Post-bottling management of oxygen to reduce off-flavour formation and optimise wine style

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Between the extremes of too much or too little oxygen after bottling lies a range of different combinations of chemical reactions and interactive wine aroma compounds that contribute to desirable varietal, regional and style differences. Achieving this balance in Sauvignon Blanc wines has some special challenges. Preserving the thiol compounds responsible for its varietal signature by minimising oxygen exposure may also increase the risk of higher accumulation of undesirable sulfur compounds. Copper fining at bottling is a tool that is often used to reduce the levels of undesirable sulfur compounds. The ‘good’ fruity thiol compounds can also be removed with copper fining and residual copper may also accelerate other oxidative reactions, resulting in further loss of the ‘good’ thiols. Understanding how aroma compounds react with oxygen under different conditions and in different wine backgrounds is necessary for informed decision-making with regard to bottling and packaging.
The diagram is intended to provide a general overview of the possibilities offered by oxygen management when it comes to modulation of wine aroma composition.

Starting from a young wine with the same aroma composition, different oxygen regimes will lead to the development of wines with different patterns of volatile components. In the case of high oxygen exposure (Figure 1, right panel), degradation of the components responsible for aromas of tropical fruit and passionfruit (e.g., 3-mercaptohexanol [3MH] and 3-mercaptohexanol acetate [3MHA]), and floral aromas (e.g., linalool) can be quite rapid, while most fruity fermentation esters decline at a rate that is not affected by oxygen availability. At the same time, the aroma compounds responsible for oxidised aroma, such as sotolon and aldehydes, accumulate at a higher rate due to the involvement of oxygen in their formation reactions, while an increase in dimethyl sulfide (DMS) appears not to be affected by oxygen. At low concentrations, DMS enhances red berry aromas but contributes negatively at high concentrations.

Under conditions of high oxygen exposure, the young wine evolves towards an aroma profile where fruity aromas are progressively replaced by the increasing contribution of DMS, aldehydes (nutty, dried fruits aromas, but also bruised apples for aliphatic aldehydes), and sotolon (spicy, nutty), while the contribution of reductive compounds, such as hydrogen sulfide (H₂S) and methanethiol (MeSH), is negligible. Further exposure to oxygen, coupled with the concomitant decline in esters due to chemical hydrolysis, results in a wine where the fruity aromas are largely lost, while the contribution of oxidised aromas from sotolon and aldehydes (particularly (E)-2-alkenals) become dominant.

Conversely, when exposure to oxygen is low (Figure 1, left panel), compounds responsible for tropical fruit aromas, such as 3MH and 3MHA, are better preserved, while the formation of oxidative compounds, like sotolon and aldehydes, is minimised. In this case, a large component of the fruity aromas of the young wine is preserved over a longer time, while an increase in compounds, such as DMS, can positively contribute to the overall complexity. However, low exposure to oxygen can eventually result in the excessive accumulation of reductive aroma compounds, such as MeSH, possibly determining reductive off-flavours.

It appears, therefore, that many key aroma compounds exhibit trends during ageing that are strongly dependent on oxygen exposure. The case of volatile sulfur compounds appears particularly interesting in view of the fact that these compounds, although having similar reactivity, exhibit very different odour properties. While H₂S and MeSH are characterised by unpleasant odours reminiscent of rotten egg and sewage, 3MH and 3MHA are characterised by pleasant tropical and passionfruit aromas, and are known to positively contribute to the aroma of many red and white wines. Therefore, any attempt to preserve the latter, desirable thiol compounds by means of oxygen management may increase the risk of higher accumulation of the former undesirable sulfur compounds.

**OXYGEN MANAGEMENT AND SAUVIGNON BLANC AROMA**

Sauvignon Blanc is one wine where sulfur compounds can be drivers for both defects and desirable qualities. This paradox represents, perhaps, one of the biggest challenges for winemakers due to the fact that compounds such as 3MH and 3MHA, along with the other powerful varietal sulfur-containing odorant 4-mercapto-4-methyl-2-pentanone (4MMP), play a prominent role in the varietal aroma.

As discussed, reducing oxygen exposure of the wine improves the stability of these compounds. The increased loss of these compounds at high oxygen exposure appears to be linked to their reaction with quinones, which are
oxidation products of polyphenolics and whose levels increase as oxygen exposure increases. This is one reason why the vast majority of Sauvignon Blanc wines in Australia and New Zealand are bottled under closures with low oxygen transfer rates (OTRs), mainly screwcaps, and low oxygen at bottling is recommended. However, these conditions can increase the risk of developing reductive aromas, as confirmed by several studies carried out at the Australian Wine Research Institute (AWRI). Due to the lack of a comprehensive understanding of the mechanisms determining accumulation of reductive aroma compounds during winemaking, winemakers often resort to pre-bottling copper fining to remove the sulfur compounds responsible for reductive off-flavours at low oxygen exposures. However, because of similar chemical reactivities, thiols such as 3MH, 3MHA, and 4MMP can also be negatively affected, resulting in an overall loss of varietal character.

The results in Figure 2, obtained during a recent trial at the AWRI, show that copper additions at bottling can severely reduce the concentration of 3MH in Sauvignon Blanc wines bottled with higher SO2 (60mg/L), while no effect was observed at an SO2 of 30mg/L. After eight months of storage, even in the wines bottled with 30mg/L of SO2, a decrease in 3MH, 3MHA and 4MMP was generally observed in copper-fined wines, which was in most cases larger than the decrease associated with the use of higher OTR closure (Figure 3). Taken as a whole, these results, besides showing the existence of complex interactions between SO2 concentrations and copper fining, highlight the fact that copper fining, although potentially useful in preventing reductive off-flavour, can have detrimental effects on the varietal aroma compounds of Sauvignon Blanc. Moreover, the exact amount of copper to add depends on the specific requirements of individual wines and can, therefore, be difficult to estimate, potentially resulting in excessive residual copper. Because copper is a very powerful oxidation catalyst, excessive copper fining can accelerate oxidation reactions, resulting in a higher risk of premature oxidation.

The data in Figure 3 show the effect of two different closures on the stability of the three thiols during the first eight months of storage. The closure type had virtually no effect on the wines without copper fining, whereas an increase in OTR became highly detrimental when copper was added at bottling. The pro-oxidant action of copper, combined with increased oxygen availability, is probably responsible for this effect, which confirms the risks associated with excessive residual copper.

Furthermore, sensory analysis of the wines from this study after 13 months of cellaring highlighted the complexity of the interactions between oxygen availability and copper fining (Figure 4). Overall, lower OTRs resulted in wines that were rated slightly higher for the reductive aroma attribute ‘struck-flint’, confirming previous observations regarding the association between screwcap and the propensity of wines to become reductive after bottling. Interestingly, in the current study, the OTR did not affect the rating of the intensity of fruitiness, indicating that there was no direct effect of oxygen alone on this attribute. However, wines stored under screwcap (low OTR) were
found to have slightly higher overall fruit-flavour intensity when copper was added at bottling.

Surprisingly, copper addition at bottling had no statistically significant effect on the struck-flint attribute in any of the wines, with closure type alone appearing to determine the level of this negative aroma attribute (Figure 4). This observation appears to contrast with the well-established practice of adding copper to remove reductive off-flavours. It might be linked to complex interactions between different aroma compounds, as previously outlined in Figure 1. Alternatively, it could also reflect the low propensity of the wine used in these trials to become reductive and, therefore, make it difficult to identify differences.

In contrast to copper’s apparent lack of effect on the struck-flint character, copper addition slightly reduced the overall fruit flavour intensity, which appears to be in agreement with the lower concentration of varietal thiols observed in these wines after eight months (Figure 2). At the same time, however, the struck-flint aroma was rated lower in these wines compared with the corresponding samples under screwcap, which highlights again the array of aroma profiles and balances that can be achieved by means of oxygen management, particularly in conjunction with other common winemaking practices such as copper fining.

CONCLUSION AND FUTURE PERSPECTIVES

Understanding the reactivity of different aroma compounds towards oxygen under different conditions is necessary for informed decision-making when bottling and packaging. While in laboratory studies the key role of oxygen in determining the evolution of different wine aroma compounds during storage has been clearly demonstrated, the knowledge regarding the significance of these reactions...
Key messages in a bottle

- Several wine aroma compounds that are important for the expression of varietal, regional and wine-style differences, are sensitive to oxidation.
- All other things being equal, reducing the amount of oxygen available after bottling will increase the likelihood of reductive characters developing in wines which have a propensity to become reductive.
- Copper fining at bottling to prevent reductive off-flavour development may not always be effective and can result in the loss of desirable compounds in Sauvignon Blanc wines.
- Residual copper in wines as a result of excessive or unnecessary copper fining, combined with oxygen exposure, can accelerate oxidative reactions.
- Individual wines will respond differently to the availability of given amounts of oxygen after bottling. Consequently, wine producers should consider factors such as their own winemaking practices and how their wines respond empirically to oxygen availability after bottling when determining the bottling variables they use for each wine, including their choice of closure.

under real winemaking conditions is still fragmented, in particular with regard to the use of oxygen management for the achievement of specific wine styles.

Research has shown that in the case of Sauvignon Blanc key aroma compounds, matrix composition plays a critical role in determining the reactivity of these compounds toward oxygen. The data presented in this study indicate that when it comes to sulfur compounds, conditions favourable to the preservation of positive aromas can also promote the development of negative compounds.

Our results also show that the widespread practice of copper fining at bottling to remove these potentially negative aromas might also reduce the levels of compounds responsible for varietal aromas. However, due to the lack of a suitable technology in the study presented here, neither oxygen concentration at bottling nor oxygen evolution during ageing were monitored, preventing a comprehensive interpretation of the data obtained. Very recently, the in-bottle measurement of dissolved and headspace oxygen in wine has become possible, and this technology is currently being integrated into our studies. In particular, we are currently investigating the effects of copper fining and antioxidant protection on oxygen evolution as well as chemical and sensory changes in Sauvignon Blanc wines.

While most studies on oxygen management have focussed on white wine aroma, only a few researchers have studied the effects of bottling conditions or OTR in red wine. Figure 1 indicates that among the compounds that respond to differences in oxygen management, there are several compounds that are known to play a key role in the aroma of red wines. One of the AWRI’s current research objectives is to unravel the changes in key aroma compounds under different oxygen regimes (particularly OTR) in Shiraz wines in relation to other key aroma compounds, such as esters, which change over time in a non-oxygen-dependent way.

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