Low-permeability closures contribute to lower sulphite levels in rosé wines and improve their aging capacity

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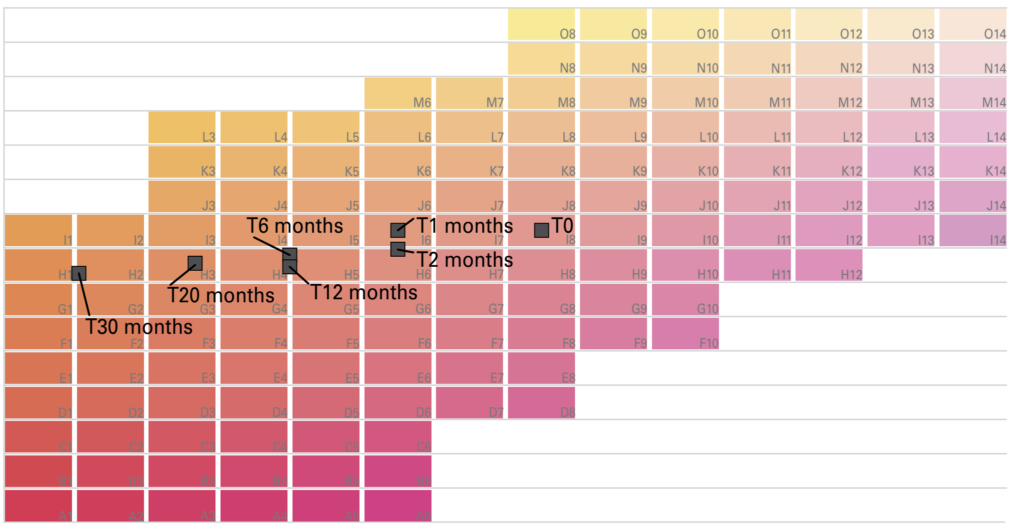
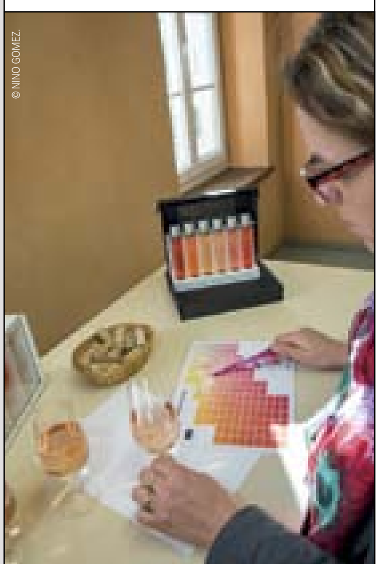
Rosé wines are appreciated for their youthful characteristics, their fresh aromas and their bright colour. However, over the months of ageing in the bottle, under the effect of oxygen and temperature, their aromas fade and the colour browns. There is measurable oxygen uptake during bottling, and that oxygen is consumed during the two to three months after bottling. This leads to a drop in the free sulphites content, increased binding with colour compounds and a decrease in aroma compounds of fermentation origin. In contrast, the oxygen introduced through the closure progressively diffuses into the wine in very small amounts. It cannot be measured but also leads to changes in wine composition. The low permeability of some closures now makes it possible to decrease the sulphite level needed to protect the wine, while still ensuring rosé wine quality. The point is to select the appropriate permeability to preserve wine potential without inducing reduction phenomena, which can negatively affect aroma expression. These studies were conducted on several types of rosé wines and can be used to identify typical cases in order to guide winemakers' choices.

Figure 1: Evolution of the apparent colour of a rosé wine stored in bottle for 30 months at 20°C.

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Wines that travel across space and time

The rosé wine market has grown steadily in the past 20 years and now represents one out of every ten bottles consumed worldwide *(growth of 31% by volume between 2002 and 2016; source: CIVP)*. These wines are increasingly being exported, and this segment currently represents 30% of wine volumes sold in the Provence region of France. Rosé wines are appreciated on all occasions, but demand is concentrated during the summer season. While the finesse and elegance of rosé wines have until now led to a focus on the fragility of these wines and the need to drink them young, the longer distribution circuits and increased demand now make it necessary to extend their shelf life and develop methods to retain the sensory characteristics appreciated by consumers for a longer time *(Masson and Cayla, 2019)*.

The trend towards lower sulphite levels in wines is a constraint in this area. Along with lower temperatures, sulphites help to delay the inexorable change in wine components over time. However, the Observatoire des Rosés du Monde *(Observatory of Rosés of the World)* put in place by the Centre du Rosé and Union des œnologues shows that winemakers are integrating this demand from the market: the average total SO_2 concentration in rosé wines has dropped from 95 to 85 mg/L in the past eight years *(Masson, 2019)*.

Slowing down the natural evolution of wines

Colour is an important factor in the attractiveness of rosé wines, and storage conditions (time, temperature, oxygen, sulphites) influence their appearance *(Cayla et al., 2013)*. The polyphenol composition of rosé wines and the resulting apparent colour depend on geographical origin, grape variety and winemaking conditions. Ducasse et *al.* (2015) showed that the proportion and quantity of the different families of anthocyanin-derived pigments are influenced by the concentration of native compounds and storage conditions. Variable temperature regimes and low sulphite levels lead in particular to an increase in

colour, owing to the lower bleaching intensity of sulphites and to increased formation of pigments that are resistant to this bleaching. This involves an increase in both colour intensity and shade. This behaviour is found in all wines, but the degree of this increase is specific to each. Over time, wines take on more colour and become oranger ***(Figure 1)***. Brown compounds are formed as time passes, and yellow colour, b*, increases more when the wine has a low sulphite level ***(Figure 2)***. Correlatively, colour intensity also increases over time, in accordance with two phenomena: the appearance of yellow compounds, but also the return of the red colour of anthocyanins, owing to a decrease in sulphite content. The average concentration of free sulphites, initially set at 15 and 25 mg/L, respectively, for the "low sulphite" and "high sulphite" batches, decreases to less than 5 mg/L and around 10 mg/L in 12 months. Furthermore, the initial colour intensity of a rosé wine (T0, ***Figure 2***) is influenced by the free sulphites content. A lightly sulphited wine appears more intense in colour, since the anthocyanins are less bleached by sulphites.
Negative changes in the colour of rosé wines represent a major commercial issue, with some bottles no longer meeting the standards expected by consumers. In general, this is also accompanied by a change in sensory profile, which evolves from fresh fruits to ripe and jammy fruits, and leads to the development of dairy and burnt notes. The aroma compounds of interest change over time. After 20 months, there is an 80% loss in acetates and ß-damascenone, along with a very significant increase in 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN). The 3-mercaptohexanol content, which contributes to citrus and exotic fruit notes, also tends to decrease over the months. Nevertheless, recent work *(Roland et al., 2016)* has revealed the equilibrium between the reduced and free forms of these compounds under the effect of storage at 20°C. It is thus possible to observe an increase over time in the measured concentration of this compound.

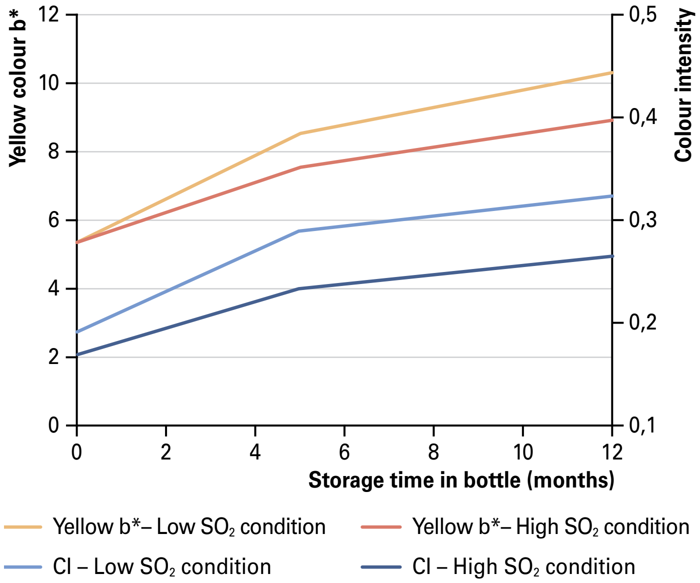
Oxygen and sulphite contents are closely dependent on each other

The oxygen present in wine after bottling has several sources:
– O_2 dissolved in the wine before bottling, owing to cellar operations (filtration, racking, transfers, etc.);
– O_2 dissolved in the wine during bottling itself;
– O_2 present in the headspace, between the closure and the wine, which is in equilibrium with the oxygen dissolved in the wine;
– O_2 transferred through the closure, as a function of its permeability, and dissolved in the wine during bottle ageing.
In the bottle, the oxygen dissolved in the wine enters into biochemical mechanisms and leads to oxidation of sulphites. This is why the free SO_2 content greatly decreases after bottling, in proportion with the O_2 content. Winemakers may intervene as a function of the equipment they dispose of (deoxygenation of the wine before racking, inerting of the bottle before filling, control of the oxygen level and good vacuum before corking), in order to minimize the quantity of O_2 in the bottle and therefore a decrease in free SO_2 concentration. As a function of this information and level of sulphite adjustment in the wine before bottling, the wine shall enjoy sulphite protection for a more or less long time. As an example ***(Figure 3)***, even though the three wines started with an identical free SO_2 content before bottling, wine 1 retains its protective sulphite level of around 20 mg/L for 12 months. In contrast, after only two months of storage, wine 3 is already below 15 mg/L of free SO_2. Consequently, the characteristics (colour, fruitiness) of wine 3 evolve much faster than those of wine 1. The phenomena governing these variations are not clearly identified but are often explained by an initial free SO_2 level (25 mg/L) that is insufficient (production/distribution constraints) and thus not rigorously stable (equilibrium between free and bound forms). If the first drop in sulphite level (first two months) is due to oxygen acquired during the bottling operation, losses are thereafter determined by the permeability of the closure.

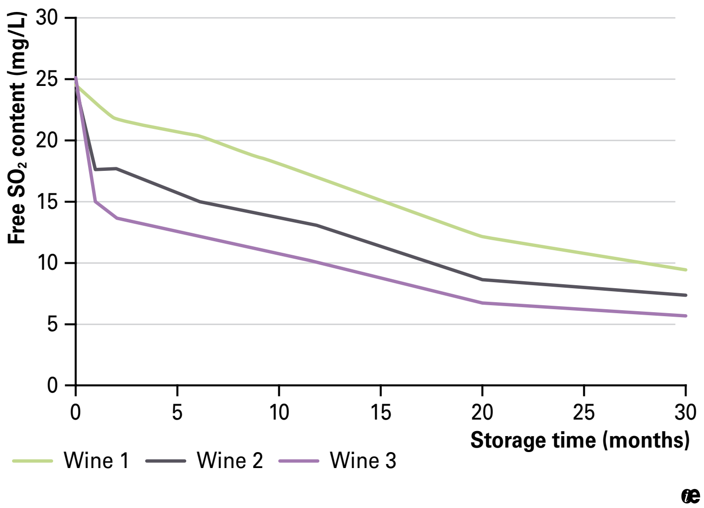
The permeability of the closure can regulate the evolution of the wine

Different methods are used to assess the permeability of a closure, i.e. the quantity of oxygen transmitted *via* the closure over time. Permeability can be broken down into two elements *(Chevalier et al, 2019)*: oxygen released after corking (OIR, or Oxygen Initial Release), due to the compression of the cork, and then passive diffusion over time (OTR, or Oxygen Transfer Rate).
The study conducted in partnership with Diam Bouchage involved four closures with

■ **Figure 2: Evolution of colour intensity** (CI) **and yellow colour** (b*) **in a rosé wine kept in bottles at 20°C in accordance with the two initial sulphite levels** (low free SO_2 target: 15 mg/L, high target: 25 mg/L).



■ **Figure 3: Evolution of free sulphites content in three rosé wines stored in bottle at 20°C.**



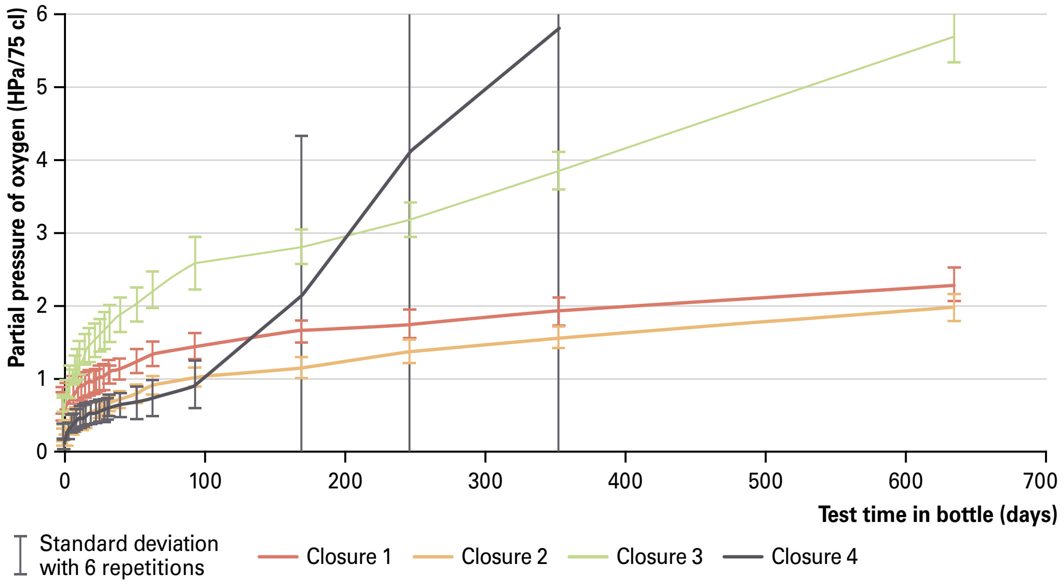
different permeability levels as assessed under standard conditions. To characterize these four closures, 75-cl bottles were equipped with luminescence probes, the oxygen level was greatly decreased, and the closure was inserted in compliance with good practices (six repetitions). Oxygen enrichment inside the bottle was monitored over almost two years ***(Figure 4,*** cumulative effect).

Closures 1 and 2 (technological corks from Diam Bouchage) are in line with expectations: closure 1 is slightly more permeable than closure 2. Closure 3 (synthetic) is the most permeable of the four closures studied and compliant with its specifications. Closure 4, made of cork, is the most impermeable in the first 90 days, and then the oxygen partial pressure greatly increases in two bottles out of the six repetitions (standard deviations are high) ***(Figure 4).*** Since natural cork is not adapted to dry conditions (bottle full of low-oxygen gas), it is possible that some of the closures may have dried out after several months of bottle ageing, thus increasing oxygen uptake in the bottle. The results show that the average permeability of these natural corks is probably between closures 1 and 2 (Diam) and closure 3 (synthetic). Technological and synthetic corks have a range of permeabilities, adapted to the varied needs of winemakers. In this study, it is not so much the closure type that is being studied as different exposures to oxygen over time, *via* the determination of permeability.

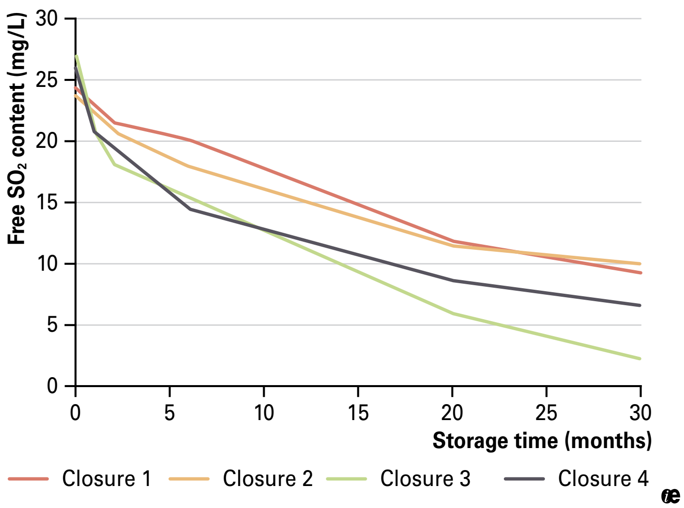
The four closures cited above ***(Figure 4)*** were used to bottle three rosé wines of varied types (origin, grape varieties, sensory profile, colour, alcohol content, pH, etc.). Wine 3 has a more intense colour and is very expressive, with grapefruit, rose and passion fruit notes among others. Its winemaking process generated limited oxygen addition, including lees ageing. It has very high contents of 3-mercaptohexanol (2,500 ng/L) and phenylethanol. Wine 2 is just as expressive but with exotic fruit, pineapple and amyl notes. This profile is confirmed by aroma analyses conducted by the Nyséos laboratory. This wine has higher concentrations of terpene alcohols, acetates and furaneol. Wine 1 has a less intense aroma and is characterised by yellow-fleshed fruits, peaches, marshmallow and rose. These wines were bottled by minimising oxygen addition (average cumulative content of 2.2 mg/L) and stored at 20°C for 30 months. Analyses were performed after 1, 2, 6, 12, 20 and 30 months, which broadly covers the usual period of consumption of rosé wines.

The first parameter evaluated over time is sulphite content ***(Figure 5).*** The free SO_2 concentrations of the batches bottled with closures 3 and 4 drop faster than with the other two stoppers. The threshold of 10 mg/L of free SO_2, commonly acknowledged as the lower limit for protection, is thus reached between 12 and 18 months for these products, whereas it occurs at 30 months for the wines aged with closures 1 and 2. The higher oxygen permeability of closure 3 explains this phenomenon. For closure 4, the average free SO_2 content after 30 months of ageing is between the values

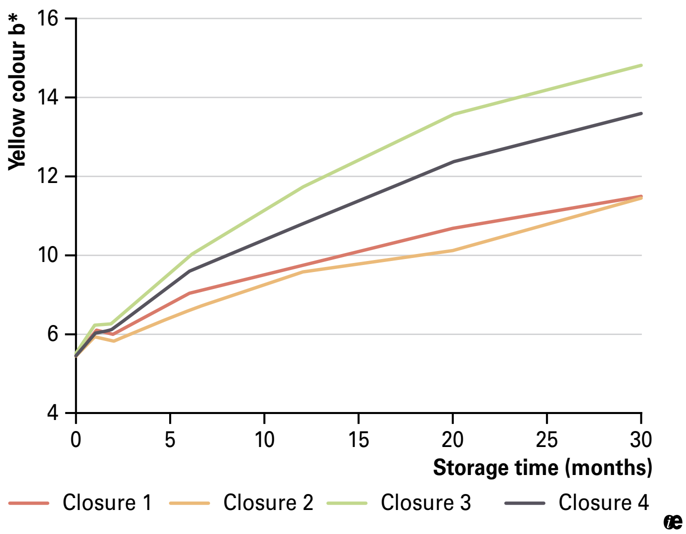
■ **Figure 4: Estimation of the permeability of closures under standardised conditions, enrichment in oxygen from the atmosphere in a bottle initially brought to a very low level.**



■ **Figure 5: Evolution of the free sulphites content in rosé wine no. 1, bottled with four stoppers with different permeability levels, stored at 20°C.**



■ **Figure 6: Evolution of yellow colour b* over time as a function of closure permeability, wine no. 2.**



for closures 1 and 2 and those for closure 3. This shows that the oxygen permeability of this batch of closures is between that of the other two types of closures in this test. Furthermore, Chevalier et *al.* (2019) showed a certain level of heterogeneity among natural cork closures, as observed after 12 months using certain indicators analysed on the three bottles opened for each type at each analytical point.

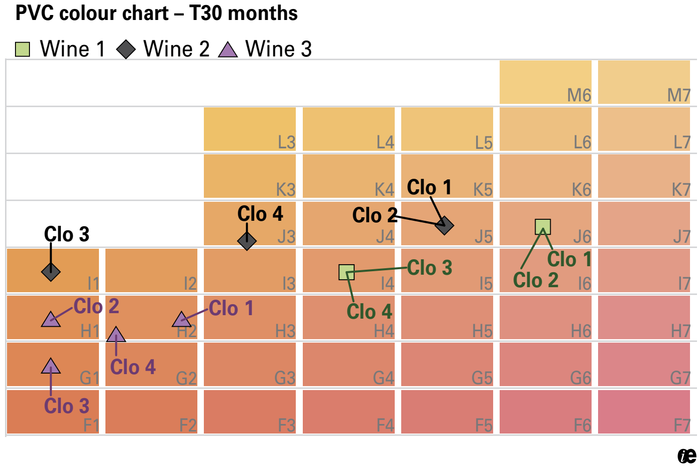
As expected, the yellow component of colour ***(Figure 6)*** increases more with closure 3, which is more permeable, regardless of the wine. Closure 4 shows intermediate behaviour, consistent with the evolution of free sulphites ***(Figure 5).*** The Diam closures (low-permeability closures 1 and 2) minimize the evolution of colour towards yellow shades. Visual consequences are assessed with the colour chart ***(Figure 7).*** The wines are quite different in appearance. Closures 1 and 2 are not, however, differentiated for the two wines that were not aged on the lees, i.e. under reductive conditions (wines 1 and 2).

For the aroma markers, most indicators are not influenced by corking conditions, since temperature is a more influential lever to minimise losses of fermentation-related compounds *(Cayla, 2012).* The concentration of 3-mercaptohexanol decreases with closure 3, which is the most permeable, for all three wine types. For the other closures, no trend can be observed over time for the three wines studied. Nevertheless, closure 4 leads to intermediate concentrations after six, 12 or 20 months, as a function of the wine.

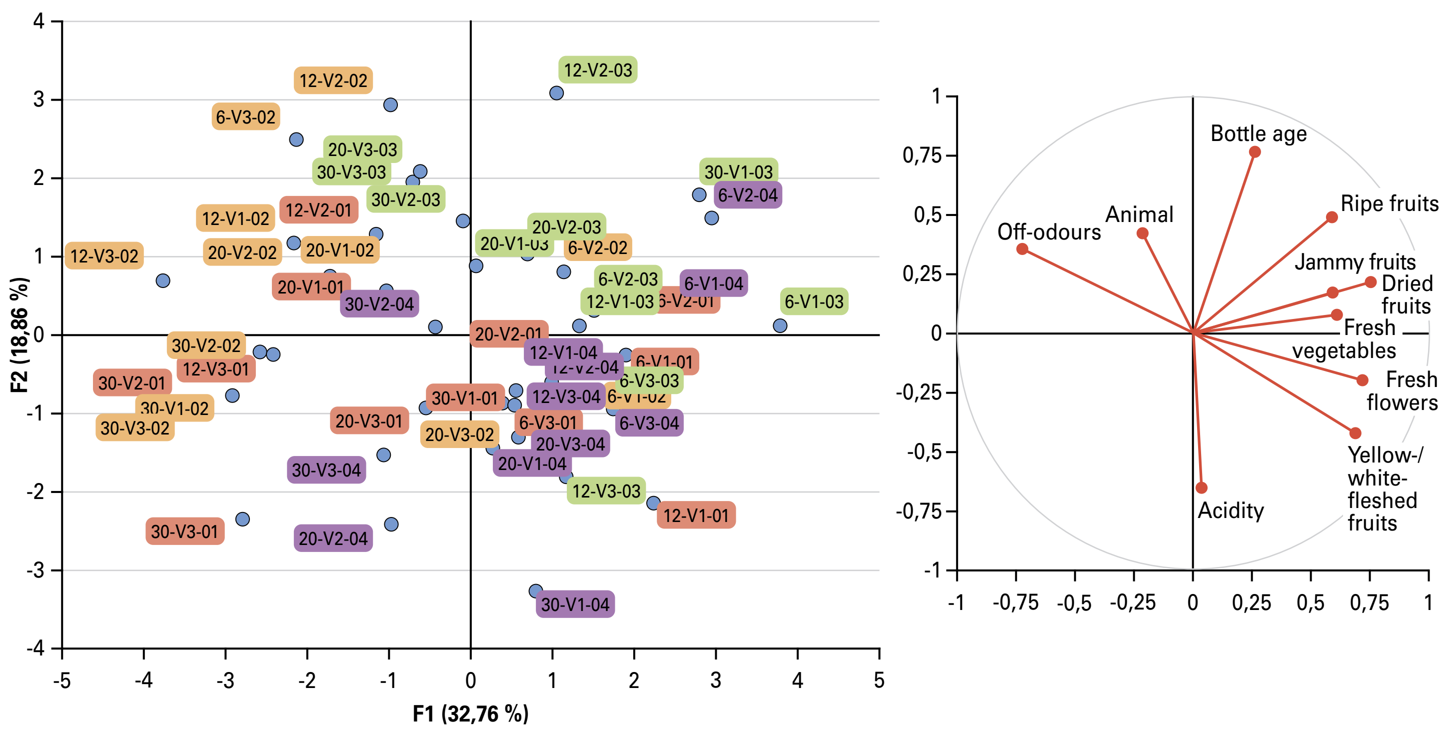
Lastly, the wines were submitted to a panel of wine professionals from Provence with extensive experience in the sensory analysis of rosé wines. The wines were tasted in black glasses, so that the tasters would not be influenced by colour. They were served at 12°C on a random basis by wine and by closure (three series of four wines). Starting with the first tasting, six months after bottling, the three wines bottled with closure 2 are marked by reduction, in particular wine 3, which was aged under reductive conditions (on the lees). This closure is the least permeable to oxygen, the bottling conditions were also controlled to minimize oxygen, and the three wines developed sulphur compounds (which were not quantified). These characteristics persist more or less until 20 months of bottle ageing for all three wines, which obtain higher scores for animal and/or burnt aromas. However, after 12 or 20 months of bottle ageing, the more permeable closure 3 gives the wines aromas of bottle age (ripe and dried fruit types), depending on the individual wine.

The representation of principal components ***(Figure 8)*** for the significant descriptors shows the dominant effect of the closure on the sensory profile of the wines. For all three wines and for most of the sensory analysis sessions, the wines bottled with closure 2 are qualified by reduction notes (animal/off-odours) and receive lower scores for jam and white- and yellow-fleshed fruits. In contrast, closure 3 leads to wines characterised by signs of bottle age, ripe fruits, dried fruits and

■ **Figure 7: Positioning of three wines on the Provence colour chart, depending on their apparent colour under standardised conditions, after 30 months of storage at 20°C.**



■ **Figure 8: Representation of axes 1 and 2 of the principal component analysis of the significant descriptors on the overall experimental plan: 3 wine types x 4 stoppers x 4 sensory analysis sessions.**



fresh vegetables. The group of wines bottled with closure 4 is identified by notes of fresh flowers and yellow-fleshed fruits. Closure 1 does not lead to any specific behaviour, which suggests that these wines do not show any reduction or premature ageing. The permeability of this closure is suitable for all three wines studied.

We can also note that the overall quality (harmony) is significant between wines only for certain series after six and 12 months of ageing. No general trend can be identified. Closure 2, however, has a negative impact on wine 3 at six and 12 months, owing to the intensity of reduction notes (matches, ripe grapefruit, etc.). This wine has a high 3-mercaptohexanol content and was bulk-aged under reductive conditions (lees ageing), thus explaining this tendency towards reduction. Closure 1 leads to the most highly appreciated wine at six months for wine 3 and at 12 months for wine 1.

Closures: the final winemaking decision

Great care is taken during the ageing of rosé wines: the use of suitable grape varieties, dedicated grape growing techniques, investment in high-performance winemaking equipment and materials. At the end of winter, the wines are "bright", just as consumers like them to be. However, bulk ageing, stabilization, bottling and bottle ageing can alter these qualities, in particular if the sulphite level is low (low protection) in order to respond to societal demands. As long as the wine is in tank, the winemaker can correct, deoxygenate and readjust the sulphite content, lower temperature, etc. and thus maintain the wine's potential. After bottling and in particular after distribution when temperature is poorly controlled, the wine reacts to the conditions to which it is exposed. Minimizing oxygen additions during bottling is the first way to minimize losses of sulphites during the first two months of bottle ageing, and this thus makes it possible to lower target sulphite levels before racking. The permeability of closures then plays a role.

With fragile products (in terms of colour and aroma expression) and for faraway markets, low oxygen permeability is recommended in order to minimize the biochemical reactions that lead to a negative impact on the product. With wines showing citrus and exotic fruit aromas, especially if the winemaking process has limited oxygen additions (case of wine 3), a closure that is too impermeable may lead to the development of sulphur compounds that persist over time. It is thus important to choose more oxygen-permeable closures in order to decrease these reduction notes, without excessively exposing the wine to premature signs of age. An intermediate permeability level is then recommended, or changes in the winemaking process should be made, in particular a decrease in free SO_2 levels at bottling (study currently in progress). Other studies are also underway at the Centre du Rosé in order to develop an easy-to-use indicator that can be used to assess the reducing power of wine. Ideally, the closure must therefore be adapted to the wine's profile, its market and distribution circuit (exposure conditions and time before consumption). ■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