Impact of oxygen permeability of stoppers on the aging of wines over a 10-year period

Part 2/3: Case of Sauvignon Blanc

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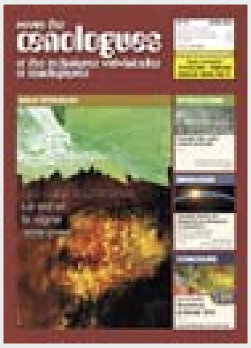

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Since Antiquity, it has been known empirically that the value of a wine increases with aging, provided that it can be stored under good conditions, namely by protecting it from air. Starting from this observation, winemakers and wine lovers developed ingenious methods to maintain such conditions. With the rudimentary techniques of their era, they were able to keep a wine for a few years and sometimes even longer for the finest wines whose reputation was similar to that of our most famous growths today.

For a long time, the use of natural cork to close wine bottles was popular with both producers and consumers. From a technical standpoint, quality criteria related to the industrial use of cork stoppers essentially applied to their visual characteristics, and then in the 1980s to their mechanical characteristics. During the 1990s, the impact of natural cork stoppers on the presence of a prohibitive off-aroma, cork taint caused by TCA (2,4,6-trichloroanisole), was demonstrated. Stricter application of natural cork stopper manufacturing processes was gradually put in place. About 15 years ago, to respond to increasing demands from winemakers concerned about the aging of their wines, the concept of Oxygen Transfer Rate, or OTR, *via* the closure was introduced. As a result, the study of the gas transfer properties *via* closures has become a major subject, since it determines the quality of bottle aging of wine *(Godden et al., 2001)*. It has been clearly established that the closure is an important parameter in the manifestation of pre-mature oxidative aging of wines, even though this phenomenon is above all determined by the quality of the raw material and by the care with which the winemaker treats it *(Lavigne et al., 2008 ; Pons et al., 2010)*.

It is now accepted that the oxygen introduced into wine during bottling is defined as the sum of the oxygen dissolved in the wine and the oxygen in the headspace *(Lopes et al., 2007; Oliveira et al., 2013)*. During bottle aging, it is also possible to distinguish between the oxygen released by the stopper itself and the oxygen originating from the outside air. To express these phenomena, OTR and a newer concept, OIR (Oxygen Initial Release), provide information about the behaviors of different types of stoppers *(Chevalier et al., 2019)*. Many studies have been conducted in recent years in order to better understand the impact of stoppers on the quality of white and red wines. The very great majority of them have followed the evolution of wines for a period of less than two years. For many wines, this period corresponds to the average length of bottle aging. However, the impact of stoppers on the aging of age-worthy wines has not been widely documented.

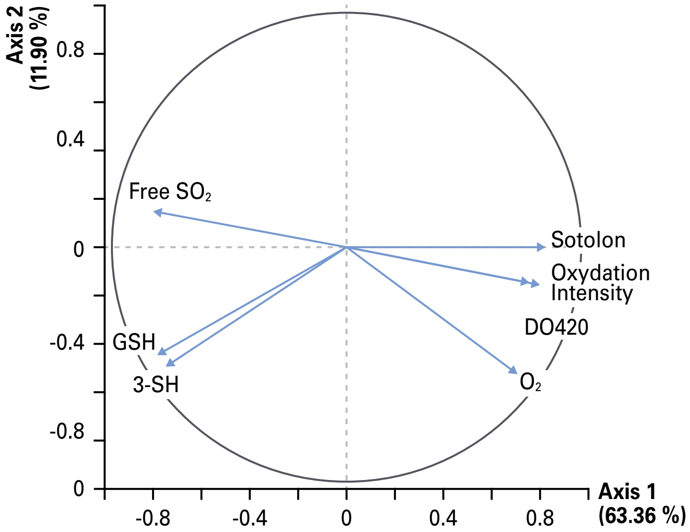
Our project is intended to study the sensory and analytical evolution of three white wines (Sauvignon Blanc from Bordeaux) over a period of 10 years, as a function of stopper type.

Table 1: Selected stoppers (x) for each growth, ranked according to their OTR value.

	OTR mg/year	I-ap	M-ap	L-ap
Saran capsule	< 0,1 [1]	x	-	-
Diam30 P0.07	0.3 [1]	x	x	x
Diam5 P0.15	0.4 [1]	x	x	x
Saranex capsule	0.5 [1]	x	-	-
Diam5 P0.35	0.6 [1]	x	x	x
Synthétic 3	0.6 [1]	x	x	x
Synthétic 1	1.5 [1]	x	-	x
Synthétic 2	4.6 [1]	-	x	-
Natural cork	0,1 – 40 [1]	x	x	x

[1] *Roberston, 2009.*

Figure 1: Representation of axes 1 and 2 of the principal component analysis of analytical and sensory results obtained during the bottle aging of three wines.



Materials and Methods

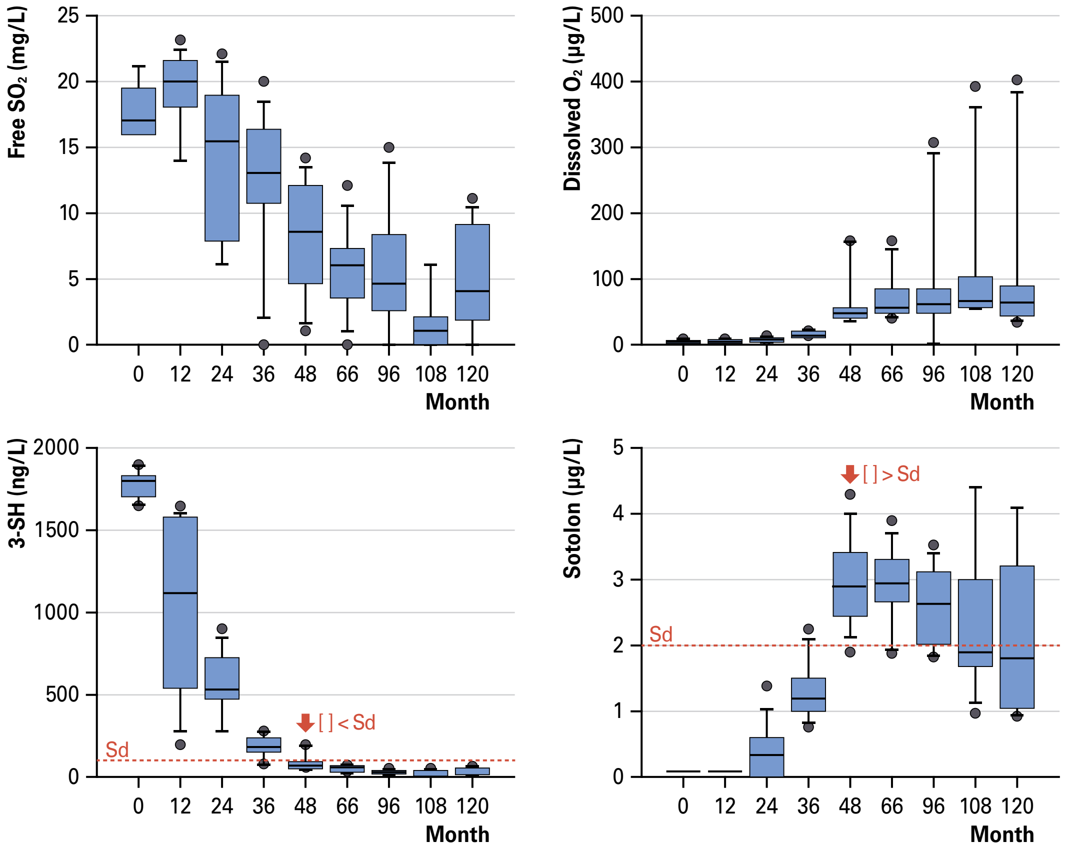
The objective of this project is to compare the evolution of three Sauvignon Blanc wines (2007 vintage) that have been corked either with traditional stoppers (natural cork of different quality levels depending on wine quality), or with several families of stoppers with different oxygen permeability values (OTR). As such, three Diam micro-agglomerated stoppers with increasing OTR values have been selected. This selection is accompanied by three synthetic stoppers and two screw caps whose theoretical OTR values, as found in the literature, are presented in ***Table 1.***

White wines of the Sauvignon Blanc varietal were selected based on their aging potential. The latter is evaluated on the basis of historical knowledge of wines from each growth. They come from appellations in the Bordeaux region. As part of this study, they are referred to as follows: "low aging potential" (l-ap), "Medium aging potential" (M-ap)" and "Long aging potential L-ap). The l-ap wine was aged on the lees in a stainless steel tank, while the two others were aged on the lees in oak barrels.

The evolution of the wines was monitored from an analytical and sensory point of view. To do this, certain chemical markers of the varietal aroma of Sauvignon Blanc wines were measured, as was their oxidative evolution. These markers are 3-sulfanylhexanol (3-SH), which has a grapefruit aroma, and sotolon, whose aroma is reminiscent of wax and honey. Other markers of oxidative evolution of wines were also measured: free SO_2 and glutathione (GSH) as well as dissolved oxygen content (Orbisphere sensor) and tint, expressed by optical density measurement at 420 nm (OD420). Each measurement corresponds to analysis of three bottles.

Figure 2: Illustration of the impact of stoppers' OTR on the intensity of yellow-orange tint of a Sauvignon Blanc wine (M-ap) **after 10 years of bottle aging** (ranking of samples as a function of OTR values in ***Table 1).***

Figure 3: Box-plot representation of the evolution of free SO_2, dissolved oxygen, 3-sulfanylhexan-1-ol and sotolon contents during the bottle aging of M-ap wine stoppered with six closures (n = 3).



At the end of this project, after 10 years of bottle aging, we completed the analytical characterization of wine aroma by measuring the content of two compounds that contribute to wine quality and also to flaws found in bottle-aged wines. These are furfurylthiol, which gives the wine a roasted note, and methional, which has an odor of boiled potatoes.

The wines were tasted at regular intervals in black glasses. A panel of internal tasters from Institut des Sciences de la Vigne et du Vin (ISVV) evaluated the intensity of oxidation in the samples as well as their preference for the samples.

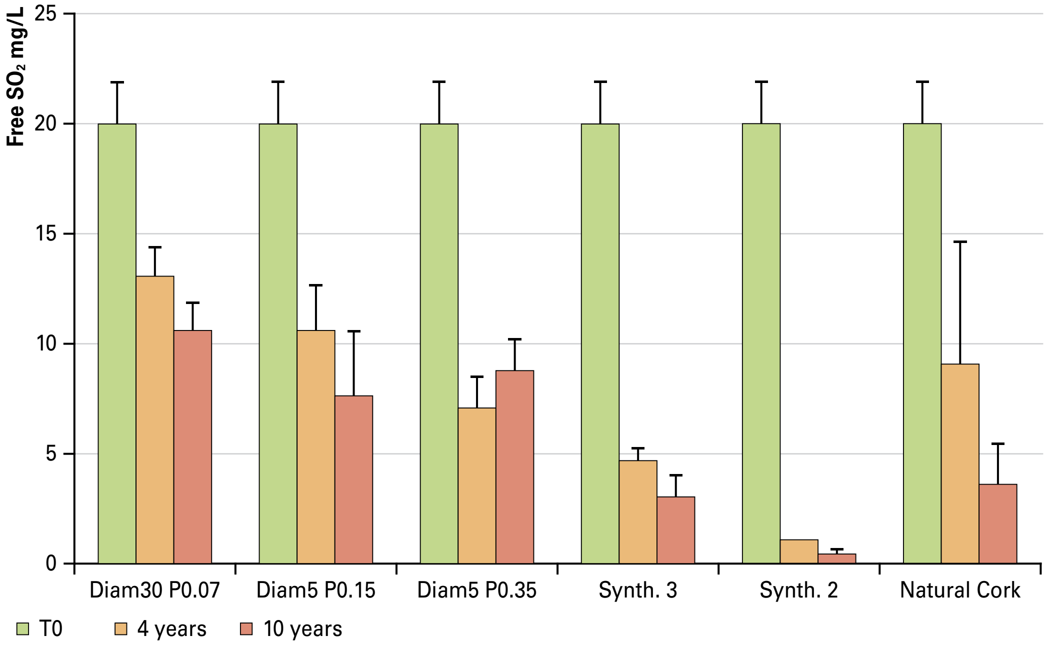
Evolution of oxidation markers of white wines during bottle aging

We monitored the evolution of several markers associated with the intrinsic quality of dry white wines. Representation of the results obtained for the three growths and all of the stoppers in the form of principal component analysis shows that the oxidation markers of the wines are well correlated with each other ***(Figure 1).*** Axis 1 represents the oxidation level and makes interpretation of the results rather easy. Low oxidation intensities are associated with high free SO_2, GSH and 3-SH contents, whereas high levels are associated with high sotolon and dissolved oxygen contents. They are also accompanied by greater perception of the oxidized character of white wines as well as a more intense yellow-orange tint ***(Figure 2)***.

As an example, we present the analytical results obtained for the M-ap growth with six stoppers ***(Figure 3)***. We show that free SO_2 decreases during bottle aging. We can note that the decrease in free SO_2 is accompanied by a great deal of scatter in the data. It is very likely that its evolution varies as a function of stopper type. Similar results are obtained for the evolution of dissolved oxygen content. Once the oxygen introduced during bottling is consumed, the dissolved oxygen contents measured after three weeks of bottle aging are less than 10 µg/L. After 10 years of bottle aging, dissolved oxygen contents are between 30 µg/L and 400 µg/L. It is possible that such ranges can lead to oxidative evolution of some of these wines.

Examination of the kinetics of evolution of aroma markers reveals that the rapid decrease in 3-SH contents during the first few years of bottle aging is accompanied by an increase in sotolon content. The scatter of their values during bottle aging may be interpreted as revealing the impact of the stopper. We note that some stoppers can preserve 3-SH contents in wines during the first few years of bottle aging ***(Figure 3)***. In contrast, after 48 months, the 3-SH values approach the aroma detection threshold (Sd 60 ng/L), making its contribution to wine aroma more limited. At the same time, we see an increase in average sotolon concentration. After 48 months of aging, levels exceed its aroma detection threshold (Sd 2 µg/L), confirming its involvement in the aroma of certain wines closed with stoppers that are too oxygen-permeable. These contents remain rather high, while presenting great variability: after 10 years of bottle aging, they are between 0.9 µg/L and more than 4 µg/L, depending on the OTR of the stoppers.

■ **Figure 4: Example of free SO_2 contents found in the M-ap wine after 4 years and 10 years of bottle aging as a function of stopper type** (n = 3).



Effect of stopper permeability on the evolution of free SO_2 content during bottle aging

As an example, the free SO_2 contents found in M-ap growth wines are presented in ***Figure 4***.

In general, the contents found in wines after 4 and 10 years are lower when the stopper's OTR value is high. Furthermore, the natural cork type shows significant scatter in values, reflecting the random character of oxygen permeability of cork stoppers. After 10 years of aging, the wine with the most permeable stopper type no longer contains any free SO_2. Conversely, the wine with the most impermeable stopper has a free SO_2 content of 11 mg/L, i.e. a decrease of only 50% from the initial value. At this level, the wine is still protected by the anti-oxidant action of free SO_2.

Effect of stopper OTR on methional and furfurylthiol contents after 10 years of bottle aging

To deepen our understanding of the precise composition of these wines, we also measured the methional and furfurylthiol (FFT) contents of all the wines after 10 years of bottle aging.

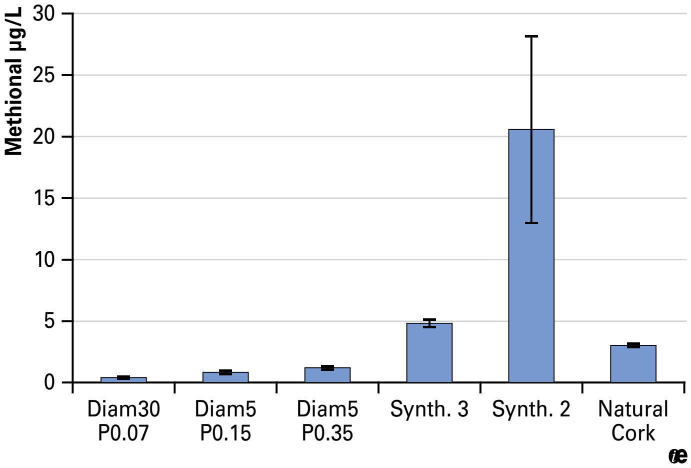
As an example, we present the results obtained for the wine with medium ageworthiness (M-ap).

Methional, a compound whose odor is reminiscent of boiled potatoes, is also a good marker of the oxidative evolution of white wines. Its aroma detection threshold is 2 µg/L. Just after bottling, this compound was measured in the wines. The contents found were all less than 0.5 µg/L. After 10 years of bottle aging, we have shown that the content of this compound reflects the oxidation level of wines as a function of the stopper's OTR value ***(Figure 5)***. The higher OTR is, the greater the methional concentration is: nearly 20 µg/L for the synth. 2 stopper, whereas wines with the least permeable stopper always have methional contents lower than its detection threshold (Sd 0.5 µg/L), even after 10 years of bottle aging.

Furfurylthiol is a sulfur compound with an extremely low aroma threshold (Sd 0.4 ng/L), and it contributes to the roasted notes found in oak barrel-aged wines and also in white wines that develop a reduction bouquet during bottle aging.

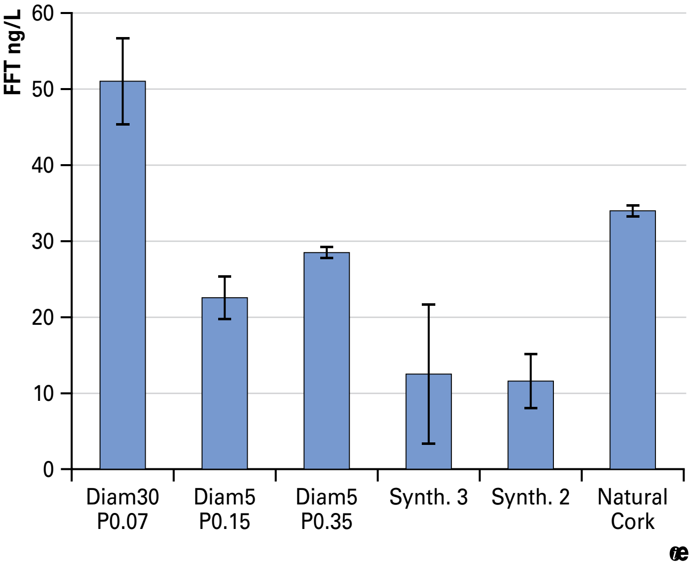
After 10 years of bottle aging, we show that the highest contents are found in the wine closed with the most impermeable cork stopper ***(Figure 6)***. At this concentration level, this compound contri-

■ **Figure 5: Methional contents found in white wines from the M-ap growth after 10 years of aging** (n = 3).



butes quite certainly to the roasted coffee notes in wines. In effect, the wine with the Diam30 P0.07 stopper contains more than 50 ng/L. The contents are lower when the OTR value of the stopper is high. The analysis of all the data has enabled us to better interpret the preference level of the wines by our panel of experts.

■ **Figure 6:** **Furfurylthiol** (FFT) **contents found in white wines from the M-ap growth after 10 years of aging** (n = 3).



Effect of stopper OTR on the intensity of oxidative character and tasters' preference

Previously, we showed that the evaluation of the oxidative character of wines throughout the experiment is very highly correlated with the sotolon and dissolved oxygen contents. The more permeable the stopper is to oxygen, the higher the quantities found in the wines will be and the more they will intervene in the oxidative mechanisms influencing evolution of wine aroma and color.

During this project, we also determined the preference of tasters during wine tasting (ranking test). As an example, we present the results obtained for the M-ap growth after 4 years and 10 years of bottle aging ***(Table 2).***

We show that the least permeable stopper for the oak barrel-aged Sauvignon Blanc wine is most preferred, regardless of bottle aging time. Similarly, the wine closed with the most oxygen-permeable synthetic stopper is the least preferred by our panel, starting at 4 years of bottle aging. After 10 years, similar results were obtained for the other two growths (low and long aging potential).

Conclusion

Started in 2008, this project was intended to provide additional insight about the impact of stopper permeability on the quality of white wines during bottle aging. To do this, we put in place an analytical and sensory approach, based on the Institute's historical knowledge about the precise characterization of the aroma fraction of wines. As such, this work includes not only the impact of the stopper on conventional markers of white wines (OD 420, free SO_2) but also on markers of the varietal aroma of Sauvignon Blanc (3-SH), markers of the oxidative evolution of these wines (sotolon, methional) as well as the markers associated with the desired evolution towards reduction bouquet (FFT). In the end, we show the importance of understanding and controlling oxygen addition during the entire bottle aging of wines.

For wines that have undergone meticulously controlled lees aging as well as careful preparation for bottling, we have shown that a stopper with low oxygen permeability should be chosen. This preserves the fruity aroma (volatile thiols) of wines, while minimizing the formation of compounds associated with oxidation notes (sotolon, methional). We show that the most impermeable cork stopper in this study (Diam30 P0.07) delays the manifestation of oxidative aging effects in white wines, while also being preferred by tasters. ■

■ **Table 2: Results of the preference ranking test from a panel of experts for wines aged for 4 and 10 years in bottle (sum of ranks).**

Time	Diam30 0.07	Diam5 P0.35	Diam5 P0.15	Synth. 3	Natural cork	Synth. 2	F	1 %	Results
4 years	37 a	46 ab	48 b	48 b	51 b	91 c	24.7	16.81	Significative
10 years	20 a	29 b	30 b	50 c	58 c	71 d	24.57	16.81	Significative

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Étude de l'influence de l'origine géographique, de la taille de grain et de la charge tannique du bois de chêne de tonnellerie sur le profil sensoriel des vins rouges