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Air saturation methodology proposal for the analysis of wine oxygen consumption kinetics

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ABSTRACT

The great heterogeneity currently present when characterizing wine consumption kinetics means that a saturation method, as well as different parameters that allow comparison between wines, need to be established. The aim of this work was to establish a robust method for a wine saturation protocol and compare different fitting models to approximate the oxygen consumption kinetics. To differentiate wines, parameters extracted from the oxygen consumption curves were studied and proposed. 72 young commercial wines (red, white and rosé) from different Spanish appellations of origin, varieties and vintages were used. The results revealed that 5 min was enough to saturate wines up to the maximum level for each one at 35 °C. The inverse curve fitting model showed the best results for all wines. Oxygen at half consumption time (O_{mid}) and time required to consume from 90% to 10% of the oxygen initially available ($\Delta t_{O\_90\_10}$) were the parameters that differentiated wines the most.

1. Introduction

The presence of oxygen is related to the phenomena that wine can undergo during the different processes of winemaking, aging and storage. The effect of these oxidation phenomena depends mainly on the concentration of oxygen present, the time of exposure to oxygen, the presence of protective agents and its composition (Ugliano, 2013) and temperature (Oliveira, Barros, Silva Ferreira, & Silva, 2015). It is usually accepted that a sudden oxidation is unfavorable, whereas a slow and continuous dissolution of oxygen can play a positive role in the evolution of wines. Therefore, the reactions occurring in wine associated with oxygen consumption have been the subject of studies and reviews detailing mechanistic aspects, reaction rates, and changes in wine composition (Bueno et al., 2018; Danilewicz & Standing, 2018; Kreitman, Danilewicz, Jeffery, & Elias, 2016; Nevares et al., 2017; Waterhouse & Laurie, 2006).

One of the most studied aspects is the oxygen consumption rate of wine (Ferreira, Carrascon, Bueno, Ugliano, & Fernandez-Zurbano, 2015; Marrufo-Curtido, Carrascón, Bueno, Ferreira, & Escudero, 2018; Nevares et al., 2017). The amount of oxygen that wines can consume when exposed to oxygen and the changes that occur, both chemically and sensorially, were evaluated in these studies. Although the approaches to establish the rate of oxygen consumption in wines were varied, that most commonly used was to saturate the wine with air. While in most cases the effect of a single saturation cycle was analyzed (Chinnici, Sonni, Natali, & Riponi, 2013; Comuzzo et al., 2015; Danilewicz, Seccombe, & Whelan, 2008; Fracassetti, Coetzee, Vanzo, Ballabio, & Du Toit, 2013; Kontoudakis & Clark, 2020; Martins, Monforte, & da Silva Ferreira, 2013; Nevares et al., 2017; Picariello, Gambuti, Petracca, Rinaldi, & Moio, 2018), there were several works in which the same wine was subjected to several consecutive saturation cycles (Bueno et al., 2018; Carrascón et al., 2018; Carrascón, Bueno, Fernandez-Zurbano, & Ferreira, 2017; Carrascón, Fernandez-Zurbano, Bueno, & Ferreira, 2015; Danilewicz & Standing, 2018; Ferreira et al., 2015; Gambuti, Picariello, Rinaldi, & Moio, 2018; Marrufo-Curtido et al., 2018). Wine composition affects the rate of oxygen consumption and for many years it was established that red wines could consume more oxygen than white wines (Danilewicz, 2016; Kreitman et al., 2016; Singleton, 1987), although other studies stated that both types of wine can consume similar amounts of oxygen (Nevares et al., 2017). The factors that most influence the rate of oxygen consumption in wine are environmental, such as storage temperature (Oliveira et al., 2015) and exposure to light (Rousseva, Kontoudakis, Schmidtke, Scollary, & Clark, 2016), and also the composition of the wine in phenolic compounds

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(Carrascón et al., 2015, 2018; Fracassetti et al., 2013), sulfur dioxide (Danilewicz & Standing, 2018; Danilewicz, 2016) and metal ion content (Cu, Fe and Mn) (Ferreira et al., 2015; Kontoudakis & Clark, 2020).

One of the critical points in the study of consumption kinetics is the air saturation procedure for wines. Some studies do not provide any information on the saturation procedure used, and in others it is very scarce; this, together with the great heterogeneity of the procedures, makes it difficult to make comparisons between the different studies. Many studies saturate the sample by stirring for a certain time, others by bubbling with air, and others with a mixture of gases. Thus, different authors (Carrascón et al., 2018, 2017, 2015; Ferreira et al., 2015; Marrufo-Curtido et al., 2018) performed agitation of the sample for 10 s, opening of the container to allow air to enter and again agitation for another 10 s, until the oxygen level of the wine reached 6 mg/L of dissolved oxygen. In this line, Garrido-Bañuelos et al. (Garrido-Bañuelos, Buica, de Villiers, & du Toit, 2019) performed agitation for 2 min, allowing air to enter every 10 s and reached levels between 7 and 9 mg/L. Rousseva et al., 2016 (Rousseva et al., 2016) and Kontoudakis & Clark, 2020 (Kontoudakis & Clark, 2020) assay extended this time to 5–10 min, to saturate up to 3–4.5 mg/L and 7 mg/L, respectively, and Martins et al. (2013) maintained agitation for one hour to reach levels of 8–9 mg/L. Other authors did not indicate a specific saturation time, but maintained agitation until no increase in oxygen concentration was observed: 7 mg/L (Fracassetti et al., 2013), 6–9 mg/L (Comuzzo et al., 2015), 6.5 ± 0.2 mg/L (Gonzalez, Vidal, & Ugliano, 2018) and 7–9 mg/L (Danilewicz, 2011; Danilewicz et al., 2008; Danilewicz & Standing, 2018; Danilewicz & Wallbridge, 2010; Garrido-Bañuelos, Buica, Sharp, de Villiers, & du Toit, 2019; Kontoudakis & Clark, 2020; Marrufo-Curtido et al., 2018; Martins et al., 2013; Monforte, Oliveira, Martins, & Silva Ferreira, 2019; Nevares et al., 2017; Rousseva et al., 2016). In other works wines were saturated by bubbling with air, such as Gambuti et al., 2018 (Gambuti et al., 2018) assay who maintained this bubbling for 10 and 15 min, respectively, reaching dissolved oxygen values of 8–10 mg/L in the former and 6.6 mg/L in the latter. Nevares et al., 2017 (Nevares et al., 2017) assay maintained this bubbling until the partial pressure of oxygen in the wine was the same as atmospheric, which is equivalent to an approximate concentration of 7 mg/L of oxygen in water at a Patm of 1013 hPa and at 35 °C. Other authors saturated with an O_2/N_2 mixture (20/80) until the wine reached 6.5 mg/L dissolved oxygen (Silva Ferreira, Hogg, & Guedes De Pinho, 2003), 7.2 mg/L (Rodrigues, Silva Ferreira, Guedes de Pinho, Bento, & Geraldo, 2007) and 8 mg/L (Oliveira et al., 2015). Some studies elicited different levels of dissolved oxygen in wine by exposing it to different volumes of air, to reach 9–11 mg/L, 22–35 mg/L or 35–55 mg/L of dissolved oxygen (Bueno et al., 2018; Marrufo-Curtido et al., 2018). Therefore, in addition to the heterogeneity of the procedures, most of the literature does not consider the importance of pressure and temperature in the process.

Based on the few works found, the solubility of oxygen in wine at room temperature (20 °C) and atmospheric pressure (1013 hPa) was assumed to be approximately 6 mL/L (8 mg/L) (Singleton, 1987) and the studies mentioned carried out saturation under these conditions, since the range of oxygen values oscillated between 6.5 and 9 mg/L in most cases. Another aspect to be considered during the procedure is to avoid oxygen supersaturation in the solution. Therefore, when wines are saturated by air bubbling, as in water, high flows (air flow rates > 1 mL/min) and very small bubbles should be avoided (Näykki, Jalukse, Helm, & Leito, 2013).

Oxygen consumption due to multiple pathways and/or reactions (Monforte et al., 2019; Oliveira, Ferreira, De Freitas, & Silva, 2011; Waterhouse & Laurie, 2006) followed a first-order reaction kinetics (Ferreira et al., 2015; Kontoudakis & Clark, 2020; Marrufo-Curtido et al., 2018; Martins et al., 2013; Oliveira et al., 2015). (Monforte et al., 2019) indicated that total consumed oxygen fitted a second-order polynomial equation related to malic acid and metal content. In a previous work, it was conducted a comparative study to fit the oxygen consumption rate based on the exponential and phenomenological models, highlighting that the latter fitted more significantly than the exponential equation described by the oxygen consumption kinetics (Nevares et al., 2017). Different statistical parameters, including the Oxygen Consumption Rate Index (OCRI) and the relationship of these parameters with the oxygen consumption capacity of the wines, were established from the oxygen consumption capacity and its derivative. Subsequently these and additional parameters have been used by (Sánchez-Gómez, del Alamo-Sanza, Martínez-Martínez, & Nevares, 2020) to differentiate wines aged in low and high oxygen transfer rate barrels.

The objective of this work was to establish the characteristic parameters of the oxygen consumption kinetics of wines. To this end a robust procedure to ensure the correct air saturation of wines needed to be developed to compare the different fitting models to approximate the oxygen consumption kinetics of different types of wines, and finally establishing the differentiating kinetics parameters.

2. Materials and Methods

2.1. Wine and sampling

A total of 72 young commercial wines from different Spanish appellations of origin, varieties and vintages (between one and three years old), red, white and rosé (24 of each type) acquired at local stores, were used. The average of the initial characteristics of the wine samples analyzed according to OIV (OIV, 2019) is shown in Table 1.

The bottles containing the wines for the experiment were opened in an oxygen-free atmosphere in a glove box from Jacomex (Dagneux, France) in which atmospheric oxygen was held under 0.002% (<3 ppm) to preserve samples for further analysis avoiding any further oxidation of the initial wines. Samples of 250 mL were collected from each wine intended for saturation and study of the oxygen consumption kinetics.

Table 1
Initial characteristics of the wine samples.

	White n = 24	Rosé n = 24	Red n = 24	F[2]
Alcohol concentration (v/v)	12.16 ± 0.82 a	12.70 ± 0.88 b	12.93 ± 0.99 b	***4.58****
pH	3.34 ± 0.10 a	3.34 ± 0.14 a	3.64 ± 0.08 b	***59.00******
TPI[1]	8.33 ± 1.04 a	10.37 ± 2.12 a	55.50 ± 10.30 b	***457.93******
Reducing sugars (g/L)	2.61 ± 2.11	2.63 ± 2.63	3.44 ± 2.87	*0.82*
Free SO_2 (mg/L)	23.58 ± 12.97	18.21 ± 11.50	19.46 ± 8.00	*1.56*
Total SO_2 (mg/L)	99.42 ± 17.07 b	79.42 ± 23.56 a	73.13 ± 24.17 a	***9.49******
Cu (mg/L)	0.14 ± 0.13	0.09 ± 0.06	0.15 ± 0.19	*1.15*
Fe (mg/L)	1.57 ± 1.48 a	1.10 ± 0.47 a	2.68 ± 1.38 b	***11.05******
DOTs (hPa)	175.06 ± 2.26 b	172.82 ± 2.81 a	172.74 ± 2.55 a	***12.81******
DOMs (hPa)	150.66 ± 7.80 c	142.56 ± 8.12 b	139.40 ± 5.06 a	***31.86 *****
DOTs / DOMs (%)	86.08 ± 4.53 c	82.49 ± 4.47 b	80.72 ± 2.986 a	***21.72 *****
DOTs - DOMs (hPa)	24.39 ± 8.02 a	30.25 ± 7.79 b	33.33 ± 5.27 c	***19.43 *****

DOTs: theoretical partial pressure of oxygen; DOMs: partial pressure of oxygen measured; DOTs / DOMs: saturation percentage reached in the wines compared to theoretical oxygen; DOTs – DOMs: difference between theoretical and measured partial pressures.

[1] TPI: Total Polyphenol Index.

[2] Significant values in bold according to: *p value < 0.05; ** < p value < 0.01; ***p value < 0.001.

2.2. Air saturation protocol of wines: A new tool for establishing the oxygen consumption curves

To establish the saturation protocol for the wines, the working conditions of the method proposed in a previous work (Nevares et al., 2017) were slightly modified. Firstly, and since the oxygen consumption measurements were made at 35 °C and in order to work at the same temperature to avoid fluctuations in oxygen concentration due to temperature variation, the air used for saturation was tempered at this temperature. The wines were also tempered in completely filled bottles, inside the same chamber used to measure the kinetics of dissolved oxygen (DO). To allow the saturation of 6 wines at once, the saturation set-up outside the tempered chamber was provided with 6 stainless steel diffusers with a pore size of 5 μm. Different saturation times were tested (3, 5, 7 and 10 min) to ensure complete saturation with all of the diffusers, seeking to balance the oxygen partial pressure in the wine with that of the atmosphere (100% air sat.). To prevent oxygen over-saturation in the equilibrated solution, high-speed air flow (i.e. air flow rates > 1 mL/min) and very small bubbles were avoided, in accordance with the procedure described elsewhere (Näykki et al., 2013). During the saturation process and in order to avoid loss of wine due to the formation of foam as well as to guarantee that the air saturation was done in an atmosphere with 100% relative humidity, temperature-controlled bottles at 35 °C with a volume three times greater than that of the liquid to be saturated were used. According to Dalton's Law and Raoult's Law the partial pressure in a gaseous mixture of each component of an ethanol-water solution, with which it is in equilibrium and which depends on the alcoholic strength of the solution, is equal to the product of the mole fraction (X) of each compound in the liquid by its vapor pressure. The saturation processes were thus carried out in equilibrium with the water-ethanol vapor saturated atmosphere. Thus, the partial pressure of oxygen (P_{O_2}) at saturation (hPa) can be calculated considering the water vapor partial pressure (P_{H_2O}) as well as the ethanol vapor pressure (P_{EtOH}):

$$P_{O_2} = 20.95\% \ (P_{atm} - X_{H_2O}P_{H_2O} - X_{EtOH}P_{EtOH}) \tag{1}$$

with the water and ethanol vapor pressures determined in bar by the Antoine formula,

$$P_v = 10^{A-B/C+T} \tag{2}$$

with the equation parameters for water being A = 5.20389, B = 1733.926 and C = −39.485 and for ethanol A = 5.37229, B = 1670.409 and C = −40.191 in the test temperature range 308.15 K (Linstrom & Mallard, 2017). During the saturation process, the DO was constantly measured with an optoluminescent oxygen meter FireSting GO2 together with a Trace Range Robust Oxygen Probe (PyroScience GmbH, Aachen, Germany). It is important to ensure that the oxygen content data are correct, as the composition of the wine significantly affects the measurement and varies depending on the type of equipment used. A compensation value (CV) was applied (by subtraction) for the error made based on the ethanol (A) and sugar (B) contents of the measured liquid with the DO measuring sensors used (del Alamo-Sanza, Pando, & Nevares, 2014):

$$CV = 2.2643 - 1.3\ A + 0.5597\ B + 1.0271\ A^2 - 0.1289\ B^2 \tag{3}$$

2.3. Measurement of DO and kinetics of oxygen consumption

The oxygen-saturated wines were then transferred onto 2 mL glass SensorVial SV-PSt5 (Precision Sensing GmbH, Regensburg, Germany), which were airtight and had an optically isolated oxygen sensor integrated at the bottom. To ensure airtightness, the original caps were replaced by caps with sampling and vent valves (Mininert precision sampling valves 13 mm screw cap; Restek Corporation, PA, United States), which have a PTFE body and an additional PTFE membrane and gasket to ensure air tightness. These sensors were read out with the SDR SensorDish® Reader and the oxygen consumption kinetic was followed by measuring DO through this device (Precision Sensing GmbH, Regensburg, Germany). The SensorVials fit into a 24-well plate, which was placed on the reader, ensuring that all samples were in the same saturation conditions. The custom-built prototype of optical chemical sensors spot PSt5 to work with wine were integrated at the bottom [Accuracy: 0.02% O_2 at 0% O_2 and 0.02% O_2 at 21% O_2 (37 °C). Resolution: 0.43% O_2 at 0% O_2 and 0.65% O_2 at 21% O_2 (37 °C)].

The oxygen consumption kinetics for each wine were then carried out in quadruplicate in order to reduce uncertainty. The remaining wine was reserved for further analysis in an oxygen-free atmosphere. To ensure that all samples were measured simultaneously in the same conditions, the device with the samples was kept in a high accuracy thermostatic chamber at a constant temperature of 35 ± 0.10 °C (Raypa Trade, Terrassa, Barcelona, Spain) in darkness. The assays were performed in groups of 48 vials simultaneously (2 SensorDish® Readers were available). The DO of the samples was measured every hour throughout the entire consumption process, finally generating a total of 288 oxygen consumption kinetics of the studied wines (72 × 4). The initial atmospheric pressure of each trial was checked with the digital barometer included in the Fibox-4 Trace device during every assay.

The oxygen sensors of each vial were calibrated according to the manufacturers' protocol, with measurements performed at two calibration points: oxygen-free water (0% air saturation) and saturated air (100% air saturation). The 0% calibration standard was prepared based on a strong reductant; in this case, 1 g sodium sulfite (Na_2SO_3) was dissolved in 100 mL of pure water (MiliQ). Since the working temperature was set at 35 °C, this was also considered for calibration. Both the saturation air and the pure water were tempered at 35 °C inside the same thermostatic chamber before the 0% calibration standard formulation.

2.4. Kinetic curve data process

To study the oxygen consumption kinetics, the curve data were preprocessed according to (Sánchez-Gómez et al., 2020) in order to obtain representative curves for each sample. To this end, each kinetic curve was preprocessed removing the initial and final data, that is, the data before the maximum and after the minimum of the curve, respectively. The curves were then resampled with a sampling period of 15 min and combined, obtaining the mean-std and mean + std curves of the four repetitions of the kinetic curves of each sample. As a result 144 curves were obtained from the 72 samples analyzed (24 for each type of wine).

The first part of the analysis of these 144 kinetic curves consisted of fitting these curves with four different fitting models that have been previously employed in other works (Ferreira et al., 2015; Marrufo-Curtido et al., 2018; Nevares et al., 2017; Sánchez-Gómez et al., 2020): exponential, inverse, second-order polynomic and phenomenological. The second part of the analysis consisted of extracting characteristic parameters that describe the kinetic curves, some of them considered in previous studies done by this group (Nevares et al., 2017; Sánchez-Gómez et al., 2020).

2.5. Statistical analysis

To study the statistically significant differences in the fitting parameters associated with the adjusting curves and in the different parameters extracted from the oxygen consumption kinetics a one-way analysis of variance (ANOVA) at the 95% probability level according to Fisher's least significant difference (LSD) was determined. Moreover, the goodness of fit of each fitting model was evaluated by means of two parameters: the Root Mean Squared Error (RMSE), which is the square root of the mean value of the difference between the real value and the model value elevated to the square, and the Pearson correlation coefficient between the real curve data and the model data. These two parameters allowed the proposed models to be evaluated: a better model has an RMSE closer to 0 or when the Pearson correlation coefficient is closer to 1. The proposed models̓ performance could also be compared with the results obtained by other authors. Consumption kinetics data were analyzed by a Stepwise linear discriminant analysis (SLDA) to find a linear combination of the variables separating the wines. In this study, the forward method was used to select the variables most useful for differentiating the wines. All statistical analyses were carried out using the STATISTICA 64 program (Stat Soft. Inc, USA).

3. Results and discussion

The wines studied were young commercial wines, which have received all kinds of treatments in order to avoid microbial growth and showed differences in their basic oenological characteristics (Table 1). The mean alcohol concentration value was significantly higher in the case of red wines compared to white and the same was found for pH value and iron content. The white wines also had a significantly higher level of total sulfur dioxide. As expected, the Total Polyphenol Index (TPI) showed a significantly higher mean value in red wines.

3.1. Wine saturation methods

First the saturation time needed to be set. For this purpose, equal amounts of wine, previously tempered at 35 °C, were saturated in sextuplicate and simultaneously in the saturation device (see Materials and Methods) for different times. The amount of dissolved oxygen was monitored during the process, recording the level reached in each of the 6 vessels for each saturation time: 3, 5, 7 and 10 min. This process was repeated for several days and with several wines. The coefficient of variation of the dissolved oxygen measurements taken simultaneously in sextuplicate after 5 min of saturation was found to be less than 1%, thus establishing that the minimum saturation time should be equal to or greater than 5 min. Likewise, it was verified that the increase, measured as an increase in partial pressure of oxygen (in hPa), which involved maintaining saturation for 7 or 10 min with respect to the minimum established in the previous guideline (5 min), did not involve an increase of more than ±3 hPa (<1% of air saturation). Given that the wines were saturated outside the tempered chamber, in order to avoid temperature changes by maintaining the samples at 35 °C during the saturation stage and subsequent measurement, a time of 5 min was considered sufficient to reach the corresponding partial air pressure and the decrease in temperature was not greater than 2 °C.

Once the saturation time was established, repeatability and reproducibility were calculated in order to validate the saturation method with the saturation device for 6 samples simultaneously. To do this, data of the time needed to reach saturation in the 12 analyses were processed as follows: the two standard deviations of the 6 triplicates (one per day) for each wine were combined (square root of the arithmetic mean of the variances) to obtain the method saturation repeatability; the standard deviation of the two mean values for each wine (one per day) multiplied by the square root of 3 was taken as the reproducibility value (if this value was greater than the repeatability - if not, that figure was also considered reproducibility) (Ortega, López, Cacho, & Ferreira, 2001). As a result repeatability was 1.07% (as RSD) and reproducibility 2.00%, both results being lower than 5% and therefore considered acceptable.

Once the protocol was defined, 6 batches were saturated on 6 different days, each one with 12 wines: white wines (batches 1 and 2); rosé wines (batches 3 and 4); and red wines (batches 5 and 6), thus a total of 72 wines. For each of the 6 wines in each batch, 250 mL were tempered at 35 °C in bottles with the same volume (~250 mL). When the first 6 wines reached the set working temperature (35 °C), they were transferred to other bottles of a larger size and also tempered at the same temperature. Wines were saturated during 5 min, as previously established. This process was repeated twice every day. Since 2 SensorDish® Readers (each one with 24 vials) were available, 4 replicates for each wine were carried out covering 12 wines each day.

3.2. Importance of the initial partial pressure reached

As indicated in the corresponding section of Materials and Methods, at the beginning of the saturation process, the atmospheric pressure was measured to determine the partial pressure of oxygen that the saturated wines should reach. Table 1 shows the theoretical partial pressure of oxygen (DOTs) that the different saturated wines should have reached in the atmospheric conditions under which the white wines (937 and 943 hPa), rosé wines (932 and 930 hPa) and red wines (933 and 936 hPa) were saturated. This took into account the error committed by the measurement system due to the presence of ethanol and sugar in the wine measured (compensation value, CV), as well as the ethanol and water vapor pressure at 35 °C depending on their alcoholic concentration. The measured oxygen partial pressure (DOMs) for each wine was also included, as well as the difference between the theoretical and measured data. Taking these data into account, it can be seen that the wines did not reach 100% air saturation according to Henry's law, resulting in 86%, 82% and 81% for white, rosé and red wines, respectively. Similarly, it can be seen that on average, the difference between the theoretical oxygen partial pressure and that achieved is significantly lower for white wines (24 hPa), followed by rosé (30 hPa), and red (33 hPa). Depending on the type of wine and despite being saturated according to the same protocol (5 min to avoid oxidation of the wines), not all were able to reach the same oxygen partial pressure, either due to the fact that the wine did not follow Henry's law, or to the dependence of the oxygen solubility on the ethanol, sugar and phenolic compound content; this point obviously requires in-depth study in the future. Different air saturation levels were observed by (Garrido-Bañuelos, Buica, Sharp, et al., 2019) when they applied 3 saturation cycles spaced 3 months apart to hydroalcoholic extracts of a Shiraz variety with different anthocyanin/tannin (A/T) ratios. This was also observed in white and rosé wines, and red wines (Carrascón et al., 2017; Ferreira et al., 2015). However, the latter authors indicated that the variation in the initial oxygen levels reached by red wines in different saturation cycles did not depend on the type of wine, and that they were related to differences in the measurement of the first saturation point and to the different viscosity of the wines affecting the rate of microbubble degassing. All these works measured dissolved oxygen in mg/L, presupposing the solubility of oxygen in water; however, it is important to point out that the solubility of oxygen in water is not the same as in wine due to the well-known influence of alcohols and other compounds on oxygen solubility. In this work, the kinetics of oxygen consumption was monitored by measuring the 72 real wines, which were saturated following the protocol described above, in hPa. Nevertheless, in order to make a comparison with other published works, the mg/L achieved were calculated assuming the solubility of oxygen in water. The average level of dissolved oxygen reached by the freshly saturated white wines was 5.23 ± 0.30 mg/L, in the rosé wines it was 4.95 ± 0.28 mg/L and in the freshly saturated red wines it was 4.84 ± 0.18 mg/L: all of them should have reached 5.33 mg/L.

3.3. Adjustment of the oxygen consumption kinetics/curves

The mean and standard deviation values for the oxygen consumption kinetics of each wine studied are shown in Fig. 1. Thus, the kinetics for the white wines (Fig. 1a), the rosé wines (Fig. 1b) and the red wines (Fig. 1c) are shown separately. In a first visual analysis, differences can be seen both between the three types of wine and within each type. Fig. 1d shows the large overlap between the different types of wines studied, which confirms Boulton's statement that there can be white and red wines that consume the same amount of oxygen (Boulton, 2011). These curves are analyzed in more detail in the following section on the basis of their most descriptive parameters.

The first step in the analysis of the oxygen consumption kinetics was their adjustment to the four different models considered and mentioned in the Materials and Methods section: exponential curve, inverse curve,

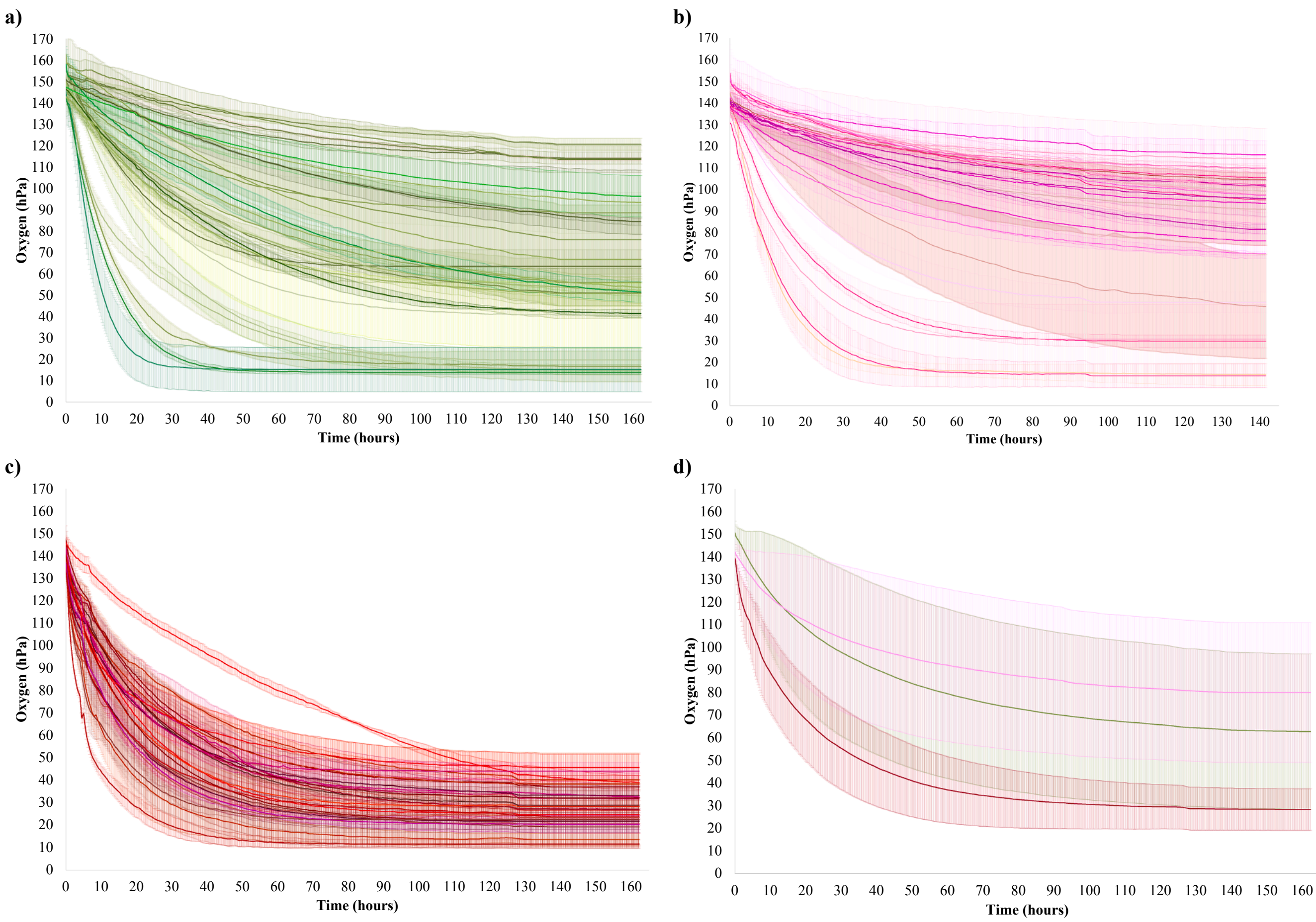

Fig. 1. Oxygen kinetics of wines: a) White n = 24; b) Rosé n = 24; c) Red n = 24; d) Average for each type of wine. Each intense-color line represents the mean value and the lighter-color vertical lines represent the standard deviation for each time. Moreover, on figures a), b) and c) each wine is represented with a different color, while on figure d) each wine type is represented with a different color (red for red, pink for rosé and green for white wine respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 2
Values of the fitting parameters associated with the four parametric adjustment curves, ANOVA results, mean Root Mean Squared Error (RMSE) and Pearson correlation coefficient obtained for white, rosé and red wines studied.

		White wines			Rosé wines			Red wines			ANOVA
		min	Max	mean ± std	min	max	mean ± std	min	max	mean ± std	F[1]
Exponential	α	104.05	162.30	135.99 ± 11.39 c	112.17	152.73	130.13 ± 9.10 b	82.06	141.89	104.67 ± 12.57 a	***107.76****
$O(t) = \alpha \cdot e^{-\beta \cdot t}$	β	0.0016	0.1273	0.0142 ± 0.0220 ab	0.0007	0.0743	0.0092 ± 0.0155 a	0.0066	0.0670	0.0195 ± 0.0137 b	***4.193****
RMSE (correlation)		5.435 (0.9675)			3.888 (0.9662)			8.373 (0.9356)			
Inverse	K	475	84,845	22246 ± 23341 b	727	178,893	41127 ± 36252 c	580	9781	3788 ± 2410 a	***26.917******
$O(t) = \frac{K}{t - t_0}$	t_0	−565	−3	−151 ± 158 b	−1374	−5	−304 ± 271 c	−89	−4	−29 ± 19 a	***27.642******
RMSE (correlation)		3.198 (0.9855)			2.564 (0.9795)			3.856 (0.9851)			
Second-order polynomic	A	0.0014	0.0971	0.0106 0 ± 0.0194 b	0.0008	0.0314	0.0055 ± 0.0070 a	0.0034	0.0344	0.0104 ± 0.0059 ab	*2.637*
$O(t) = A \cdot t^2 + B \cdot t + C$	B	−6.850	−0.408	−1.581 ± 1.341 a	−3.583	−0.201	−1.003 ± 0.833 b	−3.382	−1.146	−1.770 ± 0.443 a	***8.551******
	C	91.68	169.12	138.45 ± 16.28 b	79.93	159.62	132.16 ± 14.73 b	68.51	144.10	105.69 ± 16.62 a	***57.402******
RMSE (correlation)		3.303 (0.9862)			2.350 (0.9855)			6.166 (0.9577)			
Phenomenological	a	755	20,972,384	5188583 ± 5213447 a	82,130	15,732,716	4424766 ± 3964134 a	170,645	15,742,643	7774946 ± 5203416 b	***6.344*****
$O(t) = \frac{a}{1 + b \cdot e^{-c \cdot t}}$	b	4	153,430	39336 ± 40534 a	565	136,210	34998 ± 33086 a	1205	179,775	76810 ± 54214 b	***13.407******
	c	0.0016	0.1406	0.0153 ± 0.0240 ab	0.0007	0.0743	0.0100 ± 0.0167 a	0.0066	0.0670	0.0212 ± 0.0138 b	***4.352****
RMSE (correlation)		6.101 (0.9695)			4.466 (0.9685)			9.466 (0.9433)			

polynomic curve and phenomenological curve (Table 2). The results of the fit of the curves in terms of Root Mean Squared Error (RMSE) and correlation coefficient are shown in Table 2. In both cases the best results were obtained with the inverse curve fit, with good results for the three types of wine. In second place was the degree two polynomial curve fit, which achieved a good fit for white and rosé wines but a poor one for red wines. In addition, it used one more constant value in its model, making it less robust and more complex than the inverse curve-based one. Finally, the fits using the exponential and the phenomenological curves were slightly worse overall than those of the other two models. Analyzing the fits from the point of view of the wines, the best fits were achieved for white and rosé wines, while red wines were the worst, the inverse curve being the one that obtained fitting results comparable to those of white and rosé wines. Therefore, in terms of fit, it can be stated that the model based on the inverse curve was the one that gave the best results when modeling consumption kinetics (Table 2).

The analysis of the adjustment parameter values of the four models considered for the kinetics of the three types of wine is included in Table 2, which shows the minimum, maximum, mean and standard deviation values of each parameter for each type of wine and the F statistic of the ANOVA test. The model parameters that presented the most significant differences between the three types of wine was parameter α of the exponential model, with an F-statistic value of 107.76 of the polynomial model with an F of 57.402 and the two parameters of the inverse model, with F values greater than 26. Analyzing the fit models as a whole, the inverse model was the only one in which all its parameters showed significant differences greater than 0.1%, while the polynomial model had one parameter with no significant differences and the other two models had one parameter with significant differences of 5% but not 1%.

In the exponential models parameter by parameter analysis α was the one with the most significant differences between the three types of wine. This parameter regulates the amplitude of the model, so it is related to the overall oxygen level over time and was higher for white wines and lower for red wines, with rosé wines in between. Parameter β regulates the concavity of the oxygen consumption curve, but in this case the differences between the 3 types of wines were only significant at 5%. For the inverse curve model both parameters had significant differences at 0.1% and the same ordering of the groups: red wines had the lowest value, followed by whites and rosés with the highest values for both parameters. In this model parameter K gives an idea of the level of oxygen (analogous to α in the exponential model) and parameter t_0 models the shape of the curve and the decay mode. Analyzing the degree two polynomial model, only the coefficients of the linear term (B) and the constant (C) showed significant differences between the three types of wine, and there were no significant differences for the coefficient of the quadratic term (A). However, on analyzing the groups generated for the two parameters with significant differences white and red wines were assigned to the same group with a lower value than rosé wines for parameter B, while red wines had a lower value than the group formed by white and rosé wines for parameter C. Therefore, none of the three parameters generated three groups that differentiated the three types of wine. Finally, the phenomenological model resulted in parameter c with significant differences at 5%, parameter a with significant differences at 1% and parameter b with significant differences at 0.1%. In addition, for the three parameters the analysis generated two groups, in which rosé wines always had the lowest parameter values, red wines the highest values and white wines had parameters a and b in the same group as the rosé wines and parameter c in an intermediate group between the other two types of wine red and white. As already mentioned, the model based on the inverse curve was the one that offered the best fitting result. Moreover, it was the only one in which its two parameters provided significant differences at 0.1% among the three types of wine and was able to sort the values of both parameters into three groups: one with lower values for reds, one with intermediate values for whites and one with the highest values for rosés (Table 2).

3.4. Parameters of the oxygen consumption kinetics of red, white and rosé wines

Once the parameters for each of the adjustment curves were studied, the 72 curves in Fig. 1 were analyzed in more detail through the 20 parameters chosen to describe the consumption curves, which are reliable and representative indicators to describe, characterize and differentiate the consumption kinetics of the wines studied (Table 3 and Fig. 2). Some of these parameters were established in previous works carried out by the UVaMOX group to differentiate white and red wines (Nevares et al., 2017) or wines aged in barrels with different oxygen transfer rates (OTR) during different times (Sánchez-Gómez et al., 2020).

In general, the different parameters presented in Table 3 collected information about aspects related to: a) oxygen consumption capacity (oxygen value parameters, indicated by the symbol O, such as O_{max} or O_{min}) b) speed or rate of oxygen consumption (time value parameters, denoted by the symbol t and those including the symbol R); c) oxygen consumption avidity (area value parameters, denoted by the symbol A). Likewise, and in order to focus the study on different parts of the curve, the parameters established addressed: I) totality of the curve: overview of the whole oxygen consumption process, the parameters corresponding to numbers (1)–(5); II) first half of the oxygen consumption process: parameters that reported the behavior of the wines in the first half of the consumption kinetics and also gave information on the convexity of the curve, allowing those wines capable of consuming oxygen more or less rapidly in this phase, slowing down or speeding up in the second half of the kinetics, to be differentiated and were numbered (6), (7), (8) and (20); III) were the parameters defining the oxygen consumption interval between 90% and 10%: these parameters avoided the interferences that the extremes of the curves (upper or lower) could cause. These parameters are labelled with subscripts 90 and 10, corresponding to numbers (9)–(15) (Table 3).

The amount of oxygen a wine can consume (ΔO_{max_min}) (Fig. 2a) reflects its capacity to consume oxygen and is significantly higher for red wines (~111 hPa) and lower for rosé wines (~62 hPa) with white wines in an intermediate position (~88 hPa) (Table 3). However, in view of the standard deviation values and the graphical representation of these kinetics (Fig. 1), this parameter varied considerably between the white and rosé wines analyzed. Most of the literature states that red wines can consume more oxygen than white ones (Danilewicz, 2016; Kreitman et al., 2016; Singleton, 1987). However, Boulton in 2011(Boulton, 2011) and later (Nevares et al., 2017) described the opposite. Nevares et al., 2017 found no statistically significant differences in oxygen consumption kinetics in the study carried out on 108 composition-controlled wines and 32 real wines, both white and red, with the amounts of oxygen consumed by white and red wines being of the same order. The results obtained in this work indicated in general that red wines consumed more oxygen, although there were white and rosé wines capable of consuming similar amounts to red wines. Therefore, the greater or lesser capacity of different wines to consume oxygen will depend on the nature of the wines being compared. The amount of oxygen consumed by the red wines ranged from 3.2 mg/L to 4.6 mg/L, with an average value of 3.9 mg/L (~111 hPa). These values were lower than those reported by other works, thus with the analysis of 15 wines, mean values of 5 mg/L were found (Ferreira et al., 2015) and values from 7.69 mg/L to 10 mg/L in a study of 8 wines (Bueno et al., 2018; Carrascón et al., 2018). For 24 white and 24 rosé wines studied, it was found that on average they were able to consume from ~ 3 mg/L and ~ 2 mg/L, respectively, these results being higher than those described by (Rousseva et al., 2016) for white wines with levels of 1 and 2.5 mg/L.

The amount of oxygen that a wine can consume (ΔO_{max_min}) is determined by the largest amount of dissolved oxygen that the wine can have under these conditions, i.e. the dissolved oxygen under saturated conditions (O_{max}) and logically by the level of oxygen that it does not consume (O_{min}) (Fig. 2a). O_{min} corresponds to the residual value of

Table 3
Maximum and minimum values of parameters extracted from the oxygen consumption kinetic curves for the different wines and ANOVA results.

Parameters				White wines			Rosé wines			Red wines			ANOVA
	Equation	*Name*	Fig. 2	min	max	*mean ± std*	min	max	*mean ± std*	min	max	*mean ± std*	F[1]
(1)	$\Delta O_{max\_min} = O_{max} - O_{min}$	ΔO_{max_min}	(a)	31.07	141.30	87.85 ± 32.91b	15.81	133.70	61.95 ± 31.47 a	91.96	132.43	111.09 ± 8.12 c	***40.66****
(2)	$O_{max} = max\{O_2(t)\}$	O_{max}	(a)	133.76	175.50	150.66 ± 7.80 c	129.34	166.91	142.57 ± 8.12 b	129.67	153.60	139.41 ± 5.06 a	***31.86****
(3)	$O_{min} = min\{O_2(t)\}$	O_{min}	(a)	4.70	123.32	62.85 ± 35.23 b	8.30	128.21	80.63 ± 33.69 c	9.59	52.18	28.38 ± 11.23 a	***40.61****
(4)	t_{0_min}: time of the last point of the oxygen curve	t_{O_min}	(b)	51.50	162.00	137.41 ± 27.01	79.25	141.50	132.17 ± 16.35	68.75	162.25	130.69 ± 22.20	*1.21*
(5)	$A_{max\_min} = \int_{t=0}^{t_{O\_min}} O_2(t)dt$	A_{max_min}	(b)	1232	19,717	11930 ± 5273 b	2108	19,105	13078 ± 4825 b	1762	12,341	6132 ± 2399 a	***35.11****
(6)	$O_{int} = (O_{max} - O_{min})/2$	O_{int}	(d)	69.23	141.48	106.74 ± 19.52 b	68.82	142.07	111.59 ± 18.80 b	69.84	98.56	83.86 ± 7.71 a	***39.75****
(7)	$t_{O_{int}} = t \text{ so that } O_2(t = t_{O\_int}) = O_{int}$	t_{O_int}	(d)	6.00	47.95	28.85 ± 12.51 b	7.44	49.37	27.47 ± 11.29 b	4.18	44.90	13.78 ± 8.03 a	***28.67****
(8)	$O_{mid} = O_2(t = t_{O\_min}/2)$	O_{mid}	(d)	6.61	134.75	75.14 ± 36.78 b	9.00	135.79	90.93 ± 34.47 c	9.89	66.74	35.19 ± 14.90 a	***43.03****
(9)	$O_{90} = O_{max} - 0.1\cdot(O_{max} - O_{min})$	O_{90}	(e)	118.73	166.67	141.33 ± 9.20 c	116.71	160.95	135.99 ± 9.24 b	114.55	141.16	126.95 ± 6.10 a	***36.72****
(10)	$O_{10} = O_{min} + 0.1\cdot(O_{max} - O_{min})$	O_{10}	(e)	18.05	126.43	71.66 ± 32.02 b	20.46	131.02	86.86 ± 30.64 c	21.73	61.40	39.50 ± 10.48 a	***40.61****
(11)	$\Delta O_{90\_10} = O_{90} - O_{10}$	ΔO_{90_10}	(e)	24.76	111.83	69.67 ± 25.92 b	12.45	105.52	49.13 ± 24.92 a	72.68	104.29	87.46 ± 5.97 c	***39.88****
(12)	$t_{O_{90}} = t \text{ so that } O_2(t = t_{O\_90}) = O_{90}$	t_{O_90}	(e)	1.50	8.75	4.36 ± 2.15 c	0.50	8.00	2.95 ± 1.70 b	0.50	6.75	1.39 ± 1.11 a	***36.37****
(13)	$t_{O\_10} = t \text{ so that } O_2(t = t_{O\_10}) = O_{10}$	t_{O_10}	(e)	15.00	123.25	85.01 ± 31.53 b	23.25	115.00	85.12 ± 25.91 b	21.25	110.00	52.03 ± 19.60 a	***25.56****
(14)	$\Delta t_{O\_90\_10} = t_{O\_10} - t_{O\_90}$	$\Delta t_{O\_90\_10}$	(e)	13.25	116.75	80.66 ± 30.04 b	21.50	112.50	82.19 ± 25.43 b	20.50	104.25	50.67 ± 18.91 a	***23.86****
(15)	$A_{90\_10} = \int_{t_{O\_90}}^{t_{O\_10}} O_2(t)dt$	A_{90_10}	(e)	759	15,186	8271 ± 4270 b	1180	14,597	9082 ± 3706 b	962	8928	3560 ± 1761 a	***36.51****
(16)	$R_{max} = max\left\{-\frac{\partial O_2(t)}{\partial t}\right\}$	R_{max}	(g)	24.69	1.95	7.82 ± 5.91 b	18.84	1.96	6.87 ± 4.37 b	30.89	5.38	15.92 ± 6.07 a	***39.12****
(17)	$R_{min} = min\left\{-\frac{\partial O_2(t)}{\partial t}\right\}$	R_{min}	(g)	0.04	10.36	1.63 ± 2.55	0.07	8.26	1.60 ± 1.91	0.03	22.23	1.73 ± 3.51	*0.03*
(18)	$t_{R\_max} = t \text{ so that } \frac{\partial O_2}{\partial t}(t = t_{R\_max}) = -R_{max}$	t_{R_max}	(g)	0.13	19.63	1.73 ± 3.46	0.13	5.88	1.41 ± 1.92	0.13	7.13	1.38 ± 2.11	*0.27*
(19)	$t_{R\_min} = t \text{ so that } \frac{\partial O_2}{\partial t}(t = t_{R\_min}) = -R_{min}$	t_{R_min}	(g)	0.38	144.38	37.14 ± 51.68 ab	0.38	115.38	21.08 ± 30.48 a	2.88	118.63	41.62 ± 39.24 b	***3.27****
(20)	$t_{A_{50}} \text{ so that} \int_{t=0}^{t_{A_{50}}} O_2(t)dt = \frac{1}{2}\cdot A_{max\_min}$	$t_{A_{50}}$	(h)	5.75	73.75	50.80 ± 17.51 b	12.50	67.50	55.09 ± 15.77 b	14.50	56.50	38.55 ± 10.91 a	***15.73****

For each parameter, different letters indicate significant differences among different wines according to the Fisher's LSD test ($\alpha < 0.05$).
(1) Total oxygen consumed (hPa); **(2)** Maximum/Initial oxygen value (hPa); **(3)** Minimum/Final oxygen value (hPa); **(4)** Total consumption time (h); **(5)** Area under the oxygen consumption curve (hPa·h); **(6)** Average oxygen value between the maximum and the minimum oxygen values (hPa); **(7)** Fall time to 50% air saturation (h); **(8)** Oxygen at half consumption time (hPa); **(9)** Oxygen value that represents 90% of the range between the maximum and minimum values (hPa); **(10)** Oxygen value that represents 10% of the range between the maximum and minimum values (hPa); **(11)** Variation between O_{90} and O_{10} (hPa); **(12)** Time when O_{90} is reached (h); **(13)** Time when O_{10} is reached (h); **(14)** Time variation between t_{O_90} and t_{O_10} (h); **(15)** Area under the oxygen consumption curve and between $t_{O\text{-}90}$ and t_{O_10} (hPa·h); **(16)** Maximum value of the oxygen consumption/ratecurve (hPa/h); **(17)** Minimum value of the oxygen consumption/rate curve (hPa/h); **(18)** Time when the maximum oxygen rate is reached (h); **(19)** Time when the minimum value of the oxygen curve rate is reached (h); **(20)** Time when the area under the kinetic curve is half the total area under the curve (h).

[1] Significant values in bold according to: *p value < 0.05; ** < p value < 0.01; ***p value < 0.001.

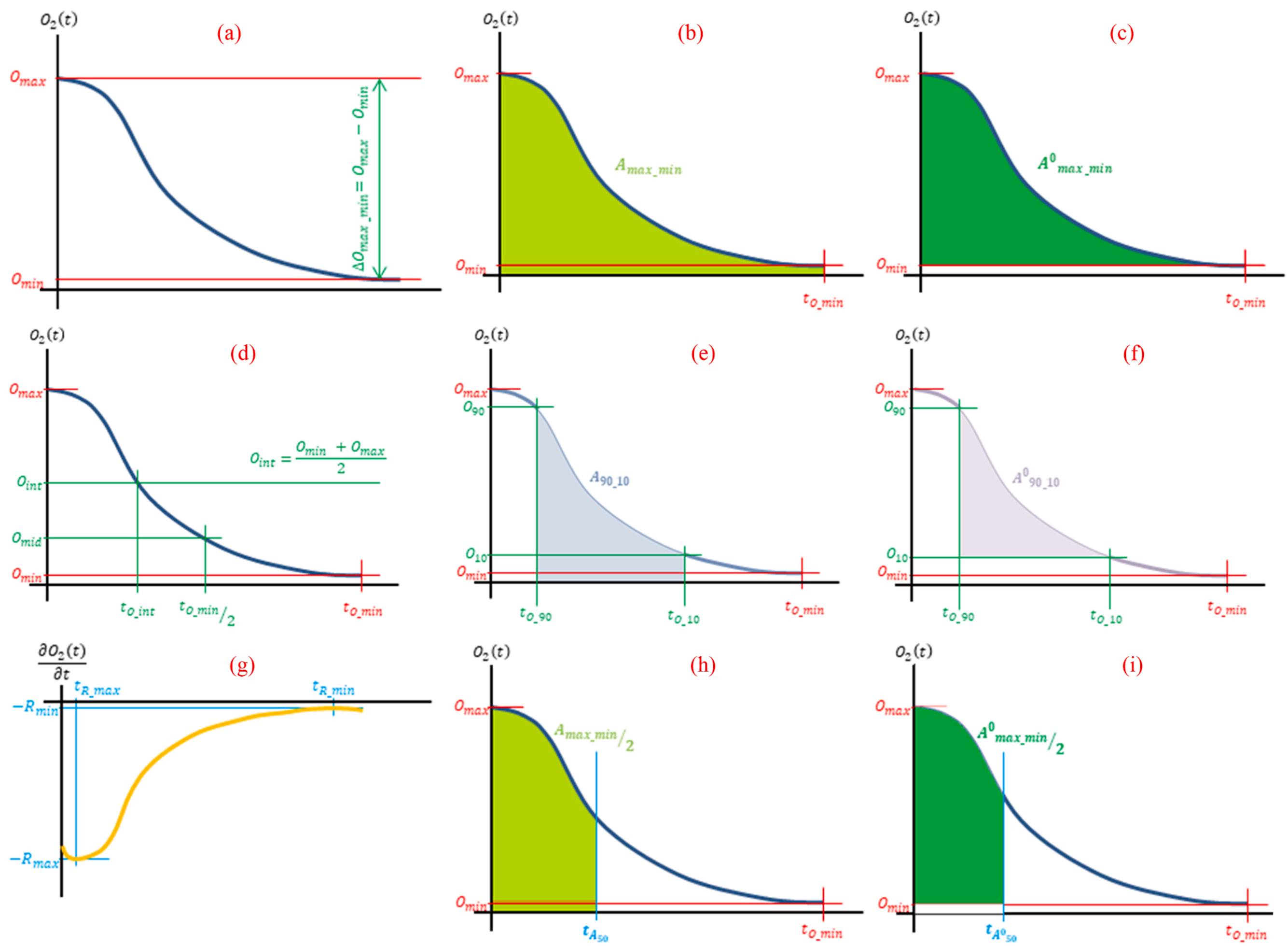

Fig. 2. Graphical representation of the parameters extracted from the oxygen consumption kinetic curves, which are presented in Table 3.

dissolved oxygen that a wine is not able to consume and is therefore the minimum or final value of the consumption kinetics. The values obtained for this parameter in the 72 wines analyzed showed that none of the wines fully consumed the available oxygen, with the red wines showing a significantly lower dissolved oxygen content at the end of the kinetics (Table 3). The standard deviation values, which reported variability among the wines analyzed, were ± 35.23 hPa for whites and ± 33.69 hPa for rosés, suggesting greater heterogeneity within these wines than in the case of red wines (standard deviation ± 11.23 hPa). The higher values of remaining oxygen, which cannot be consumed, are related to: a) a lower presence of compounds to react with oxygen, as indicated by (Garrido-Bañuelos, Buica, Sharp, et al., 2019) in their study conducted with three extracts with different ratios of Anthocyanins/Tannins (A/t), where the initial oxygen levels were between 6 and 9 mg/L; b) higher or lower presence of different additives (sulfur dioxide, ascorbic acid or glutathione), as evidenced by (Comuzzo et al., 2015), using two white wines, where the initial oxygen level was between 7.29 ± 0.14 and 8.25 ± 0.19 mg/L; c) concentration of metals (Cu and Fe), demonstrated by (Rousseva et al., 2016) in the study based on 6 white wines, where the initial dissolved oxygen was between 3 and 4 mg/L. (Carrascón et al., 2017; Ferreira et al., 2015) first studied 4 white and 3 rosé wines, and secondly 15 red wines; they observed that as a wine was subjected to various saturations, reaching initial dissolved oxygen concentrations of 6 mg/L in both studies, the remaining oxygen increased, and more noticeably, in white and rosé wines, reflected the decrease in their ability to consume oxygen. However, in the case of the 72 commercial wines analyzed in this work, no significant correlations were found between the residual dissolved oxygen content and the initial copper or iron content of the wines, although there seemed to be more of a relationship with iron than with copper, and the red wines had a significantly higher iron content (Table 1). The correlation between the initial copper and iron level and residual oxygen in white wines was −0.0184 and −0.3064, respectively, in red wines 0.0184 and −0.0171, respectively, and in rosé wines −0.0094 and −0.3824, respectively.

In relation to the dissolved oxygen present in the wines in the first phase of the consumption kinetics, it should be noted that the highest average values of O_{int} (half of the oxygen consumed, Fig. 2d) and O_{mid} (oxygen consumed at half the total oxygen consumption time, Fig. 2d) found in white and rosé wines indicated a lower oxygen consumption capacity in the first half of the process than in red wines. This result was also reflected by the higher convexity of the kinetic curve found in the red wines (Sánchez-Gómez et al., 2020) recorded in parameter O_{mid}which, with lower values in red wines, indicated a greater oxygen consumption capacity at the beginning of the process (Table 3). According to the values of this parameter, on average, the red wines had consumed approximately 75% of the total amount of oxygen consumed, significantly higher than that found in the rosé and white wines (Table 3). This amount is significantly higher than that found for white wines (50%) and especially for rosés (36%). These values show that the red wines analyzed had a significantly higher oxygen consumption capacity than whites and rosés in the first half of the process.

The parameters describing the curve limited between 90% and 10% of the variation of ΔO_{max_min} confirmed that the reds had a greater oxygen consumption capacity at the beginning of the kinetics, with a value of O_{90} (Fig. 2e) in relation to a higher O_{max} (9%) (Table 3). In the case of parameter O_{10} (Fig. 2e) white and rosé wines presented relative percentages of 52% and 61%, respectively, and 52% and 61%, respectively, for O_{max}. The amount of oxygen consumed ΔO_{90_10} (Fig. 2e) reported that the 24 red wines consumed approximately 87 hPa of the total of 111 hPa on average, while for the 24 white wines this consumption was 69 hPa of the total of 88 hPa and in the case of the 24 rosé wines it was 49 hPa of 62 hPa. Thus, the consumption capacity of the red wines in this interval indicates that they consumed 80% of the total oxygen, which was significantly higher than that consumed by the white and rosé wines

In relation to the parameters considered at different times, no statistically significant differences were found in the total time taken by the different types of wines to consume the maximum level of dissolved oxygen available (Table 3). t_{O_min} (Fig. 2b) was the total time taken by the different types of wine to consume the maximum level of dissolved oxygen available (Table 3). This result was due to the wide heterogeneity obtained within each type of wine. Thus, this parameter ranged from 51.50 to162.00 h for white wines, from 79.25 to 141.50 h for rosé wines and from 68.75 to 162.25 h for red wines. It is interesting to note that red wines consumed most of the available oxygen in 4 days (Fig. 1). (Oliveira et al., 2015) concluded that oxygen depletion is faster at higher temperatures (35 and 40 °C) and that oxygen consumption depends on the initial oxygen concentration. For the 72 wines of this experiment, the results of the correlations between both parameters (t_{O_min} and O_{max}) indicated that the higher the initial oxygen level, the longer the consumption time (r = 0.2259 and *p value* = 0.0065). However, for each type of wine individually the positive correlation between both parameters was only significant in rosé wines (r = 0.3265 and *p value* = 0.0235), so the type of wine will condition this. The relationship with temperature has been addressed by different authors, although the great variability described in the literature could be explained by the characteristics of the wines. Moutounet and Mazauric (2001) indicated that an air-saturated red wine took 25 h to consume dissolved oxygen when at 13 °C, whereas this was reduced to 3 h when the temperature was raised to 30 °C. This slowdown in oxygen consumption was also described by different authors in red wines: while some wines consumed up to 8.2 mg/L in one day, others took a week to consume the same amount of oxygen at 25 °C (Ferreira et al., 2015), or between 12 and 17 days at 20 °C (Danilewicz & Standing, 2018). In the case of white and rosé wines published results varied, ranging from 7.5 days for wines at 25 °C (Carrascón et al., 2017) to 5–16 days for different white wines to consume 5 mg/L at 22 °C (Gonzalez et al., 2018).

In relation to the time required to reach the oxygen level, called the O_{int} (Fig. 2d) level, referred to as t_{O_int} (Nevares et al., 2017), it was found that red wines needed half the time of white and rosé wines (Table 3). The red wines analyzed consumed 50% of the total available oxygen in approximately 13 h on average, while for white and rosé wines this time doubled to ~ 29 and ~ 27 h, respectively.

As regards time (t_{O_90}) (Fig. 2e), white wines took slightly more than 4 h to reach O_{90} and this was significantly shorter for rosé and red wines: 3 and 1 h, respectively (Table 3). At the other end of the scale, the time required to reach O_{10} (t_{O_10}) (Fig. 2e) was similar for whites and rosés (~85 h), but was reduced to 52 h for reds. Thus, the red wines studied would need slightly more than 50 h on average to consume 90% of the oxygen. However, although the latter time showed no differences between whites and rosés, the shorter time shown by the rosés for O_{90} shown higher capacity by rosé wines to consume oxygen during the first few hours. Over time this capacity slowed down and became equal to that of white wines, as indicated by parameter t_{O_90}which showed no differences between rosé and white wines. The time interval between the indicated oxygen levels ($\Delta t_{O_90_10}$) gives information on the time it took for the wines to consume 80% of the total oxygen content ΔO_{max_min}. These values were very similar to those of t_{O_10}. The time interval between the indicated oxygen levels (90–10) gives information on the time it took for the wines to consume 80% of the total amount of oxygen, although it was not significant, but the rosé wines took longer to consume this percentage, even though the total amount consumed was lower (ΔO_{max_min}) and they had a higher avidity at the beginning of the process compared to the white wines.

The above parameters related to the oxygen consumption rate were obtained directly from the curve and have been shown to be e of interest for the differentiation, characterization and description of the different wines. However, they may not be sufficient to differentiate or highlight other aspects of each kinetic. Thus, parameters that reflected the rate of oxygen consumption, such as the minimum and maximum oxygen consumption rate (R_{min} and R_{max}, Fig. 2g), obtained from the first derivative of the consumption kinetics, and the times at which they were reached (t_{R_min} and t_{R_max}, Fig. 2g) are described below. The R_{max} parameter, denoted as ***min_der*** in the work of (Sánchez-Gómez et al., 2020), produced the maximum rate of consumption, this being higher when the wine consumed oxygen more rapidly. This was the case for red wines, whose mean value of R_{max}(~16 hPa/h) was approximately double that for white wines (~8 hPa/h) and rosé wines (~7 hPa/h). The main responsible for these higher consumptions are phenolic compounds and metals, whose values were significantly higher in red wines (Table 1), thus favoring a higher rate of oxygen consumption. Moreover, being young red wines, it is conceivable that oxygen is more involved in acetaldehyde-mediated reactions to form new, more stable polymeric pigments, consequently modifying tannin reactivity (Picariello et al., 2018). Other authors described different rates in oxygen consumption in red wines, from rates of 8.2 mg/L. day (Ferreira et al., 2015) to 1.95–6.83 mg/L. day (Carrascón et al., 2018). Of note is the work of (Marrufo-Curtido et al., 2018) where a first segment of explosive consumption with rates of 0–159 mg/L. day lasting about 30 min was defined, followed by rates between 0.90 and 60.7 mg/L. day with a duration of between 1 and 3 h. In the case of white and rosé wines rates of 0.258–0.833 mg/L. day for 20 and 30 days were described (Carrascón et al., 2017). Fig. 3 collects the results obtained in this work on the evolution of the oxygen consumption rate (hPa/h) calculated as the difference in oxygen content (hPa) between two given time instants divided by the corresponding time difference. In the first 8 h the oxygen consumption rate was significantly higher in red wines and decreased rapidly from 12 hPa/h to 3.13 hPa/h (13.9 mg/L.day to 3.6 mg/L.day). In the case of white and rosé wines, the rate of oxygen consumption in the first hours was lower, decreasing from consuming 6.5 hPa/h (7.5 mg/L.day) in the first hour to 2.5 hPa/h (2.9 mg/L.day) at 8 h. The situation for rosé wines was similar, from an oxygen consumption rate of 5.3 hPa/h (6.1 mg/L.day) in the first hour to 1.3 hPa/h (1.5 mg/L.day) after 8 h. The rate of oxygen consumption slowed down in the three types of wines in the following period from 8 to 25 h, remaining higher in the case of red wines (from 3.13 to 1.33 hPa/h, 3.8 to 1.5 mg/L.day), followed by the whites, whose rate went from 2.5 to 1.13 hPa/h (2.9 to 1.3 mg/L.day) and finally the rosés, which showed the lowest rate of oxygen consumption decreasing from 1.3 to 0.75 hPa/h (1.5 to 0.9 mg/L.day). Subsequently, after two days, the differences in the oxygen consumption rate of the wines studied was significantly reduced (Fig. 3b), showing an oxygen consumption rate of 0.55, 0.45 and 0.56 hPa/h (0.6, 0.4 and 0.6 mg/L.day) for white, rosé and red wines, respectively, which was reduced to 0.08, 0.03 and 0.09 hPa/h (0.09, 0.03 and 0.1 mg/L.day) at the end of the test at 160 h.

At the other extreme, the minimum value of the oxygen consumption rate (R_{min}) gives information about the slowdown in oxygen consumption, which was similar for the three types of wines studied: 1.63, 1.60 and 1.73 hPa/h (1.9, 1.8 and 2 mg/L.day) for whites, rosés and reds, respectively (Table 3). This minimum consumption rate was reached at time t_{R_min} and reflected the moment of greatest flattening of the curve. In the case of the 24 white wines studied, it occurred on average at 37 h, while for rosés it was at 21 h and for reds at 41 h. Due to the variability among the different wines analyzed, there were no significant differences between white and red wines, although reds presented a higher mean value, indicating a longer period of time with a high oxygen

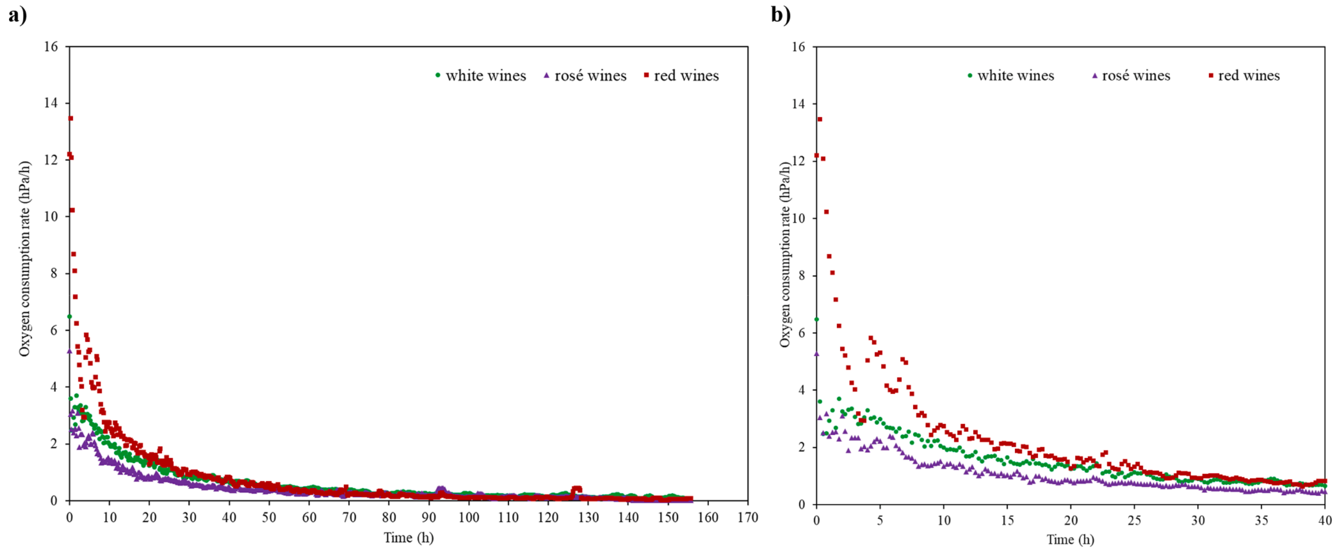

Fig. 3. Evolution of the average oxygen consumption rate (hPa/h) of red, white and rosé wines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

consumption rate, especially compared to rosé wines.

A_{max_min} is called $t_{A_{50}}$ o t_{OCRI} in the work of (Nevares et al., 2017), it is defined as the time in which the area under the curve is half of the total area. This time increased for wines with a low oxygen consumption rate or for those that were not able to consume all the dissolved oxygen. Therefore, as described above, this time was shorter for red wines (Table 3). The product of ΔO_{max_min} and t_{O_min} is the area under the curve (A_{max_min}), and establishes the relationship between the capacity and the rate of oxygen consumption of a wine: the lower the value, the greater the avidity for oxygen consumption or the lower the value of remaining oxygen (O_{min}.). It is necessary to narrow down its interpretation in terms of oxygen consumption capacity (ΔO_{max_min}) and speed (t_{O_min}).

By limiting the value of the area between 90% and 10% of the variation of ΔO_{max_min} (A_{90_10}) (Table 3), the reading gave the same results as for the previous parameter: greater avidity for oxygen consumption even when the extremes of the curves were not taken into account. In percentage terms, this area accounted for almost 70% of A_{max_min} for whites and rosés, reducing this value to almost 60% for reds. This could be explained by the results obtained for O_{90} which indicated that the latter wines consumed 9% of the total initial oxygen (O_{max}), while for whites and rosés these values were lower (6% and 5%, respectively).

3.5. *Consumption kinetics parameters characteristic of white, rosé and red wines*

Discriminant analysis allows us to extract the most significant parameters of the consumption kinetics of the different types of wine. Fig. 4 presents the coefficients which represent the correlations between the variables and the discriminant functions and are commonly used in order to interpret the "meaning" of discriminant functions. Fig. 4 represents samples in a scatterplot for the two discriminant functions. Of the 20 parameters obtained from each curve, SLDA model selected 14 variables that allowed for good wine differentiation and those with the highest discrimination capacity were 7 in order of significance (Fig. 4): O_{mid}, t_{O_90}, A_{max_min}, O_{int}, $t_{A_{50}}$, $\Delta t_{O\_90\_10}$, t_{O_min}, which are related to the

a)

	Function 1	Function 2	*p-value*
O_{90}	0.4772	-0.3178	*0.1546*
O_{max}	0.5273	-0.0467	*0.4732*
t_{O_90}	0.4104	-0.2037	***0.0030***
$t_{A_{50}}$	0.1236	-0.3254	*0.0142*
t_{O_int}	0.2795	-0.3786	*0.5005*
R_{max}	0.2727	-0.4698	*0.1947*
ΔO_{max_min}	0.2257	-0.4658	***0.0062***
O_{mid}	0.2014	-0.5545	***0.0004***
R_{min}	-0.0043	0.0103	*0.0723*
O_{int}	0.2502	-0.5250	***0.0087***
$\Delta t_{O\_90\_10}$	0.2135	-0.3650	***0.0206***
t_{O_min}	0.0790	-0.0056	***0.0476***
A_{90_10}	0.2377	-0.4772	*0.2356*
t_{R_min}	-0.0417	0.1420	*0.2598*
Eigenvalue	3.1028	1.6555	
Cum.Prop*	0.6521	1.0000	

*Cumulative proportion of explained variance

b)

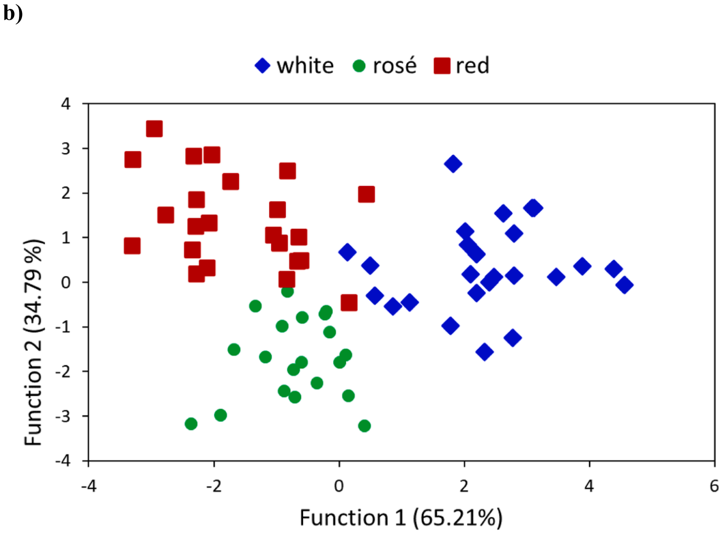

Fig. 4. Variable coefficients for the discriminant function variables (a) and plot of scores for wine differentiation using discriminant functions 1 and 2 (b).

amount of oxygen consumed O_{mid}, ΔO_{max_min}, O_{int}, and the time invested in consuming this amount of oxygen, t_{O_90}, $t_{A_{50}}$, $\Delta t_{O\_90\_10}$, t_{O_min}. Red and rosé wines are positioned on the negative axis of function 1 which explains 65.21%, while white wines are positioned on the positive side with importance of the variables O_{max}, O_{90} and $\Delta t_{O\_90\_10}$. It was found that the most significant variable was O_{mid} which represented the oxygen content present in the wine, therefore unconsumed, when just half the time necessary to consume all the available oxygen had been spent. Taking red wines as a reference, white and rosé wines were found to have a O_{mid} 2.2 and 2.6 times higher. In the same way, on average white wines required twice as much oxygen consumption time as red wines, i.e. A_{max_min} than red wines, so the area under the curve described between the highest and lowest oxygen level was very large, since white wines took much longer to move from one point to another. This was reflected in the parameter $\Delta t_{O\_90\_10}$ which indicated that white wines took three times as long to go from 90% to 10% of the oxygen initially available as red wines, and parameter $t_{A_{50}}$, which reflected the time in which half of the area under the curve was reached, showed that for white wines this time was 30% longer. This result was due to the fact that, in the first half of the kinetics of red wines, the rate of oxygen consumption was very high compared to the rate in white and rosé wines.

Therefore, these results characterize the consumption kinetics of a wine and indicate whether it is a white, rosé or red wine, with the oxygen level at the middle of the kinetics (O_{mid}) and the time required to consume from 90% to 10% of the initially available oxygen ($\Delta t_{O\_90\_10}$), two variables with values of 78.9 and 4.4 for white wines, double and triple that for red wines, with 35.5 and 1.4, respectively. This indicated that, based on the 72 wines analyzed, when a wine presents values of O_{mid} and $\Delta t_{O\_90\_10}$ close to 78 and 4.4, it is very likely that it is a white wine; while in the case of red wine it will present values of O_{mid} and $\Delta t_{O\_90\_10}$ close to 35 and 1.4.

4. Conclusions

The study of the development of a method for wine saturation at 35 °C has shown that 5 min are sufficient for wines to reach the maximum initial oxygen level: this will differ and will depend on the wine. The importance of atmospheric pressure in the saturation phase has been proved, so this parameter needs to be considered in the comparison between wine saturations.

The best fitting model of the consumption kinetics for the 3 types of wines studied, was the inverse curve. A total of 20 parameters were established to describe the oxygen consumption kinetics of a wine. The parameters with the greatest discriminatory capacity were those related to the amount of oxygen consumed O_{mid}, $A_{max_min}$and $O_{int}$and the time invested in consuming this amount of oxygen t_{O_90}, $t_{A_{50}}$, $\Delta t_{O\_90\_10}$, t_{O_min}. These results characterize the consumption kinetics of a wine and indicate whether it is a white, rosé or red wine, with the oxygen level at the mid-point of the kinetics (O_{mid}) and the time required to consume from 90% to 10% of the initially available oxygen ($\Delta t_{O\_90\_10}$) being the two variables that contributed most to the differentiation.

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CRediT authorship contribution statement

Maria Del Alamo-Sanza: Conceptualization, Methodology, Formal analysis, Supervision, Project administration, Funding acquisition. **Rosario Sánchez-Gómez:** Investigation, Writing - original draft, Writing - review & editing. **Víctor Martínez-Martínez:** Formal analysis, Writing - review & editing. **Ana Martínez-Gil:** Writing - review & editing. **Ignacio Nevares:** Conceptualization, Methodology, Formal analysis, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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