Technical notes

Measuring oxidative aroma compounds in wines

Oxidation is one of the most common wine faults and can occur at different stages of the winemaking process, as well as after a wine has been bottled. 'Honey', 'sherry', 'cardboard', 'cooked vegetable', 'cider', 'woody', and 'hay' are some of the characteristic aroma descriptors of oxidised wines. Alongside the development of these aromas, the oxidation of major wine compounds can also result in significant undesirable colour changes. It is commonly believed that acetaldehyde is the main aroma compound generated during wine oxidation. Acetaldehyde is found in wines at concentrations around 80 mg/L in whites and 30 mg/L in reds, and is by far the most abundant aldehyde in wines (McCloskey and Mahaney 1981). A high concentration of acetaldehyde is a particular feature of sherry wines, where it commonly found at around 300 mg/L (Cortes et al. 1998), well above its reported aroma threshold of 0.5 mg/L (Guth 1997) and it can be produced at relatively high levels during fermentation. However, although acetaldehyde plays an important role in the oxidation process, notably in further reactions with other compounds, its direct sensory contribution seems to be rather insignificant (Escudero et al. 2002).

On the other hand, other aldehydic compounds such as phenylacetaldehyde and methional have been shown to be important in the aroma of oxidised wines. Their aromas are described as 'honey- and potato- like' respectively, and their odour thresholds are as low as 1 and 0.5 μg/L (Escudero et al. 2000), up to 1000 times lower than that of acetaldehyde. In addition to those two compounds, several long chained aldehydes such as (*E*)-2-nonenal, (*E*)-2-octenal, (*E*)-2-hexenal, as well as benzaldehyde, furfural, hexanal and some alcohols have been found in increased concentration in wines exposed to oxygen (Balboa-Lagunero et al. 2011; Escudero, Cacho and Ferreira 2000; Escudero et al. 2002). The (*E*)-2-alkenals, with their 'green', 'fatty', and 'nutty' odour descriptors, are all characterised by having very low odour thresholds, with (*E*)-2-nonenal (the one described as 'sawdust') having a threshold as low as 0.17 μg/L (Chatonnet and Dubourdieu 1998). In addition, the aroma of aged fortified wines has been shown to be related to increased concentrations of the compound sotolon, which seems to be most closely related to the 'rancio' (nutty-like) flavour descriptor (Collin et al. 2012; Martin et al. 1992; Silva Ferreira, Barbe and Bertrand 2003).

The formation of these oxidation-related aroma compounds generally occurs well before any colour changes. Hence, measuring these compounds can be an indication of the onset of oxidation at earlier stages. For most research studies involving oxidative effects, indirect measures such as loss of sulfur dioxide or spectral measures to assess the extent of browning have been used. Until recently, analytical methods for oxidative aroma compounds have not been available at the AWRI. Since these compounds generally occur in wines at very low concentration and are difficult to quantify it is essential to use a highly sensitive and selective analytical method.

A comprehensive new GC-MS/MS method has recently been developed through a collaboration with Agilent Technologies which allows the simultaneous quantification of 18 volatile compounds involved in wine oxidation. The compounds include the (*E*)-2-alkenal compounds that occur at trace concentrations ((*E*)-2-hexenal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E*)-2-nonenal), various 'Strecker aldehydes' (methional, phenylacetaldehyde, 3-methylbutanal, 2-methylpropanal), methionol, eugenol, maltol and furans (sotolon, furaneol and homofuraneol).

Samples from a trial where a Semillon wine was bottled under different closures (two natural corks, two synthetic closures and a screw cap) and stored at approximately 15°C for 14 years, were recently analysed using the new method. The colour differences observed among the samples clearly showed a range of levels of oxidation, with the wine colours ranging from a light yellow in the case of those sealed with screw caps, to a dark brown for wines under the synthetic closures.

Most of the oxidation-related compounds analysed were found to vary significantly among the wines bottled with different closures. Figure 1 shows the concentrations of methional and phenylacetaldehyde in the wines. The concentrations of these aldehydes were highest in the most oxidised wines (under synthetic corks) and lowest in the least oxidised wines (under screw cap), with greater variation in the wines under the natural corks, as indicated

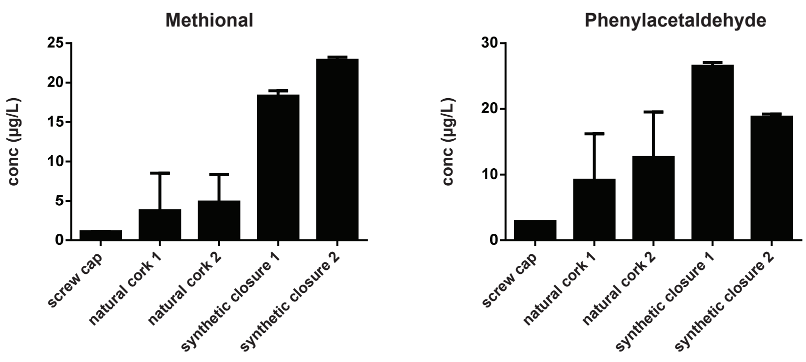

Figure 1. Concentration (µg/L) of methional and phenylacetaldehyde in white wines bottled under different closures after 14 years of storage.

by the larger error bars. The levels of these two compounds in the wines under cork and synthetic closures were significantly greater than their aroma thresholds, suggesting a likely contribution to the aroma of these wines.

The concentration of 3-methylbutanal, a malt-smelling compound, was also measured (Figure 2) and found to vary greatly depending on the type of closure used. In particular, when the wines were sealed with screw cap there was a very low concentration of this compound, while higher concentrations were found in the other wines, particularly when a synthetic closure was used.

Other measured compounds, including the (*E*)-2-alkenals with different chain lengths, were also found to vary in agreement with the degree of oxidation observed in the wines sealed with the different closures. In particular concentrations of (*E*)-2-hexenal and (*E*)-2-nonenal were found to vary across the wines however their overall levels were relatively low compared to the aroma thresholds, suggesting that their sensory significance is likely to be negligible.

Another compound measured was sotolon, the key odorant of aged sherry wines, ports and botrytised wines, that has also been reported as a contributor to the oxidative off-flavour of table wines (Escudero, Cacho and Ferreira 2000; Martin et al. 1992). Despite the high degree of oxidation in the wines analysed, sotolon was only detected in the wines sealed with synthetic closures, where it was found in concentrations around its odour threshold (15 µg/L). In the less oxidised samples it was detected at concentrations below its quantification limit, suggesting that in this set of wines it is not a major contributor.

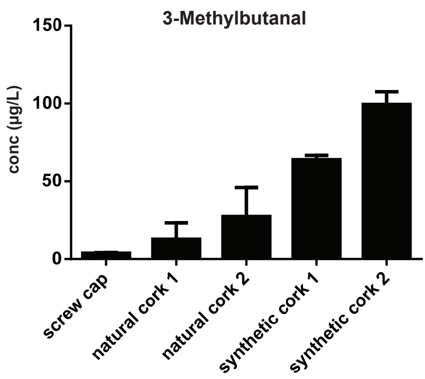

Figure 2. Concentration (µg/L) of 3-methylbutanal in white wines under different closures after 14 years of storage.

In summary, the newly developed GC–MS/MS method has been used to simultaneously quantify 18 oxidation-related compounds in wines at mg/L, μg/L and ng/L levels. By analysing a set of white wines characterised generally by pronounced oxidation but also by large differences in the levels of oxidation, the role of a range of flavour compounds contributing to oxidative aroma has been investigated. The compounds phenylacetaldehyde and methional, two compounds described in the literature as important in oxidised wines, were detected at high concentrations in the most oxidised samples, indicating them as key contributors to oxidative off-flavour in this set of white wines. The new method for oxidation-related compounds will be published shortly in a peer-reviewed journal, and will then be available to the Australian wine sector through AWRI Commercial Services.

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