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Oxygen gas transfer through oak barrels: a macroscopic approach

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ABSTRACT

The oak barrel maturation step is nowadays strongly rooted in the production of quality wines. Two main physico-chemical phenomena contribute to the modification and improvement of wine: the solubilisation of volatile and non-volatile wood compounds concomitant with the dissolution of oxygen from the air into the wine. Indeed, wood is a porous material and gas transfer (especially oxygen transfer, expressed as oxygen transfer rate or OTR) through oak barrels, is an intrinsic parameter which ensures wine oxygen supply during maturation. Due to its oenological impact, it has been actively studied over recent decades using several approaches based on the same principle: the monitoring of oxygen in a model wine solution in the barrel. This project aimed at assaying barrel OTR by using a new tool based on the theoretical knowledge of gas transfer through porous materials. An oxygen concentration gradient was created on each side of a barrel kept in an airtight stainless-steel tank. The concentration of the oxygen in the atmosphere around the barrel was monitored in order to quantify oxygen transfer, thus the avoiding common drawbacks of interactions between dissolved oxygen ingress kinetics and the consumption of oxygen in the liquid phase by wood components. This study reports for the first time, the diffusion coefficient of entire oak barrels (*Q. sessilis*) to be between 10^{-10} and 10^{-9} m²/s, and it contributes to increasing knowledge on the complex phenomena driving oxygen ingress during the maturation of wine in barrels kept in cellar conditions. The results highlight the important role of wood moisture content in oxygen transfer, and provides a simple and reliable parameter to monitor it: the weight of the barrel. Following methodology developed by the authors, the OTR of a new oak barrel was found to be 11.4 mg/L per year. Taking into account the oxygen released through the wood pores, a new barrel will contribute 14.4 mg/L per year of oxygen to the wine, of which 46 % in the first three months of aging.

KEYWORDS

Permeability, oak barrel, oxygen, transfer, OTR, aging, oxidation, wine.

INTRODUCTION

For centuries, wooden barrels have been used to store, carry and sell wines. Nowadays, it is well known and described from a chemical point of view that maturation in oak barrels profoundly modifies the intrinsic composition of wines and shapes their quality. These modifications result from complex phenomena associated with the solubilisation of volatile and non-volatile compounds in the wine, accompanied with the slow ingress of small quantities of oxygen (Boidron *et al.,* 1988; Michel *et al.,* 2011). For these reasons, oak barrels are considered as active vessels. For decades, numerous studies have contributed to a better understanding of the barrel aging impact on the colour, aroma and taste of wine (Chatonnet and Dubourdieu, 1998; Prida and Chatonnet, 2010; Shinkaruk *et al.,* 2019; Marchal *et al.,* 2016; Michel *et al.,* 2016).

Oxygen ingress or the oxygen transfer rate (OTR) through oak barrels is another important parameter to take into account when interpreting the chemical modification of wines aged in oak barrels. This micro-oxygenation phenomenon was first observed as early as 1931 by Ribéreau-Gayon, who used a basic chemical approach involving a sulfite solution kept in barrels. Since then, much research has been carried out in this area, sometimes leading to inconsistent results; thus, questions raised almost a hundred years ago about how much oxygen a barrel can bring and the way in which the oxygen transfer takes place are still a matter of debate (Table 1). Depending on the experimental protocol, as well as the measurement system, OTR values can range from 5 to 45 mg/L per year (Frolov-Bagreev and Agabal'iants, 1951; Vivas and Glories, 1997; Kelly and Wollan, 2003; Nevares and del Alamo-Sanza, 2014; del Alamo-Sanza and Nevares, 2014; Prat-García *et al.,* 2020). Nevertheless, it is widely accepted that the oxygen absorbed by wine during maturation in barrels comes from the atmospheric air and from the pores of the oak wood barrel (del Alamo-Sanza and Nevares, 2014; Qiu, 2015; Vivas and Glories, 1997).

Regarding the oxygen intake of wine from the air, the total amount of oxygen transferred through the barrel corresponds to the sum of three potential entry points: the stave, joints and bung. The contribution of the oak staves depends on the permeability coefficient of the wood, and that of the joints on their quality (machining profile) and pressure (number of steel strapping) (Qiu *et al.,* 2018). Using the same analytical approach as Ribéreau-Gayon (1933), a study conducted almost 25 years ago showed that 21 % of the oxygen entered through the bung, 63 % through the gaps between the staves, and only 16 % through the staves (Vivas and Glories, 1997). It was estimated that the amount of annual oxygen entry was from 10 mg/L per year for five-year-old barrels to 45 mg/L per year for new very fine grain barrels. More recently, Nevares *et al.* (2014) confirmed that oxygen is transferred through the oak wood of wine barrels in a study using optical sensors and a high-resolution colour camera. Additional experiments led the same team (del Alamo-Sanza *et al.,* 2017) to conclude that oxygen ingress via the bung was negligible, while 46 to 72 % of oxygen ingress occurred via the oak wood, meaning that wood is a much more important entry point than the gaps between the staves. In the field of material science, oak wood can be considered as a porous solid. The flow of fluids through wood is only possible in two ways: via bulk flow, according to Darcy's law, and via diffusive flow, according to Fick's law. As oak wood is not permeable to liquid, bulk flow can be limited to the first millimetres of wood impregnation - where the voids are interconnected - due to hydrostatic pressure. At the same time, diffusion of gases and vapor occurs through the cell lumen and boundaries. Sorz and Hietz (2006) showed that the oxygen diffusion coefficient of *Quercus robur* wood is 21 times higher in the axial direction than in the radial direction (6.9×10^{-8} *vs* 32×10^{-8} m²/s). They also found diffusion through the wood at 40 % gas content to be five times higher than diffusion through wood at 15 % gas content, thus highlighting the role of wood moisture content in gas transfer. Similar results were obtained by del Alamo-Sanza and Nevares (2014) in a study using a fine-grain American oak (*Q. alba*) barrel: most of the oxygen was dissolved in the first two months after barrel filling, followed by a steady state phase characterised by low continuous oxygen ingress. A total of 11.62 mg/L of oxygen was dissolved during the year. Using luminescence technology, Martínez-Martínez *et al.* (2019) estimated the OTR to be between 7.3 and 8.9 mg/L a year for *Q.petraea* wood samples. A more recent study (Prat-García *et al.,* 2020) showed oxygen transfers of 11.9 to 22.8 mg/L per year in barrels made out of oak wood staves classified according to image analysis. Furthermore, Qiu *et al.* (2018) found that gaps between staves were an important entry point for oxygen ingress; by measuring oxygen transfer with a permeameter trough stave junction, they concluded that transfer is strongly dependent on the pressure applied between staves, as well as the quality of the contact surface. Indeed, at 20 bar of pressure between staves, they measured a very limited oxygen transfer, in contrast to that measured at 3 bar.

The second source of oxygen ingress is wood pores. As reported by several authors (Plötze and Niemz, 2011; Diaz-Maroto and Tahir, 2019), the porosity of oak wood is known to be approximately 0.6. Once in contact with wine, the oxygen naturally contained in oak wood cells is desorbed progressively as the first millimetres of wood are flooded; about 10 mg/L of oxygen is thereby provided in the first month of aging in a standard 225 L barrel (Qiu *et al.,* 2018). This observation has also been reported for aging using stave and chips by Pons *et al.* (2014) and García-Estévez *et al.* (2017). These authors also highlighted the difference between the theoretical oxygen quantity released by wood and the lower measured dissolved oxygen content due to oxygen consumption by ellagitanins or hydrosoluble compounds. Prat-García *et al.* (2020) recently reported an oxygen release of 1.3 to 1.8 mg/L due to desorption nine days after barrel filling. When wood staves are impregnated with a model solution or wine, two antagonistic dynamic

TABLE 1. Examples of OTR data obtained from entire oak barrels and expressed as the amount of oxygen brought to the wine during aging according to the results found in the literature over a 90 years period.

Oxygen Transfer Rate per year	Barrel type	Method	Authors
5 mg/L	Sealed barrels	Kinetics of $SO4^{2-}$ formation	Ribéreau-Gayon (1933)
15 to 45 mg/L	Sealed barrels	N-A*	Frolov-Bagreev and Agabal'iants (1951)
28 mg/L	Unsealed barrels	Kinetics of $SO4^{2-}$ formation	Vivas and Glories (1997)
36 mg/L	Sealed barrel, bunghole on the side		
45 mg/L	Silicone bung to ensure an airtight seal		
19.5 mg/L	New barrels Limousin (wild grain)		
28 mg/L	New barrels Centre (tight grain)		
10 mg/L	5-year-old used barrels, Centre (tight grain)		
32 ± 5.6 mg/L	New barrels, American Oak (*Q. alba*)	dissolved oxygen optoluminescent dipping probe	Nevares *et al.* (2014)
27 ± 2.3 mg/L	New barrels, French Oak (*Q. petraea*)		
11.3 ± 0.9 mg/L	4 new medium grain American Oak barrels	Dynamic one-year OTR measurement in a barrel	del Alamo-Sanza and Nevares (2014)
11.7 ± 1.5 mg/L	4 new tight grain American Oak barrels	Measurement with a dissolved oxygen optoluminescent dipping probe	
8.2 ± 0.5 mg/L	4 new tight grain French Oak barrels		
22.8 mg/L	High OTR barrel (*Q. petraea*)	Classification of wood by image analysis of staves	Prat-García *et al.* (2020)
11.9 mg/L	Low OTR barrel (*Q. petraea*)	Measurement with a dissolved oxygen optoluminescent dipping probe	
14.4 mg/L	Commercial barrel (*Q. petraea*)		

* Not Available

phenomena occur with quite similar kinetics. In the particular case of oak wood chips, the air trapped in the wood pores is quickly released in the first three days, and the dissolved oxygen in the model solution increases (Pons *et al.,* 2014). In parallel, hydrosoluble wood compounds are released and oxidation reactions start. According to García-Estévez *et al.* (2017), the majority of air trapped in the wood pores of oak chips is released after 5 to 10 days, and the oxygen consumption in the model solution becomes higher than the oxygen released until all dissolved oxygen is consumed after 55 days. Knowing that red wine contains a lot of compounds highly reactive to oxygen, including the ellagitanins released during oak-wood aging, these observations underline the limits to the technique for measuring dissolved oxygen content in wine when it comes to quantifying oxygen transfer in active vessels.

The aim of the present study was thus to develop a new method for oak barrels adapted from traditional membrane permeability measurement techniques for commercial cork stoppers (Karbowiak *et al.,* 2010). A macroscopic approach was used based on the hypothesis that the barrel can be considered as a ‟membrane" separating the wine from the atmosphere and for which the classical diffusion laws apply. A hermetic tank was built, and the barrel was stored inside it to study gas/gas transfer. The results of the analysis of gaseous oxygen variation within the atmosphere surrounding the barrel could contribute to significantly improving knowledge of oxygen transfer during wine aging in barrels.

MATERIALS AND METHODS

1. Gas measurement

A NomaSense O_2 P6000 and a Pst 3 sensor (Nomacorc, USA) were used to monitor the evolution of oxygen concentration in the tank and the barrel. The measurement range was 0-100 % O_2, and the detection limit was 0.03 % O_2 (according to the manufacturer). For the oxygen compensation measurements, the system unit was stored inside the tank in order to record the internal temperature and pressure at the same time. The probe was placed at bung height in the same place for all the experiments. The system was calibrated using CO_2 (4.5 grade, Linde AG, Germany) and atmospheric air at 20.95 % O_2. During the experiment, the measurements were automated and recorded every 10 min.

2. Hermetic tanks

Two stainless steel hermetic tanks tailored to contain a barrel were manufactured by BELLOT Company (Gradignan, France). A door at one end of the tank and sealed with elastomer joints and vacuum PTFE grease gave access to the barrel inside. A small trap door was located on the top of the tank for CO_2, O_2 and air injection. Figure 1 shows the tanks in opened and closed positions. The total volume of a tank was 1522 L (according to the manufacturer).

3. Barrel selection

A total of 10 brand-new 225 L classic Bordeaux barrels with 6 hoops and made out of French oak wood (*Quercus petraea)* were provided by Seguin Moreau Cooperage (Cognac, France).

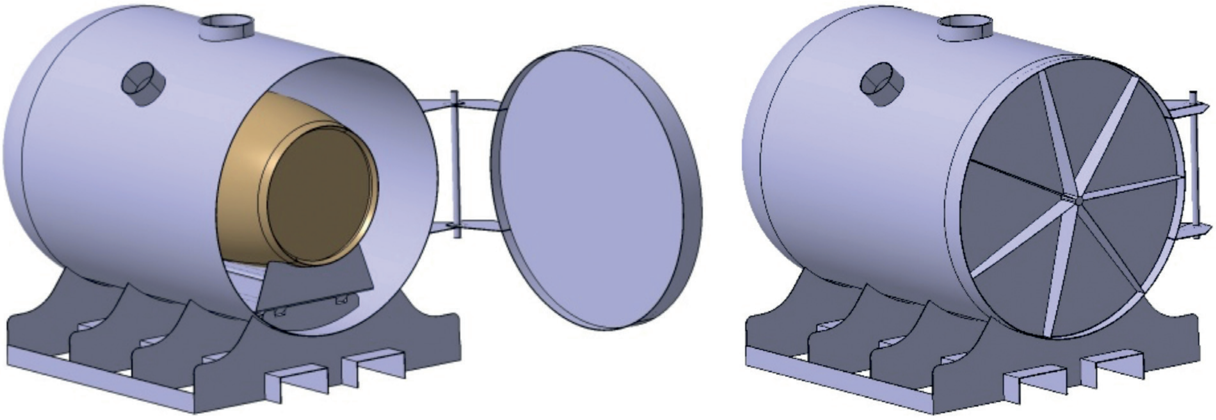

FIGURE 1. Schematic representation of the stainless-steel tanks in open (loading position) and closed (ready to assay OTR) positions.

Each barrel had undergone a water pressure test by the manufacturer to ensure the absence of leakage. They were delivered with a silicone bung of 50 mm in diameter. Table 2 gives detailed information about the barrels as provided by the cooper. The external volume of each barrel selected for the study was calculated using parabolic formula; the volumes varied from 283 to 287 L depending on the stave thickness of the barrels. The average weight of a standard 21 mm barrel was 38.5 kg at delivery. Before each assay, the external surface of the oak barrels was cleaned with absolute ethanol in order to prevent the development of mould during the experiment in the closed tank.

TABLE 2. Characteristics of the brand-new 225 L oak wood barrels.

Barrel code	Weight (kg)	Stave thickness (mm)	Toasting*	Grain**
B1	38.9	21	medium-long	Fine
B2	36.8	15	medium-long / open	Fine
B3	44.6	27	medium-long	extra-fine
B4	55.5	34	medium-long / open	Fine
B5	36.9	21	medium-long	Fine
B6	37.7	21	medium-long	Fine
B7	40.4	21	medium-long	Fine
B8	38.2	21	medium-long	Fine
B9	46.9	27	medium-long	Fine
B10	37.9	21	medium-long	Fine

* According to the manufacturer.

** According to the manufacturer, extra-fine (< 2 mm) and fine (2–3 mm).

4. Barrel hydration protocols

In order to evaluate the effect of hydration protocols on OTR level, a different protocol was followed for each of three barrels of identical stave thickness and toasting level: 1) The bottom of Barrel 6 was filled with 20 L of cold water (15 °C) and then closed with the bung; the barrel was stored vertically for 12 hr then turned upside down and left for another 12 hr, 2) Barrel 5 was completely filled (225 L) with cold water (15 °C) and then the bung hole was closed with a bung; the full barrel was left for 48 hr and then emptied, and 3) Barrel 7 was hydrated for 12 and 22 min using a vapour generator (Vapo-Clean from R-tech Solutions, France) capable of producing 30 kg/h of vapour; the vapour was released inside the barrel through a stainless-steel stick output. All the remaining barrels were simply filled with cold water during the desired time in order to reach different moisture contents. They were then weighed before the OTR measurement.

5. Moisture content calculation

Wood is a hygroscopic material; i.e., wood gains or loses moisture from the air and/or the liquid depending on the conditions of the surrounding environment. Water can migrate into wood in three ways: i) as a fluid through the cell lumens via capillary tension, ii) as vapour through the cell lumens, and iii) via molecular diffusion through the cell walls. The moisture content of wood can be calculated from the relationship between the mass of water in the wood and the mass of the wood without the water. As the absolute dry mass of a barrel remains unknown, we calculated a relative variation of moisture content (ΔMC; Eq.1), based on the difference between the actual barrel mass (m_h) and the lowest barrel mass (m_i).

$$\Delta MC(\%) = \frac{m_h - m_i}{m_i} * 100 \qquad \text{(Equation 1)}$$

6. Diffusion coefficient and OTR calculation

As soon as they come into contact with liquid, extractable oak wood compounds, like lignanes, coumarines, ellagitanins and lactones, progressively dissolve in the liquid phase. As a consequence, when using an oxygen dipping probe in the liquid, the total oxygen ingress evaluation could be distorted by the consumption of oxygen by these compounds (García-Estévez *et al.,* 2017; Pons *et al.,* 2014; Pascual *et al.,* 2017), as well as by the dynamic evolution of the barrel moisture content during the measurement. In the present study, this was overcome by working in the gas/gas phase for barrel characterisation, as is already widely-applied in research in oenology for the monitoring of gas/gas OTR of stoppers. A barrel-tank characterisation system equivalent to a membrane characterisation system, with two individual spaces separated by oak wood of the barrel (Figure 2), was used in this study.

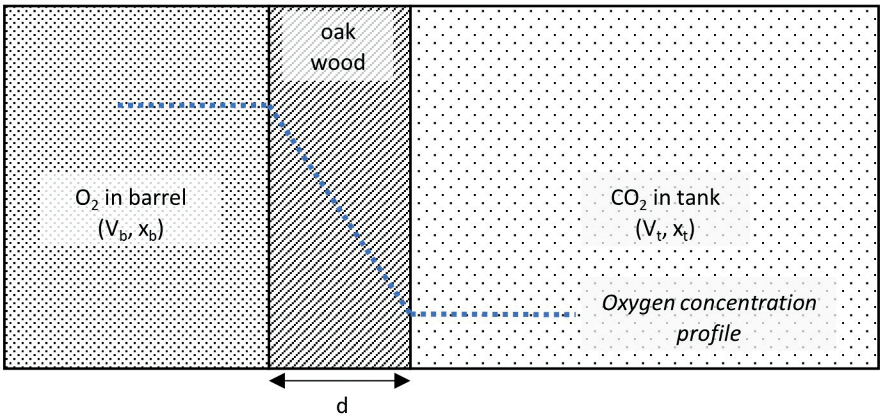

FIGURE 2. Schematic representation of the barrel-tank characterisation system, with the oxygen concentration gradient at a given time between the barrel saturated with O_2 and the vat saturated with CO_2 (d = thickness of the stave).

The initial trials were conducted with new oak barrels filled with CO_2 (< 1 % O_2) and surrounded by atmospheric air (21 % O_2), but the time required to reach a steady state to perform one measurement was 20 days and was thus not suitable to study multiple barrels. This parameter was excessively long due to the relatively low oxygen concentration gradient and to the low permeability of oak wood to oxygen. Therefore, in order to decrease the time required for each experiment, the barrels were filled with air saturated by approximately 90 % oxygen, then closed tightly with a silicone bung before storage in the middle of the tank. Once the tank was closed, it was filled with CO_2 (O_2 dropped to approximately 3 % saturation). A high oxygen gradient concentration was thereby created between the inside of the barrel and the inside of the tank, increasing the flow of oxygen through the wood and allowing the diffusion coefficient to be determined within 4 to 7 days. In this experiment, the diffusion of oxygen occurred from the inside to the outside of the barrel; it was important to measure the quantity of oxygen passing through the barrel without modifying the integrity of the barrel by passing probes through the wood.

The permeation of gases through the wood with a thickness *d* (m) was calculated with an equation (eq.2) based on Fick's first law (Ruiz de Adana *et al.,* 2005; Sorz and Hietz, 2006):

$$V_t \frac{dx_t}{dt} = \frac{A \cdot D}{d}\left(x_{final} - x_t\right) \qquad \text{(Equation 2)}$$

where $V_t \, . \, dx/dt$ is the volumetric flow of gas transported per unit time (m^3/s) from the inside of the barrel (volume V_b) to the outside (volume V_t). This is proportional to the oxygen fraction gradient ($\Delta x = x_{final} - x_t$, where x_{final} is the oxygen fraction at equilibrium and x_t the oxygen fraction recorded over time) from the outside of the barrel to its inner surface *A* (m^2). The constant *D* is the diffusion coefficient (m^2/s). In such a closed system, the principle of mass conservation applies and the final concentration (at equilibrium) can be calculated as follows (eq.3):

$$x_t \cdot V_t + x_b \cdot V_b = x_f(V_t + V_b) \qquad \text{(Equation 3)}$$

Equations 2 and 3 were merged (eq.4) and solved by using boundary conditions (eq.5):

$$\int_{x_t^0}^{x_f} \frac{dx_t}{x_f - x_t} = \beta \cdot D \cdot \int_0^t dt \qquad \text{(Equation 4)}$$

$$f(x_t) = ln\left(\frac{x_t - x_f}{x_t^0 - x_f}\right) = -\beta \cdot D \cdot t \quad \text{(Equation 5)}$$

$$\text{With } \beta = \frac{A}{d \cdot V_t}\left(1 + \frac{V_t}{V_b}\right)$$

The diffusion coefficient of barrel D was obtained from the experimental data x_t = f(t) plotted according to Equation 5. This linearisation method allowed D to be calculated from the experimental data acquired in a short time.

From the obtained coefficient D, it was possible to estimate the Oxygen Transfer Rate (OTR) of oxygen passing from atmospheric air to the wine via wood of the oak barrel. The concentration of dissolved oxygen inside the barrel was assumed to be close to 0 mg/L (the oxygen consumption rate in the wine is faster than the oxygen ingress rate), and the dissolved oxygen concentration at the interface between air and wet wood to be proportional to the partial pressure of oxygen in the atmospheric air, according to Henry's law. However, the saturated concentration of oxygen in wine depends on multiple parameters, such as temperature, type of wine or alcohol content. In this study, an oxygen concentration of 7.4 mg/L was used for all the calculations (with wine at 19 °C), as used by Devatine *et al.* (2007). It was possible to estimate the OTR by inserting the experimental diffusion coefficient into equation 2 (eq.6):

$$OTR = D \cdot \frac{A \cdot 7.4}{d \cdot V_b} \qquad \text{(Equation 6)}$$

RESULTS AND DISCUSSION

1. Gas tightness test

The gas tightness of stainless-steel tanks is of primary importance for the development of a gas/gas transfer method. In this study, two tanks were submitted to a gas tightness test before use. With the main end door closed, CO_2 was injected through the top hole until the concentration of O_2 inside the tank had decreased from around 21 % to lower than 5 %. The trap door of the top hole was then closed. The concentration of O_2 was monitored for three weeks. For both tanks, the gas tightness was calculated to be lower than < 0.001 %/day. This very low transfer enabled the gas exchange in each barrel to be accurately monitored.

2. Initial diffusion coefficient of brand-new barrels

The diffusion coefficient of 10 brand new barrels - described in Table 1 - was measured using the tank system described earlier. An example of data processing is given in Figure 3, where the function of oxygen fraction in the tank (x_t) is plotted against time, according to equation 5. In this case, a high coefficient of determination (R^2 = 0.999) was obtained for a diffusion coefficient of 1.94×10^{-9} m²/s.

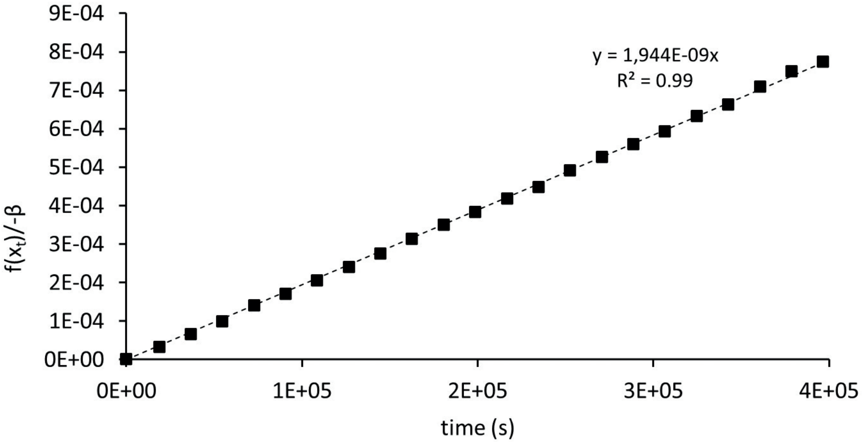

FIGURE 3. Example of experimental data linearisation $f(x_t)/-\beta = f(t)$. The slope represents the diffusion coefficient D in m²/s.

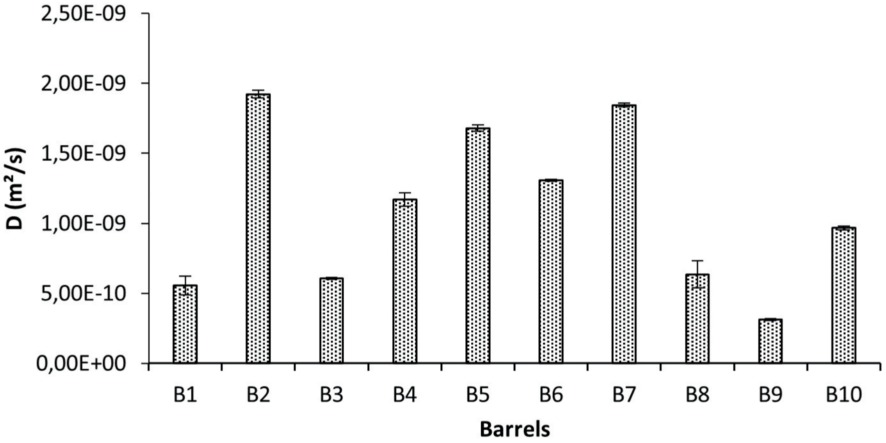

FIGURE 4. Example of the diffusion coefficients of 10 new oak barrels (Q. *sessilis*).

The initial D values of the 10 barrels ranged from $3{\cdot}10^{-10}$ to $2{\cdot}10^{-9}$ m²/s (Figure 4) with a good repeatability in the two measurements for each barrel. These results show that the D-values of barrels can be very heterogenous when the barrels are used for the first time. The main factor that could explain this range is wood moisture content, as similarly reported for oak barrels by Nevares *et al.* (2014) and for corks by Fonseca *et al.* (2013). Indeed, some barrels were stored in our lab for weeks before D measurement, while others were characterised immediately at delivery. This result indicates the importance of barrel moisture content before use in order to ensure the homogeneity of the diffusion coefficient.

3. Influence of barrel preparation on diffusion coefficient

Oak wood, like many natural products, is considered to be a hygroscopic material: it naturally absorbs or releases moisture in the form of water vapour from or to the air. Empirically, an expression of this phenomenon – which is well known by wine makers – is that when empty oak wood barrels are stored for a long time, they lose their watertightness (and thus start leaking), and they thus need to be filled with water before use. Coopers deliver finished barrels as quickly as possible, and the winemakers are advised to do barrelling at their earliest convenience after reception.

Coopers usually also recommend that the brand-new barrels be soaked before being filled with wine. The main reason is to swell the wood and thus avoid any leakage of liquid by forming a tight seal. Another reason is to remove residual sawdust and the harshest of the tannins. The manufacturers recommend several ways to soak the barrels; for example, filling them with a few litres of hot water and bunging them for two hours; actively rinsing for five minutes with hot water; filling them with cold water and leaving for 24 or 48 hours; or filling with hot water and leaving for 24 hours. All these processes have different cost in terms of water consumption and labour, and their impact on the diffusion coefficient is not precisely described in literature.

In this experiment, each of three barrels (21 mm thickness) was prepared following one of the following procedures generally recommended by coopers and described earlier in the barrel hydration protocols section. For each treatment, the water consumption, the relative humidity percentage corresponding to the increase in barrel mass after the hydration process (ΔMC) and diffusion coefficient (D) were determined after each treatment, as summarised in Table 3. As can be seen, the diffusion coefficients of the three barrels were reduced by a factor of 10 compared to the corresponding control barrels. Water consumption is shown to be equivalent when comparing the vapour and 20 L hydration treatments, but with vapour treatment reducing the preparation time from 24 h to 12 min. The diffusion coefficient of the 48 hours whole barrel treatment was found to be similar to a 22 min vapour treatment, but with the latter consuming only 11 L of water instead of the 225 L consumed in the former. As a consequence, vapour treatment seems to be a great alternative for winemakers in terms of water and time saving.

TABLE 3. Impact of hydration protocol (vapour, entire and 20 L barrel bottoms hydration) on the diffusion coefficient of new oak barrels.

Barrel	Preparation mode	Preparation time	Water consumption (L)	ΔMC (%)	D (m²/s)
6	Hydration of barrel bottoms (20L)	Control	0	0.0	1.4×10^{-9}
		24 h	20	1.9	3.8×10^{-10}
5	Whole barrel hydration	Control	0	0.0	1.8×10^{-9}
		48 h	225	4.3	2.0×10^{-10}
7	Water vapour	Control	0	0.0	2.0×10^{-9}
		12 min	6	2.0	3.4×10^{-10}
		22 min	11	3.2	1.7×10^{-10}
		42 min	21	4.2	1.1×10^{-10}

4. Impact of the oak barrel moisture content on the evolution of the diffusion coefficient

During the previously described experiment, we observed that the diffusion coefficient decrease was concomitant with a relative mass increase. Therefore, in order to evaluate the relationship between the moisture content and the diffusion coefficient of a barrel more precisely, the diffusion coefficient of an oak barrel (B1) was evaluated at different levels of moisture content (Figure 5).

As reported by other authors (del Alamo-Sanza and Nevares, 2014; Sorz and Hietz, 2006; Vivas *et al.,* 2003), this trend indicates that the moisture content of wood has a fundamental role in the oxygen diffusion coefficient of a barrel.

In order to further support our observation, we extended our experiment to include nine more barrels from our selection. These were weighed and monitored at two different moisture contents for different diffusion-coefficients (initial "i" and hydrated "h"). As the absolute humidity content (not measured in this study) of the barrels would have been required to compare them, the ratio of the two diffusion-coefficients (initial and hydrated) for each of the nine barrels was calculated and plotted against the corresponding ΔMC (Figure 6).

Regardless of the thickness of the staves, the Dh/Di ratio of all the barrels seems to be highly correlated to ΔMC through an exponential function. Such behaviour has been observed for conifers by Sorz and Hietz (2006), even though they found a more linear relationship for *Quercus* wood. However, in this study, the measurement is based on an entire wood barrel, and the exponential decrease in diffusion based on moisture content can be explained by a combination of multiple phenomena occurring simultaneously. First, when a barrel is filled, a physical expansion of the wood caused by the absorption of liquid occurs.

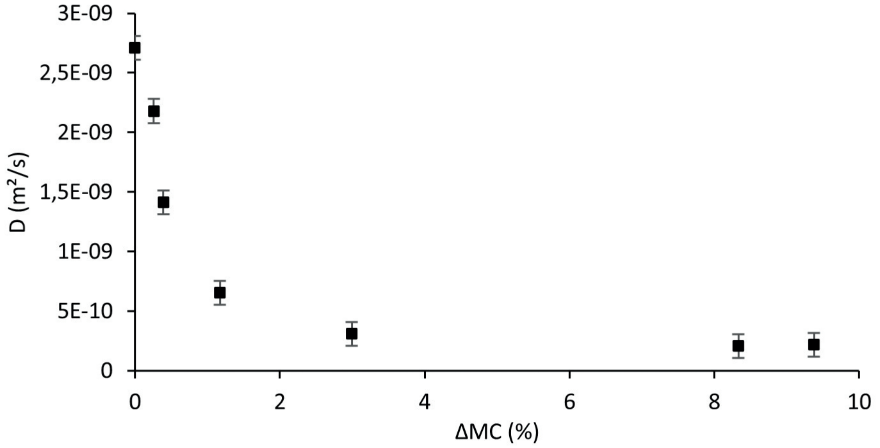

FIGURE 5. Evolution of the diffusion coefficient D of oak barrel B1 according to the relative increase in moisture content (ΔMC).

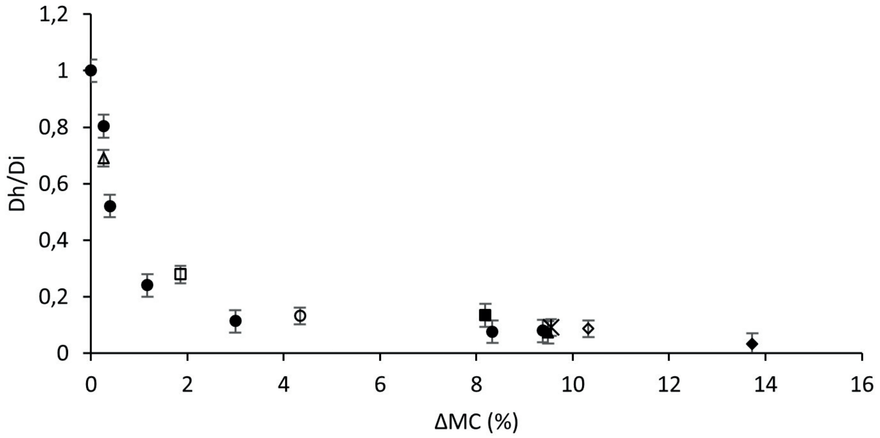

FIGURE 6. Ratios of initial (Di) and hydrated (Dh) diffusion-coefficients of 9 new oak barrels ●(B1) ◇ (B2) ■ (B3) ○ (B5) ∗ (B4) □ (B6) ◆ (B8) ▲ (B9) △ (B10) against their corresponding ΔMC.

As a consequence, the pressure between the staves may increase, thus decreasing oxygen transfer (Qiu *et al.,* 2018). In parallel, the increase in MC during hydration is due to the advance of the moisture from the inside of the barrel (which is in contact with the liquid) to the outside of the barrel (which is in contact with the air). As described by Singleton (1995), the liquid saturates the cells and vessels of the wood in a free fluid state. Progressively and towards the outside, the free liquid decreases and the gas content of the lumens increases. At a certain point, there is no more free liquid and the lumens are filled with gas and vapor only. The more waterlogged the wood is, the lower the diffusion coefficient. Ruiz de Adana *et al.* (2005) established a model to describe this phenomenon and calculated a diffusion coefficient of $1.05x10^{-11}$ m²/s for the internal side of the stave and $1.33x10^{-8}$ m²/s for the external side. These results correspond well to the measured global coefficients in the present study (from $2x10^{-10}$ m²/s for the "hydrated" state to $3x10^{-9}$ m²/s for the "dry" state). However, the diffusion coefficient of oxygen is known to be $2x10^{-5}$ and $2x10^{-9}$ m²/s in air and water respectively (Sorz and Hietz, 2006). In water only and in dry wood, the two oxygen diffusion coefficients were found to be rather similar, making it impossible to determine which one is limiting the diffusion. In terms of hydrated wood, there is a difference in an order of magnitude of 2 or 3 between the two diffusion coefficients, meaning that the interactions between cell walls and water are the main limiting diffusion factors in this case.

Figure 7 shows the evolution of ΔMC in barrel B1 over hydration time when completely filled with water. The moisture content shows a high correlation with hydration time ($R^2=0.986$) through a derivation of the Lucas-Washburn equation (Fries & Dreyer, 2008; Zhmud *et al.,* 2000) which originally described the penetration depth

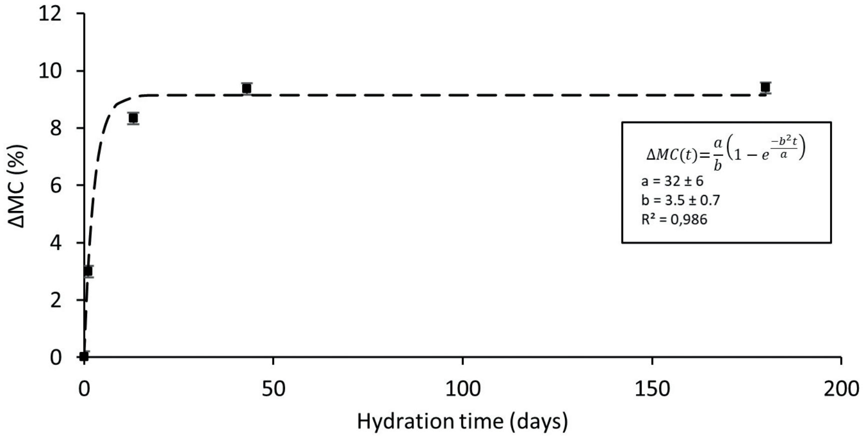

FIGURE 7. Evolution of the relative moisture content (ΔMC) over hydration time when barrel B1 was completely filled with water.

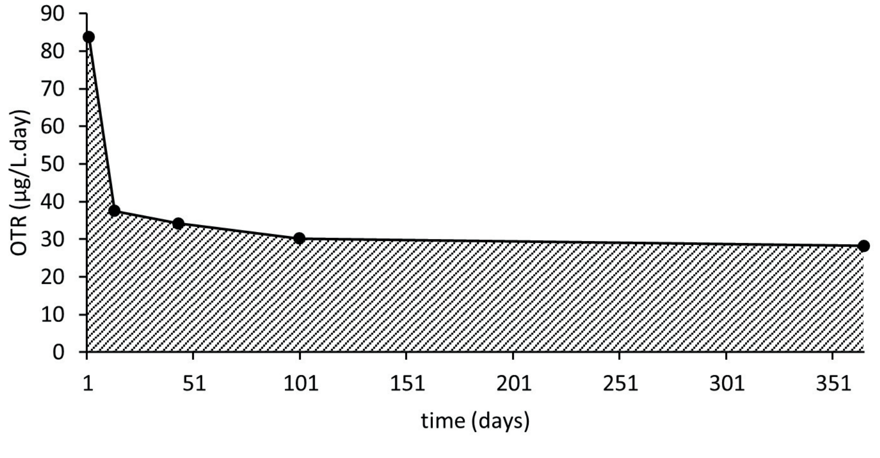

FIGURE 8. Evolution of the barrel OTR (µg/L.day) during aging over time since filling.

of water according to the time in porous media by capillarity. In accordance with the latest (at the time of writing) results in the literature (Roussey *et al.,* 2021), this result confirm that barrels need around 20 to 40 days to enter into a pseudo steady state in terms of moisture content, and as a consequence, in terms of OTR.

5. Total dissolved oxygen intake

In order to evaluate the annual dissolved oxygen intake using the new method described in this study, an example is given of a calculation based on the results obtained from Barrel 1. By using the results obtained from Figures 5 and 6, it is possible to calculate the diffusion coefficient according to the time since filling. This coefficient can be used to evaluate an OTR in mg/L.day (eq. 6) through the barrel during wine aging.

When applying the trapezoidal rule, an integration of the curve representing this OTR over time since filling (Figure 8) results in a total OTR of 11.4 mg/L per year. Moreover, if the volume of air contained in wood pores is assumed to be completely desorbed in the wine as it impregnates the barrel, the amount of desorbed oxygen per litre of wine ($m_{dO2/L}$) after barrel filling can be calculated as follows:

$$m_{dO2/L} = \frac{\Delta MC \cdot m_{barrel} \cdot M_{O2} \cdot \varphi \cdot P_{O2air}}{\rho \cdot V_b \cdot R \cdot T}$$

where m_{barrel} is the mass of the barrel, φ the wood porosity, M_{O2} the molar mass of molecular oxygen, P_{O2air} the partial pressure of oxygen in the atmosphere, ρ the density of wine, V_b the volume of wine in the barrel, R the ideal gas constant and T the temperature. Under the experimental conditions of the present study, barrel B1 (with a theoretical porosity of 0.6 and a ΔMC of up to 4 kg, and under atmospheric pressure at 15°C) desorbed a maximum of 3 mg of oxygen per litre of wine around 30 days after barrel filling. Taking into account the calculated OTR and the estimated amount of oxygen desorbed from the wood pores, the total intake of oxygen can be estimated as being 14.4 mg/L during the first year. This means that around 21 % of the oxygen is released as a result of wood porosity. Similar results have recently been observed by Prat-García *et al.* (2020) with an average dissolved oxygen release of 1.3 to 1.8 mg/L via wood porosity nine days after barrel filling, and an average OTR of 14.4 mg/L per year for commercial barrels, leading to a total intake of 16 mg/L of oxygen in the first year.

CONCLUSIONS

Possessing knowledge of oak barrels OTR is essential for winemakers and researchers. Using insights into membrane science, a new method for measuring the OTR was developed based on the analysis of gaseous oxygen concentration in the atmosphere surrounding a barrel in a hermetic tank. Fick's law was used to determine the diffusion coefficient of entire oak barrels. A very high correlation between this coefficient and the wood moisture content (weight variation) was observed. This model could allow the total amount of oxygen transferred to the wine at any time to be estimated by simply knowing the initial parameters of the barrel (its diffusion coefficient and weight at delivery) and the time since barrel filling. In addition, the application of vapour for preparing new barrels prior to first-time use has an impact on the diffusion coefficient; the data shows that by following this vapour protocol, time and water can be saved during the barrel preparation step, thus contributing to improved oxygen management during maturation and, ultimately, better sensory quality control.

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