Exposure of red wine to oxygen post-fermentation

— If you can't avoid it, why not control it?

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IN THIS MODERN and economically competitive society it is increasingly important to consistently produce wine to definable specifications and styles. Process management throughout the production stage is crucial in achieving repeatability and control. Lack of control comes, in part, from a lack of knowledge of key factors influencing sensory perception of high quality wine—and therefore an inability to modulate them as required—and fluctuations in processing variables that affect these factors. One such variable is oxygen. We know little about the exact impact on wine quality of low levels of oxygen exposure, although detrimental effects of excessive exposure are well established. Traditionally, the ability to control the amount of exposure has been limited by the inherent variability of physical operations such as racking and topping up, and enclosures such as oak barrels and closure/bottle combinations.

Oxygen is an essential component of modern red wine production, particularly in the control of yeast activity, sulfur off-odour management and fermentation-derived volatile composition (Julien et al. 2000; Torrea and Henschke, unpublished). The importance of oxygen after the completion of fermentation is, however, less well understood. The maturation period is traditionally characterised by a predominance of essentially non-aerobic conditions, interspersed by brief exposure to oxygen during periodic racking and wine transfer (Jackson 2000, Ribereau-Gayon et al. 2000). The sometimes positive and, thereafter, unstoppable negative effects of excessive oxygen exposure to wine are clearly apparent after the bottle is finally opened.

It is clear that there is some degree of continuous oxygen exposure throughout the lifetime of a wine, at least in more traditional storage vessels such as oak barrels and glass closed with either natural bark cork or more recent synthetic alternatives (Ribereau-Gayon et al. 2000, Caloghiris et al. 1997, Moutounet et al. 1998, Vivas and Saint-Cricq de Gaulejac 1999, Godden et al. 2001). Although little conclusive data are available, a comparison of the estimated oxygen permeation rates of various storage vessels employed throughout the lifetime of a wine suggests that wine is exposed to oxygen in decreasing amounts with each successive stage (Table 1). No satisfactory method to estimate oxygen permeation into barrels and closures under natural conditions is available at present, to our knowledge. Hence, estimations of oxygen permeation through natural bark corks in horizontal storage positions using sulfur dioxide data (Casey 1994, Keenan et al. 1999), or permeation through barrels filled with model wine, might not be accurate given that sulfur dioxide and oxygen both can be lost through multiple pathways (Ribereau-Gayon et al. 2000, Singleton 2000). While the rate of oxygen permeation through natural bark cork has been reported to be variable

TABLE 1

Process/Receptacle	Rate (mg/L/year)	Amount (mg/L)	Reference
Bottle closures (white wine)			
Natural cork, inverted	0.85		Keenan et al. (1999)
Stelvin, inverted	0.61		Keenan et al. (1999)
Natural cork, horizontal	1.18		Casey (1994)
Barrel storage			
New barrels	20-45		Vivas (1997)*
Old barrels	10		Vivas (1997)*
Microoxygenation			
1 month at 10 mL/L/month then 4 months at 5 mL/L/month		42	McCord et al. (2002)
0-5 mL/L/month, 3-6 months		≤ 42	Otto (2002)
30-40 mL/L/month up to 4 weeks prior to completion of MLF		42-56	Loch (2002)
Operations			
Wine transfer		2-6	Vivas (1997)*
Racking		3-5	Vivas (1997)*
Full saturation			
20 degrees Celsius		8.4	Moutounet and Mazauric (2001)

*Doctoral thesis of Nicholas Vivas, as reported by Ribereau-Gayon et al. (2000).

Table 1. Oxygen exposure of wine during storage and operations. Reported rates of oxygen permeation through wine storage vessels and oxygen additions as a result of standard winemaking operations are listed as mg/L/year (rates) or mg/L (single additions).

(Caloghiris et al. 1997) and while examples of so-called 'random oxidation' are observed in our problem solving activities, a recent study did not reveal any statistically significant differences in variability (as judged by sulfur dioxide levels in replicate samples) regardless of the orientation of storage (Godden et al. 2001). It is clear, however, that the oxygen level inside oak barrels is strongly dependent on several parameters including barrel age, oak type and storage practices (Vivas and Saint-Cricq de Gaulejac 1999, Perez-Prieto et al. 2003).

This review aims to briefly consider two important stages of red wine production where there recently have been developments towards controlling the degree of oxygen exposure. Although some studies seeking to establish correlations between oxygen exposure and sensory outcomes have been conducted, there is as yet little insight into cause and effect and it is clear that more research is needed.

CONTROLLED EXPOSURE OF OXYGEN DURING STORAGE

Recently, a technique known as microoxygenation (here abbreviated as MOX) has been developed in the Madiran region of France (Lemaire et al. 2002, Moutounet et al. 1995). MOX can be defined as the controlled continuous or semi-continuous addition of small doses of oxygen to wine. In most applications, the rate of oxygen addition is adjusted so that it is lower than the rate of 'consumption' by chemical reactions, thereby avoiding an increase in the concentration of measurable dissolved oxygen (Moutounet et al. 1995). In theory, it allows one of the main missing components of bulk tank maturation (compared with traditional small-scale barrel storage), the supposed slow diffusion of oxygen through the barrel (Moutounet et al. 1998, Vivas and Saint-Cricq de Gaulejac 1999), to be added. Hence, together with the possible addition of oak components (McCord 2002), it can be argued that the benefits of barrel storage, to some extent, now can be reproduced in tank (Ribereau-Gayon et al. 1983, Moutounet et al. 1995). Both the continuous slow permeation of oxygen through the barrel and small discontinuous additions of oxygen, mimicking racking and topping up practices, could, in theory, be catered for with the same equipment. If wine quality is improved compared to traditional tank storage under more reductive conditions, the next step is to evaluate qualitative differences between MOX treated wines and traditional barrel management. Such differences, if any, can then be weighed against cost differences associated with new barrel purchase, evaporative loss (Moutounet and Mazauric 2001), labour costs, maintenance and operations of barrels and MOX equipment (Paul 2002 and Work 2003), as well as more efficient use of natural oak resources.

MOX is commonly employed after the termination of alcoholic fermentation, at any stage up until bottling. In practice, high rates of oxygen addition (up to 110 mg O_2/L/year; Loch 2002) are used early pre-MLF (malolactic fermentation), while lower rates are reported post-MLF (Lemaire et al. 2002, Otto 2002, Loch 2002, Table 1). Reported effects include an increase in colour density, softer mouthfeel, increased fullness, reduced green/herbaceous aroma attributes, and greater intensity of aroma attributes regarded as grape-derived (so-called 'varietal aroma') (Paul 2002, Zoecklein et al. 2003, Rieger 2000, Moutounet et al. 1995, Atanasova et al. 2002). In addition, MOX has reportedly been used to aid the completion of sluggish fermentations or aid in restarting stuck fermentations (Zoecklein et al. 2003 and Loch 2002).

MOX studies so far—a focus on phenolic compounds

Although several studies and reviews of the role of oxygen in wine production have been published (Singleton 1987, Singleton 2000, Danilewicz 2003), very limited information from rigorous studies has yet been published about sensory and compositional effects of MOX and MOX-like treatments. In fact, no formal sensory study or analyses of aroma compounds in MOX-treated wines has, to our knowledge, yet been reported in a refereed journal. Some of the major influences of MOX treatment, such as changes to overall mouth-feel and astringency by informal sensory evaluation and changes to visual properties (Zoecklein et al. 2003, Moutounet et al. 1995 and Atanasova et al. 2002) are, at least in part, associated with phenolic compounds. For example, the majority of the visual impact of aged wine (more than 3 years old) is due to 'pigmented polymers' (Somers 1971, Degenhardt et al. 2000, Schwarz et al. 2003). Likewise, the majority of compounds responsible for astringent sensations in red wine are thought to be due to a hugely complex group of polymeric phenols (more commonly known as tannins or proanthocyanidins) (Gawel 1998), possibly including the pigmented sub-group thereof, namely 'pigmented polymers' (Hayasaka et al. 2003, Hayasaka and Kennedy 2003). A direct link between polymeric phenols present in wine and perceived astringency has not yet been shown conclusively to date, although numerous papers suggest that they are responsible for the perception of astringent sensations (Arnold et al. 1980, Gawel 1998, Brossaud et al. 2001, Vidal et al. 2003).

A general trend in analytical results of MOX-treated wines is a decrease in the concentration of anthocyanins, concomitant with an increase in total colour density (Moutounet et al. 1995, Atanasova et al. 2002, McCord 2002). Methods to characterise polymeric phenols, such as the mean degree of polymerisation (mDP) or HCl index (Glories 1978, Kennedy and Jones 2001), have either shown no differences (Atanasova et al. 2002) or an increase in the average molecular weight of polyphenolic compounds occurring concurrently with MOX treatment (Moutounet et al. 1995). McCord (2002) reported a small increase in the proportion of polymeric pigments to polymeric phenols and an increase in affinity of phenolics to protein in response to MOX treatment. Similar results have been found in repetitive oxygen addition studies (Vivas and Glories 1996, Castellari et al. 2000), while comparisons between tank and barrel storage have been less clear cut (Ho et al. 2001, Perez-Prieto et al. 2003). Most of these analytical results are not compatible with reported effects suggesting that oxygen additions result in a reduction in perceived astringency, given the current theory that the astringency of a polyphenolic extract in model wine solution is greater the higher the mDP, as recently demonstrated by Vidal et al. (2003). Unfortunately, none of the above analytical studies included a formal sensory evaluation.

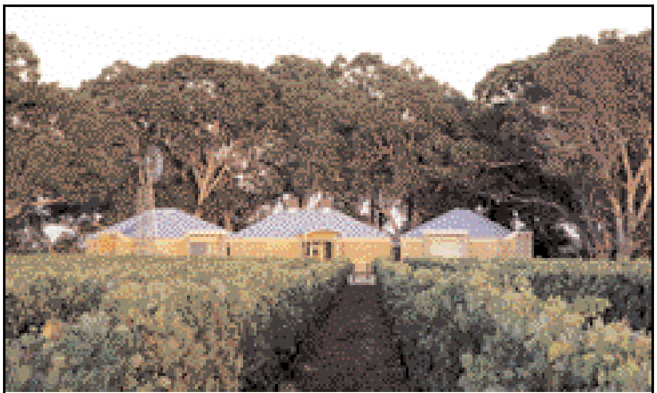
Is acetaldehyde the (only) link between oxygen and phenol composition?

Acetaldehyde, generated by the oxygen-catalysed oxidation of ethanol in the presence of wine phenolics (Wildenradt and Singleton 1974), is regarded as a key MOX-responsive element that might act as a link between oxygen and structural modification of wine phenolics (Atanasova et al. 2002). However, free acetaldehyde is 'consumed' and quantitative analyses are, therefore, difficult to interpret. Nevertheless, acetaldehyde is known to stimulate the formation of three main types of polymeric phenols in wine or model wine solutions: pyranoanthocyanins (Timberlake and Bridle 1976), pyranoanthocyanin-flavanol (Francia-Aricha et al. 1997) and ethyl-bridged anthocyanin-flavonol or flavanol-flavanol adducts (Fulcrand et al. 1996, Salas et al. 2004). A link between acetaldehyde production (generated by yeast) and the accumulation of the anthocyanin-derived pigment Vitisin B in wine was recently described (Morata et al. 2003, Eglinton et al. 2004). In model solutions, higher molecular weight 'pigmented polymers' are rapidly formed if reactions between acetaldehyde and phenolic compounds are allowed to continue (Es-Safi et al. 1999, Rivas-Gonzalo et al. 1995), eventually resulting in the formation of insoluble precipitates (Bakker et al. 1993). The insolubility of some acetaldehyde-derived flavanol-anthocyanin polymers (Escribano-Bailon et al. 2001) might, at least in part, explain observed losses of astringency (Zoecklein et al. 2003) as a result of overall losses of astringent material (Haslam 1980). This might partly explain why several authors have failed to detect any (Remy et al. 2000, Hayasaka and Kennedy 2003) or low levels of ethyl-linked anthocyanin-derivatives in wines greater than 1 year old (Hayasaka et al. 2004, Lee et al. 2004) although losses due to degradation may also play a role in reducing the levels of these compounds (Hayasaka et al. 2004). Even if present, we still don't know the sensory significance of any low molecular weight pigmented oligomers, nor their relative importance as intermediates in the formation of larger 'pigmented polymers' that remain soluble in commercial wine. Given the overwhelming impact of monomeric anthocyanins in young wines and polymeric pigments in older wines on perceived wine colour, it is difficult to believe that low molecular weight anthocyanin-flavanol adducts play anything but a minor role for wine colour in most commercial wines (Schwarz et al. 2003).

Thus, at present, the only well-known possibility for MOX to influence polymeric phenol composition is via acetaldehyde. Notably, it is possible that oxygen could influence other chemical reactions that directly or indirectly influence phenolic compounds as described by Singleton (2000), Danilewicz (2003) and Remy et al. (2000). The impact of such latter reactions on wine composition has not been investigated. Interestingly, yeast vary greatly in their ability to produce acetaldehyde during alcoholic fermentation, and such differences might also have an impact on polymeric phenol composition in a manner similar to those reported for MOX treatments (Eglinton et al. 2000, Eglinton et al. 2004, Morata et al. 2003). The microbiological interaction is complicated further by the fact that many lactic acid bacteria are capable of degrading acetaldehyde (Osborne et al. 2000).

Which wines to MOX, how much and when to stop

MOX is already commonly used within the Australian wine industry although a clear substantiated consensus view of the real effects and possible benefits is yet to emerge. Our limited discussions with winemakers practising MOX have highlighted a need for methods to estimate which wines will benefit positively from MOX, how much oxygen to add, and when to stop treatment. Such methods are important in an effort to manage the outcome of the controlled addition of oxygen, without having to resort solely to sensory evaluation well in advance of commercial release. Several other issues that warrant consideration include the possible increased risks for microbial spoilage (Ciani and Ferraro 1997, Bartowsky et al. 2003), interactions with oak wood additives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(Vivas and Glories 1996, McCord 2002), long-term effects and studies into actual economic gains.

Given the widespread use, it would appear that there are sensorial changes as a result of MOX treatment, although this is yet to be shown by a formal sensory evaluation. However, studies so far have not been able to detect differences in phenolic composition that explain reported sensory differences between treatments. This might reflect the current lack of knowledge and analytical techniques that effectively can explain the sensory impact of polymeric phenols in a complex and varying matrix. Alternatively, humans might be able to perceive very subtle differences, which our analytical machinery yet cannot detect. Whichever way we look at it, there is a need for further research on the topic. Preliminary studies into the effect of MOX have been initiated at the AWRI in collaboration with a major Australian wine company. The aim of our study is to confirm if MOX treatment has any measurable effect and, if so, use existing methods to describe what that effect might be. Guided by this initial trial, we will develop a plan for more comprehensive experimentation, in consultation with practitioners across the wine industry. Subject to the availability of resources, we aim to obtain an insight into how MOX treatments can be monitored so as to determine what wines to MOX, how much to MOX and when to stop.

CONTROLLED EXPOSURE OF OXYGEN IN THE BOTTLE

Notwithstanding very recent promising innovations introduced by some players in the cork industry, there has in the New World been a moderate, but obvious, shift away from the absolute stronghold that natural cork previously had on wine packaged in glass bottles. A range of alternative closure technologies, which might vary in such aspects as degree of market acceptability, oxygen permeation rate, ability to carry out 'flavour scalping' and their propensity to contribute 'taints' of varying character are now available and used by the industry (Capone et al. 2003, Godden et al. 2001). For example, roll-on tamper evident screw cap closures (ROTE) have recently become a popular alternative for Australian and New Zealand white wines (Anonymous 2001, Francis 2003). In the recent large comparative 'closure trial' study carried out by the AWRI, greater retention of free SO_2 (Godden et al. 2001), lower levels of oxidised aroma characters and higher levels of aroma characters described as 'rubbery' or 'struck flint' (which might, in part, be influenced by low levels of oxygen) (Francis et al. 2003) of the Semillon wine used in this study, suggested that ROTE closures are less permeable to oxygen than natural cork. With regard to the observed 'rubbery' or 'struck flint' sensory attribute, formation of sensorially active compounds, which are not noticeable at bottling, in response to changes in the environment and/or time is obviously only possible if the correct precursors are present, unless the closure itself is chemically contributing to the aroma. Although ROTE closures might be well suited to certain white wine styles (Anonymous 2001), red wines that contain large quantities of phenolic compounds could respond differently to small changes in the rate of oxygen permeation than white wine.

Informal sensory assessments of the Semillon wine used in the AWRI closure study (Godden et al. 2001) after copper, cadmium and copper/ascorbate fining suggested that a combination of mercaptans and di-sulfides were responsible for the observed 'struck flint' or 'rubbery' aroma (Francis et al. 2003). A range of sulfur compounds such as sulfides, thiols (mercaptans) and disulfides have previously been described as 'rubbery' (in addition to other attributes) at wine-like concentrations. These include dimethyl sulfide, ethyl mercaptan, 2-mercaptoethanol, carbon disulfide and diethyl disulfide (Goniak and Noble 1987, Rauhut 1993, Mestres et al. 2000, Ferreira et al. 2003). The level of such compounds can be modulated by changes in the environment. For example, the concentration of dimethyl sulfide was negatively affected by oxygen permeation in bottled Champagne wine (Vasserot et al. 2001) but positively affected by a single discontinuous addition of oxygen to port wine (Ferreira et al. 2003). In contrast, levels of 2-mercaptoethanol were lowered in response to oxygen treatment in the latter study, highlighting the importance of degradation in addition to formation. It is not implausible that all of the aforementioned aroma compounds potentially responsible for 'rubbery' aroma will respond differentially to changes in oxygen exposure. Yet another source of sulfur compounds in bottled wine is the oxygen-unrelated hydrolysis of thioesters to corresponding mercaptans with lower odour thresholds than their precursors (Leppännen et al. 1980). Unfortunately, exhaustive studies that attempt to identify key impact sulfur-containing odours associated with reduced conditions and their respective precursors in wine remain limited (Rauhut 1993, Mestres et al. 2000, Ferreira et al. 2003). A more rigorous study into cause-effect relationships between reductive environments, aroma compounds and sensory attributes associated with reduced environments are needed. A detailed insight into consumer acceptability of 'struck flint' or 'rubbery' aroma attributes in wines would also be beneficial.

Assessing the effect of oxygen at bottling: an AWRI red wine screw cap study

A next logical step, in an effort to overcome any possible side-effects associated with the reduced oxygen exposure of ROTE closures, is to, in controlled fashion, modify either the continuous ingress of oxygen (Eric et al. 1976, Vasserot et al. 2001) or, alternatively modulate the amount of oxygen present at bottling. One study into the effect of variations in oxygen exposure was recently initiated at the AWRI. A commercial Cabernet Sauvignon wine from the 2002 vintage was bottled in December 2002 with a ROTE seal and headspaces of 4, 16 and 64 mL air, equivalent to 16, 53 and 104 mm of distance from the top of the bottle to the surface of the wine, respectively. As a comparison, the same wine was also bottled and sealed with natural cork (Reference 2) and a synthetic closure using vacuum insertion and ullages of 6 mL and 5.4 mL, respectively. The wines are being stored upright at the Hickinbotham Roseworthy Wine Science Laboratory under controlled temperature (18°C) and humidity (60-80%). Extensive chemical and sensory analyses are planned throughout this long-term study and full details will be published elsewhere. Preliminary results indicate that differences in sulfur dioxide content could be observed among some of the treatments (Figure 1a). The substantial initial drop in sulfur dioxide is most likely related to the amount of oxygen present in the headspace at bottling.

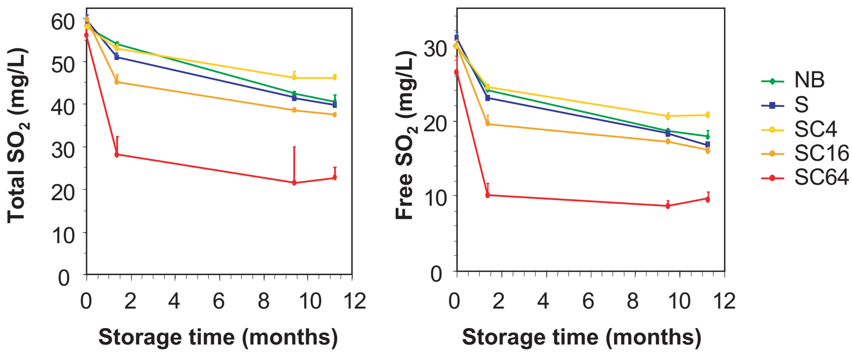

Figure 1a. Total and free sulfur dioxide through the storage period for the red wine screw cap experiment. Closure abbreviations are: NB = natural bark, S = synthetic, SC = screw cap (4,16 or 64 mL of headspace).

HPLC analyses of key phenolic compounds or compound groups in these wines 12 months after bottling revealed that the concentration of 'pigmented polymers' and tannins were not different in wines sealed with different closures (Compare NB, S and SC16; Figure 1b). Differences in the rates of oxygen permeation of bottle closures are expected to

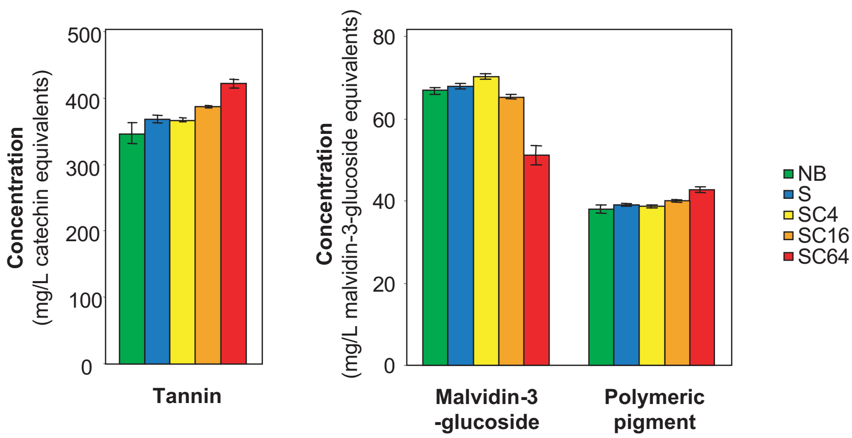

Figure 1b. Phenolic data of the red wine screw cap study. The concentration of tannins (280 nm) and polymeric pigments (520 nm) was estimated essentially as described in Peng et al. (2002), with slight modifications to be reported elsewhere. Abbreviations are as explained in the legend of Figure 1a.

be much lower than the quantities of oxygen introduced during typical MOX-treatment of red wines (Table 1) and this might explain why no differences in the quantity of phenolic compounds could be found between the different closures. However, ullage volume did have a slight impact on the polymeric phenol content and the concentration of malvidin-3-O-glucoside was concomitantly lower the greater the headspace (SC4 vs SC16 and SC64) as expected from earlier studies (Vivas and Glories 1996, Castellari et al. 2000) (Compare SC4, SC16 and SC64; Figure 1b). It is important to note that classical C18-HPLC analysis can give information regarding concentration but not composition of polymeric phenols in wine. For example, the average distribution of the molecular weight of individual compounds (mDP) might not have changed although the total quantity of polymeric phenols has changed. However, it can be expected that both the quantity and composition of polymeric phenolics potentially can have an influence on sensory perception, as shown by Vidal et al. (2003).

Sensory panel data obtained through duo-trio difference testing (by aroma only), performed six months after bottling revealed that there were no statistically significant differences between wines in bottles sealed under natural cork and any of the wines in bottles sealed with ROTE. However, nine months after bottling, significant differences could be found between the wine sealed under ROTE with 64 mL ullage and the wine sealed with natural cork and also with the ROTE with 16 mL of ullage.

Sensory descriptive analysis (13 aroma attributes, four palate attributes) was conducted after 12 months post-bottling and there were found to be no statistically significant differences among the treatments for any of the attributes rated except 'reduced' and 'oxidised' (bruised apple, aldehydic) (Figure 2). There was no significant difference for any attribute between the natural cork closed wine and the wine sealed with the ROTE with the intermediate headspace volume. The wine bottled with the ROTE closure with the smallest headspace volume was rated as highest in 'reduced' aroma, while the wine sealed with the ROTE closure with the largest headspace was rated as significantly higher in 'oxidised' aroma than the wine sealed with the other closure types. It should be noted that the average scores for both of these attributes were very low (less than 1.5 on the 0 to 9 intensity scale used), especially in relation to the other attributes rated; for example overall fruit intensity was rated with a mean score of approximately 4.5 for each of the wines of each closure on the 0 to 9 intensity scale used. Thus the results indicate that any struck flint/rubbery or oxidised aromas were relatively subtle features of the wine at 12 months post-bottling. In studies of this sort there is always the need to distinguish whether differences that might be detected as statistically significant are in fact of practical importance. Nevertheless, these data provide information that can be used to judge whether bottling wines under ROTE with a small, or conversely a large, air headspace volume, might be desirable.

The overall conclusion from the sensory and the phenolic chemical data obtained from this study to date is that these red

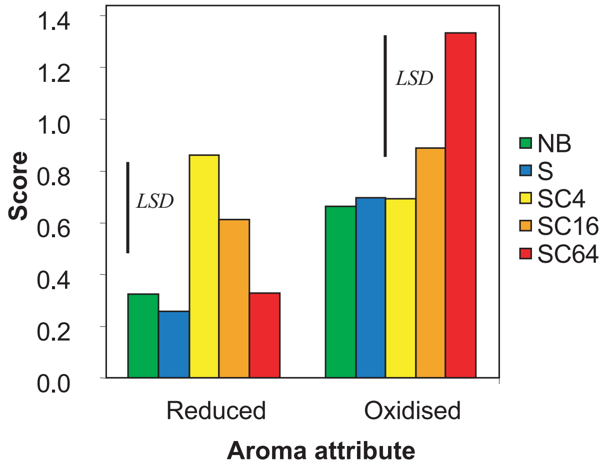

Figure 2. Descriptive analysis data of the red wine screw cap study. Mean data for the two attributes that were statistically significantly different across the treatments are shown, together with the Least Significant Difference (LSD, P=0.05) value. The attributes were rated on a scale of 0-9, with a level of 9 indicating a strong intensity. Abbreviations are as explained in the legend to Figure 1a.

wines sealed with the different treatments differed only slightly. Further data obtained over the next year of the wine's life will shed more light as to whether differences in oxygen level at bottling and closure type might substantially affect the flavour of the red wine used in this study. The ability to generalise from the results of this study to other red wines will also be established with further, extended investigations.

CONCLUSION

There is an interesting link between the post fermentation processing and bottling stages of wine production, with overlapping implications. For example, MOX could be used to potentially reduce or eliminate the content of sulfur-containing precursors (Moutounet et al. 1995) that later in development can become the source of derivatives with sensory impact (Francis et al. 2003). On the other hand, preliminary data indicate that differences in initial oxygen content at bottling also can have an effect on the composition of polymeric phenols, similar to that of MOX treatment, thereby suggesting that the evolution of compositional changes to wine phenolics to a certain extent can be modulated by a conscious choice of bottling practice. In parallel with the shift to the use of ROTE closures for white wines, Godden et al. (2001) conducted a thorough evaluation of this practice to add to the knowledge generated by the study of Rankine and colleagues decades earlier (Eric et al. 1976). In contrast, it appears that MOX is already used in the industry despite the absence of a similar thorough study in relation to this technique, a situation that to a lesser extent also applies to the use of ROTE closures for red wines. Although this increases the risk of the introduction of these techniques, the fact that innovative industry practitioners are adopting both MOX and use of ROTE closures for red wines now, will allow industry to evaluate this technology quicker and also help the define the issues that an extensive research approach must address. While we do not preempt the outcomes of such future studies, it would be tempting to believe that the enhanced control exerted over exposure of wine to oxygen in turn will facilitate the production of wine to tighter consumer informed specifications than is currently possible.

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