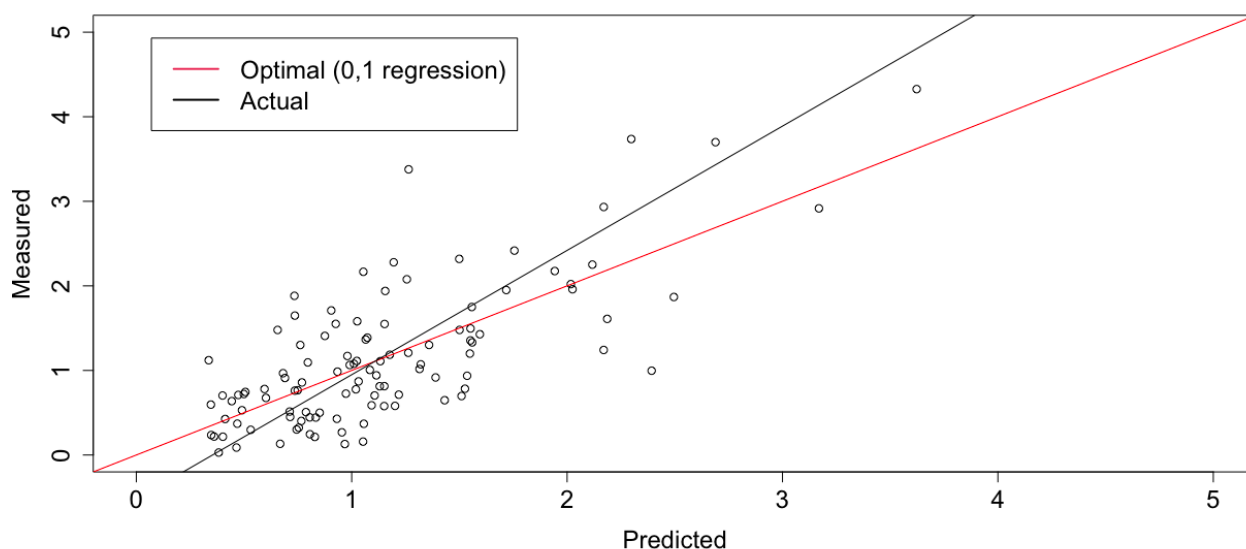


Figure 31 Plot of measured versus predicted values for olfactory perception of oxidized aroma by applying PLS to cyclic voltammetry data. Intercept: -0.53; R^2 : 0.52; RMSE: 0.56.

Table 29 Results of PLS analysis related to the parameters analyzed by sensory analysis, by the use of untreated data and by the application of first derivative ($f(x)$) of cyclic voltammetry, UV and visible spectra.

		Cyclic voltammetry data	Cyclic voltammetry data, first derivative	Anodic trace data	Anodic trace data, first derivative	UV spectra	UV spectra, first derivative	Visible spectra	Visible spectra, first derivative
Olfactory perceived quality	Intercept	-2.62	-3.80	-3.11	-3.78	-3.80	-3.92	-3.84	-3.85
	R ²	0.35	0.06	0.23	0.07	0.08	0.05	0.07	0.05
	RMSE	0.83	1.00	0.90	0.99	0.98	0.99	0.98	1.00
Olfactory reduced aroma	Intercept	-1.07	-1.28	-0.85	-1.27	-1.31	-1.27	-1.45	-1.55
	R ²	0.41	0.30	0.53	0.30	0.36	0.28	0.18	0.16
	RMSE	0.80	0.88	0.71	0.87	0.86	0.85	0.91	0.96
Olfactory oxidized aroma	Intercept	-0.53	-0.93	-0.88	-0.91	-0.92	-0.93	-1.12	-1.11
	R ²	0.52	0.17	0.22	0.19	0.19	0.18	0.01	0.01
	RMSE	0.56	0.74	0.72	0.73	0.74	0.74	0.81	0.81
Retro nasal perceived quality	Intercept	-2.59	-1.06	-3.58	-3.53	-3.47	-3.75	-3.53	-3.55
	R ²	0.34	0.73	0.09	0.11	0.13	0.07	0.12	0.10
	RMSE	0.80	0.51	0.94	0.93	0.87	0.91	0.88	0.93
Retro nasal reduced aroma	Intercept	-1.37	-0.93	-1.01	-1.45	-1.20	-1.22	-1.11	-1.41
	R ²	0.21	0.46	0.42	0.16	0.25	0.24	0.30	0.19
	RMSE	1.05	0.86	0.90	1.08	0.86	0.86	0.83	1.06
Retro nasal oxidized aroma	Intercept	-0.63	-0.63	-0.63	-0.72	-0.90	-0.74	-0.88	-0.87
	R ²	0.30	0.30	0.29	0.20	0.00	0.18	0.03	0.03
	RMSE	0.62	0.62	0.62	0.66	0.75	0.68	0.74	0.73

Application of partial least squares (PLS) to forecast carbonyl compounds.

Finally, the carbonyl compounds were analyzed using PLS, Table 30. This class of compounds plays a crucial role in the study of the state of evolution of wine, since they are the result of oxidative processes, therefore also related to the characteristics of the packaging.

Based on the results obtained (Table 30), UV and visible spectra do not allow to develop a predictive model enough robust, while CV has shown good potential in forecasting the amount of different carbonyl compounds.

The information regarding the content of acetaldehyde is also quite good. Acetaldehyde is produced during fermentation and can also form in the bottle over time. The PLS analysis of the entire voltammetry trace yielded positive results for acetaldehyde, by the application of the first derivative, Figure 32.

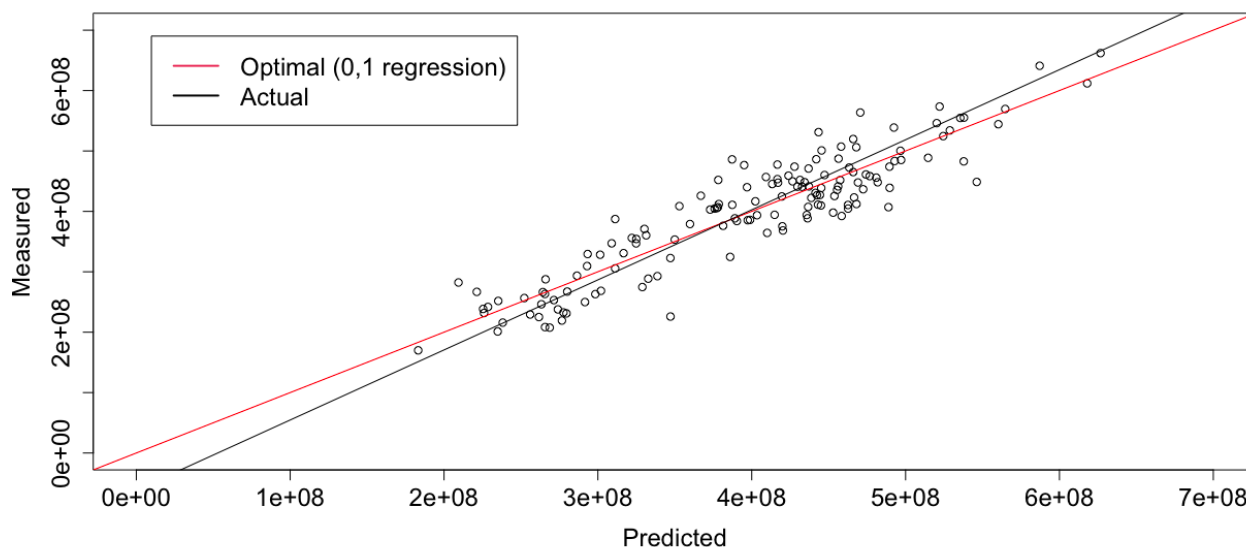


Figure 32 Plot of measured versus predicted values for acetaldehyde content (absolute area) by applying PLS to cyclic voltammetry data pre-processed by first derivative. Intercept: -59250000; R^2 : 0.85; RMSE: 39092454.

Furthermore, the UV spectra data, pre-processed by means of the first derivative, also showed good results in PLS analysis for acetaldehyde, Figure 33.

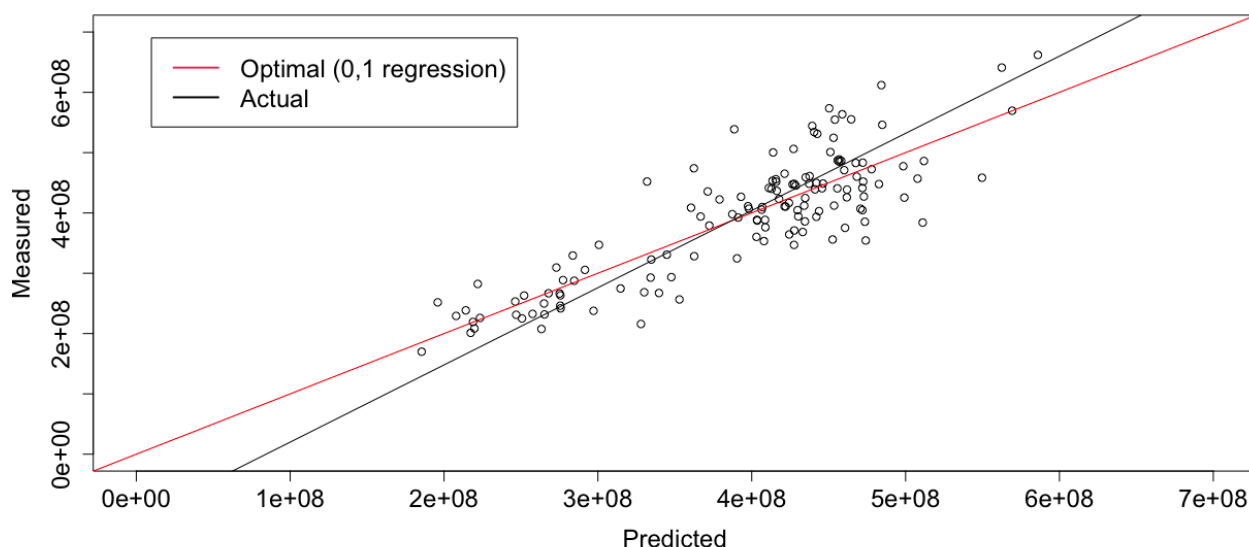


Figure 33 Plot of measured versus predicted values for acetaldehyde content (absolute area) by applying PLS to UV spectra data pre-processed by first derivative. Intercept: -108000000; R^2 : 0.72; RMSE: 53343560.

The models obtained for acetaldehyde content were compared. The best results were related to the use of cyclic voltammetry data, pretreated by means of a first derivative, with a discrete dispersion of samples along the regression.

In order to enhance the outcomes, it is essential to implement supplementary statistical methodologies to reduce the discrepancy associated with the RMSE value. This will enable the estimation of more accurate predicted values.

Also remarkable are the data obtained for the aldehydes related to the Strecker reaction, such as 2-methylbutanal, 3-methylbutanal, and phenylacetaldehyde (Table 30).

Table 30 Results of PLS analysis related to carbonyl compounds analyzed, by the use of untreated data and by the application of first derivative ($f(x)$) of cyclic voltammetry, UV and visible spectra.

		Cyclic voltammetry data	Cyclic voltammetry data, first derivative	Anodic trace data	Anodic trace data, first derivative	UV spectra	UV spectra, first derivative	Visible spectra	Visible spectra, first derivative
Formaldehyde	Intercept	-1322000	-1292000	-1303000	-1318000	-1234000	-1286000	-1628000	-1595000
	R ²	0.19	0.21	0.20	0.19	0.25	0.22	0.00	0.02
	RMSE	1307184	1292084	1297399	1305105	1275051	1301819	1450443	1435632
Acetaldehyde	Intercept	-86730000	-59250000	-12880000	-12030000	-20230000	-10800000	-39020000	-35900000
	R ²	0.78	0.85	0.37	0.69	0.48	0.72	0.01	0.09
	RMSE	47296354	39092454	57633560	55708882	73023950	53343560	100320735	96222547
Acetone	Intercept	-5381000	-2859000	-1034000	-1094000	-1656000	-1629000	-2146000	-20992000
	R ²	0.76	0.87	0.53	0.51	0.26	0.27	0.04	0.06
	RMSE	4954782	3611521	6868801	7065616	8743784	8671342	9895681	9769737
Butanal	Intercept	-7623000	-8271000	-9261000	-9253000	-16160000	-16700000	-20950000	-22650000
	R ²	0.68	0.65	0.61	0.61	0.31	0.28	0.12	0.05
	RMSE	8809034	9175526	9709414	9705136	12597210	12802976	14602147	15184773
Propionaldehyde	Intercept	-7101000	-6189000	-7014000	-4927000	-11850000	-12150000	-12930000	-12910000
	R ²	0.45	0.52	0.46	0.62	0.13	0.11	0.01	0.01
	RMSE	16992730	15863735	16888259	14154309	21871592	22149534	22932915	22912459
Butanone	Intercept	-3732000	-2653000	-4459000	-3644000	-4382000	-4737000	-4727000	-4775000
	R ²	0.22	0.45	0.07	0.24	0.11	0.04	0.02	0.01
	RMSE	6198296	5225857	6775074	6124661	6759735	7028317	6975426	7010883
Pentanone	Intercept	-318800	-406100	-372500	-582100	-538000	-599700	-783300	-760100
	R ²	0.59	0.48	0.53	0.26	0.31	0.23	0.01	0.04
	RMSE	407752.9	460243.5	440786.1	551023.4	535583.1	565463.8	639170.3	629661.2

continue

2-methylbutanal	Intercept	-3131000	-2806000	-3773000	-3375000	-7355000	-6997000	-9344000	-10040000
	R ²	0.70	0.73	0.65	0.68	0.30	0.33	0.13	0.06
	RMSE	3500016	3313622	3842412	3633922	5357561	5225810	6046561	6267039
3-methylbutanal	Intercept	-1701000	-1814000	-2400000	-2426000	-3702000	-3728000	-5481000	-5439000
	R ²	0.70	0.68	0.58	0.58	0.35	0.35	0.05	0.06
	RMSE	1834457	1894658	2179403	2191071	2758902	2768364	3293476	3280651
Hexanal	Intercept	-1352000	-1433000	-1638000	-1917000	-2952000	-3153000	-4426000	-4260000
	R ²	0.70	0.68	0.63	0.57	0.33	0.29	0.02	0.05
	RMSE	1527274	1572566	1681276	1818957	2299968	2377216	2762929	2711544
Glycolaldehyde	Intercept	-4716000	-6489000	-6012000	-6468000	-7321000	-7571000	-9354000	-9321000
	R ²	0.51	0.32	0.37	0.33	0.16	0.14	0.03	0.03
	RMSE	8584017	10069605	9692302	10052672	10505571	10683301	12089522	12068476
Furaldehyde	Intercept	-2970000	-3230000	-5222000	-4636000	-8935000	-8929000	-11600000	-11460000
	R ²	0.75	0.73	0.57	0.62	0.26	0.26	0.05	0.06
	RMSE	4965706	5178455	6584139	6203579	8775525	8772429	9812954	9752316
Benzaldehyde	Intercept	-1727000	-2278000	-2023000	-1935000	-2252000	-2480000	-2683000	-2744000
	R ²	0.41	0.22	0.31	0.34	0.23	0.15	0.09	0.06
	RMSE	2419143	2778699	2618187	2560640	2817599	2956434	3015506	3049591
Phenylacetaldehyde	Intercept	-31000	-22480	-26150	-21770	-48740	-49220	-59770	-63170
	R ²	0.53	0.65	0.60	0.67	0.25	0.24	0.09	0.04
	RMSE	38522.1	32803.5	35381.8	32285.5	49409.7	49649.2	53490.8	54992.1
Methylglyoxal	Intercept	-1389000	-1316000	-1602000	-1850000	-2585000	-2756000	-3552000	-3284000
	R ²	0.65	0.67	0.60	0.54	0.34	0.29	0.11	0.18
	RMSE	1284789	1250292	1379560	1482593	1758909	1816177	2054163	1975180

Investigation of correlations between cyclic voltammetry and changes of analyzed parameters

Furthermore, one of the objectives of the present project is to evaluate the potential of cyclic voltammetry in predicting the evolution of white wine samples after bottling.

To achieve this, we analyzed the correlations between the integral of cyclic voltammetry, related to the first sampling point, and the distance on the factorial plane based on the PCA for different parameters, related to the first (three months) and last (fourteen months) sampling points.

Correlations between the changes related to the different parameters analyzed and cyclic voltammetry are shown in Table 31. The correlation is particularly significant regarding the variation of the samples in terms of the CIE lab parameters, the category of evolution markers (composed by the POM test and the absorbance at 420 nm), as well as the variation related to the volatile fraction.

This demonstrates that there is a relationship between cyclic voltammetry and the variation related to the analytical parameters considered. The results obtained are promising for the future development of a forecast model based on an analytical method that can be performed in a simple way and with portable instrument, such as cyclic voltammetry.

Table 31 Correlation matrix of the cyclic voltammetry integral range of the first sampling point and the distance on the factorial plane, based on PCA, of the different parameters analyzed between the first and last sampling points (two and fourteen months after the start of the project). Evolution markers is composed by POM test and absorbance at 420nm.

Integral range (mV)	Chemical parameters		SO ₂		Cie Lab		Evolution markers		Volatile compounds		Carbonyl compounds	
Anodic trace	-0,21	ns	0,64	**	0,2	ns	-0,84	***	-0,5	*	-0,72	***
0 - 100	-0,64	**	-0,05	ns	-0,86	***	-0,11	ns	0,63	**	-0,15	ns
100 - 200	-0,02	ns	0,46	*	0,37	ns	-0,58	**	-0,43	*	-0,53	*
200 - 300	0,09	ns	0,41	ns	0,5	*	-0,48	*	-0,62	**	-0,43	*
300 - 400	0,32	ns	0,22	ns	0,78	***	-0,32	ns	-0,72	***	-0,22	ns
400 - 500	0,28	ns	0,23	ns	0,76	***	-0,38	ns	-0,73	***	-0,25	ns
500 - 600	0,23	ns	0,29	ns	0,7	***	-0,44	*	-0,72	***	-0,31	ns
600 - 700	0,2	ns	0,31	ns	0,66	***	-0,47	*	-0,69	***	-0,35	ns
700 - 800	0,2	ns	0,29	ns	0,68	***	-0,49	*	-0,64	**	-0,34	ns
800 - 900	0,14	ns	0,37	ns	0,61	**	-0,56	**	-0,6	**	-0,42	ns
900 - 1000	-0,17	ns	0,6	**	0,26	ns	-0,81	***	-0,49	*	-0,68	***
1000 - 1100	-0,3	ns	0,64	**	0,09	ns	-0,88	***	-0,47	*	-0,76	***
1100 - 1200	-0,35	ns	0,62	**	0,05	ns	-0,89	***	-0,47	*	-0,76	***
1200 - 1300	-0,37	ns	0,62	**	0	ns	-0,89	***	-0,44	*	-0,76	***

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'.

4. Conclusion

Some chemical parameters, such as sulfur dioxide and color, have historically been used for their effectiveness in assessing the evolution potential of a wine. In the present study, these parameters were found to be crucial in evaluating the effect of evolution.

In the present work, were also applied methods to evaluate the volatile component and the content of carbonyl compounds, in particular, the first showed significant differences over time, depending on the use of different closures and different wine typologies, but in particular the second group of compounds was very effective to evaluate the evolution during the experiment. Additionally, strong correlations were found between the content of free sulfur dioxide and the presence of carbonyl compounds, confirming the importance of these compounds, which are linked to oxidative pathways, for evaluating the evolution potential.

The use of cyclic voltammetry, an electrochemical analysis used in enology in recent times, was also effective for the purposes of this research project.

Cyclic voltammetry, UV, and visible spectra were processed using PLS to develop models for the prediction of the parameters analyzed in the present study in cross-validation, and further studies with a larger number of samples seem to be necessary to evaluate this tool for predicting enological parameters. This process yielded good results for various parameters, including free sulfur dioxide, color (measured by absorbance at 420nm and the b^* parameter relative to CIE Lab), flavanols, TPI, acetaldehyde, ethyl esters, alcohols, and carbonyl compounds.

Furthermore, the cyclic voltammetry also demonstrated significant correlations with the changes in the analyzed parameters. This information is crucial for the development of a future forecast model, which could also be effective for the prediction of the evolution of a white wine.

It is important to note that the analyses were conducted on various bottles, and certain analytical methods may have varied depending on the samples.

Furthermore, the Covid-19 pandemic had a significant impact on the sensory analysis, resulting in the loss of information from the initial sampling point.

Finally, to obtain more accurate evaluations, it is necessary to implement the study with a larger number of samples. This will allow a better evaluation of the impact of variety, closure, and enological techniques. Additionally, implementing the population and application of further statistical analysis could lead to a better assessment of the analytical techniques, which will also allow the development of more structured and robust models.

As discussed, with appropriate calibrations, cyclic voltammetry could be an important additional tool to obtain a rapid screening of the analyzed wine and also provide an indication relative to the susceptibility of the sample to evolution effects.

Evaluation of oxygen management and the effect of different closures on the evolution of white wines

1. Aim of the project

The aim of this project was to investigate and evaluate strategies to improve the evolution of bottled white wines. To improve the evolution potential, a contactor membrane was utilized to manage the amount of dissolved oxygen at the bottling stage. Additionally, four different closures were tested, a technical cork and three different screw caps with three different liners, which resulted in different closure properties, especially oxygen transfer rate (OTR).

Different analytical techniques were used to evaluate the evolution in order to obtain a complete overview of the parameters related to the evolution of the samples, including parameters conventionally used for evaluating wine aging, such as wine color, sulfur dioxide, volatile compounds, flavanols. Additionally, cyclic voltammetry (CV) and the analysis of carbonyl compounds were also performed as non-conventional indicators. CV in particular, is of great interest in several fields due to its short analysis time and ease of execution compared to other methods. Three different sampling points were managed to analyze wines, at four-month intervals.

2. Materials and Methods

Samples

Pinot gris DOC delle Venezie, vintage 2020 was used. Two treatments were applied: a control, untreated, and the treated with a contactor membrane by Mastermind Remove and the use of polypropylene membranes with a nominal porosity of 0,05 μm (Ju.Cla.S. S.r.l., Pescantina, VR) to manage dissolved gases. The concentration of dissolved oxygen was respectively 1.2 mg/L and 0.3 mg/L.

Wine was bottled using a GAI 3005 TOP (GAI Macchine Imbottigliatrici Spa, Ceresole Alba, Italy), in 750 mL flint bordolese bottles. Four different closures were used, a technical cork (C) as a control and three screw caps produced by Korked S.r.l. (San Giorgio in Bosco, Italy), characterized by different lines, Saranex (S), and two experimental liners named liner M and Z. The codification of the samples can be found in Table 32.

Samples were stored at a temperature of 20 ± 5 °C and a relative humidity of 70 ± 10 % until analysis.

Table 32 Codification of the samples used in the experiment according to the treatments performed and the closures used.

Samples code	Closure	Treatment	Relative Estimated OTR*
C	Cork	Control / Untreated	n.k.
C_c	Cork	Treated with Contactor membrane	n.k.
S	Saranex	Control / Untreated	+++
S_c	Saranex	Treated with Contactor membrane	+++
M	Liner "M"	Control / Untreated	++
M_c	Liner "M"	Treated with Contactor membrane	++
Z	Liner "Z"	Control / Untreated	+
Z_c	Liner "Z"	Treated with Contactor membrane	+

n.k. = not known; *indicated by the supplier

The analyses were carried out at four-month intervals, starting from the third month after bottling.

The study start was delayed due to logistical reasons related to the presence of pandemic COVID-19.

Methods

For the present project, the same methods and reagents were used as for the previous one (

Materials and Methods) In addition, dissolved oxygen was measured as described in the following paragraph.

Determination of dissolved oxygen

The concentration of dissolved oxygen was determine using an OxySense® 325I fluorimeter managed by the software OxySense GEN-III version V1.2.1 and using O2xyDot® sensors glued inside some of the collected bottles (OxySense Inc., Denver, MA, USA), as described by Comuzzo et al. (2015).

3. Results and discussion

Evaluation of dissolved oxygen concentration after treatment to manage dissolved gases

The use of contactor membranes is a recently approved technology, which is currently being used on a marginal level. This treatment is highly effective in removing dissolved gases, resulting in a significant reduction in gas concentration. This is particularly important for wine production, where the concentration of oxygen in the bottle is crucial. Several studies have evaluated the use of membrane contactors for the treatment of wine, in particular the study by Vidal et al. (2010), which used different operating modes and recorded a significant reduction in the concentration of oxygen, in particular through the use of vacuum with a reduction of about 88% of the dissolved oxygen content. The study by Vidal et al. (2010) also reports that no significant differences were found in the results of the chemical analyses carried out to evaluate ethyl alcohol content, color and sulfur dioxide concentrations. However, significant differences were found in the amount of some esters in the volatile component, although these differences did not have a significant effect on the sensory evaluation. The loss of volatile compounds mainly depends on the properties of the membrane, mainly the pore size. The pores of a contactor membrane used for gas removal generally have an average nominal pore diameter between 0.03 and 0.05 μm , which allows the passage of gases, but also of low molecular weight volatile molecules.

The thesis project demonstrated a net reduction in the amount of oxygen during bottling by using the contactor membrane. Gas measurements taken during bottling revealed a carbon dioxide concentration of 1500 mg/L and a dissolved oxygen concentration of 1.2 mg/L, while the treated samples with the contactor membrane were reduced to values of 900 mg/L for carbon dioxide and 0.3 mg/L for dissolved oxygen, after bottling. The measurements were taken on the bottling line at the end of the filtration stage, which appears to be a stage during which an increase in dissolved gases can occur.

After a brief stop (three days) to allow the samples to reach stability, which amounted to three days, the dissolved oxygen concentration was measured and then repeated periodically until the end of the experiment. A significant difference was observed in the first measurement between the treated samples and the control samples, except for the samples bottled with cork (Figure 34). This may be due to the possible release of oxygen from the cork after its compression during corking. Regarding the screw caps, the samples showed an increase of oxygen compared to the measurements made at the bottling stage, but still significantly less than the increase recorded in the samples with cork.

It is important to consider that there is an increase in dissolved oxygen during the bottling process, and the results obtained could have been further improved if the screw caps had been inerted.

However, the samples with cork closures showed a faster consumption of dissolved oxygen and at 95 days after bottling, showing a lower dissolved oxygen concentration than the samples with the screwcap closures.

Finally, the screw caps showed a lower dissolved oxygen concentration from day 144, which tended to be more constant, with values close to the absence of dissolved oxygen; the same trend was found for the cork caps, but with higher values. This trend was observed for both treatments.

The data demonstrate that contactor membrane treatment is effective in reducing dissolved oxygen concentration. However, the use of the appropriate closure is important to optimize the process, even in the short term. The differences among closures seemed limited to the first three-four months after bottling; after five months, screw caps determined a very low oxygen amount in the bottles, while technical cork led to a slightly higher concentration, which nevertheless remained also quite constant for the remaining part of the experiment.

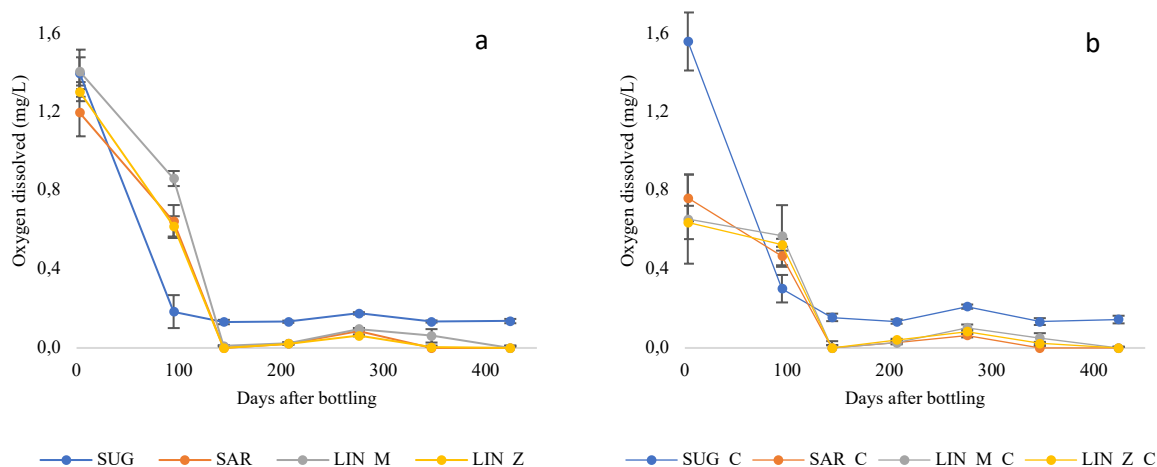


Figure 34 Studies of dissolved oxygen concentration by the different closures used in the study and by the management of dissolved oxygen by the use of a contactor membrane at bottling, figure a control and b contactor. Abbreviation C: cork; S: Saranex; M: liner 'M'; Z: liner 'Z'.

Evaluation of the effect of treatments on chemical parameters

To obtain a complete view of the evolution based on the analyzed parameters, Factor Analysis was followed by PCA, in which the most significant variables were selected in order to obtain the most accurate description of the system, best explaining the variance among the analyzed samples. For the factor analysis, 0.6 was chosen as the limit for the factor loadings.

The Figure 35 and Figure 36 show the results of the PCA analysis, which makes it possible to assess how the change was most pronounced between the first and second sampling points, three and eleven months after the start of the project, respectively. During the period of the experiment, a change in the sulfur dioxide concentration was obtained, mainly related to the total amount. Sulfur dioxide is the primary antioxidant used in enology to protect wine from oxidative processes, and its reduction led to an increase in color, as measured by absorbance at 420 nm. This reduction also led to a decrease in the most easily oxidized phenolic component, under the category flavanols. An additional result appears to be a reduction in the evolution potential values due to oxidation of the oxidizable fraction over time in the matrix, as assessed by the POM test.

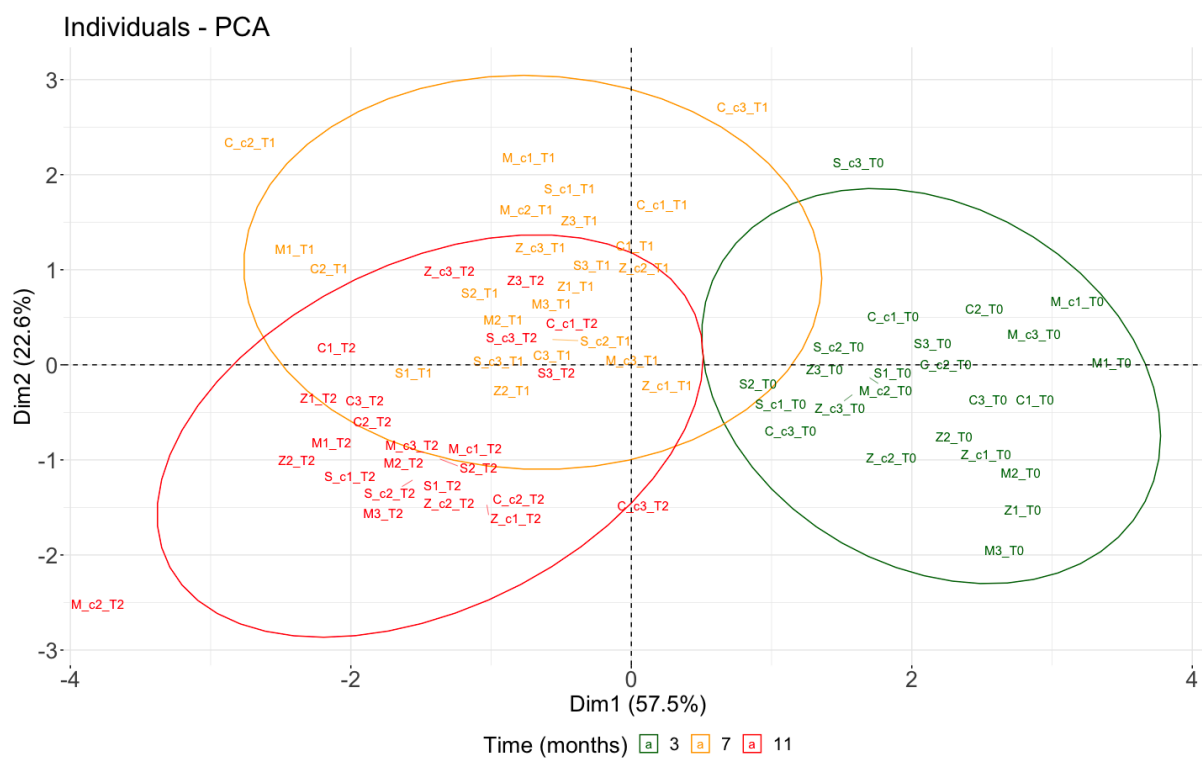


Figure 35 Score plot based on the chemical parameters analyzed. The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.

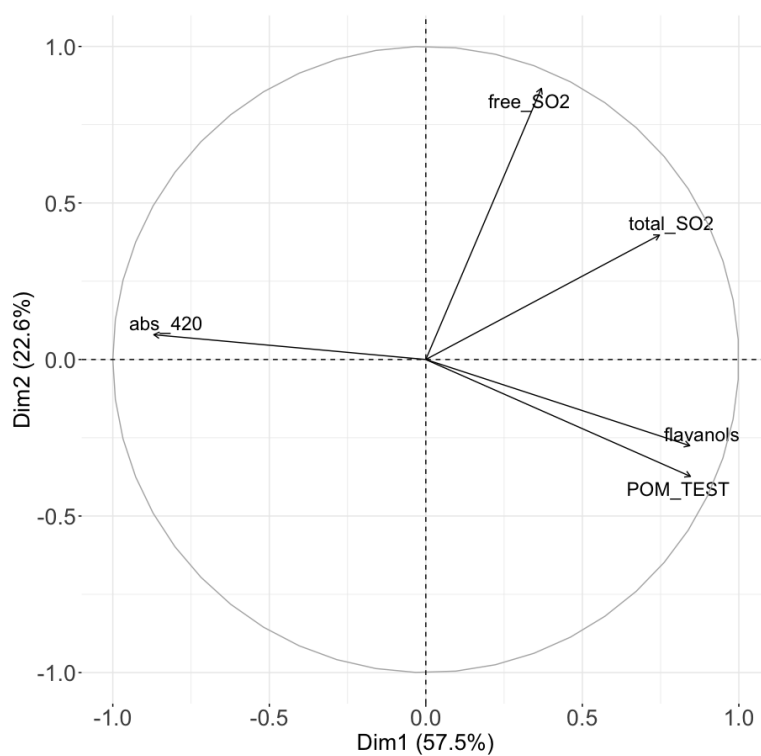


Figure 36 Loading plot of the chemical parameters analyzed.

The individual sampling points were analyzed using analysis of variance (ANOVA) to highlight the main differences related to the use of different closures and the effect of treatment, both separately and in combination. Significant differences were found in numerous parameters (Table 33).

Table 33 The impact of closure (C), treatment (T), and their combined effect (C X T) on the chemical parameters analyzed throughout the whole experiment.

Variables	Effect of the Closure (C)				Effect of the Treatment (T)				C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T	
Oxygen (mg/L)	0.17	0.19	0.27	0.20	ns	0.22	0.19	ns	ns
Total thiols (µg/L)	141.5	136.5	135.0	132.1	ns	132.6	139.9	ns	ns
Flavanols (mg/L)	9.0	8.6	9.3	9.3	ns	8.9	9.1	ns	ns
Free SO ₂ (mg/L)	10.0	9.3	9.3	8.9	ns	8.5	10.2	ns	ns
Combined SO ₂ (mg/L)	94.5	91.3	88.8	91.1	ns	92.7	90.2	ns	ns
Total SO ₂ (mg/L)	104.5	100.6	98.1	100.0	ns	101.2	100.4	ns	ns
POM test (%)	33	29	34	33	ns	33	31	ns	ns
L*	98.40	98.90	98.79	98.65	ns	98.80	98.56	ns	ns
a*	-0.75	a -0.62	b -0.61	b -0.73	a *	-0.66	-0.69	ns	ns
b*	4.91	4.78	4.89	4.80	ns	4.88	4.81	ns	ns
TPI	5.6	ab 5.7	b 5.4	a 5.5	ab *	5.6	5.4	ns	ns
abs 420 nm	0.073	0.069	0.072	0.068	ns	0.072	0.069	ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Analyses at the first sampling point, performed three months after bottling (due to logistical and pandemic problems), cause a loss of information on initial changes. However, the initial wine was the same for all samples, so significant differences appear to be minimal.

Three months after bottling (Table 34), significant differences were found in the amount of dissolved oxygen based on the type of closure used. The M liner closure had higher values, while the cork closure had lower values. Additionally, the treatment of samples by the contactor membrane resulted in lower values, although not statistically significant.

The differences in flavanol content, despite marked as significant, were poorly relevant from the practical point of view. Also free SO₂, at the first sampling point showed minor variations depending on closure and gas management treatment.

Table 34 The impact of closure (C), treatment (T) and their combined effect (C X T) on the chemical parameters analyzed at the first sampling point, after three months after bottling.

Variables	Effect of the Closure (C)								Effect of the Treatment (T)					C X T	
	Cork		Saranex		Liner M		Liner Z		C	Control		Treated			T
Oxygen	0.24	a	0.56	b	0.72	c	0.57	b	***	0.58		0.47		ns	*
Total thiols	168.4	c	160.4	ab	164.4	bc	156.8	a	***	159.2	a	165.9	b	***	*
Flavanols	9.9	a	10.0	a	11.9	b	11.2	b	***	10.9		10.7		ns	ns
Free SO ₂	10.8		11.7		11.9		8.7		ns	9.9		11.7		ns	ns
Combined SO ₂	101.0		97.2		94.9		96.5		ns	99.0		95.8		ns	ns
Total SO ₂	111.8		108.8		106.8		105.3		ns	108.9		107.5		ns	ns
POM test	69	b	42	a	62	b	60	ab	**	67	b	50	a	**	ns
L*	99.10		99.20		99.30		99.25		ns	99.26		99.16		ns	ns
a*	-0.57		-0.56		-0.57		-0.56		ns	-0.54	b	-0.58	a	***	*
b*	4.17		4.10		4.06		4.04		ns	4.09		4.09		ns	ns
TPI	5.6	ab	5.7	b	5.1	a	5.2	ab	*	5.5		5.3		ns	ns
abs 420 nm	0.060		0.058		0.056		0.056		ns	0.058		0.058		ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

As previously reported, analyses conducted during the second sampling point, seven months after the start of the experiment, indicated a reduction in dissolved oxygen content (Table 35). Furthermore, the effect of evolution resulted in a decrease in various parameters, including total thiol compounds, flavanols, sulfur dioxide, and oxidizability. In this study, it was found that free sulfur dioxide concentration remained generally constant between three and seven months from bottling. Contrary, we observed a decrease of the combined fraction and such increase had a negative impact on the total SO₂ concentration. The POM test indicated a significant reduction in oxidizability potential, but no significant variations were recorded among the different closures or treatments employed. Additionally, there was a slight increase in absorbance at 420 nm, the parameter used to evaluate yellow color change, between the first two samplings, with no significant differences between samples.

Table 35 The impact of closure (C), treatment (T) and their combined effect (C X T) on the chemical parameters analyzed at the second sampling point, after seven months after bottling.

Variables	Effect of the Closure (C)								Effect of the Treatment (T)				C X T		
	Cork		Saranex		Liner M		Liner Z		C	Control		Treated		T	
Oxygen (mg/L)	0.13	b	0.03	a	0.03	a	0.03	a	***	0.05	a	0.06	b	**	ns
Total thiols (μg/L)	139.2		129.6		129.3		131.6		ns	127.8	a	137.0	b	*	ns
Flavanols (mg/L)	8.6	c	7.5	a	7.7	ab	8.3	bc	**	7.9		8.1		ns	ns
Free SO ₂ (mg/L)	14.6		10.6		12.6		11.3		ns	10.7		13.9		ns	ns
Combined SO ₂ (mg/L)	89.2		89.3		87.6		90.6		ns	90.0		88.3		ns	ns
Total SO ₂ (mg/L)	103.8		99.9		100.3		101.9		**	100.8		102.2		ns	ns
POM test (%)	8		19		16		19		ns	15		16		ns	ns
L*	97.47		98.81		98.53		98.50		ns	98.59		98.06		ns	ns
a*	-1.00	a	-0.60	b	-0.55	b	-0.92	a	***	-0.75		-0.79		ns	ns
b*	5.25		4.84		5.04		4.79		ns	5.04		4.92		ns	ns
TPI	5.4		5.5		5.4		5.5		ns	5.4		5.5		ns	ns
abs 420 nm	0.082		0.070		0.076		0.068		ns	0.076		0.072		ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Finally, at the third sampling point, eleven months after the start of the experiment (Table 36), stability was reached in the dissolved oxygen values, comparing them with the situation found at seven months after the start of the experiment. A reduction in the concentration of total thiol compounds was observed, with significant differences based on treatment, a higher amount of total thiol content was detected in the samples treated with contactor membrane. There was no reduction in flavanols when comparing the last sample point with the previous one. However, a reduction in sulfur dioxide concentration was recorded, primarily due to a significant decrease in the free fraction, which led to an increase in color-related values, assessed by absorbance at 420 nm. No significant differences were found between the different samples for these parameters. However, a significant difference in color was observed, which can be attributed to the effect of closure.

Table 36 The impact of closure (C), treatment (T) and their combined effect (C X T) on the chemical parameters analyzed at the third sampling point, after eleven months after bottling.

Variables	Effect of the Closure (C)								Effect of the Treatment (T)					C X T
	Cork		Saranex		Liner M		Liner Z		C	Control		Treated		
Oxygen (mg/L)	0.13	d	0.00	a	0.06	c	0.01	b	***	0.04		0.05	ns	ns
Total thiols (μg/L)	116.7	b	119.3	b	111.3	a	107.8	a	***	110.7	a	116.9	b	*** *
Flavanols (mg/L)	8.5		8.2		8.2		8.3		ns	8.0		8.6	***	***
Free SO ₂ (mg/L)	4.6		5.6		3.4		6.7		ns	5.0		5.1	ns	ns
Combined SO ₂ (mg/L)	93.2		87.5		83.9		86.2		ns	88.9		86.5	ns	ns
Total SO ₂ (mg/L)	97.8		93.0		87.3		92.8		ns	93.9		91.6	ns	ns
POM test (%)	21		27		23		19		ns	17	a	28	b	** *
L*	98.62		98.70		98.52		98.20		ns	98.57		98.46	ns	ns
a*	-0.67	b	-0.71	a	-0.72	a	-0.72	a	***	-0.70		-0.71	ns	ns
b*	5.32	a	5.40	a	5.58	b	5.56	b	***	5.52	b	5.42	a	** **
TPI	5.7		5.8		5.6		5.7		ns	5.8		5.6	ns	ns
abs 420 nm	0.078	a	0.078	ab	0.083	b	0.080	ab	*	0.081		0.079	ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Finally, the data obtained about the first and last sampling point were processed by PCA, calculating the factorial coordinates and the distances on the factorial plane of PCA between the two sampling moments for a given sample (Table 49), as shown in Figure 37 and Figure 38.

The M liner closure, both in control and through the use of the contactor membrane, recorded the highest variation, which resulted in a significant reduction in flavanols, but also in total sulfur dioxide and, finally obtained a difference between the samplings that tended to be greater in terms of color.

The samples that were subjected to dissolved gas management based on contactor membrane in combination with agglomerated cork closure, but also Saranex closure without the use of contactor membrane, showed the least variation. This is linked to a slight reduction related to the concentration of the flavanol group, a higher content of free sulfur dioxide compared to the average and also a slight total fraction of sulfur dioxide loss compared to the other samples, finally difference related to the POM test were also found, which in the last point was slightly higher than in the rest of the samples analyzed, thus with a greater potential for oxidizability and a tendency to a lower color.

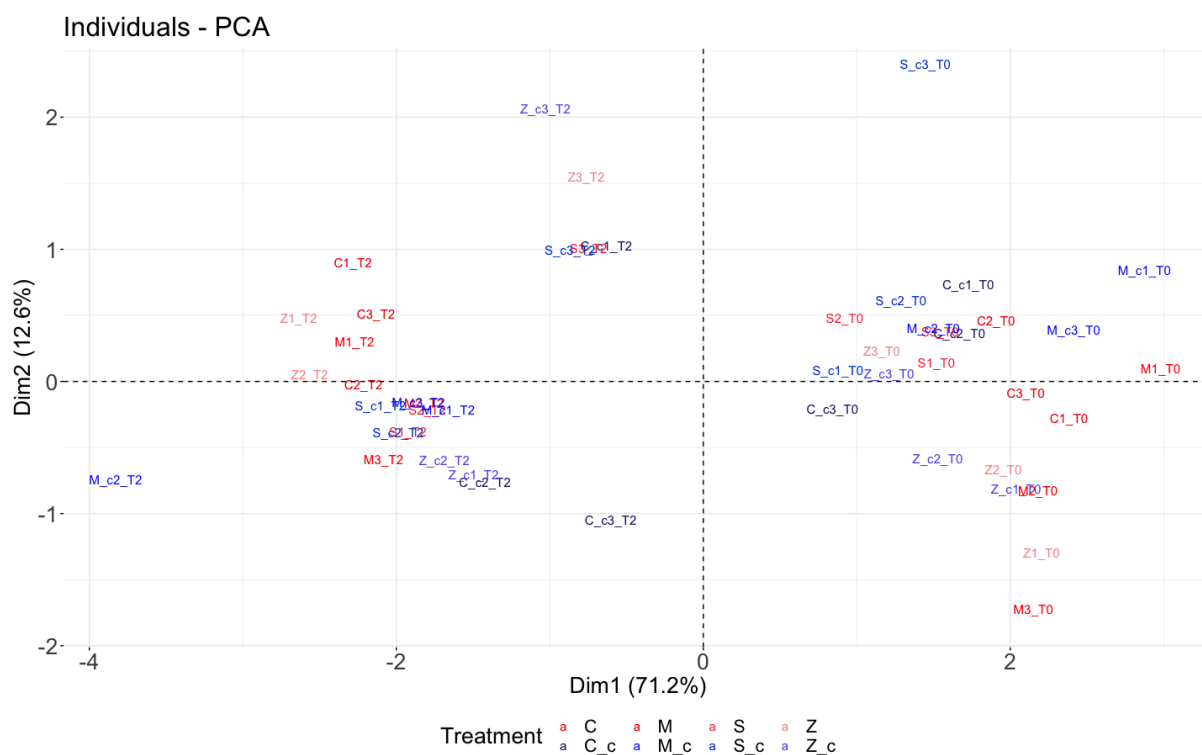


Figure 37 Score plot of the samples, based on the chemical parameters analyzed, to analyze the behavior between the first (T0) and the last sampling point (T2). The legend displays the different treatments applied.

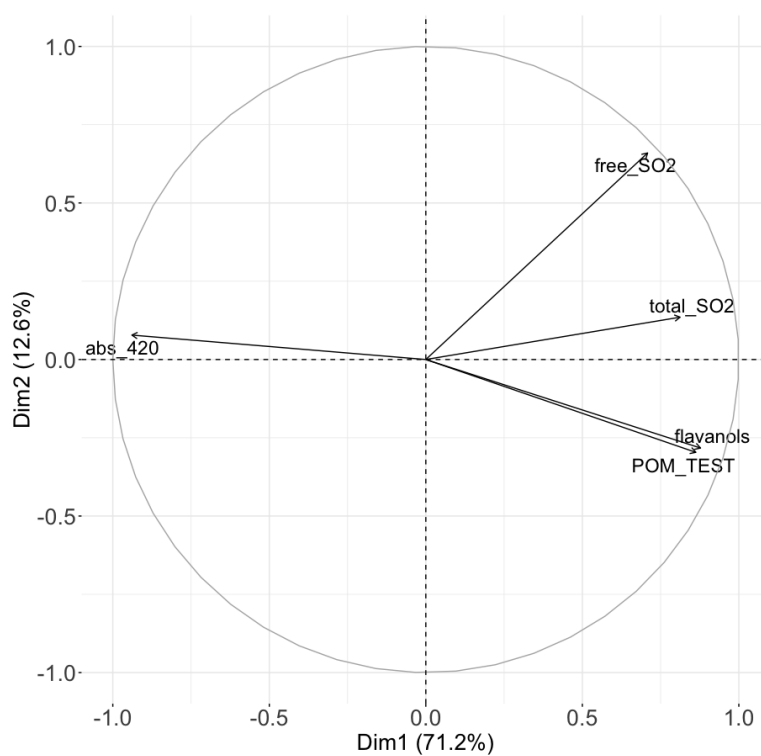


Figure 38 Loading plot of the chemical parameters analyzed.

Evaluation of the effect of treatments on volatile composition

The PCA was performed using the volatile composition data obtained during the experiment, as shown in Figure 39 and Figure 40. The volatile compounds were categorized according to Table 4.

The main reduction was observed between the first and the second points of sampling, with a smaller variation between samples, while at the final sampling point there was an increase in the concentration of the volatile components in the category relative to the markers of evolution.

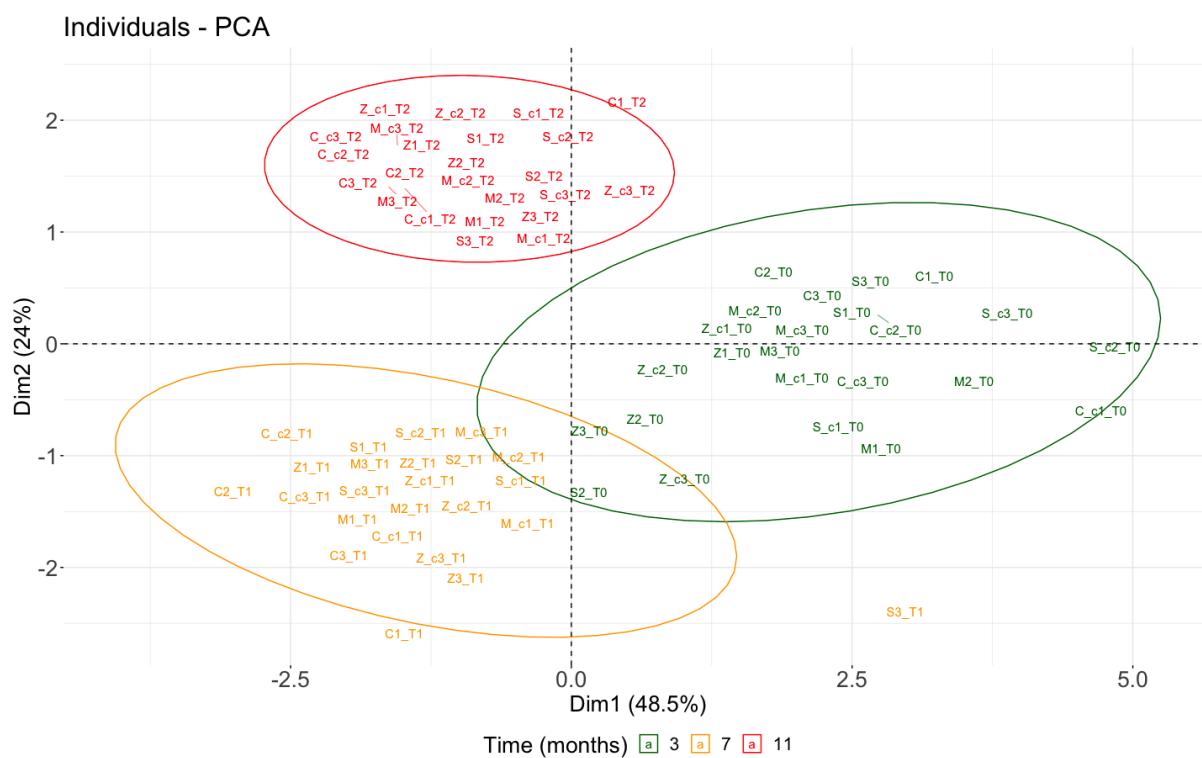


Figure 39 Score plot based on the classification of volatile compound groups concentration ($\mu\text{g/L}$), according to different sampling points. The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.

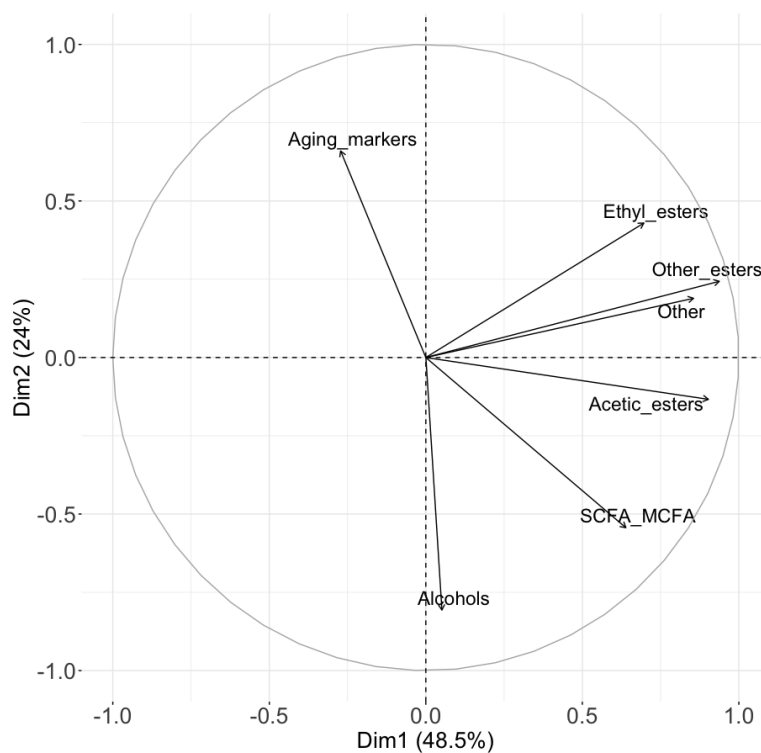


Figure 40 Loading plot of the concentration ($\mu\text{g/L}$) of volatile composition based on the volatile group classification. Abbreviation SCFA_MCFA: Short and Medium Chain Fatty Acids.

The analysis of variance was performed on the data obtained. Only the difference based on the closure turns out to be significant, for the concentration in ethyl esters, with higher values for the Saranex closure, and for short and medium chain fatty acids, with values tending to be higher for the screw caps, particularly the Saranex closure.

Regarding the analysis of the different sampling points, no significant differences result from the combined effect of closure and treatment (Table 37).

Table 37 The impact of closure (C), treatment (T), and their combined effect (C X T) on the concentration (µg/L) of volatile composition analyzed, classified in groups, throughout the whole experiment.

Variables	Effect of the Closure (C)								Effect of the Treatment (T)				C X T	
	Cork		Saranex		Liner M		Liner Z		C	Control	Treated	T		
Ethyl esters	2316.7	a	2604.8	b	2413.3	a	2304.5	a	**	2367.2	2452.4	ns	ns	
Acetic esters	509.6		522.9		503.4		498.8		ns	499.8	517.6	ns	ns	
Other esters	15.7		17.6		16.4		14.8		ns	15.8	16.5	ns	ns	
Aging markers	9.4		11.0		11.0		9.8		ns	10.3	10.3	ns	ns	
Alcohols	390.4		403.1		400.9		389.1		ns	397.8	394.0	ns	ns	
SCFA_MCFA	117.8	a	146.5	b	134.3	ab	127.6	ab	*	131.3	131.8	ns	ns	
Other	93.7		88.1		89.4		87.9		ns	90.6	88.9	ns	ns	

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Specifically, during the first sampling, there was a significant difference in ethyl esters between the different closures, with higher values observed for cork, but it should be noted that the Z liner was very different from the other closures. This trend is also observed in the category of other esters and other compounds, as shown in Table 38.

The application of the treatment resulted in significant differences in the concentrations of ethyl esters, acetic esters, aging markers, and short- and medium-chain fatty acids, which were higher in samples treated by contactor membrane. A general reduction of concentration was observed in all groups in the study based on the evolution of wines made by Ling et al. (2019). Higher amounts of volatile compounds may indicate a more effective preservation of the samples.

Table 38 The impact of closure (C), treatment (T), and their combined effect (C X T) on the concentration ($\mu\text{g/L}$) of volatile composition analyzed, classified in groups, at the first sampling point, after three months after bottling.

Variables	Effect of the Closure (C)								Effect of the Treatment (T)					C X T	
	Cork		Saranex		Liner M		Liner Z		C	Control		Treated			T
Ethyl esters	2664.4	b	2645.0	b	2563.3	b	2217.5	a	**	2432.0	a	2613.1	b	*	ns
Acetic esters	734.9		769.5		731.3		704.9		ns	712.9	a	757.5	b	*	ns
Other esters	22.8	b	21.3	ab	21.1	ab	17.2	a	*	19.8		21.4		ns	ns
Aging markers	7.1		6.4		8.0		5.4		ns	5.9	a	7.5	b	*	ns
Alcohols	389.2		388.6		392.3		373.1		ns	376.4		395.2		ns	ns
SCFA_MCFA	146.9		156.0		155.6		131.5		ns	138.9	a	156.1	b	*	ns
Other	117.8	a	112.4	a	107.6	a	105.7	a	*	112.2		109.6		ns	ns

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

At the following sampling point, seven months after the start of the experiment (Table 39), there was a general decrease in the concentration of the different volatile components, with the except of aging markers and alcohols, which showed an increase in concentration.

There were smaller significant differences within the second sampling point, particularly in the concentrations of ethyl esters based on closure. The lowest values were related to the use of cork, which experienced a marked decrease compared to the previous sampling point. The other closures better preserved this group of compounds, as well as the other esters categories.

Table 39 The impact of closure (C), treatment (T), and their combined effect (C X T) on the concentration ($\mu\text{g/L}$) of volatile composition analyzed, classified in groups, at the second sampling point, after seven months after bottling.

Variables	Effect of the Closure (C)								Effect of the Treatment (T)				C X T
	Cork		Saranex		Liner M		Liner Z		C	Control	Treated	T	
Ethyl esters	1939.6	a	2439.7	b	2215.4	ab	2157.2	ab	**	2162.4	2213.6	ns	ns
Acetic esters	403.9		408.2		385.5		400.9		ns	400.0	399.2	ns	ns
Other esters	9.8	a	15.2	c	13.2	bc	12.1	ab	***	12.4	12.7	ns	ns
Aging markers	7.2		9.8		8.9		8.4		ns	8.8	8.4	ns	ns
Alcohols	438.0		448.0		437.9		438.7		ns	448.2	433.1	ns	ns
SCFA_MCFA	116.4		160.6		138.3		140.9		ns	142.6	135.6	ns	ns
Other	77.1		68.8		76.1		69.7		ns	72.8	73.0	ns	ns

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

Comparing the last sampling point, at eleven months (Table 40), with the previous one, there was an increase in concentrations of aging markers, with higher concentrations found in screw caps. In terms of the treatment effect, control samples registered a higher concentration.

Finally, after eleven months, significant differences were observed in the concentration of ethyl esters, aging markers, and short- and medium-chain fatty acids between the samples with screwcaps and in particular between the samples with Saranex liner. Regarding the application of contactor membrane, no significant differences were found except for the group of compounds classified as evolution markers, which were found to be slightly present with the use of the treatment.

Table 40 The impact of closure (C), treatment (T), and their combined effect (C X T) on the concentration ($\mu\text{g/L}$) of volatile composition analyzed, classified in groups, at the third sampling point, after eleven months after bottling.

Variables	Effect of the Closure (C)								Effect of the Treatment (T)				C X T		
	Cork		Saranex		Liner M		Liner Z		C	Control		Treated		T	
Ethyl esters	2346.1	a	2729.7	b	2461.1	a	2538.7	ab	**	2507.1		2530.7	ns	ns	
Acetic esters	390.0		391.1		393.6		390.7		ns	386.5		396.2	ns	ns	
Other esters	14.5		16.4		15.0		15.0		ns	15.1		15.4	ns	ns	
Aging markers	13.8	a	16.8	b	16.0	ab	15.7	ab	*	16.3	b	14.9	a	*	ns
Alcohols	343.8		372.7		372.5		355.6		ns	368.6		353.7	ns	ns	
SCFA_MCFA	90.1	a	122.8	b	108.9	b	110.3	b	***	112.4		103.6	ns	ns	
Other	86.1		83.0		84.6		88.3		ns	87.0		84.1	ns	ns	

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

To evaluate the overall effect of treatments that had the greatest impact on the volatile component, the distances on the factorial plane based on PCA (Figure 41 and Figure 42) was calculated, based on data from the third and eleventh month after bottling (Table 49).

The sample sealed with cork and the treatment related to gas management showed the greatest change, with a significant reduction in the content of ethyl and acetic esters, as well as short and medium chain fatty acids. Regarding the samples that showed less variation during the experimentation, the M and Z liners, both combined with dissolved gas management, were characterized by a lower loss

of ethyl esters, particularly the Z liner. Additionally, they had a lower impact on the evolution of alcohols and other ester groups.

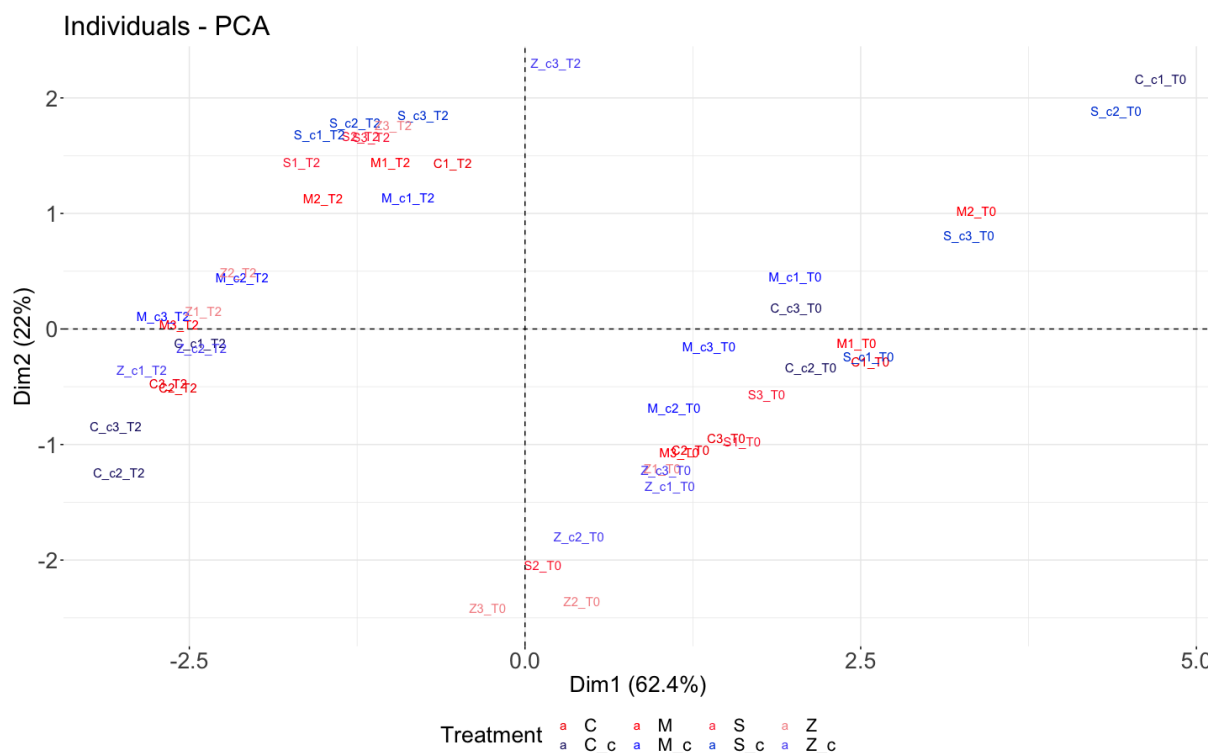


Figure 41 Score plot based on the classification of volatile compound groups concentration ($\mu\text{g/L}$), according to different sampling points, to analyze the behavior between the first (T0) and the last sampling point (T2). The legend displays the different treatments applied.

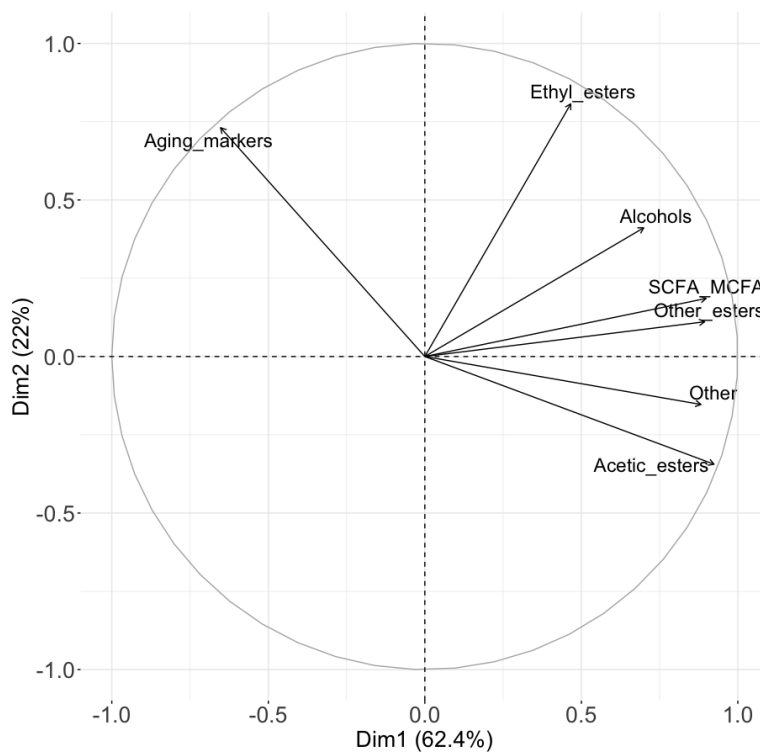


Figure 42 Loading plot of the concentration ($\mu\text{g/L}$) of volatile composition based on the volatile group classification. Abbreviation SCFA_MCFA: Short and Medium Chain Fatty Acids.

Evaluation of the effect of treatments on the parameters analyzed by sensory analysis

During the experiment, a sensory analysis was carried out to evaluate the perception of the evolution-related characteristics.

As previously described for other variables, the greatest change appears to be related to variations obtained between the first and second sampling points Figure 43 and Figure 44. Although the second sampling point at seven months after the start of the project appears to be more characterized by notes of reduction, which are correlated with the generalized reduction in the volatile component, it has less impact given the explained variance of dimension 2. The third sampling point, at eleven months from the start of the experiment, shows an oxidation character, in agreement with the increase of compounds related to the category of evolution markers.

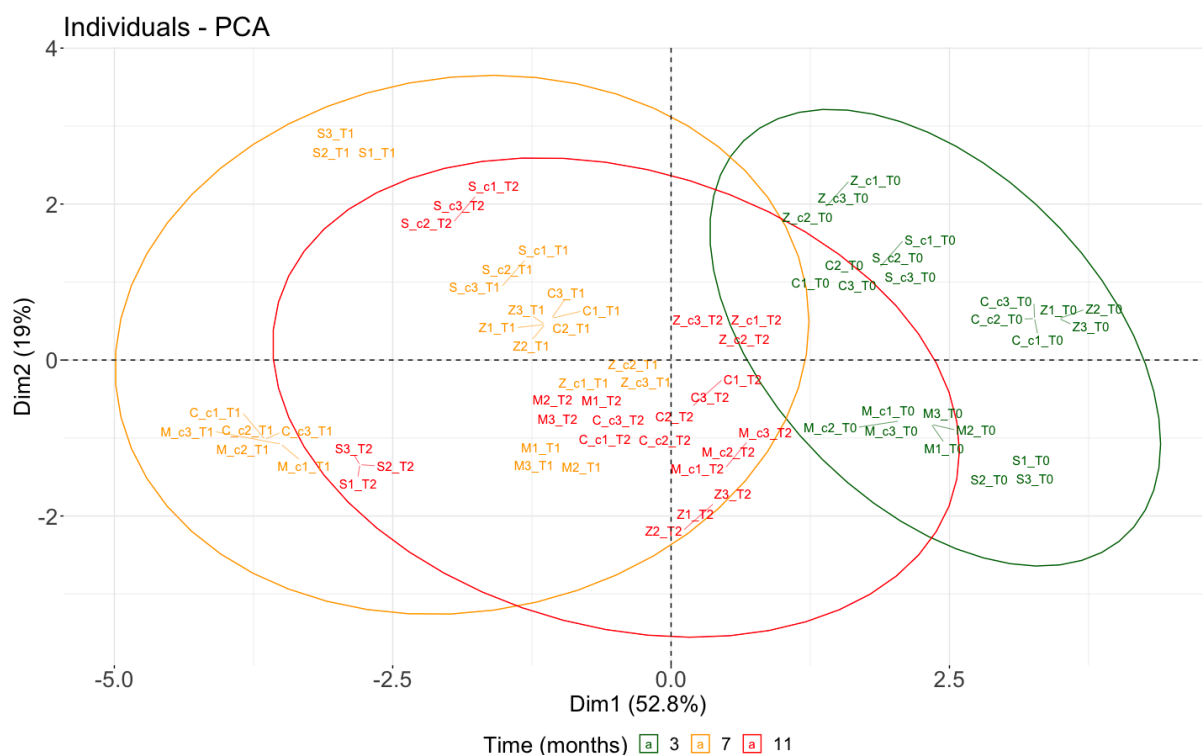


Figure 43 Score plot based on the parameters analyzed through the sensory analysis. The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.

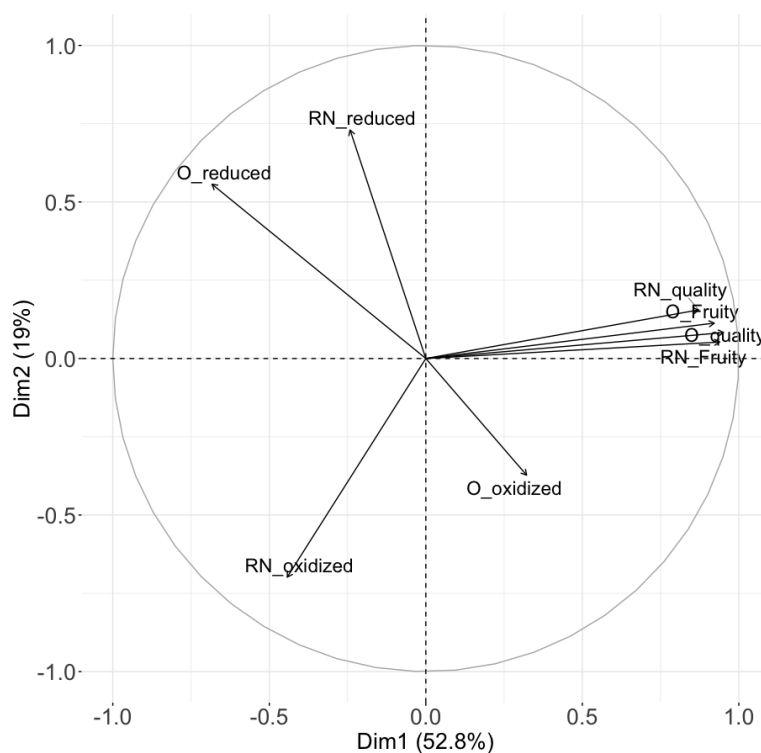


Figure 44 Loading plot based on the sensory analysis. Abbreviation *O_quality*: Olfactory perceived quality; *O_reduced*: Olfactory reduced aroma; *O_oxidized*: Olfactory oxidized aroma; *O_fruity*: Olfactory fruity aroma; *RN_quality*: Retro nasal perceived quality; *RN_reduced*: Retro nasal reduced aroma; *RN_oxidized*: Retro nasal oxidized aroma; *RN_fruity*: Retro nasal fruity aroma.

The analysis of variance carried out on the sensory analysis data, shown significant differences on closure application in terms of both olfactory and retro-olfactory reduced descriptors, as well as in terms of the retro-olfactory oxidized parameter (

Table 41). The Saranex liner was found to be more susceptible to oxidized scent occurrence compared to the liner M, while the latter recorded higher values for reduced perception, particularly during retro-nasal.

The treatment showed low significant difference, except for the higher oxidation perceived during retro-smell in the control, untreated sample.

Table 41 The impact of closure (C), treatment (T), and their combined effect (C X T) on the parameters analyzed by sensory analysis, throughout the whole experiment.

Variables	Effect of the Closure (C)				Effect of the Treatment (T)				C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T	
Olfactory perceived quality	4.87	4.45	4.99	5.13	ns	4.93	4.79	ns	ns
Olfactory reduced aroma	1.48	1.50	1.59	1.31	ns	1.41	1.53	ns	***
Olfactory oxidized aroma	0.69 a	1.17 b	0.72 a	0.68 a	***	0.77	0.86	ns	ns
Olfactory fruity aroma	3.32	3.08	3.00	3.42	ns	3.33	3.07	ns	ns
Retro nasal perceived quality	4.17	4.33	4.17	4.63	ns	4.37	4.28	ns	ns
Retro nasal reduced aroma	1.04 ab	1.06 ab	1.31 b	0.81 a	***	1.16 b	0.95 a	*	***
Retro nasal oxidized aroma	0.60 bc	0.73 c	0.44 a	0.52 ab	***	0.55	0.60	ns	***
Retro nasal fruity aroma	2.79	2.86	2.90	2.99	ns	2.91	2.87	ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Analyzing the sampling in more detail the first sampling point, it can be seen that no significant differences were observed in the data analysis related to the first sampling point (Table 42).

Table 42 The impact of closure (C), treatment (T), and their combined effect (C X T) on the parameters analyzed by sensory analysis at the first sampling point, after three months after bottling.

Variables	Effect of the Closure (C)				Effect of the Treatment (T)				C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T	
Olfactory perceived quality	6.05	5.52	5.94	6.14	ns	6.08	5.75	ns	ns
Olfactory reduced aroma	1.93	2.28	1.95	1.21	ns	1.80	1.89	ns	ns
Olfactory oxidized aroma	0.66	0.54	0.58	0.70	ns	0.45	0.79	ns	ns
Olfactory fruity aroma	5.02	4.99	4.36	4.68	ns	4.77	4.76	ns	ns
Retro nasal perceived quality	4.49	5.18	4.72	5.02	ns	4.92	4.78	ns	ns
Retro nasal reduced aroma	0.68	1.12	1.10	0.44	ns	0.92	0.75	ns	ns
Retro nasal oxidized aroma	0.73	0.70	0.40	0.58	ns	0.53	0.66	ns	ns
Retro nasal fruity aroma	4.32	4.09	4.09	3.89	ns	4.05	4.14	ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Comparing the sensory analysis values obtained after three and seven months, it is possible to observe a significant reduction in the perceived quality values and fruity character (Table 43). This phenomenon was more pronounced in the samples that were sealed with cork closures. These samples received slightly higher scores for perceived quality and fruity character, while receiving lower scores for the perception of oxidized and reduced characteristics. Regarding the treatment, the control group received slightly higher scores, indicating a more open and ready wine, which is consistent with the data obtained at the first sampling point.

However, no significant differences were observed in the second sampling point.

Table 43 The impact of closure (C), treatment (T), and their combined effect (C X T) on the parameters analyzed by sensory analysis at the second sampling point, after seven months after bottling.

Variables	Effect of the Closure (C)				Effect of the Treatment (T)				C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T	
Olfactory perceived quality	3,81	4.21	4.08	4.32	ns	4.20	4.01	ns	ns
Olfactory reduced aroma	1,45	0.79	1.65	1.42	ns	1.18	1.48	ns	ns
Olfactory oxidized aroma	1.00	1.63	0.89	0.88	ns	1.12	1.08	ns	ns
Olfactory fruity aroma	1.74	2.16	1.81	2.79	ns	2.38	1.87	ns	ns
Retro nasal perceived quality	3.87	4.05	3.37	4.18	ns	4.13	3.61	ns	ns
Retro nasal reduced aroma	1.46	0.93	1.54	0.97	ns	1.07	1.39	ns	ns
Retro nasal oxidized aroma	0.71	0.85	0.54	0.58	ns	0.69	0.66	ns	ns
Retro nasal fruity aroma	1.66	2.37	1.85	2.31	ns	2.12	1.97	ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

At the final sampling point (Table 44), a slight increase in perceived quality was observed for the analyzed samples, except for the Saranex liner, which registered a higher value of oxidized aroma during olfactory perception compared to other closures.

Table 44 The impact of closure (C), treatment (T), and their combined effect (C X T) on the parameters analyzed by sensory analysis at the third sampling point, after eleven months after bottling.

Variables	Effect of the Closure (C)				Effect of the Treatment (T)			C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T
Olfactory perceived quality	4.75	3.63	4.94	4.92	ns	4.52	4.60	ns
Olfactory reduced aroma	1.05	1.43	1.19	1.30	ns	1.27	1.21	ns
Olfactory oxidized aroma	0.42 a	1.34 b	0.69 ab	0.45 a	*	0.75	0.71	ns
Olfactory fruity aroma	3.19	2.09	2.81	2.78	ns	2.85	2.59	ns
Retro nasal perceived quality	4.13	3.76	4.42	4.68	ns	4.06	4.44	ns
Retro nasal reduced aroma	0.97	1.13	1.30	1.01	ns	1.49	0.72	ns
Retro nasal oxidized aroma	0.37	0.64	0.39	0.39	ns	0.42	0.48	ns
Retro nasal fruity aroma	2.40	2.13	2.78	2.77	ns	2.55	2.49	ns

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

Finally, distances on the factorial plane were calculated based on the PCA (Table 49), shown in Figure 45 and Figure 46, using data from the first and last sampling points. The liner M closure exhibited the least overall variation considering both treatments, while the liner Z samples with dissolved gas management showed the least variation over time.

The oxygen present in the closure may have been released into the bottle, in the case of cork, resulting in higher levels of dissolved oxygen in these samples compared to those with screw caps, as shown in Figure 45 and Figure 46.

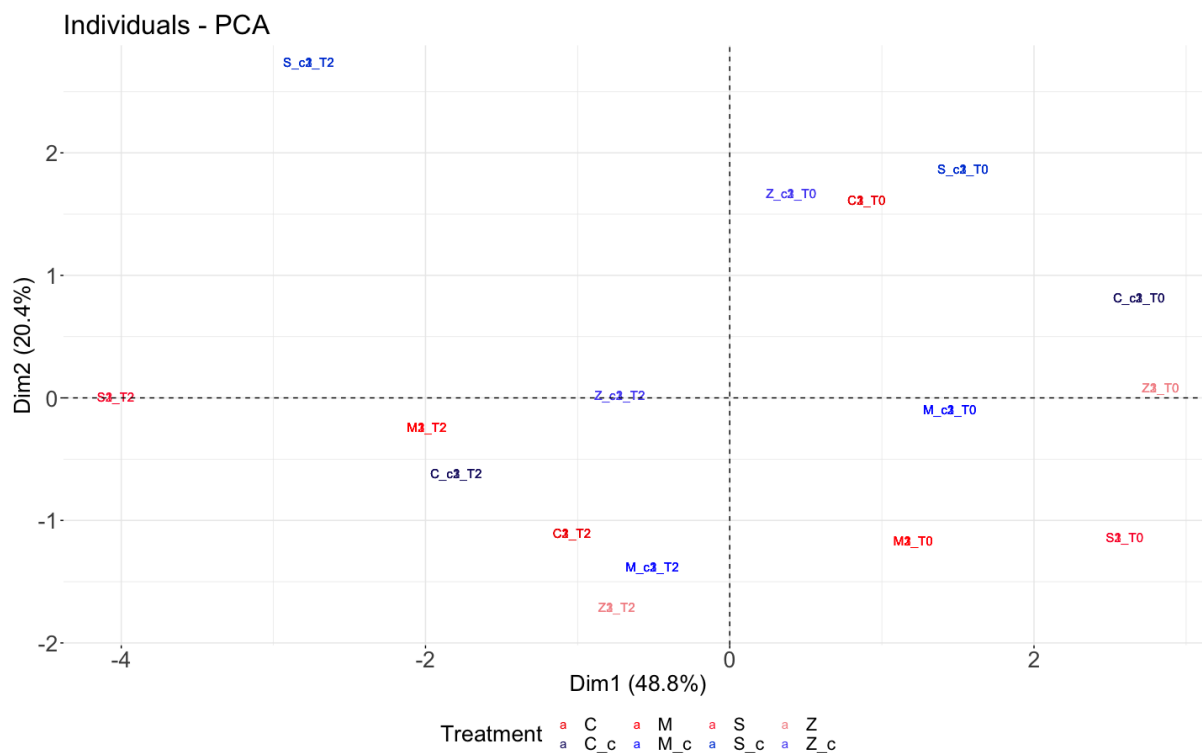


Figure 45 Score plot based on the parameters analyzed through the sensory analysis, to analyze the behavior between the first (T0) and the last sampling point (T2). The legend displays the different treatments applied.

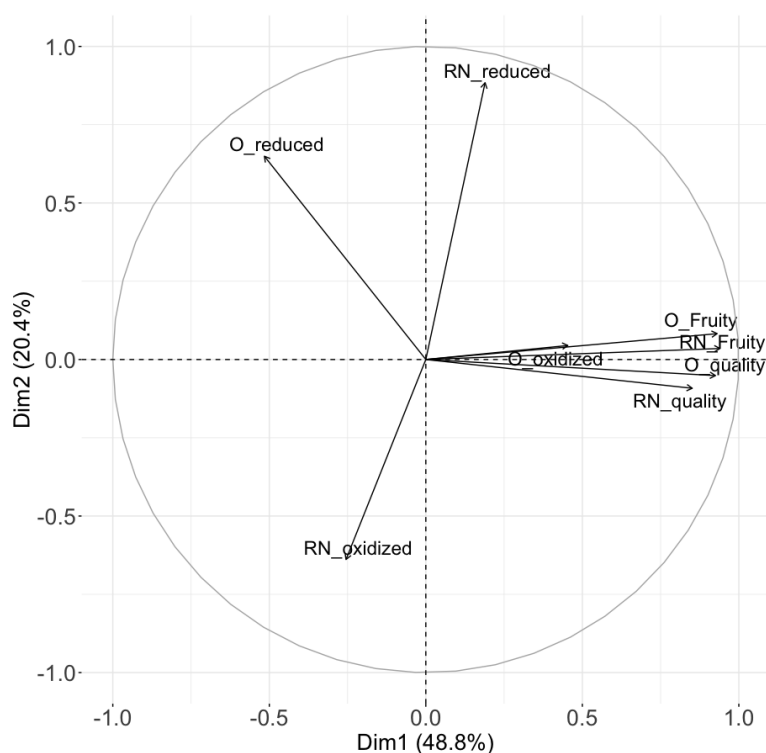


Figure 46 Loading plot base on the sensory analysis. Abbreviation O_quality: Olfactory perceived quality; O_reduced: Olfactory reduced aroma; O_oxidized: Olfactory oxidized aroma; O_fruity: Olfactory fruity aroma; RN_quality: Retro nasal perceived quality; RN_reduced: Retro nasal reduced aroma; RN_oxidized: Retro nasal oxidized aroma; RN_fruity: Retro nasal fruity aroma.

Evaluation of the effect of treatments on the composition of carbonyl compounds

As discussed before carbonyl compounds, are a group of molecules derived from evolution related processes. In this study, the PCA analysis in Figure 47 and Figure 48, showed a good clustering of the samples analyzed, based on sampling points. At the first sampling point, three months after the start of the experiment, the samples appear to be homogeneous. However, at the second sampling point, there are significant differences in the screw-cap samples presented by the liner M, which have a higher concentration of carbonyl compounds compared to the other samples. There were no differences found regarding the treatments. At the final sampling point, after eleven months, there was a significant increase in acetaldehyde, glycolaldehyde, 2-furaldehyde and methylglyoxal contents. However, the use of the contactor treatment for oxygen management and the liners M and Saranex resulted in a better performance, with a lower total content of carbonyl compounds.

According to the collected data, liner M consistently recorded higher levels of carbonyl compounds compared to the other closures (Table 45).

However, when evaluating the effect of treatment, the content seems to be higher in the control samples, but not significantly different from the treated samples.

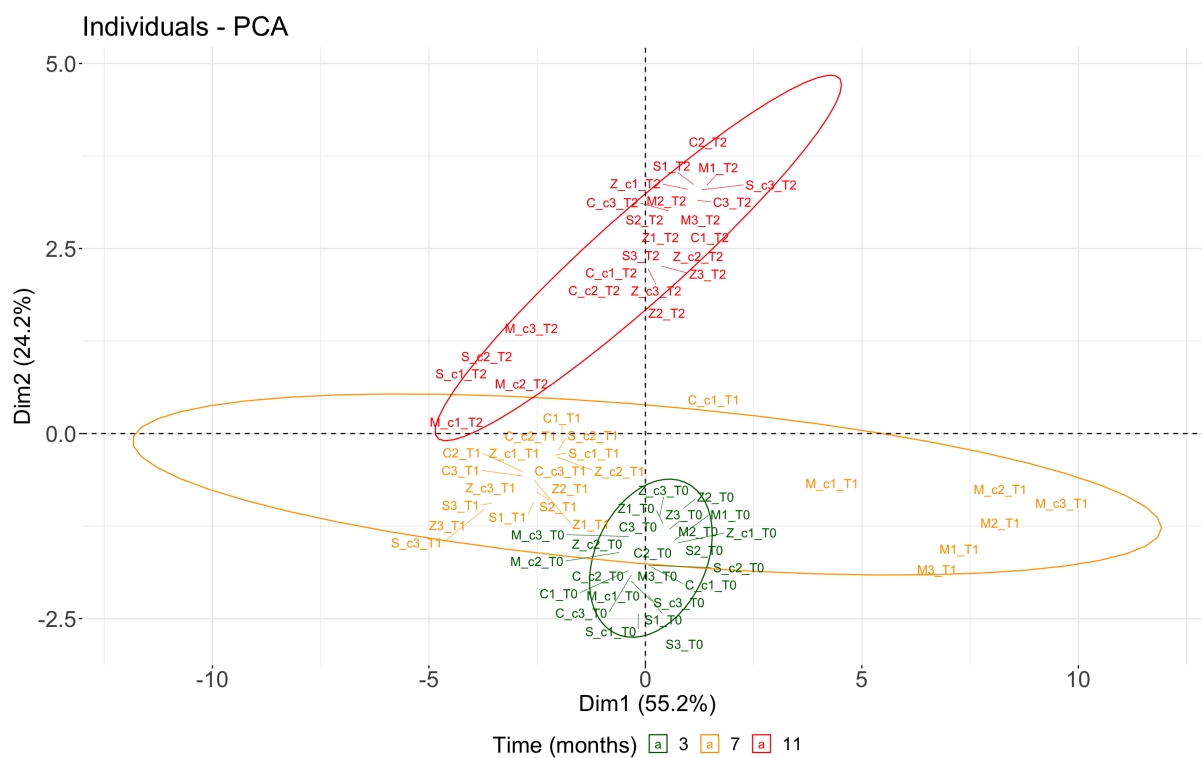


Figure 47 Score plot based on the absolute area of carbonyl compounds. The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.

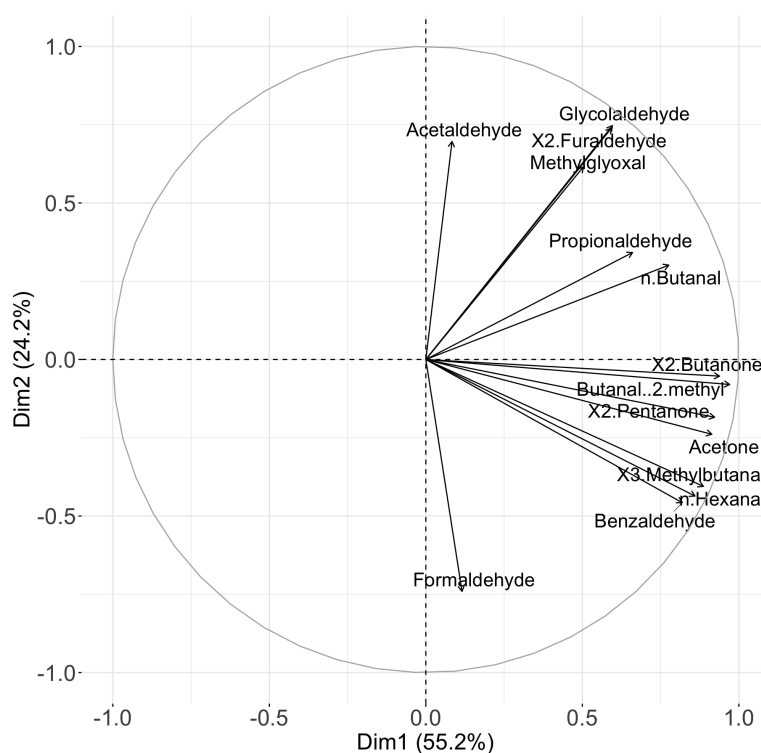


Figure 48 Loading plot based on the absolute area of carbonyl compounds.

Table 45 The impact of closure (C), treatment (T), and their combined effect (C X T) on the absolute area of carbonyl compounds, throughout the whole experiment.

Variables	Effect of the Closure (C)					Effect of the Treatment (T)			C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T	
Formaldehyde	2786236	2981602	2474346	2265684	ns	2749473	2504461	ns	ns
Acetaldehyde	539437347	551604043	543292198	558175332	ns	555084756	541169704	ns	ns
Acetone	24920720	b 21690144	a 30360694	c 22487214	ab ***	25160474	24568911	ns	ns
n-Butanal	16366804	b 14729945	a 19454309	c 15573608	ab *	16866293	16196040	ns	ns
Propionaldehyde	12416423	c 8452405	a 10327924	b 8996274	a ***	10329306	9767207	ns	ns
2-Butanone	2188502	a 1975325	a 2894206	b 2203349	a **	2480994	2149696	ns	ns
Pentanone	465549	a 424577	a 905613	b 455683	a ***	585902	539810	ns	ns
2-Methylbutanal	8612407	a 8633923	a 12651856	b 9130017	a ***	10123430	9390671	ns	ns
3-Methylbutanal	11369751	a 12092853	a 16060335	b 12247277	a **	13426703	12458405	ns	ns
n-Hexanal	9200532	a 9960779	ab 13807810	c 10505082	b **	11083128	10653974	ns	ns
Glycolaldehyde	1091169	1159159	1417399	1176882	ns	1298743	1123561	ns	ns
2-Furaldehyde	5439174	4529249	6446003	4558284	ns	5589153	4897203	ns	ns
Benzaldehyde	734789	a 825985	a 1181349	b 823990	ab **	948335	834722	ns	ns
Methylglyoxal	4278202	3987713	4360626	4251805	ns	4287573	4151600	ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

As previously discussed, the data obtained during the first sampling point showed sufficient homogeneity among the different treatments used (Table 46). Significant differences were highlighted in the evaluation of variance based on closure. However, it is not possible to identify which type has been most affected by the evolution. This group of compounds requires extended periods of evolution or high temperatures to accumulate substantial amounts of these substances, ultimately affecting the sensory aspect. As a general trend, it is important to note that the untreated samples showed higher values for the absolute area of carbonyl compounds, although this difference does not appear to be statistically significant.

1

Table 46 The impact of closure (C), treatment (T), and their combined effect (C X T) on the absolute area of carbonyl compounds at the first sampling point, after three months after bottling.

Variables	Effect of the Closure (C)								Effect of the Treatment (T)					C X T	
	Cork		Saranex		Liner M		Liner Z		C	Control		Treated			T
Formaldehyde	5181829	b	5414575	b	3781196	a	3256197	a	***	4554512		4262387		ns	ns
Acetaldehyde	536576878		541807526		547233898		561833801		ns	555540621		538185431		ns	ns
Acetone	25641620		24689884		26478566		24496384		ns	25866203		24787024		ns	ns
n-Butanal	11653411	a	12838611	ab	13247720	b	13212491	b	**	12804834		12671282		ns	ns
Propionaldehyde	10872441	b	9674066	a	9412421	a	10076677	ab	**	10102711		9915091		ns	ns
2-Butanone	2334584	a	2372808	ab	2613861	b	2582644	b	**	2595797	b	2356152	a	**	**
Pentanone	545314		543107		566599		549803		ns	542763		559649		ns	*
2-Methylbutanal	9789845	a	10497536	b	10744824	b	10828108	b	**	10648520	a	10281637	b	*	ns
3-Methylbutanal	14311290	a	16217171	c	14593556	ab	15946739	bc	**	15845642	b	14688736	a	**	ns
n-Hexanal	11654278	a	13562667	b	13006351	b	14652671	c	***	13123647		13314336		ns	**
Glycolaldehyde	797987		912391		886768		933597		ns	992361	b	773011	a	***	ns
2-Furaldehyde	2978304	b	2325346	a	2110333	a	2270152	a	**	2638922	b	2203145	a	**	ns
Benzaldehyde	974202		1197253		1071596		1145352		ns	1247212	b	946990	a	***	ns
Methylglyoxal	4427795		4126755		3798039		4296488		ns	4218367		4106171		ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

2

The data from the first and second sampling points were compared and a slight increase in the overall content of carbonyl compounds was observed (Table 47). The analysis of variance revealed numerous significant differences, and the liner M showed an overall significant increase in the different compounds analyzed.

From a treatment specific point of view, the differences were slight and limited to only two compounds, propionaldehyde and methylglyoxal. Contactor treatment, although not significant, led to more carbonyl compounds.

1 Table 47 The impact of closure (C), treatment (T), and their combined effect (C X T) on the absolute area of carbonyl compounds at the second sampling point, after seven months after bottling.

Variables	Effect of the Closure (C)						Effect of the Treatment (T)						C X T		
	Cork		Saranex		Liner M		Liner Z		C		Control			Treated	
Formaldehyde	2007126		2316512		2459727		1964541		ns	2329553		2044400		ns	ns
Acetaldehyde	503893134		511190406		505391949		511781700		ns	503779534		512349060		ns	ns
Acetone	24253100	a	20344805	a	44892053	b	20374722	a ***	26486923		28445417		ns	ns	
n-Butanal	18959908	b	14479335	a	29359669	b	14907883	a ***	18533350		20320047		ns	ns	
Propionaldehyde	10899748	a	6247871	a	12912573	b	6498359	a ***	8590997	a	9688279	b *	ns		
2-Butanone	1531617	a	1505994	a	4242025	b	1517729	a ***	2214218		2184465		ns	ns	
Pentanone	336247	a	288517	a	1734822	b	303067	a ***	693524		637802		ns	ns	
2-Methylbutanal	6361455	a	6136149	a	18489417	b	6263332	a ***	9213203		9411974		ns	ns	
3-Methylbutanal	9722399	a	9413130	a	23982267	b	9349906	a ***	12738549		13495301		ns	ns	
n-Hexanal	7861622	a	7620993	a	20595028	b	7591149	a ***	10632691		11201704		ns	ns	
Glycolaldehyde	833115	a	877316	a	1760993	b	841564	a ***	1043908		1112586		ns	ns	
2-Furaldehyde	4760900	a	3651136	a	9890997	b	3347524	a ***	5278782		5546497		ns	ns	
Benzaldehyde	638257	a	691061	a	1861800	b	647067	a ***	926671		992421		ns	ns	
Methylglyoxal	2825469	a	3011775	a	4469588	b	2836565	a ***	2993053	a	3578646	b ***	ns		

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Finally, the analysis of the results obtained in the latter sampling point showed a separation of the samples (Table 48). Specifically, the Saranex and liner M showed a slight increase in the content of carbonyl compounds. Significant differences were found in the analysis of variance regarding the treatment aimed at managing dissolved gases, which provided greater protection against evolution, resulting in a lower overall concentration of carbonyl compounds.

After evaluating the combined effect of the treatment and closure, significant differences in various compounds based on the analysis of variance were found. The combination of Saranex and liner M, along with the use of the contactor membrane, was the most effective on wine preservation from oxidative processes.

Table 48 The impact of closure (C), treatment (T), and their combined effect (C X T) on the absolute area of carbonyl compounds at the third sampling point, after eleven months after bottling.

Variables	Effect of the Closure (C)								Effect of the Treatment (T)					C X T	
	Cork		Saranex		Liner M		Liner Z		C	Control		Treated			T
Formaldehyde	1169752		1213720		1182115		1576314		ns	1364353		1206598		ns	ns
Acetaldehyde	577842030	a	601814196	a	577250748	a	600910496	a	*	605934113	b	572974622	a	***	ns
Acetone	24867440	b	20035742	a	19711463	a	22590534	ab	**	23128297	b	20474292	a	**	*
n-Butanal	18487094		16871888		15755539		18600449		ns	19260695	b	15596789	a	***	**
Propionaldehyde	15477080	c	9435279	ab	8658777	a	10413785	b	***	12294209	b	9698252	a	***	*
2-Butanone	2699305	c	2047172	ab	1826731	a	2509673	bc	***	2632967	b	1908473	a	***	ns
Pentanone	515087	b	442106	a	415420	a	514180	b	***	521418	b	421979	a	***	***
2-Methylbutanal	9685920		9268083		8721327		10298611		ns	10508568	b	8478402	a	***	**
3-Methylbutanal	10075563		10648259		9605182		11445187		ns	11695918	b	9191178	a	***	**
n-Hexanal	8085695		8698678		7822053		9271426		ns	9493045	b	7445881	a	***	*
Glycolaldehyde	1642404		1687769		1604436		1755486		ns	1859961	b	1485087	a	*	*
2-Furaldehyde	8578319		7611266		7336681		8057175		ns	8849754	b	6941966	a	**	**
Benzaldehyde	591908		589642		610650		679550		ns	671121	b	564754	a	*	**
Methylglyoxal	5581342		4824610		4814249		5622361		ns	5651298	b	4769983	a	*	**

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

Based on the data from the three and eleven-month samplings (Figure 49 and Figure 50), the greatest difference was related to the use of dissolved gas management and the use of Saranex liners. Instead, it is due to a smaller increase in such compounds during the experiment. The variance analysis indicates that the M liner has the lowest concentration of these compounds.

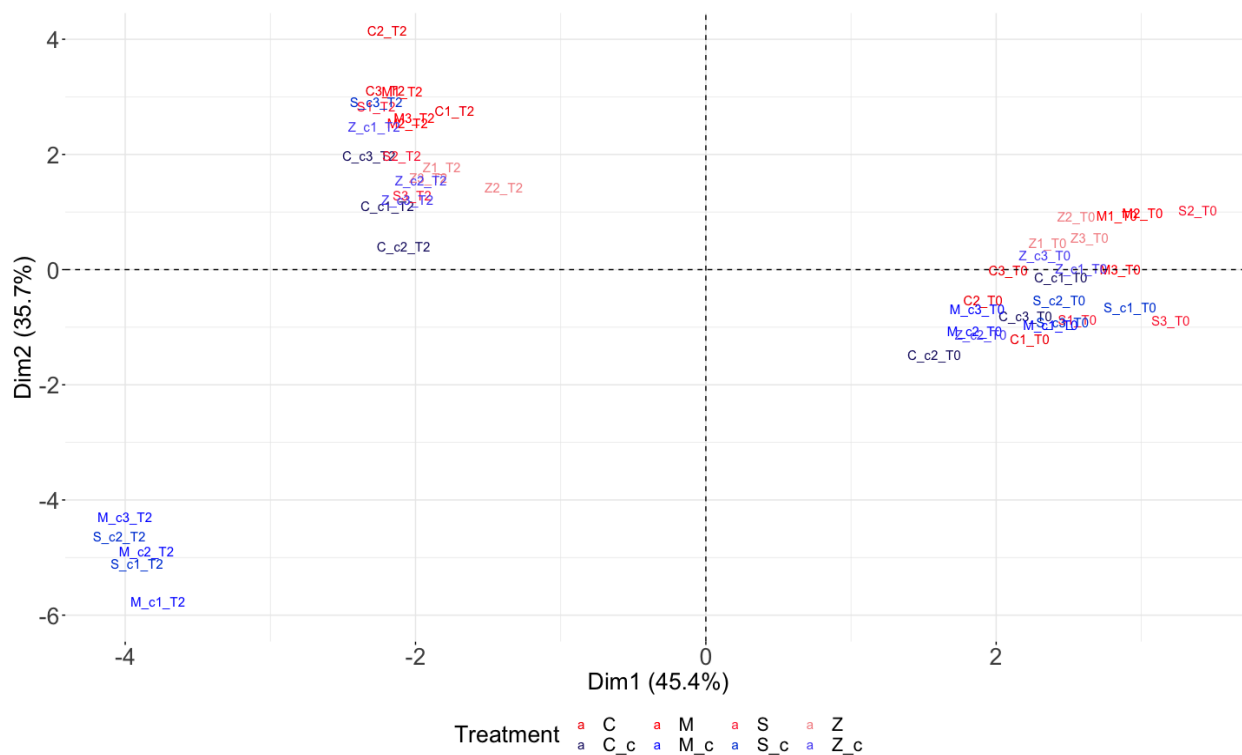


Figure 49 Score plot based on the absolute area of carbonyl compounds, to analyze the behavior between the first (T0) and the last sampling point (T2). The legend displays the different treatments applied.

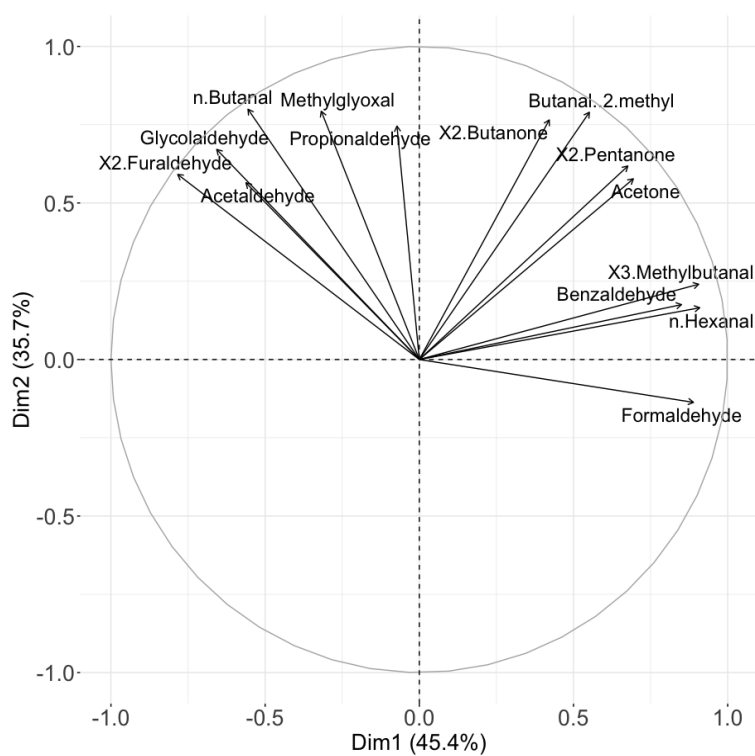


Figure 50 Loading plot based on the absolute area of carbonyl compounds.

Table 49 Distances on the factorial plane based on the PCA of the different categories of parameters analyzed; values reported represent the average relative to the analyzed replications.

	chemical parameters	volatile composition	sensory analysis	carbonyl compounds
C	4,41	3,86	3,33	5,71
C_c	2,44	5,97	4,71	4,73
S	2,88	3,9	6,73	5,77
S_c	3,04	4,79	4,38	7,3
M	4,56	4,18	3,32	5,4
M_c	4,8	3,48	2,33	7,19
Z	4,02	3,91	4	4,34
Z_c	3,25	3,64	1,99	4,88

Evaluation of the effect of treatments on cyclic voltammetry

Finally, the obtained results from the cyclic voltammetry analysis are not in accordance with the expectations. The literature and experimental experience suggest a gradual reduction in the anodic plot related to the analysis throughout the project. However, as shown in the related PCA in Figure 51 and Figure 52, the change in the anodic plot is reverse to the trend.

At the first sampling point, three months after the start of the experiment, the samples treated by the contactor membrane recorded a voltammogram that tended to be slightly higher, and therefore potentially higher in evolutionary potential. At the second sampling point, there was a significant increase in voltammogram with high sample dispersion. However, the control samples tended to record a higher current along the anodic trace. At eleven months, there is no discernible treatment pattern, but the liner M and Saranex consistently recorded higher current values.

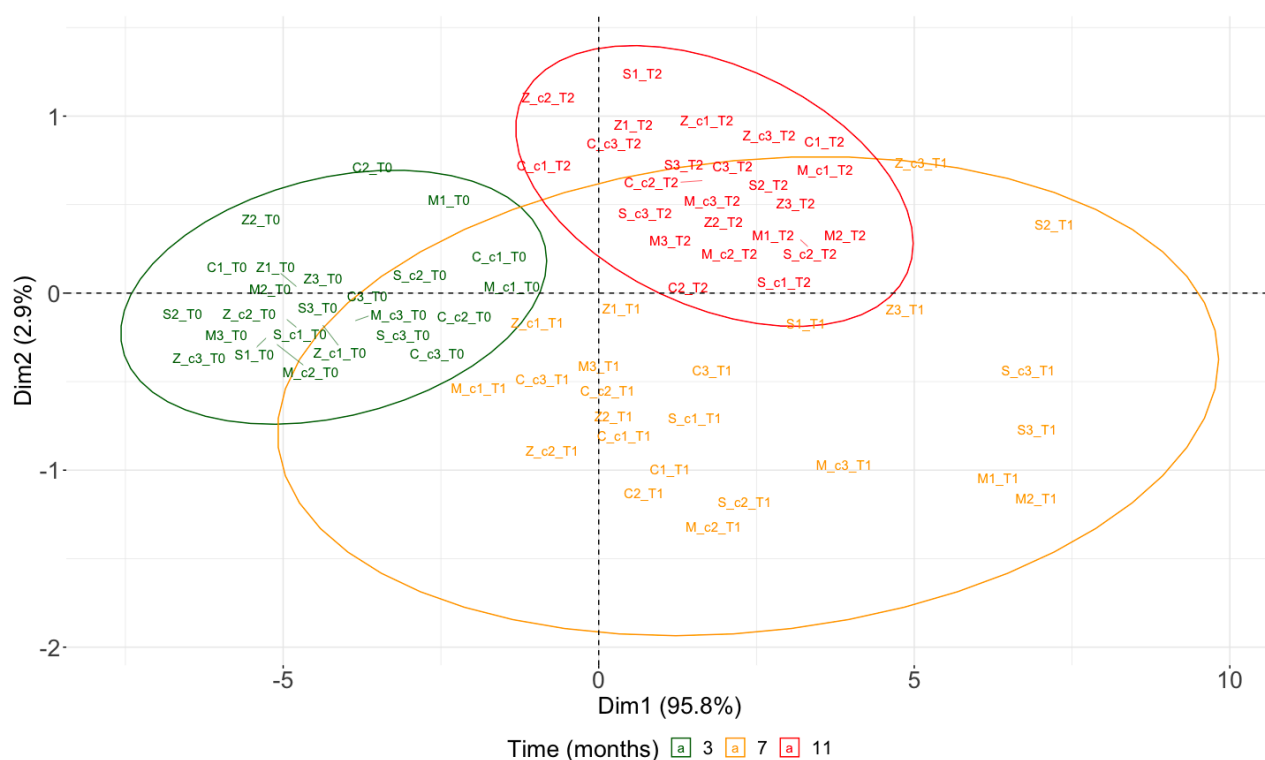
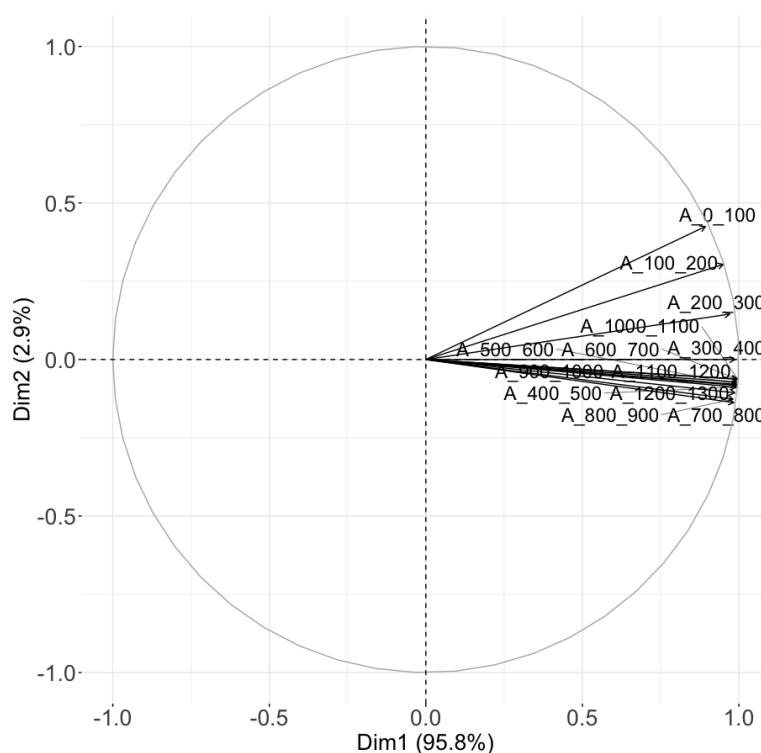


Figure 51 Score plot based on the cyclic voltammetry. The groups were clustered according to the different sampling points. The legend displays the time, in months, for each sampling point from the start of the experiment.



However, Saranex and liner M recorded values that were generally higher than cork and liner Z. This represents a higher evolution potential of the bottled wine.

Table 50 The impact of closure (C), treatment (T), and their combined effect (C X T) on the parameters obtained cyclic voltammetry, throughout the whole experiment.

Variables	Effect of the Closure (C)				Effect of the Treatment (T)				C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T	
A_0_100	85.1	98.9	92.6	94.3	ns	95.2	90.2	ns	ns
A_100_200	171.7	192.0	183.82	173.9	ns	185.6	175.1	ns	ns
A_200_300	413.5	460.3	448.4	407.5	ns	442.4	422.5	ns	ns
A_300_400	733.6	759.9	750.4	716.3	ns	742.3	737.8	ns	ns
A_400_500	1008.5	1049.6	1040.0	991.1	ns	1025.0	1019.6	ns	ns
A_500_600	1371.6	1435.7	1421.6	1354.0	ns	1401.9	1389.5	ns	ns
A_600_700	2035.4	2153.2	2133.3	2011.1	ns	2098.2	2068.2	ns	ns
A_700_800	2829.2	2934.9	2919.2	2804.0	ns	2878.8	2864.9	ns	ns
A_800_900	3538.4	3706.0	3689.3	3529.9	ns	3634.9	3596.9	ns	ns
A_900_1000	4575.8	4844.7	4826.5	4569.3	ns	4746.1	4662.1	ns	ns
A_1000_1100	6294.2	6717.2	6693.2	6268.4	ns	6571.4	6415.0	ns	ns
A_1100_1200	9202.0	9817.1	9782.8	9113.7	ns	9602.9	9354.8	ns	ns
A_1200_1300	13695.0	14503.8	14462.1	13501.6	ns	14208.9	13872.4	ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

In the cyclic voltammetry anodic trace integral, significant differences were observed between 300 and 400 mV, 700 and 800 mV, and finally between 1200 and 1300 mV at the first sampling point (Table 51). Samples sealed with cork closure were found to have a larger integral area in these parts of the curve.

Regarding the dissolved gas management treatment, the integral was found to be significantly different between 400 and 1300 mV for samples treated with a membrane contactor.

Table 51 The impact of closure (C), treatment (T), and their combined effect (C X T) on the parameters obtained cyclic voltammetry at the first sampling point, after three months after bottling.

Variables	Effect of the Closure (C)				Effect of the Treatment (T)				C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T	
A_0_100	62	41	51	39	ns	46	51	ns	ns
A_100_200	125	95	110	92	ns	101	110	ns	ns
A_200_300	286	241	273	239	ns	250	269	ns	ns
A_300_400	628	a 553	a 584	a 545	a *	559	595	ns	ns
A_400_500	884	819	851	809	ns	814	a 867	b *	ns
A_500_600	1211	1135	1176	1117	ns	1124	a 1195	b **	ns
A_600_700	1739	1639	1706	1614	ns	1623	a 1726	b **	ns
A_700_800	2564	b 2420	ab 2501	ab 2380	a *	2398	a 2534	b **	ns
A_800_900	3197	3030	3128	2969	ns	2995	a 3167	b *	ns
A_900_1000	4026	3792	3930	3696	ns	3748	a 3974	b *	ns
A_1000_1100	5395	5058	5234	4899	ns	4994	a 5299	b *	ns
A_1100_1200	7765	7276	7477	7019	ns	7172	a 7597	b *	ns
A_1200_1300	11630	b 10962	ab 11153	ab 10543	a *	10779	a 11364	b *	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

The differences between the obtained data are less significant when compared to the sampling point at three months from the beginning of the experiment (Table 52).

Table 52 The impact of closure (C), treatment (T), and their combined effect (C X T) on the parameters obtained cyclic voltammetry at the second sampling point, after seven months after bottling.

Variables	Effect of the Closure (C)				Effect of the Treatment (T)				C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T	
A_0_100	73	129	99	111	ns	114	92	ns	ns
A_100_200	161	244	200	197	ns	217	183	ns	ns
A_200_300	426	a 584	b 505	ab 461	ab *	526	463	ns	ns
A_300_400	772	a 905	b 851	ab 807	ab *	861	806	ns	ns
A_400_500	1062	1232	1166	1094	ns	1175	1102	ns	ns
A_500_600	1433	1678	1580	1487	ns	1597	1492	ns	ns
A_600_700	2149	2542	2373	2217	ns	2403	2238	ns	ns
A_700_800	2979	3393	3232	3081	ns	3264	3079	ns	ns
A_800_900	3726	4319	4100	3888	ns	4146	3871	ns	ns
A_900_1000	4835	5720	5405	5061	ns	5464	5046	ns	ns
A_1000_1100	6697	8004	7530	6983	ns	7609	6998	ns	ns
A_1100_1200	9877	a 11723	a 11051	a 10209	a *	11140	10291	ns	ns
A_1200_1300	14788	a 17216	b 16355	ab 15153	ab *	16432	15324	ns	ns

ns: 'not significant'; p < 0.05: '*'; p < 0.01: '**'; p < 0.001: '***'

At the final sampling point, this mechanism persists for some samples, resulting in greater homogeneity among the treatments used and no significant differences between the analyzed samples (Table 53).

Table 53 The impact of closure (C), treatment (T), and their combined effect (C X T) on the parameters obtained cyclic voltammetry at the third sampling point, after eleven months after bottling.

Variables	Effect of the Closure (C)				Effect of the Treatment (T)				C X T
	Cork	Saranex	Liner M	Liner Z	C	Control	Treated	T	
A_0_100	119	126	127	131	ns	124	127	ns	ns
A_100_200	228	236	240	232	ns	237	231	ns	ns
A_200_300	527	554	565	521	ns	550	534	ns	ns
A_300_400	800	820	815	796	ns	805	811	ns	ns
A_400_500	1078	1097	1101	1069	ns	1084	1088	ns	ns
A_500_600	1470	1493	1508	1456	ns	1483	1481	ns	ns
A_600_700	2217	2277	2319	2201	ns	2268	2240	ns	ns
A_700_800	2943	2991	3023	2950	ns	2973	2980	ns	ns
A_800_900	3691	3768	3838	3731	ns	3762	3752	ns	ns
A_900_1000	4865	5020	5143	4949	ns	5025	4964	ns	ns
A_1000_1100	6789	7088.7	7314	6922	ns	7109	6948	ns	ns
A_1100_1200	9962	10450.6	10819	10112	ns	10496	10176	ns	ns
A_1200_1300	14666	15332.8	15878	14807	ns	15414	14928	ns	ns

ns: 'not significant'; $p < 0.05$: '*'; $p < 0.01$: '**'; $p < 0.001$: '***'

The results obtained from the voltammetry test will not be further discussed due to their anomalous nature compared to the literature.

To investigate this phenomenon, ethanol content and pH value of the samples, which could have affected the measurements, were evaluated, but no significant differences were found between the samples.

4. Conclusion

The management of dissolved gases, principally the management of oxygen in the bottling stage, through the use of contactor membranes, is an enological technique of recent application, for which not many studies have been published. However, it is an efficient technique for reducing the dissolved oxygen content in bottled wine, which helps to preserve the wine in the short term. The investigation carried out show that the effect is also present in the long term. The reduction of dissolved oxygen content is optimized by using screw caps instead of cork closures.

Furthermore, this technique did not have a negative impact on the volatile component, which involves similar devices but different membrane characteristics. Specifically, the use of the contactor membrane resulted in higher quality ratings in sensory analysis and a lower presence of carbonyl compounds, which are linked to oxidative pathways as described in previous chapters and which may be used as markers of evolution.

From the closure perspective, basing on the analyses performed, there are no clear differences between the closures used, except for the analysis of carbonyl compounds, that resulted less present with liner 'M' and Saranex, resulting in a lower oxidative impact on the samples.

Further experiments are necessary to understand the interaction between contactor membrane treatment, different available closures, and their relationship with different enological production techniques and approaches. Finally, more extensive experiments could provide further information on the evolution for different factors.

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