Validating the Oxygen Performance of a Wine Closure

Tim Keller and Annegret Cantu. VinPerfect Inc.,
831 Latour Court, Suite B1, Napa, Ca 94558, USA.
Email:acantu@vinperfect.com

VinPerfect™
YOUR WINE DESERVES NO LESS

ABSTRACT

Oxygen plays a key role in wine chemistry and aging as it affects the stability and sensory properties of wine. Amongst the current choices of wine closures the discussion of oxygen permeability has come to the forefront, but there is little agreement as to what methods are appropriate for measuring oxygen transmission rates (OTR) in a wine context or even what the target OTR should be. Given the high number of reported faults in bottled wines stemming from over, or under oxidation, the ability to measure oxygen transmission through a closure and to insure that a given closure is delivering the intended oxygen dose is of significant commercial importance for the wine industry as a whole. Our research has two main objectives. 1. experimentally test our theories about optimal wine oxidation levels. 2. Confirm that our closures perform within that range.

To accomplish these objectives, wine enclosures are tested with model wines bottled in clear glass where oxygen ingress is measured by different oxygen testing methods, and a variety of commercial wines fitted with closures of known oxygen permeability characteristics, which can be tested for post-bottling SO_2 decline and other chemical parameters.

We will present **(i)** the **theory** behind our targeted level of in-bottle wine oxygenation, **(ii)** our **material and methods** for validating it, and **(iii)** the **results of our research to-date** in creating a closure that reliably delivers oxygen within that range.

INTRODUCTION – Theory behind VinPerfect's targeted OTR range

How do we know how much oxygen a wine needs?

It is important to understand that trying to have one "optimal" amount of oxygen is not realistic. However, it is possible to define a range of oxygen ingress rates that might be advantageous to wine quality. The approach is to consider multiple products that address different rates of oxygen ingress and then further let the winemaker decide what is right for the wine.

Looking at the current closure market there is no product that consistently performs within that range we target. Synthetic corks admit too much oxygen, screw caps admit too little oxygen, and natural cork is very inconsistent (see Figure 1.) (5, 9)

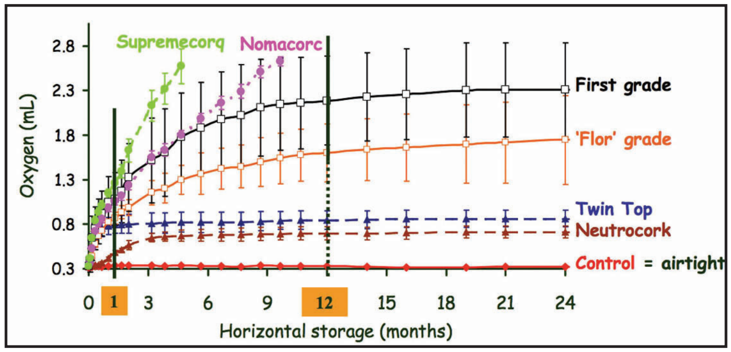

Figure 1. Oxygen ingress true closures (9).

VinPerfect's defined ranges are associated to the problems a wine will bear post-bottling, too much and a wine might prematurely oxidize, lose varietal characteristics, decrease in pleasant aromatic compounds and increase in aldehydes (1, 3, 6, 11, 12). Too little oxygen and a wine might under develop and is in danger of forming reduced aromas (3, 7, 8, 10, 13).

Further considerations are that the customer does not see wine as a perishable product. How long should a wine last before becoming oxidized? For most wines, a storage of below a year is adequate, but it should be possible to store a wine at least five years before becoming oxidized.

How do we define shelf life of a wine?

(1) Wine is protected against oxidation products by free SO_2. We take the mass ratio of SO_2 and O_2 into consideration ($2 SO_2 + O_2 \rightarrow 2 SO_3$), where 1 mg/L of O_2 will consume 4 mg/L of SO_2 (2, 5)
(2) Most wines are bottled at 30 mg/L free SO_2
(3) When free SO_2 drops below 10 mg/L wines' capacity of binding aldehydes is significantly lowered and oxidations products start to appear (2).
(4) As a consequence of points (1) - (3), and considering the "lightest" kind of wine, e.g. a white wine, following oxygen transmission for our upper and lower limits can be extracted:
For a wine decline in free SO_2 from 30 mg/L to 10 mg/L, the minimum O_2 required is 5 mg/L, which gives us a shelf life of 4 years and an O_2 annual ingress of 1 mg/L. It is harder to define the lower limit clearly, but with an annual ingress of 0.5 mg/L, a shelf life of 10 years is established, which insures against reduction problems (Figure 2).

MATERIALS AND METHODS

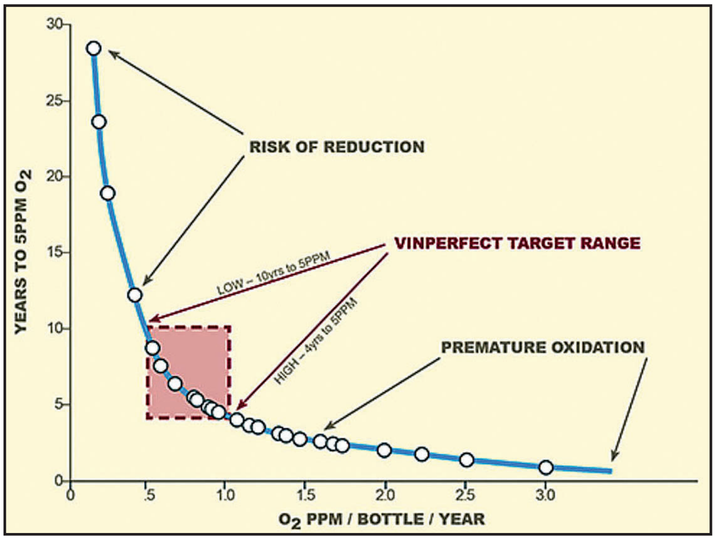

Figure 2. VinPerfect's shelf life reasoning -- years to 5 ppm.

How does the winemaker choose an oxygen level within this range?

If we consider the light white wine example, which is the most vulnerable to oxidation, a winemaker should probably utilize a closure closer to the low-oxygen end of the range at 0.5 ppm per year. Conversely, a red wine with elevated phenolic content and therefore a higher oxygen absorption capacity could benefit more from an oxygen rate close to 1 ppm per year. A red wine has less to risk from the upper oxygen limit.

In the end, the selection of a closure's oxygen transfer rate for a wine's post-bottling life is an extension of the winemaker's style. So, we would not consider to make specific suggestions of oxygen transfer rates for various varieties.

In summary for deliberation, for an age worthy red wine 1 ppm per year will allow gradual development in the bottle for 10 to 20 years, without being starved of oxygen or over-exposed. For white wines, the selection of a low oxygen closure means that even the lightest white may last 10 years or more. The range we have selected is right in the center of the average cork oxygen performance range when the bottle is stored properly but without its inconsistency (Figure 1).

Figure 3. VinPerfect's Closure System

Method for Ingress Determination:

Wine bottles were filled with deoxygenated model wine solution (12% ethanol, distilled water, tartaric acid, adjusted to pH 3.6). Non-invasive oxygen sensors from NOMASense and MOCON OpTech (see figure 4, 5 and 6). are placed mid-way and in the headspace the same 375 mL wine bottles. Wine bottles are inverted, stored in a temperature controlled cabinet at 20° and measured weekly for O_2 ingress. Total packaged oxygen is calculated and expressed as mg/L.

Figure 4. NOMASense O_2 Trace (Presens-Fibox 3LCD trace v 7 oxygen anlayzer using Pst6 oxygen sensing ports (range 0–1.8 mg/L and 0–4.2% O_2).

Calibration is performed by using a provided factory calibration sheet specific to the Pst6 sensors used.

Figure 5. a) MOCON OpTech-O_2 Analyzer and b) Calibration Card

Calibration is performed with a MOCON OpTech-O_2 CalCard (see Figure 2b)

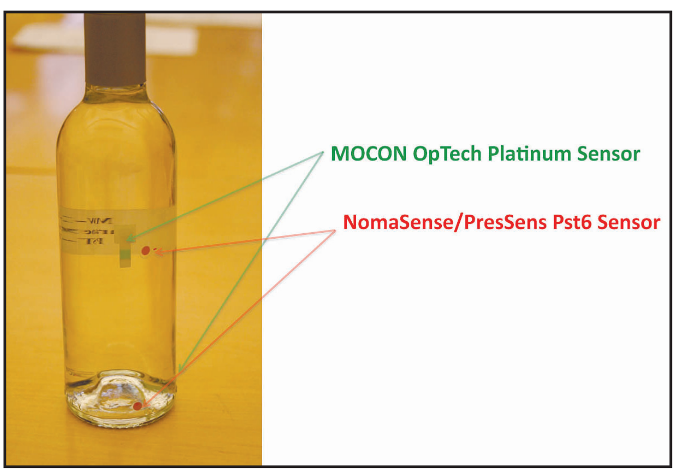

Figure 6. Non-invasive oxygen sensors MOCON OpTech and NOMASense side by side in solution and in the headspace

ACKNOWLEDGEMENTS

MOCON Inc

RESULTS OF RESEARCH TO-DATE

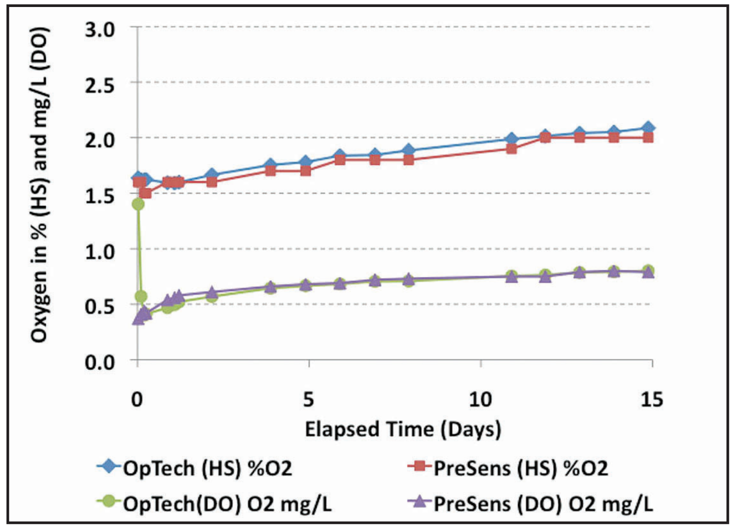

Figure 7. Comparison Trial OpTech O_2 Analyzer versus NOMASense O_2 Trace measuring head space (HS) and dissolved oxygen (DO) over time in wine.

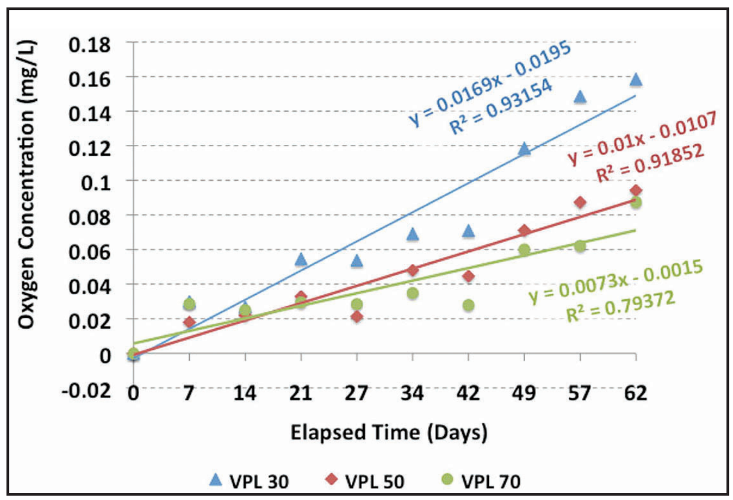

Figure 8. Three levels of liners metalization.

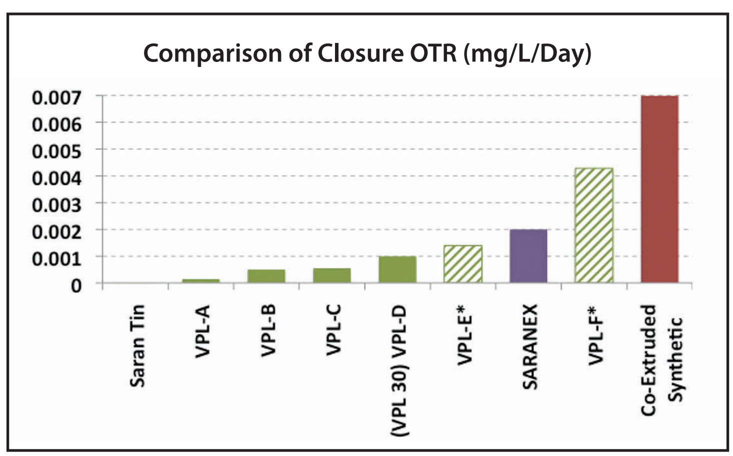

*Figure 9. VinPerfect comparison of closure OTR (mg/L/day) and prediction for *New Liner Material.*

CONCLUSIONS

> Both NOMASense and MOCON OpTech oxygen analyzers show almost identical performance in measuring head space and dissolved oxygen and work excellent and a wine-like-solution. The MOCON instrument has the advantage of being more cost efficient for sensors and the instrument itself. MOCON OpTech is also more user-friendly, and includes software to record and track data easily.

> There is an inverse correlation between the optical density of the films used in the VinPerfect prototypes and the OTR of the resulting closure. The higher the optical density, the lower the OTR. This indicates a method of positive control of oxygen through the varying of metalization level.

> Preliminary results show low coefficients of variation in O_2 ingress for VinPerfect's liner prototypes indicating consistency.

> Measurements of inserted closures with high initial DO did not render useful results with this method since the rising O_2 started to approach equilibrium with the outside environment, reducing the driving force O_2 transmission. These closures should be tested with a larger volume bottle, or better yet, closures should be depleted of contained O_2 by storing them before the test in an O_2 void environment. Further, the first two weeks after bottling should be kept in an inert environment to complete the recovery phase without atmospheric O_2 interference and to keep the equilibrium driving force equal to real-world conditions.

> Some screw capped samples across manufacturers were shown to have variants not explained by the composition of the liner. In these cases it was found that defects in the sealing-surface of the bottle were present, highlighting the fact that the cap liner is only half of the seal, and underscoring the importance of the vigilance in glass quality.

> Further research needs to be performed:

- Trials with inserted closures on larger bottles
- Correlation of OTR measured via this method, with SO_2 changes observed in real wines
- Correlation of wine composition, color and sensory to differences in the SO_2 depletion of wines with closures of known OTR.

REFERENCES

(1) Blanchard et al., 2004. Reactivity of 3--Mercaptohexanol in Red Wine: Imp of Oxygen, Phenolic Fractions, and Sulfur dioxide. Am. J. Enol. Vitic. 55, 115--120

(2) Boulton et al., 1996. Principles and Practices of Winemaking. Chapmann&Hall, New York.

(3) Caillé et al., 2010. Sensory Characteristics changes of red Grenache Wines submitted to Different Oxygen Exposures Pre and Pos Bottling. Analytica Chimica Acta. 660, 35--42.

(4) Crochiere. et al., 2007. Measuring Oxygen Ingress During Bottling/Storage. Practical Winery & Vineyard, 1--5.

(5) Danilewicz et al., 2008.Mechanisms of Interaction of Polyphenols, Oxygen and Sulfur Dioxide in Model Wine and Wine. Am. J. Enol. Vitic. 59, 128--136.

(6) Escudero et al., 2002. Sensory and Chemical Changes of Young White Wines Stored under Oxygen. An Assessment of the Role Played by Aldehydes and some Other Important Odorants. Food Chem. 2002, 77, 325-331.

(7) Godden et al., 2001. Wine Bottle Closures: Physical Characteristics and Effect on Composition and Sensory Properties of a Semillion Wine. Performance up to 20 Months Post--Bottling. Aust. J. Grape Wine Res., 7, 62–105.

(8) Kwitatkowski et al., 2003 The Impact of Closures, including Screw Cap with Three Different Headspace Volumes, on the Composition, Colour and Sensory Properties of a Cabernet Sauvignon Wine During Two Years' Storage. Aust. J. Grape Wine Res., 13, 81–94.

(9) Lopes et al., 2006. Impact of Storage Position on Oxygen Ingress through Different Closures into Wine Bottles. J Agric Food Chem, 54, 6741--6746.

(10) Lopes et al., 2009. Impact of Oxygen Dissolved at Bottling and Transmitted Through Closures on the Composition and Sensory Properties of a Sauvignon Blanc Wine during Bottle Storage. J.Agric. Food Chem., 57, 10261--10270.

(11) Oliveira et al., 2002Development of a Potentiometric Method to Measure the Resistance to Oxidation of White Wines and the Antioxidant Power of their constituents. J. Agric. Food Chem. 2002, 50, 2121– 2124.

(12) Singelton, 1979. Oxygen with Phenols and related Reactionsin Musts, Wines and Model Systemes – Observations and Practical Implications. Am. J. Enol. Vitic. 38, 69--77.

(13) Skouroumounis et al., 2009. The Impact of Closure Type and Storage Conditions on the Composition, Colour and Flavour Properties of a Riesling and a Wooded Chardonnay Wine during Five Years' Storage. Aust. J. Grape Wine Res., 11, 369–384.