Oxygen transmission through different closures into wine bottles

BY Paulo Lopes, Cédric Saucier, Pierre-Louis Teissedre, Yves Glories
Faculté d'Oenologie de Bordeaux, Université Victor Segalen Bordeaux 2 UMR 1219 INRA.
Talence Cedex, France
pdl@net.sapo.pt

Ageing of wine is extremely dependent on the amount of oxygen 0a wine receives during the winemaking process.[1] Opportunities for oxygen exposure include contact during vinification prior to bottling, oxygen pick up during transfer to the filler, in the bottling line, in the headspace (dependent of volume, pressure, and gas composition), and oxygen ingress through the closure during post-bottling storage. The latter depends on the oxygen barrier provided by the closure used.

To summarize our experiment, a non-destructive (a single bottle can be analyzed without compromising the closure seal) colorimetric method was developed to measure oxygen ingress from 0.25 to 2.5 mL into wine bottles. This method infers oxygen ingress through a closure by direct colorimetric scan of flint wine bottles (375 mL) containing indigo carmine solutions that gradually changes color from yellow to indigo as oxygen reacts with the reduced indigo carmine. This method measures the oxygen ingress through

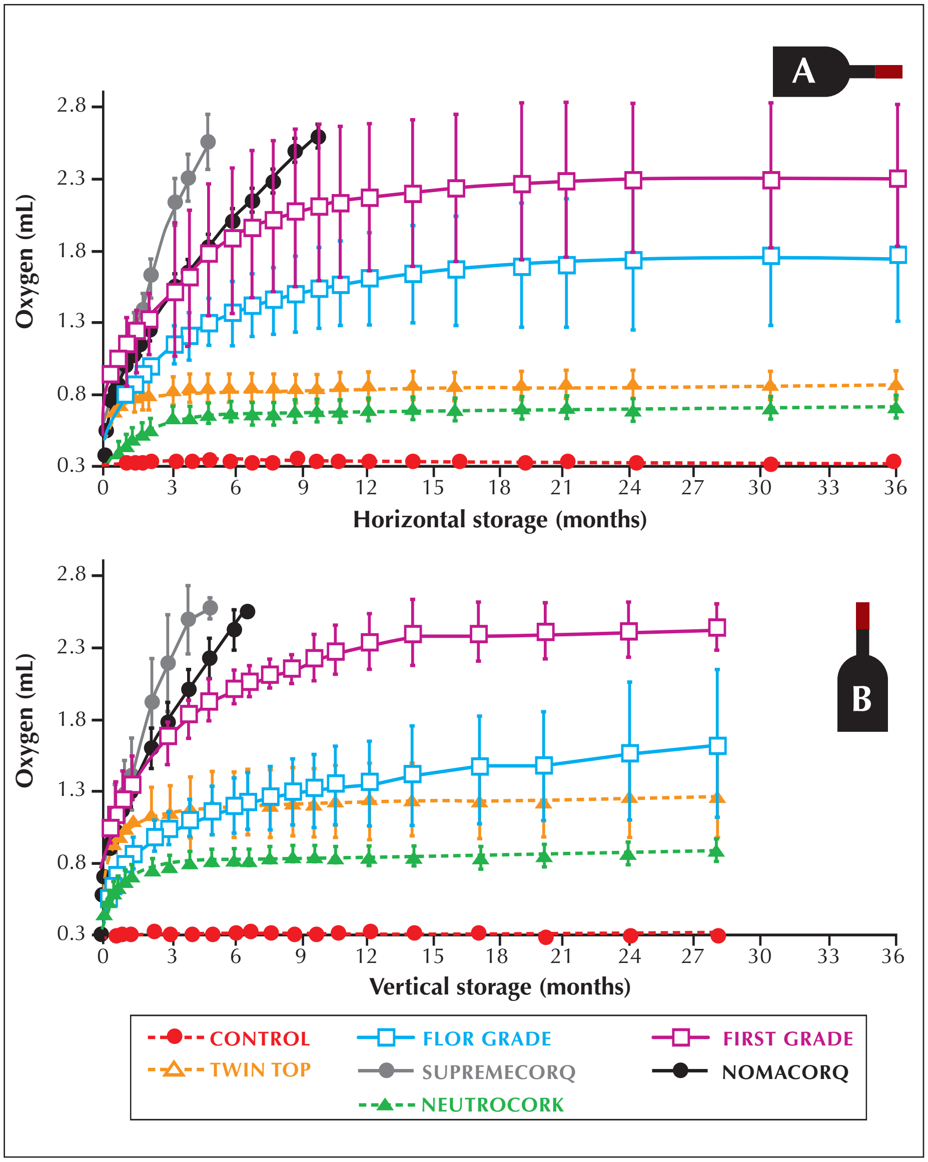

Figure I. Kinetics of oxygen ingress through different closures into wine bottles stored in horizontal position over 36 months (A) and vertical position over 28 months (B). Error bars represent the standard deviation of four replicates.

different closures over the time under identical conditions to wine bottle ageing. Details concerning this methodology are provided in Lopes *et al*.[2]

Closures tested include: two natural cork stoppers (45 x 24 mm), the best grade ("flor"), and the intermediate grade (first); two "technical" cork stoppers (Twin Top and Neutrocork); two synthetic closures, Nomacorc classic closure (43 x 22 mm) and Supremecorq 45™; and four different screw-cap (saran-tin liners) closures (Stelvin, Auscap, Cospak, and CSA).

An airtight bottle containing a reduced indigo carmine solution, sealed by flame, was used as a control. Four bottle replicates of each of the sealing systems were assessed. All bottles were sealed and then stored horizontally and vertically under constant temperature of 20 +/-1ºC and constant relative humidity of 65 +/-1%. More details regarding closures, bottling, and storage conditions are available in Lopes *et al*.[3]

This report provides results of the total oxygen ingress through different cylindrical and screw-cap closures into wine bottles after bottling up to 36 and 18 months of horizontal storage, respectively. The impact of bottle orientation over 28 months of storage was also assessed.

Table I: Full ranges of oxygen ingress rates (µL/day) through screw caps, "technical" and natural cork stoppers, and synthetic closures, during the first month and the subsequent months of storage.

Closure Type	First month	Storage: Horizontal	Storage: Vertical
Screw caps (tin liner)	<500[a]	0.2–0.7	—
"Technical" corks	15–40	0.1–0.4	0.1–0.9
Natural corks	25–45	1.7–6.1[b] 0.1–2.3[c]	0.5–4.4[b] 0.1–2.7[c]
Nomacorc synthetic closure	30–40	6	8–9
SupremeCorq synthetic closure	35–45	11–15	11–12

[a] at moment of bottling
[b] from 2 to 12 months of storage
[c] from 12 to 36 months (horizontal) and 12 to 28 months (vertical) storage

Results

Figure I shows the kinetics of oxygen ingress through different closures into wine bottles stored horizontally and vertically over 36 and 28 months, respectively. It can be observed that only the control (bottle sealed by flame) was completely airtight, while other closures were permeable to oxygen. Oxygen pickup through cylindrical closures was much more important in the first month than in the following months of storage. This latter period was extremely dependent on the oxygen barrier properties of each closure. Probably, the important increase in color change during first month is likely to be due to oxygen within closures that diffuses out of the closure during compression. The oxygen entrained at fill was negligible (less than 9µg/L, measured by polarographic probe).

"Technical" cork stoppers (Twin Top and Neutrocork) exhibited a low level of oxygen permeation (0.1 to 0.4 µL per day, Table I). In contrast, synthetic closures, Nomacorc and Supremecorq, exhibited the highest oxygen permeation, reaching a limit of quantification for our method (2.5 mL of oxygen) within 140 and 290 days, respectively (Figure IA).

Natural cork stoppers exhibited medium levels of oxygen permeation. On average, the best grade of natural cork stoppers ("flor") exhibited lower oxygen ingress than the intermediate one (first grade) (Figure IA). This latter grade presented some variability among four replicates, which can perform as well as the natural "flor" grade or similar to the less permeable Nomacorc synthetic closures.

The oxygen permeation patterns for natural corks differed from other closures. Generally, oxygen ingress through natural corks decreased over time, mainly between the second and twelfth month (1.7 to 6.1 µL per day), then rose gradually (0.1 to 2.3 µL per day) until completion of the study at 36 months (Table I). These data shows that natural corks' permeation varied by a factor of 3.5 between two and 12 months and 23 in the following months, which are substantially lower than the oxygen transmission rates and 1000-fold variation reported by other studies.[1,4]

The main reason for this difference is the methodology used to measure oxygen permeation of natural corks (moisture-sensitive). Our method measures oxygen ingress through natural corks inserted in commercial glass bottles filled with an aqueous indigo carmine solution, while the Mocon method, used by other researchers, is based on measurement of oxygen transmission rates through corks inserted in a cut bottleneck without liquid contact.

The contact with liquid is an important factor in oxygen transmission through corks irrespective of bottle orientation. Even in upright storage, the relative humidity inside a bottle is maintained at 100%, which allows the absorption of considerable amounts of moisture by the corks.

Oxygen diffusion through screw-cap closures differed from cylindrical closures. The apparent entry of oxygen into wine bottles was substantially higher during bottling than in the following 18 months of storage. This appeared to be due to the insertion of oxygen contained within the screw-cap in bottle headspace at the time of sealing. After bottling, screw-caps allowed the ingress of consistent low amounts of oxygen (0.2 to 0.6 µL per day, Table I) with no significant differences between manufacturers.

The different oxygen barrier properties of each type of closure tested explain the large divergence in composition and sensory properties of wines sealed with different closures reported by several recent studies.[5,6,7] These studies showed that oxygen ingress rates exhibited by synthetic closures, result in wines with a high level of browning and high-oxidized aroma scores.

On the other hand, too low oxygen ingress rates, as shown by screw-cap closures and glass ampoules, promotes the development of rubbery or struck flint sulfide-like aroma characters (post-bottling reduction). Generally, cork stoppers presented intermediate performance.[6,7]

Another finding was that bottle storage orientation (upright or lying down) had little impact on oxygen ingress through most of the closures into wine bottles, at least over the first 28 months of the experiment under controlled conditions of temperature and humidity (Figure IB, Table I). These results agree with those recently reported by G. K. Skouroumounis *et al.* showing that no storage effect on the composition and sensory properties of white wines over five years, when the storage conditions are constant and controlled.[7]

Conclusion

Different closures and sealing systems tested in this study resulted in a large divergence of oxygen barrier properties. After 18, 28, and 36 months of storage, only the control bottle (bottle sealed by flame) was air-tight. Other closures displayed different levels of oxygen permeation: low in screw-caps and "technical" corks, intermediate in conventional natural cork stoppers, and high in synthetic closures.

Judging by our findings and other recent research, it is clear that ageing of wine in bottle occurs under micro-oxygenation. However, the current issue is how much oxygen transmission is required from a closure for wines to age correctly in bottle, without oxidation or reduction prob-

Bottle #1 [left] (control) contains indigo carmine solution after 36 months of horizontal storage. Bottle #2 contains indigo carmine solution sealed with "technical" Netrocork® cork stopper after 36 months of horizontal storage. Bottle #3 contains indigo carmine solution sealed with natural cork stopper after 36 months of horizontal storage. Bottle #4 [right] contains indigo carmine solution sealed with Nomacorc Classic® synthetic closure after 10 months of horizontal storage.

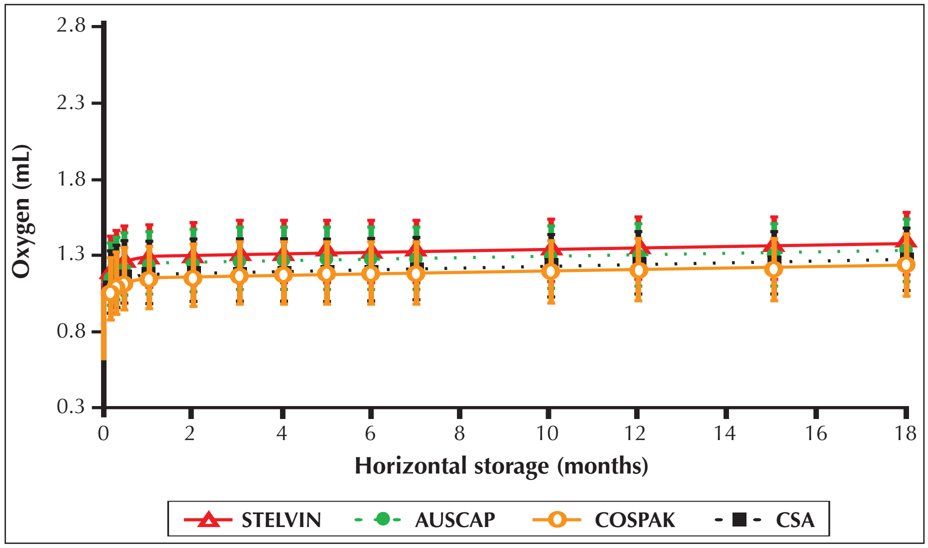

Figure II. Kinetics of oxygen ingress through screw cap closures into wine bottles stored horizontally during 18 months. Error bars represent the standard deviation of four replicates.

lems. This will depend on grape varieties, winemaking practices, bottling procedure, closure performance, and storage conditions.

The bottom line is that only a better understanding of the wine chemistry and the sources of oxygen will enable us to determine the optimal amount of oxygen needed for wine to develop properly in the bottle. ■

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