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Chapter 8

CHEMICAL AND SENSORY DISCRIMINATION OF DIFFERENT KINDS OF WHITE WINE AGING AND ENOLOGICAL MEASURES TO IMPROVE WHITE WINE FLAVOR STABILITY: A REVIEW

Volker Schneider
Schneider-Oenologie, Weiler bei Bingen, Germany
Email: Schneider.Oenologie@gmail.com

ABSTRACT

Fruity white table wines are sensitive beverages whose flavor stability during storage and aging is a major concern in the wine industry. Only a few among them age in a way considered positive by hedonic criteria, while the overwhelming majority of them undergo chemical reactions leading to four distinctive kinds of aging characterized by wine industry professionals as oxidative aging, atypical aging, post-bottling reduction flavor, and petrol flavor. Each of these specific ways of aging has its own set of sensory descriptors, impact compounds, and reaction mechanisms. They add to nonspecific aging reactions occurring in any wine and end up shaping the peculiar sensory profile of an aged white wine. All of them are associated with fruit composition, but vinification procedures and storage conditions exert a severe effect on the rate of their formation and the intensity of their ultimate sensory impact. After fermentation, the time point of filtration, careful protection against uncontrolled oxygen uptake before, during and after bottling, the rational use of sulfur dioxide and ascorbic acid, the choice of the bottle closure, and the storage temperature are the most important technical variables affecting aging reactions. This chapter presents the most recent knowledge about the specific impact of these variables on each form of aging with the purpose of optimizing flavor stability and typicity during storage with regard to grape variety and origin. It also provides clues for a precise sensory identification of the different types of white wine aging in linguistic terms, which is necessary to characterize and communicate which type of aging is present.

Keywords: wine, oxidative aging, atypical aging, petrol flavor, reduction flavor, oxygen

INTRODUCTION

The market value of fruity white wines is intrinsically bound to their distinctive varietal aroma. Much enological knowledge is dedicated to its production, while much less attention is paid to its preservation. However, white wines are sensitive products. They are subject to a far more pronounced aging than red wines. Usually, the sensory outcome of this aging process is opposed to current quality perceptions; white wines aged in a positive way constitute rare exceptions. The limited shelf life of white wines after bottling is a global problem.

All wines change during storage. A gradual decay of fruity aroma attributes, particularly of those produced by the fermentation metabolism of yeast, is common to all kinds of wine and considered unavoidable. This process is referred to as maturation. In addition to that, distinctive aging flavors appear in white wines in a subsequent phase. Their occurrence adversely affects the sensory pattern and quality features initially intended to be produced by the winemaker.

In order to take targeted measures for optimizing white wine shelf life and flavor stability, it is mandatory to differentiate the different kinds of aging flavor according to their sensory characteristics and chemical pathways. For this purpose, there is a need of specific terms applied in descriptive sensory analysis whose precise use depends on sensory training and experience of the professional tasters involved. Unfortunately, and to much disfavor of wine quality control, sensory terms are frequently misused, abused, or exchanged among themselves. As an example, the term “oxidized” gives no information about whether there is the typical smell of free acetaldehyde involved in the aromatic pattern as it occurs in the absence of free sulfur dioxide, or whether the smell is evoked by other oxidation products generated in the presence of free sulfur dioxide. Misunderstandings caused by imprecise language use often lead to wrong decisions when it comes to choose enological counter-measures for preventing or remedying premature aging flavors.

According to sensory criteria, there are five different kinds of white wine evolution. Four of them are considered as characterized by specific aging flavors and discussed in this chapter:

- A general decrease of fermentation aromatics, especially acetates of higher alcohols and ethyl esters of fatty acids resulting from yeast metabolism. This decay is largely attributed to acid-ester hydrolysis equilibrium and particularly pronounced during the first weeks and months after alcoholic fermentation.
- Typical or oxidative aging giving rise to a wine commonly called maderized or simply oxidized. It is reminiscent of the odor of hay, straw, nuts, cooked vegetables, boiled potatoes, black tea, honey, and wet soil. Additionally, the smell of free acetaldehyde reminding bruised apple may appear and mask these olfactory attributes when free sulfur dioxide has been decreased to nil by oxygen uptake. An increase of astringency on the palate and an intensification of color may occur simultaneously, but must not do so.
- Atypical aging resulting from the conversion of a phytohormone called indole-3-acetic acid into 2-aminoacetophenone and other by-products reminding mothballs, soap, floor polish, acacia blossom, and laundry in wines produced from stressed fruit.

- Post-bottling reduction flavor leading to the formation of volatile sulfur compounds, particularly mercaptans, whose stinky smell is reminiscent of burnt rubber, cooked cabbage, rotten eggs, and garlic. Its appearance is fostered when wines prone to produce it are bottled using bottle closures with low oxygen ingress.
- Petrol flavor, calling to mind gasoline, kerosene, and dry apricots, related to an acidic hydrolysis of grape-derived precursors like carotenoids in wines obtained from a very limited number of grape varieties such as Riesling.

Oxidative aging with its commonly known sensory pattern is the most typical form of aging of white wines, while the other variants of aging are considered more or less defective deviations from normal wine evolution. The frequently encountered confusion between typical and atypical aging is a particularly serious problem in enology with far reaching consequences.

TYPICAL OR OXIDATIVE AGING

Reactions and Compounds Involved

The oxidation of wines has quite different consequences for white and red wines. Oxygen uptake is usually required for the maturation of red wines, but it seldom improves white wines where the preservation of the fruity, vegetative, or mineral aromas responsible for varietal or geographical character is sought.

Oxidative aging is the kind of white wine aging that has always been known and, therefore, is considered as typical aging as opposed to atypical aging. While there has been extensive knowledge about the degradation of fruity aroma compounds occurring in any kind of wine, reaction pathways and end products involved in oxidative aging have been less investigated during a long time. Recent results, however, indicate that besides oxidation, sugars and amino acids are also involved through slowly proceeding reactions of caramelization and those of the Maillard type.

Reactions of amino acids on one hand and dicarbonyl compounds (e.g., diacetyl) and ketones (e.g., acetoine) on the other hand leading to the formation of odor-active compounds have been shown. Especially, sulfur-containing amino acids like cysteine are able to yield various pyrazines, thiazoles, thiazolidines, and oxalones from the Maillard and Strecker reactions under mild pH and temperature conditions. The products formed present complex odors of nut, popcorn, roasted hazelnuts, sulfur, and dry fruits (Marchand et al., 2000, Pripis-Nicolau et al., 2000). Independently of these findings, lactones produced by a completely different pathway have been made responsible at least partially for the characteristic smell of oxidized wines (Muller et al., 1973).

Under oxidative conditions, coupled oxidation of vicinal di- and trihydroxyphenols yields acetaldehyde and higher aldehydes substantially contributing to the aroma of Sherry wine (Wildenradt and Singleton, 1974) and, at lower concentrations, also to that of other white wines.

The non-enzymatic formation of aldehydes is a consequence of wine oxidation and compromises the quality of white wines conceived as fruity (Baro and Quiros Carrasco, 1977). In Riesling wines, it has been shown that under conditions of oxidative storage, a large array of compounds is produced that is not observed when storage takes place in the absence of oxygen ingress. These odor-active compounds comprise aldehydes including benzaldehyde, furfural, 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), and acetaldehyde (Simpson, 1978).

An increase of saturated and unsaturated carbonyl compounds as well as methyl ketones was observed when wine was stored in wooden barrels allowing oxygen ingress. Under these conditions, the typical smell of the oxidized wine was ascribed to 2-nonanon and 2-undecanone (Ferreira da Silva and Bertrand, 1996).

In another study, 22 new odor-active compounds were found after oxidation of six different white wines. Four of them were present in all wines and 14 in more than half of the wines. Several of these compounds displayed an objectionable, oxidized smell. Using descriptive analysis of the oxidized wines, 15 of the odor attributes proved to be affected by oxidation, whereby the overall aroma feature changed by 60%. There was an oxidation pattern common to all oxidized wines (Escudero et al., 2000 a). The aroma feature of oxidized wines was primarily ascribed to higher aldehydes as methional, a strong odorant displaying an off-flavor reminiscent of cooked vegetables. It is probably produced by peroxidation of methionol or via Strecker degradation of methionine mediated by *o*-quinones formed during wine oxidation (Escudero et al., 2000 b; Ferreira da Silva et al., 2003).

In a subsequent work, the same authors showed the intensity of the cooked vegetables odor to correlate with the concentrations of 2-nonenal, eugenol, benzaldehyde, and furfural, while acetaldehyde did not vary significantly during oxidation (Escudero et al., 2002). However, other research groups confirmed the role of the afore-mentioned methional as a key compound in the aroma feature of oxidation-spoiled white wines, along with phenylacetaldehyde, 3-(methylthio)propionaldehyde, 4,5-dimethyl-3-hydroxy-2(5H)-furanone (sotolon) (Silva Ferreira et al., 2002; Silva Ferreira et al., 2003 a; 2003 b; Silva Ferreira, 2007), benzaldehyde, furfural, and other higher aldehydes derived from unsaturated fatty acids (Ferreira et al., 1997). The concentrations of these compounds correlated with the oxygen uptake and the intensity of odor descriptors like boiled potatoes, farm-feed, hay, wood, and honey. Extension of these studies confirmed the sensory importance of a wide array of (E)-2-alkenals for flavor deterioration of oxidation-spoiled white wine (Culleré et al., 2007). Additionally, 2,5-furandicarbaldehyde, furyl hydroxymethyl ketone, and hydroxymaltol have been identified as further chemical markers of oxidative aging in barrels, especially of the honey descriptor. Stirring the lees decreased their concentration (Lavigne-Cruege et al., 2000).

Decreases in acetate esters and many ethyl esters produced by yeast metabolism are a well-known phenomenon during the aging of wine and largely attributed to their hydrolysis-esterification equilibria. They are responsible for the rapid loss of fermentation-derived aromas in young wines. In white wine bottled in the presence of air, aroma esters decreased more than after bottling under nitrogen, proving the impact of oxidation on ester equilibria (Patrianakou and Roussis, 2013). Similar findings have been reported for terpenols and norisoprenoids, grape-derived aroma compounds that impart floral aromas (Ferreira da Silva et al., 2002). These results demonstrate that oxidative aging comprises, beyond the synthesis of off-flavor related

compounds, also the decay of fruity-floral aroma compounds much sought after in young white wines.

As a whole, the available studies on typical white wine aging flavor suggest that some of the underlying reactions can take place under anaerobic conditions. However, they also stress the role of oxygen uptake and subsequent reactions of oxidation leading to the formation of many and varied carbonyl compounds like higher aldehydes as odor-active compounds. At low concentrations, these compounds may add to the complexity of a wine but as they increase, they begin to detract from wine quality and become ultimately responsible for the aroma pattern of typically aged white wines. The German expression "Firne," sometimes encountered in the international literature and barely translatable, describes very precisely this kind of odor pattern without ruling out the presence of free sulfur dioxide.

The multifarious carbonyls generated in this way may be accompanied and partially masked by free acetaldehyde with its typical smell reminiscent of over-ripe bruised apples and sherry easily detected by wine industry professionals. Its presence is a common wine fault related to the absence of any free sulfur dioxide as it might occur after its complete oxidation by oxygen ingress or in wines without sulfites added. More precisely, free acetaldehyde and free sulfur dioxide exclude one another since they almost spontaneously form an odorless hydroxysulfonate addition product. The small dissociation constant ($K_D = 5 \times 10^{-6}$) for this reaction explains why the equilibrium favors the formation of product. Therefore, the smell of free acetaldehyde disappears as soon as sulfites are added in an amount large enough to bind it entirely and to ensure some free sulfur dioxide in excess. The reaction is completely reversible.

Oxidative aging proceeds in the presence of free sulfur dioxide used as the traditional antioxidant in the wine industry, but is strongly accelerated in its absence. It is imperative to distinguish the smell of free acetaldehyde from that of oxidative, typical aging, even though both of them might occur simultaneously. In contrast to free acetaldehyde easy to deal with in wine stabilization by addition of SO_2, the higher aldehydes responsible for the smell of typical aging are largely unreactive. They do not bind to sulfur dioxide to produce an odorless addition product to any useful extent, nor are the reactions leading to their formation reversible.

Because of the diversity and low reactivity of the compounds involved, they are difficult to remove from wine. Some minor improvement of wines affected by the odor of typical aging is possible using fining with activated charcoal or yeast lees obtained from young wines. More specific fining agents are not available, nor do other fining materials commonly used in the wine industry show any effect.

Influence of the Phenolic Composition

There are many organic compounds in wine that are potential targets for oxidation processes. Odor-active aromatic components constitute one group of them, but they are not the main initial substrate of oxidation. Contrarily, when wine picks up atmospheric oxygen, polyphenolic compounds are the primary reactants that are oxidized, a process that initiates a cascade of chemical transformations. The oxidation of phenols is catalyzed by transition metals

present in any wine. It generates hydrogen peroxide. Under a competitive scenario containing free SO_2 and ferrous ions as in wine, the major part of hydrogen peroxide is scavenged by SO_2 that, in turn, is oxidized to sulfate. A minor proportion of hydrogen peroxide undergoes metal-catalyzed reduction, referred to as the Fenton reaction. This reaction yields hydroxyl radicals that can oxidize almost all wine components not directly oxidizable by molecular oxygen, e.g., alcohols to the respective aldehydes (Wildenradt and Singleton, 1974; Singleton, 1987; Waterhouse and Laurie, 2006; Du Toit et al., 2006; Danilewicz, 2007; Elias and Waterhouse, 2010; Oliveira et al., 2011; Danilewicz, 2012). SO_2 exerts its protective function in oxidizing wine by scavenging hydrogen peroxide, thereby diverting it from the Fenton route.

Phenolic compounds originating from grapes can basically be divided into the non-flavonoid and the flavonoid fraction. The non-flavonoid phenols, which are hydroxybenzoic and hydroxycinnamic acid derivates, derive from the grape juice and are the principal phenolic molecules in white wines at concentrations ranging typically from 100 to 200 mg/L. Even though they may display bitterness and astringency, they do not do so in white wines since their concentration is close to the sensory detection threshold (Smith and Waters, 2012). Thus, they contribute at best to volume and weight on the palate without major gustatory and chromatic implications during wine aging (Singleton and Noble, 1976; Arnold et al., 1980; Vérette et al., 1988).

Flavonoid phenols are extracted from grape seeds, skins, and stems during crushing, skin contact, and pressing. Depending on wine making conditions, concentrations in white wines are highly variable in a range from 0 to 50 mg/L and not directly related to the more comprehensive total phenol content. In young white wines, they comprise essentially catechin and epicatechin as colorless monomers displaying some astringency and bitterness. During aging, they undergo oxidative polymerization resulting in an increase of bitterness, astringency (Noble, 1994), and white wine color, with the appearance of browning at the extreme. In the absence of flavonoid phenols, white wines are not able to develop substantial browning (Rossi and Singleton, 1966; Simpson, 1982; Lee and Jaworski, 1988; Fernández-Zurbano et al., 1995; Fernández-Zurbano et al., 1998; Schneider, 1998).

Aromatic degradation begins long before any color change can be observed. The color increase of white wines reflects profound alterations in taste and smell, and the potential to increase color is related to the potential of developing premature typical aging. Furthermore, a negative correlation between the concentration of flavonoid phenols and aroma stability during white wine aging has been reported under conditions of comparable oxygen uptake, suggesting that odorless flavonoids act as a catalyst in oxidative aging as perceived by smell. However, there is no correlation between total phenol content and aroma stability (Schneider, 2000). This behavior is entirely different from what happens in a red wine matrix. For the production of fruity white wines with a satisfying shelf life, reducing or eliminating flavonoid phenols and browning potential is of major enological interest.

Given the impact of flavonoid phenols on taste, smell, color, and shelf life of white wines, various analytical methods have been proposed to assay their content and identify wines prone to premature oxidative aging. They are based on accelerated browning tests (Singleton and Kramling, 1976; Müller-Späth, 1992), spectral evaluation in the ultraviolet area (Somers and Ziemelis 1985), or direct flavonoid measurements by spectrophotometry (Kramling and Singleton, 1969; Pompei and Peri, 1971; Zironi et al., 1992; Schneider, 1995). A rapid

spectrophotometric assay using 4-(dimethylamino)-cinnamaldehyde as chromophore is considered the most sensitive and specific method for measuring flavonoid phenols under conditions of industrial routine control (Schneider, 1995). For optimal shelf life, readings obtained by this assay should not exceed 5 mg/L expressed as catechin units. All these analytical approaches gain advantage over sensory evaluation since they allow for the detection of flavonoids in young wines where they are not yet sufficiently polymerized to display perceptible astringency. The measurement of total phenols is too unspecific and does not provide any information upon the flavonoid content.

Influence of Juice Processing

Flavonoid phenols can be reduced by fining. For that purpose, the wine industry makes use of various fining agents when the flavonoid content elicits disturbing astringency or compromises the wine's shelf life. Bench trials are usually performed to determine sensorially the proper dosing for the required task at a given moment. Consequently, only the most polymerized, astringent, and reactive flavonoids are removed, while their less astringent fraction remains behind and capable of reproducing astringency at a later point of time. In contrast, the analytical determination of flavonoid phenols allows also embracing monomeric precursors of more astringent compounds that would be formed later and adjusting the amount of fining agent to remove them, thus achieving more sensory stability in the long term. It is important to note, however, that phenols are not the only cause of astringency and bitterness in white wines (Smith and Waters, 2012).

PVPP (polyvinylpolypyrolidone) has been shown to be the most effective fining agent to remove both monomeric and polymerized flavonoid phenols (Sims et al., 1995; Barón et al., 1997). It can be used preventatively or as a cure for removing astringency or browning. Alternatively, proteinaceous fining as agents as casein, gelatin, or plant-derived proteins are used. The effect of gelatin depends on its specification (Cosme et al., 2008; Cosme et al., 2012). In many contemporary low-phenol white wines, it tends to show limited effectiveness in reducing flavonoid phenols and astringency. These wines lack flavonoids on a level of concentration and polymerization that would enable them to react with gelatin. This is in contrast to the effectiveness of gelatins in red wines displaying flavonoid concentrations higher by two powers of ten. Used without silica dioxide (kieselsol) as counter-fining, gelatins also pose a serious risk of over-fining in white wine, rendering the wine unstable with respect to heat-labile proteins (Schneider, 2006 b). Casein, potassium caseinates, and isinglass obtained from fish bladder take a mid-position in this context and precipitate completely. Similar to gelatins, their effect on flavonoid removal depends on their molecular weight distribution and surface charge density (Cosme et al., 2008; Braga et al., 2007).

All fining agents are reputed to strip aromatic compounds from wine, be by adsorption by the fining agent (Voilley et al., 1990; Moio et al., 2004), be by volatilization or oxidation during the fining procedure (Schneider, 2005 a). None of them is specific to the flavonoid phenol fraction since non-flavonoids are removed simultaneously (Cosme et al., 2012).

Elevated flavonoid concentrations in white wines are the result of deficiencies in grape and juice processing. Grinding and shredding of the grape tissues by severe mechanical fruit treatment has been one of the primary causes of enhanced flavonoid extraction from seeds, skins, and stems, during decades. In the meantime, there is a general trend towards a mechanically more gentle fruit processing. Thus, crushers, stemmers, and presses, the latter more and more designed as gently operating pneumatic presses, have reached a high degree of development minimizing flavonoid extraction and do not allow for much more improvement. However, skin contact and pumping of crushed fruit to the press continue to be critical points of flavonoid extraction in the course of grape processing. Many wineries act on that by treating the juices with proteinaceous fining agents. Instead of promoting their use, future research should focus more upon helping winemakers improve fruit and juice handling and make such agents dispensable.

Juice clarification is considered an important means for improving shelf life, cleanliness, and fruitiness of white wines (Singleton et al., 1975; Houtman and Du Plessis, 1981). The precursors of future off-flavors and phenol-derived astringency are partially bound to juice solids and would dissolve in the alcoholic medium after the onset of fermentation. They are reduced by juice clarification to a variable extent. Comparing static sedimentation, centrifugation, flotation, and filtration of juices, the technical means used were considered less important than the effect achieved, measured as residual turbidity before inoculation. It should not exceed 0.6% w/w (Seckler et al., 2000) or 100 NTU (nephelometric turbidity units) (Schneider, 2005 b; Nicolini et al., 2011). Juices with less than 20 NTU residual turbidity are prone to fermentation problems.

The solubility of flavonoid phenols in juice after pressing is strongly affected by the redox regimen. Reductive grape processing by use of an inert gas increases the contents of total phenols and monomeric flavonoids (Cáceres-Mella et al., 2013). In the absence of inert gas and sulfites, phenols easily undergo enzymatic oxidation induced by polyphenol oxidase. Thereby, flavonoids are oxidized by the enzymatically generated caffeoyltartaric acid quinones, polymerize (Cheynier and Ricardo da Silva, 1991), and precipitate as solids. Although juice oxidation lowers all kinds of phenolic compounds, sensory results on the palate are mainly derived from the removal of flavonoids and the decrease of astringency they elicit. In contrast, sulfite addition inactivates polyphenol oxidase and maintains flavonoids in solution, thus enabling them to undergo chemical oxidation in the wine and generate drastic flavor changes during aging. Comparing wine made from oxidized juice with a flavonoid-containing reference, sensory differences increase during aging. The reference undergoes a more dynamic evolution that the wine obtained from oxidized juice does not display. The more reductive juice processing is conducted, the more prone the wine is to oxidative aging. Thus, juice oxidation is primarily an investment in the long-term behavior of wines (Schneider, 2008 a).

Oxidized juice has a brown color. When it is clarified by filtration, the filtrate displays the typical green-yellow color of standard white wines. This observation demonstrates that the compounds responsible for the brown color are precipitated solids that can be removed mechanically. The sensorially perceptible effects of juice oxidation are neutralized by the reductive conditions during alcoholic fermentation and adsorption by yeast. After fermentation, wines show the normal bright color (Schneider, 1998).

In order to remove flavonoids completely, juice hyperoxidation (Schneider, 1998) has been developed. Thereby, oxygen is deliberately added to juice instead of SO_2. Subsequently, the precipitated phenolic material is removed by thorough juice clarification. Otherwise, it would redissolve in the alcoholic medium after fermentation. Juice clarification by flotation with air allows for simultaneous hyperoxidation and clarification in one single step (Schneider and Chapron, 1992; Sindou et al., 2008). Hyperoxidation is considered particularly beneficial for removal of elevated flavonoids from juices after skin contact (Cheynier et al., 1989; Ho et al., 1999), but can be replaced by passive oxidation, i.e., simple eschewal of pre-fermentation SO_2 additions, when low-flavonoid juices are obtained from gentle grape processing without previous skin contact time (Schneider, 2008 a).

Undoubtedly, the initial purpose of juice oxidation and hyperoxidation is largely met. However, there is a prevalent fear of aroma losses induced by juice oxidation. While it is beyond question that aroma losses do occur in cultivars known for their high contents of oxygen-sensitive varietal thiols like Sauvignon Blanc (Coetzee and Du Toit, 2012), reports on other varieties are conflicting.

Comparing wines obtained from oxidized vs. SO_2-protected juices, higher varietal aroma intensity and overall quality was reported for the lots obtained from hyperoxidized juices in Chardonnay (Cheynier et al., 1991; Cheynier et al., 1989), Parellada, Muscat, and Chardonnay (Artajona et al., 1990), Riesling (Wilson et al., 1993), as well as in Riesling and Gewürztraminer (Bailly, 1990). Lower aroma intensity after juice oxidation was found in Grenache (Cheynier et al., 1989), Pinot noir (Blanck, 1990), several varieties grown in various European countries (Guedes de Pinho et al., 1994; Dubourdieu and Lavigne, 1990) and California (Singleton et al., 1980; Ough and Crowell, 1987). Lower aroma intensity but a softer mouthfeel brought about by juice oxidation was reported for Riesling, Müller-Thurgau, and Gewürztraminer from Germany (Schmidt et al., 2003). Changes in the aroma profile without any decrease of varietal aroma intensity were observed in Chardonnay (Cejudo-Bastante et al., 2011) and Riesling (Schneider, 1996) after juice oxidation. No significant differences were found for several varieties grown in Italy (Nicolini et al., 1991), Alsace (Meistermann, 1990), and Washington State (Nagel and Graber, 1988).

The inconsistency of these results may be partially explained by low initial juice flavonoid contents obviating the need for juice oxidation, differences in residual turbidity after juice clarification, different time points of sensory evaluation during the course of wine aging, and different concepts of quality (Schneider, 1998). Clearly, juice oxidation is not as bad as its reputation and can contribute to white wine flavor stability. As an enzymatically induced reaction, it is much more specific than the chemical oxidation of wine and cannot be compared to it. From a sensory point of view, it is also more specific for flavonoid removal than the use of fining agents. Oxidizable substrate removed by juice oxidation is not available for wine oxidation.

Influence of Wine Antioxidants

In addition to controlling the rate of oxygen entry into wines, winemakers make almost universal use of sulfur dioxide (bisulfite in solution) additions to control oxidation. Sulfites do not react with oxygen directly but with the hydrogen peroxide that is produced when phenols are oxidized to quinones. It largely reduces the quinones back to the original phenols, too, thus removing quinones from further browning and aroma degradation processes. Under these conditions, the oxygen and SO_2 molar ratio should be 1:2, according to one mole equivalent of SO_2 reacting with hydrogen peroxide and a second one with the quinone (Danilewicz et al., 2008), and leading ultimately to the oxidation of 4 mg SO_2 by 1 mg O_2. However, when SO_2 losses were related to the amount of oxygen consumed in ten dry white wines stored in tightly sealed reaction vessels until total oxygen depletion, the SO_2 losses by oxidation averaged only 2.55 mg SO_2 per 1 mg O_2, accounting for only 63% of the oxygen consumed. The remaining 37% of oxygen had irreversibly vanished in reactions of oxidation (Schneider, 2006 a). This finding demonstrates that quinones and hydrogen peroxide are not reduced entirely by SO_2. It explains why there is always some oxidative aging in the presence of typical levels of free SO_2. The sulfite oxidation stoichiometry requires more substantiated data in order to better predict SO_2 losses by oxidation and help facilitate SO_2 adjustment with especial respect to post-bottling SO_2 stability.

Bottling wines with excessively high levels of free SO_2 is not an adequate way to solve problems with premature oxidative aging. Wine samples containing 35 vs. 55 mg/L free SO_2 showed equal concentrations of aromatic volatiles after seven months of storage at 20°C (Roussis et al., 2007). Bottling wines with free SO_2 levels high enough to prevent oxidation completely when oxygen is taken up would result in wines with an objectionably pungent odor of SO_2.

Hydrogen peroxide not scavenged by SO_2 is partially converted by catalytic iron into hydroxyl radicals, stronger and less selective oxidants that react with almost all organic wine components in proportion to their concentration and with little selectivity for antioxidant properties (Waterhouse and Laurie, 2006). This reaction is generally believed to produce the numerous electrophilic oxidation products, mainly aldehydes and ketones, responsible for the typical aroma profile of oxidative aging in white wines.

Sulfur dioxide is difficult to replace in current winemaking. In addition to its activity as antioxidant, it also exhibits antimicrobial activity and improves flavor by binding acetaldehyde. In order to enhance its protection against oxidation, the additional supplementation with ascorbic acid is considered from time to time. As ascorbic acid is readily oxidized by dissolved oxygen, it can be used for its direct removal, a role that is not ascribed to SO_2. However, ascorbic acid additions to wine have a controversial history in that pro-oxidative effects have been observed and ascribed to the formation of hydrogen peroxide and oxygen radicals following the initial antioxidant activity (Bradshaw et al., 2003). This is analogous to what happens when polyphenols oxidize. More precisely, ascorbic acid does not make oxygen disappear without a trace but just accelerates its conversion into more reactive oxygen species. Eventually, oxygen ends up where it does without ascorbic acid. On the other hand, there is no doubt that it can rejuvenate oxidized wines in certain circumstances. This apparent

contradiction suggests that ascorbic acid can display either pro-oxidative or reductive effects depending on age and oxidation state of the wine (Peng et al., 1998).

Even though the crossover between the antioxidant and pro-oxidant roles of ascorbic acid has not yet been precisely identified, storage conditions under limited oxygen uptake after bottling have shown no pro-oxidative effects. While some storage trials have shown little benefit to wine browning from its addition (Marks and Morris, 1993), it led to no difference in aroma or to more fruity aromas after three or more years of bottle storage in other trials, with a slight increase of color due to ascorbic acid degradation products (Skouroumounis et al., 2005; Morozova, 2013). Clearly, ascorbic acid additions may provide some complementary protection of fruity aromas against oxidative aging when used in conjunction with adequate levels of free SO_2. On the other hand, they do not act as an effective means to cope with problems of premature oxidative aging. The occasionally held belief that they do so stems from confusion with another kind of white wine aging called atypical aging, which is discussed later in this chapter.

Related protection is provided by free glutathione, a tripeptide with a free sulfhydryl moiety in its cysteine residue, which confers unique redox and nucleophilic properties. Instead of reacting directly with dissolved oxygen, it reacts with oxidized phenols in preference to varietal aroma compounds such as thiols. Therefore, its role and application as a reducing agent in wine have recently received significant commercial interest. Naturally occurring glutathione concentrations in white wines are highly affected by vinification procedures and range from non-detectable to as high as 70 mg/L (Fracassetti et al., 2011). Since glutathione is not a legal additive, glutathione-enhanced winemaking products such as inactive dry yeast preparations are proposed in order to overcome glutathione deficiencies. There is analytical evidence that additions of pure glutathione preserve better fruity varietal aroma compounds like 3-mercaptohexanol, terpenes, and volatile esters (Fragasso et al., 2010; Papadopoulou and Roussis, 2001; Papadopoulou and Roussis, 2008; Roussis et al., 2007; Roussis et al., 2009; Ugliano et al., 2011). However, sensory evidence of better aroma preservation was only obtained when glutathione had been added in the form of inactive dry yeast preparations instead of pure glutathione (Aguera et al., 2012; Schneider, 2013 a; Andújar-Ortiz et al., 2014). These findings suggest that this mechanism of protection against oxidative aging is more complex than one could expect from a mere glutathione enhancement. However, they hold promise and give reason to anticipate further development.

Post-fermentation yeast lees display numerous features exploited in enology. One of them is their reducing properties. They are related to the ability of nonviable yeast cells to consume considerable amounts of dissolved oxygen. The oxygen uptake rate of yeast during aging on yeast lees has been quantified as between 0.003 and 0.011 mg O_2/h for 10^9 yeast cells from the second to the sixth month of aging at 14°C. The initial levels of oxygen consumption rate and the gradual and irregular decay of these rates were strongly dependent on yeast strains, with 11 to 100% of the initial oxygen consumption rate left after four months of aging (Fornairon et al., 1999). In later works, this oxygen consumption was ascribed to a largely non-respiratory pathway using the oxygen for oxidation of membrane lipids (Salmon et al., 2000), leading to the production of lipid peroxides and unknown end products and thus confirming identical findings on brewers' yeast (Peddie et al., 1991).

Transferring this behavior to practical winemaking conditions, it has been shown that suspended yeast cells at a concentration corresponding to 300 NTU turbidity as occurring in turbid young wines are able to consume a total of around 50 mg/L O_2. This corresponds to approximately six times the oxygen saturation concentration of around 8.5 mg/L O_2. The average oxygen consumption rate was 0.5 mg O_2/L/h for a yeast concentration corresponding to 50 NTU or the typical turbidity of young wines several months after the end of alcoholic fermentation, respectively. This rate is strongly reduced when free SO_2 levels exceed 20 to 30 mg/L. It falls to nil after pasteurization, demonstrating the enzymatical mechanism involved (Schneider, 2005 c).

In conclusion, suspended light yeast lees are able to withdraw a large fraction of dissolved oxygen from chemical oxidation of wine compounds depending on yeast strain, yeast concentration, age, and free SO_2. Filtration cancels this effect. This shows that delayed filtration is a useful tool to protect wine against premature oxidative aging by uncontrolled oxygen uptake during storage and stabilization procedures. It is even more useful when producing wines without the addition of sulfites. Under conditions of barrel aging, it has been shown that carbonyl compounds responsible for the smell of oxidative aging are less produced when total lees are stirred weekly (Lavigne-Cruech et al., 2000).

Influence of Oxygen Pickup and Bottle Closure

Since none of the antioxidants used in the wine industry gives satisfying protection against oxidative aging of white wines, the most obvious solution would be to limit their oxygen uptake. However, working under controlled inert conditions as in the brewing industry is not yet very common in wineries. Thus, it is important to have a survey of the different points where oxygen entry takes place, the magnitude of these amounts, and the sensory changes they bring about after primary fermentation has finished.

When wine picks up oxygen, there are two different processes involved:

- Dissolution of atmospheric oxygen in the liquid depending on pressure and temperature. Oxygen saturated wine holds around 8 mg/L O_2 at 20°C and normal pressure. The oxygen dissolved as a gas can be measured. There are not yet any sensory consequences.
- Chemical binding of the dissolved oxygen to wine compounds. The bound oxygen has disappeared and cannot be measured any more. Sensory consequences appear.

Chemical oxygen binding follows a first-order reaction kinetics fitting a negative exponential function. Depending on wine composition and temperature, it takes several days to several weeks until all dissolved oxygen is depleted. There are two possible reaction models occurring in wine:

- The dissolution of oxygen in the wine is faster than its bonding; an increase of dissolved oxygen is measured.
- The dissolution of oxygen in the wine in slower than its bonding; no dissolved oxygen can be detected.

The concentration of dissolved oxygen measured by analytical means corresponds to the instantaneous difference between dissolution rate and bonding rate.

To be able to pick up oxygen from the atmosphere, a surface of the wine must be exposed to the air. The surface can be static or turbulent. A static surface of a wine-like model solution allows the transfer of 21 mg O_2/m^2/day at 20°C and 8 mg O_2/m^2/day at 7°C, respectively. Lower temperatures reduce the dispersion speed of dissolved oxygen within the liquid, thus cancelling out the effect of higher oxygen solubility. A turbulent surface enhances oxygen uptake by two to three decimal powers, depending on the intensity of the turbulence (Schneider, 2015).

Key sources for oxygen pickup include racking, pumping, mixing, fining, excess headspace, cold stabilization, filtration, and bottling. Table 1 summarizes the range of oxygen uptake during cellar operations as measured by various research groups (Vidal et al., 2001; Vidal et al., 2003; Vidal et al., 2004; Valade et al., 2006; Valade et al., 2007; Castellari et al., 2004; Calderón et al., 2014).

Table 1. Range of oxygen uptake during standard winery operations

Operation	**mg/L O_2 picked up**
Racking	0.37 – 6.6
Pumping into bottom-filled tanks	0.1 – 0.2
Pumping into top-filled tanks	2.0 – 4.0
Centrifugation	0.35 – 1.2
Diatomaceous earth filtration	0.1 – 0.7
Pad filtration	0.04 – 0.5
Cross-flow filtration	0.2 – 1.5
Membrane filtration	0.1 – 1.3
Continuous cold stabilization	1.2 – 2.8
Electrodialysis	0.28 – 1.3
Bottling	0.38 – 7.0

The large variance of oxygen uptake reported in Table 1 is to some extent due to the variability of wine volumes treated. Dissolution of oxygen occurs above all at the beginning of a wine transfer when the hose lines are still empty or at the end when they are drained. Hence, on a mg/L basis, small wine volumes take up more oxygen from the air contained in the circuit than large volumes. A better awareness of the levels of oxygen incorporated by different cellar operations will help take adequate means to protect wines from oxidative aging. In spite of the relatively low oxygen uptake at most operations, the magnitude of the cumulative exposure to oxygen during wine storage and stabilization is decisive. Good cellar practice (Schneider, 2004) to limit oxygen uptake by white wines include the following recommendations:

- Top the containers until they spill over. The quality of the topping depends on the area size of the wine surface in contact with the atmosphere. It does not depend on the missing wine volume or the height of the empty space.
- When topping is not possible, blanket the headspace with inert gas, taking into account one needs an inert gas volume corresponding to three to five times the headspace volume to reduce headspace oxygen satisfactorily.
- Prefer tall, slender tanks to short, wide containers to reduce the surface: wine ratio.
- Limit wine movements as much as possible.
- When transferring wine, limit the length of hoses and avoid unnecessary hose couplings.
- Secure loose hose connections.
- Avoid leaky pump seals.
- Before transfers and filtrations, first pump water throughout the whole system to remove any air pockets in tubing's and filter, dumping the water on the floor. Connect the inlet hose to the wine without sucking air. Taste on the fly using a three-way valve fixed to the destination tank. When the cut is ready to be made, the valve is switched to connect to the destination tank. When finished, repeat the operation pushing through with water to displace the wine in the system.
- If venting with water is not possible, purge treatment circuits with nitrogen or argon to displace air before the start of operations.
- Adjust pump capacity to tubing diameter in order to avoid turbulences in hoses and in the destination tank by maintaining a laminar flow rate not exceeding 1.5 m/sec.
- Transfer from the bottom of one tank to the bottom of the destination tank, avoiding splashing the wine from the top and excessive turbulence on the wine surface.
- When working on small wine volumes, purge the destination container with inert gas before the start of operations.
- Avoid the use of compressed air or pumping over for mixing wine. Tank mounted propeller mixers screwed onto a tank fitting, e.g., a shut-off valve near the bottom of

the container, provide the most efficient and gentle mixing with minimal oxygen uptake.

- Oxygen uptake during cellar operations correlates with losses of carbon dioxide and aromatics by volatilization. The more carbon dioxide is preserved, the less burdensome cellar treatments are for the wine.

While there are abundant data on oxygen pickup under practical winery conditions, there are surprisingly few studies upon the impact of a defined amount of oxygen on the aroma of white wines. Such sensory studies are complicated by the possibility that an unknown percentage of the oxygen be consumed by residual yeast cells or because wines displaying reduction flavor may improve after oxygen uptake. In bottled Riesling, a significant decrease of fruity varietal aroma was reported three months after it had been supplied with 11.5 mg/L O_2 from a controlled headspace (Morozova, 2013). Under comparable conditions, the same effect was observed on six wines from different white cultivars two months after supply of 10 mg/L O_2 (Schneider, 2015). In both cases, sufficient time was admitted to get all oxygen reacted with the wine.

Once a wine is bottled, the most important factors affecting its future development include bottle closure, headspace volume and composition, the history of the wine, the levels of free SO_2 and dissolved oxygen it is bottled with, and the bottle storage temperature. The impact of oxygen is so dramatic that the same wine exposed to different oxygen levels at and after bottling can result in completely distinct products. The decline of SO_2 after bottling is a rough measure of the amount of oxygen the wine is exposed to into the bottle.

One of the largest sources of oxygen ingress occurs during bottling operations and the steps shortly before. These steps aim at preparing the wine for bottling and usually include blending, mixing for SO_2 adjustment and tartrate stabilization, and filtration. The oxygen already dissolved in the wine at the moment of bottling depends on the mastering of good cellar practice and is often underestimated.

In standard bottles, 1 cm of headspace height corresponds to approximately 2.9 mL of air volume containing 0.86 mg oxygen. If this amount of oxygen is entrained into a bottle of 750 mL wine, the wine oxygen content will increase by 1.15 mg/L. On a mg/L basis, it is more in smaller bottles and less in bigger bottles. The headspace acts as an oxygen reserve for the wine that is to say that as the wine binds dissolved oxygen, there is a diffusion of headspace oxygen into the wine. Current technologies to reduce headspace oxygen levels include nitrogen sparging pre- and/or post-filling, vacuum pre- and/or post-filling, and CO_2 snow dropping pre- and/or post-filling.

These technologies are particularly important when the use of screw caps requires a larger headspace volume. For sealing with corks, vacuum corkers are commonly used. Otherwise, much of the headspace air would be compressed and remain in the bottle when the cork is driven (Kontoudakis et al., 2008).

Bottle closures show large differences in their permeability to atmospheric oxygen, measured as oxygen transmission rate (OTR). Screw caps and agglomerated cork stoppers are on the low side with $\leq$ 1 mg O_2/year, while synthetic stoppers tend to display highest OTR

ranging from 3 to 7 mg O_2/year. However, there is continuous development towards screw caps and synthetic stoppers with graduated OTR levels geared to different kinds of wine, eradicating the one-sided tendency to OTR levels too high or too low for certain types of wine. Conventional natural cork stoppers occupy an intermediate position with an OTR ranging from 1 to 4.8 mg O_2/year (Lopes et al., 2006; Lopes et al., 2007; Silva et al., 2011; Oliveira et al., 2013). However, during the first year of bottle storage, natural corks can transmit higher and additional amounts of oxygen initially entrapped in the cork tissue. Furthermore, because of the inherent variability of a natural product like cork, there are considerable differences of OTR between cork grades as well as between individual corks within a given batch (Caloghiris et al., 1997; Oliveira et al., 2013), contributing sometimes to random oxidation (Waters and Williams, 1997).

It is commonly admitted that wines bottled with closures with different OTR will exhibit different sensory and chemical characteristics. It is also acknowledged that fruity white wines require bottle closures with a consistently low OTR, and that these closures also foster the appearance of post-bottling reduction flavor if a wine is prone to produce it (Godden et al., 2001; Godden et al., 2005; Skouroumounis et al., 2005; Schneider, 2006 c; Lopes et al., 2009; Ugliano, 2013). The reduction problem associated with ultra-low OTR closures will be approached in a subsequent section of this chapter. However, the OTR of the bottle closure is not the only criterion deciding upon the degree of post-bottling oxygen exposure of wine. The effect of a low closure OTR can be relativized or cancelled out when the wine is bottled with a high level of dissolved oxygen (Dimkou et al., 2013) or a high headspace oxygen level (Dimkou et al., 2011).

In a Sauvignon Blanc wine, the combination of both high oxygen dissolved at bottling and the use of closures with a high OTR produced most oxidative aging as measured by sensory and analytical means after two years of storage. Conversely, bottling under more airtight conditions using screw caps with Saran-tin liner led to highest contents of varietal thiols but also high levels of H_2S responsible for a dominating reduced character, while natural cork stoppers and screw caps with Saranex liner presented only negligible reduced or oxidized characters (Lopes et al., 2009). Screw caps fitted with Saran-tin liner display an OTR close to nil, while those with a Saranex liner show an OTR of approximately 1 mg O_2/year (Vidal et al., 2011). Therefore, it is evident that minor differences in bottle closure OTR can affect evolution and aging of white wine after bottling.

As a summary, it can be stated that under typical industry conditions, the wine after bottling is exposed to oxygen from five different sources: Oxygen already dissolved in the wine before bottling, oxygen uptake during filling, oxygen contained in the gaseous headspace, oxygen diffusion through the bottle closure, and oxygen released from cylindrical closures compressed in the bottleneck. The sum of these five components is commonly referred to as total package oxygen (TPO). It is the amount of oxygen in a bottle that is available to react with the wine in that bottle. The adjustment of free SO_2 before bottling must take into account all oxygen subsets comprised in this crucial parameter. Yet, increasing SO_2 levels at bottling are not a proper measure to prevent sensory damages going along with uncontrolled high TPO levels.

Controlling oxidative aging requires essentially careful oxygen management before and at bottling. Currently, TPO levels in the wine industry use to be far higher than what is technically and commercially possible. On the other hand, wine is more resilient to oxygen than other

beverages as beer. Therefore, it is likely more valuable for wineries to focus initially on striving for consistent total oxygen pickup than for the absolute lowest possible TPO (Crochiere, 2007).

Influence of Storage Temperature

The Arrhenius equation states that the rate constant of a chemical reaction is exponentially related to the temperature. For bottled wine, the relative rates of oxygen uptake, browning, and SO_2 decline have been shown to increase with increasing temperature (Ough, 1985). Yet, the effect of storage temperature on wine post-bottling evolution is one of the least considered topics in enology and scarcely taken into consideration by wine quality management. While considerable efforts are made to optimize the generation of aromas by temperature control during alcoholic fermentation, much less care is taken to preserve these aromas by temperature control after fermentation and bottling. Even though it is well known that higher temperatures decrease the shelf life of all kind of food and beverages, storage temperature of sensitive white wines is a widely neglected issue in the wine industry and trade.

For oaked and unoaked Chardonnay wines, significant differences in aroma were detected after they had been stored at 40°C for five to nine days and compared to the respective controls held at 5°C. Upon heating, floral and fruity notes decreased, while the intensity of the honey, rubber, and tobacco attributes increased gradually during the first 30 days of heat exposure. Few further changes in aroma occurred when heat storage was extended to 45 days (De la Presa-Owens and Noble, 1997). In a similar study imitating the effect of shipping conditions, four white varietal wines were exposed to 40°C for three weeks and compared to the references held at 20°C. Significant sensory differences were observed. The wines stored at 40°C displayed higher concentrations of vitispirane, *p*-cymene, and TDN, which are characteristic of aged wines, as well as reductions in several esters and acetates, (Robinson et al., 2010).

Other sensory investigations on Chardonnay and Semillon wines showed that storage at 45°C for three weeks in the absence of air decreased the floral aroma character and enhanced attributes such as oak, honey, and smoky characteristic for bottled-aged white wines. However, heat treatment at 90°C for several minutes produced wine not significantly different from the control (Francis et al., 1994). This finding suggests that short-time thermal treatment under controlled conditions like flash-pasteurization affects wine quality to a lesser extent than long-term exposure to elevated temperatures in the bottle storage area. In contrast, most wine industry professionals are more concerned about the heat load imposed during thermal processings than during bottle storage.

Monitoring the heat exposure of wine during commercial shipments across the USA, bottles equipped with temperature data loggers were placed in different positions within a shipping container. The accumulated heat exposure was calculated and compared to that of wine stored under ideal cellar conditions. As a result, it was shown that wines were exposed to heat during transport that corresponded to an added bottle age between 1 and 18 months when compared with conventional cellar storage (Butzke et al., 2012).

High storage temperatures act in a synergistic way with oxygen on the decrease of terpenols, norisoprenoids, and volatile esters imparting fruity-floral aromas, and on the development of off-flavors reminiscent of honey, boiled potatoes, and farm-feed associated with the presence of phenylacetaldehyde and methional (Ferreira da Silva et al., 2002). Similarly, the combined effects of heat and oxygen were confirmed when Chardonnay was stored in bottles with different closures and in bag-in-box containers at three different temperatures for a period of three months. Under these conditions, wines stored in bag-and-boxes at 40°C showed particularly high increases of oxidized aroma and color when compared to bottles sealed with low OTR-closures and stored at the same temperature (Hopfer et al., 2012).

Short-term storage trials conducted at a temperature of 40 to 45°C might not necessarily reflect the temperature impact in a more realistic temperature range. After storage trials of bottled Italian white wines at 4, 15, and 25°C, shelf life was found to be longer than two years at 4°C, ca. 20 months at 15°C, and only 7-9 months at 25°C (Barbanti et al., 1997). In bottled white wines made from four different cultivars grown in Germany, significant losses of fruity varietal aromas and a coincident increase of oxidative aging by smell were observed at 22°C when compared to 12°C after ten months of storage. It was also shown that high temperature and flavonoid phenols act synergistically on the process of typical aging (Schneider, 2000). In typical Austrian white wine, almost no aroma changes were observed after storage for one year at 2 and 10°C, while storage at 20°C for four months produced losses of fruity varietal aroma considered perceptible by average consumers (Stöckl, 2013). Comparing storage of Sauvignon Blanc wines for 12 months at 5, 10, 18°C and at room temperature, a temperature of 18°C and higher led to excessive temperature-related hydrolysis of esters, including the prominent varietal thiol 3-mercaptohexan-1-ol acetate responsible for the passion fruit-type aroma of that cultivar. Concurrently, woody, smoky, buttery, and canned asparagus notes increased (Makhotkina et al., 2012).

As a whole, the results mentioned above provide a large body of evidence that white wines should be stored at temperatures well below 20°C, and that exceptions from this rule are only admissible for short periods as required for transport. Otherwise, the impact of temperature on aging risks being a seriously limiting factor of white wine shelf life even in the absence of oxygen.

ATYPICAL AGING

Sensory Identification and Compounds Involved

Atypical aging (ATA), also known as untypical aging, is an aroma defect occurring in *Vitis vinifera* white wines and first referred to by anecdotal reports from Germany around 1990. In the meantime, it has been observed in most wine growing countries worldwide. However, the attention paid to it by producers and consumers is highly variable and does not necessarily

reflect the frequency of its real occurrence in a given wine growing area. It is not assumed to be a distinctive fault in some countries, and may even be considered as an intrinsic expression of terroir in others.

The connection of this off-flavor to some kind of aging process is misleading since ATA may also appear in rather young white wines within a few weeks or months after alcoholic fermentation and addition of sulfur dioxide. Consequently, its existence may be not expected or simply be ignored due to deficient sensory training. The sensory identification of ATA is complicated by its diverse forms of aromatic expression evoked by variable amounts of underlying odoriferous compounds in a complex flavor matrix.

2-aminoacetophenone (AAP) has been described as the chemical marker and sensory impact compound of ATA (Rapp et al., 1993). In spiking trials conducted by various researchers, increasing amounts of AAP added to sound wines showed positive correlations with perceived ATA intensity. Respective correlation coefficients were specified as r=0.80 (Christoph et al., 1995) and r=0.66 (Schneider, 2013 b), whereas in wine obtained from a long-term field study, AAP concentration accounted for only 30% of sensory atypical aging intensity (Linsenmeier et al., 2007 a). According to these authors, and depending upon the wine matrix, the detection threshold varies from 0.5 to 1.5 µg/L AAP. Strongly aromatic wines are able to integrate greater than 1.5 µg/L AAP, while meager wines might be rejected as tainted by ATA with less than 0.5 µg/L AAP.

Contrary to spiking trials with AAP, when wines actually affected by ATA are submitted to descriptive sensory analysis, they usually show a poor correlation between AAP concentration and perceived ATA intensity. The aroma patters are also different from those elicited by pure AAP. Additions of AAP alone fail to produce the whole sensory spectrum of ATA, although it is clearly involved in the off-flavor in many wines, particularly in Europe. These results strongly suggest not only masking effects but also the participation of compounds other than only AAP (Cheng et al., 2004; Christoph et al., 1995; Fischer and Sponholz, 2000; Gessner et al., 1995; Linsenmeier at al., 2007 a; Schneider, 2013 b; Simat et al., 2004). However, while these conclusions were obtained under European cool-climate conditions, AAP was reported to be below the sensory detection threshold in wines described as tainted by ATA under specific New York growing conditions (Cheng et al., 2004). These authors ascribe the perception of ATA to a lack of varietal flavor. Confusing the lack of any flavor with ATA has also been reported from the European context (Schneider, 2013 b). Differences of the expression of this flavor defect at different stages of the wine age and differences in language use make it difficult to compare descriptions.

On occasion, ATA is mistaken as a reduction flavor. More often, however, ATA and reduction flavor occur simultaneously since viticultural stress factors are a common cause for both kinds of defect (Rauhut et al., 2003). When ATA is masked by reduction flavor, it can only be detected after copper fining removes its underlying volatile sulfur compounds. A sample treatment with copper ions better reveals ATA and helps identify it. Frequently, ATA is also confounded with typical aging. While both may occur simultaneously in some wines, their aroma patterns are totally different. Clearly, sensory bias and the lack of semantic precision are responsible to a great extent for conflicting results in ATA research.

In wines affected by ATA, a plethora of olfactory attributes can be detected (Christoph et al., 1995; Fischer and Sponholz, 2000), which, with the purpose of sensory classification, can be divided in two groups. Group I includes mothballs, naphthalene, laundry detergent powder, soap, floor polish, furniture polish, jasmine, acacia blossom, lemon blossom, dry linen, and fusel alcohols. This odor pattern is reinforced by high concentrations of free sulfur dioxide. Group II includes damp towel, wet wool, dirty dishrag, washing machine, and urine deposits. This aroma profile marks the sensory transition to reduction flavor and may complicate the sensory identification of ATA (Schneider, 2013 b). In either case, the fruity, floral, or mineral varietal aromatics disappear to a great extent, a process partially driven by the decay of short-lived fermentation-derived aromatics. Thus, the sensory intensity of ATA will increase over time. On the palate, tainted wines often come out meager and thin, displaying a metallic bitterness, some astringency, and a light color.

In affected wines, the attributes of either one or the other group can be dominant or occurring concurrently. They interact with different aroma compounds present in the normal aroma matrix of the wine, resulting in a kind of mixed flavor. Taking into account these different sensory characteristics of ATA as well as diverging perceptions among tasters, it seems unfeasible to evaluate ATA as the intensity of a not precisely defined sensory attribute (Fischer and Sponholz, 2000). There are many ambiguous sensory terms that tend to lack meaning. Additions of AAP to sound wines evoked only aroma attributes referred to in group I above and described as acacia blossom and mothballs, whereas the “stinky” descriptors of group II could not be generated in any wine (Schneider, 2013 b). The group II set of descriptors is assumed to be more related to other compounds like indole and skatole (3-methylindole) resulting from the catabolism of the common precursor indole-3-acetic acid (IAA). However, most of these compounds were reported to occur in ATA-tainted wines below their sensory threshold (Christoph et al., 1995; Gessner et al., 1999 a; Rauhut et al., 2003). Only the role of skatole is controversial (Linsenmeier et al., 2007 a; Hühn et al., 1999). No reliable data on its sensory impact are available but since it displays a strong fecal odor, it would be able to elicit the olfactory attributes of group II.

Microbiological Formation of 2-Aminoacetophenone Is Not Significant

AAP is partially responsible for the “foxy” smell of non-*vinifera* varieties, but does not occur in grapes and juices from *V. vinifera* (Acree et al., 1993). During fermentation of natural *V. vinifera* juices, it is produced from IAA as the precursor with a conversion rate too low to produce more than 0.01 µg/L AAP. These amounts are clearly below the odor threshold (Simat et al., 2004). The formation of AAP by yeast is not a significant contributor to the AAP found in wine as long as fermentations are carried out by *S. cerevisiae* strains in natural musts. This corroborates the general finding under commercial winemaking conditions that the synthesis of odor-active amounts of AAP and the appearance of ATA are not the direct consequence of yeast metabolism and that they cannot be observed immediately after fermentation without further interventions on the wine. This may not always be the case when juices are submitted

to spontaneous fermentation involving non-*Saccharomyces* strains (Sponholz et al., 1997; Simat et al., 2004).

Chemical Conversion of Indole-2-Acetic Acid into 2-Aminoacetophenone

Indole-2-acetic acid (IAA) is a phytohormone occurring in grapes and one of the intermediate products of the tryptophan metabolism of yeast, but the only one able to act as a potential precursor of AAP (Hoenicke et al., 2002 a). Therefore, it could be assumed that the concentration of unbound IAA in young wines should be of relative importance for the propensity of the wines to produce AAP. However, the significance of these concentrations is not conclusive. In one study, there was a significant but low correlation found between the content of unbound IAA prior to SO_2 addition and the amount of AAP in the wine, indicating that 30 to 50% of the AAP concentration might be traced back to the amount of the precursor IAA. This indicates that relevant factors other than the amount of unbound IAA must influence AAP formation (Simat et al., 2004). In other investigations, neither total IAA in the must nor unbound IAA in the wine showed a positive correlation with the formation of AAP. There was even a negative correlation between IAA in juice and perceived ATA in wine. Thus, the appearance of ATA seems not to be linked to a higher amount of IAA in the fruit, must, or wine (Hoenicke et al., 2001; Hoenicke et al., 2002 b). Although IAA is the precursor of AAP, its amount is not a reliable means to predict the propensity of a wine to produce ATA. Matrix effects are more important since they control the conversion of IAA into AAP. This is particularly demonstrated in red wines. Although IAA levels in red wines are approximately 10 times higher than levels in white wines (Bonerz et al., 2008), they never display ATA.

The first step in the conversion of IAA into AAP is a non-enzymatic oxidation in which the pyrrole ring of IAA is oxidized by oxygen radicals formed during the aerobic oxidation of sulfite to sulfate. By decarboxylation before or after pyrrole oxidation and cleavage of the indole ring, a complex reaction sequence comprising 3-methylindole (skatole) and 2-formylacetophenone gives rise to the appearance of AAP. Without previous addition of SO_2, the reaction does not take place; sulfite triggers the chemical conversion of IAA into AAP (Christoph et al., 1998; Christoph et al., 1999; Hoenicke et al., 2002 a; Hoenicke et al., 2002 b).

It has been shown that especially superoxide radicals are responsible for the formation of AAP and other compounds by pyrrole ring cleavage of IAA. Antioxidants with a superoxide radical scavenging activity such as phenolic compounds can reduce the tendency to ATA formation. Their amounts seem to depend on the ripeness of the grapes. Wines made from late harvested fruit revealed significantly higher antioxidative capacity and lower sensory ratings for ATA than wines from early harvested grapes. Red wines are protected against ATA by their high tannin content acting as a radical scavenger (Hoenicke et al., 2002 b). Alcohol is assumed to play a role in the reaction pathway, but wine pH was shown to have no influence (Schneider, 2014).

The formation of oxygen radicals bringing about this conversion requires the intermittent availability of dissolved oxygen. In adding controlled amounts of oxygen to model solutions containing a typical concentration of 100 µg/L IAA, is was shown that levels of as low as 0.15 to 0.5 mg/L O_2 were sufficient to produce the typical smell of ATA. These minute amounts are inevitably taken up even when wines are carefully protected against oxygen ingress during cellar operations (cf. Table I), but far too low to elicit any oxidative aging. They explain why, despite the involvement of oxygen, ATA must be distinguished from oxidative aging from a sensory and chemical point of view (Schneider, 2013 c). Consequently, post-fermentation oxygen management does not affect the appearance of ATA nor does the variable oxygen transmission rate of bottle closures.

Viticultural Origins and Countermeasures

Numerous technical reports on empirical evidence refer to over cropping, premature harvest, drought, green cover, and reduced fertilization as the main viticultural factors triggering ATA. These factors induce a physiological stress in the vine or impact ripeness adversely with the appearance of ATA as a result. However, exceptions to the rule exist for each of these factors. Frequently, they are linked one to another, thereby making it difficult to identify one factor as the sole cause of ATA.

Ripeness

Wines obtained from late harvested grapes tend to be less afflicted by ATA than those produced from early harvested fruit from the same plot (Gessner et al., 1995; Hoenicke et al., 2001; Hoenicke et al., 2002 b; Simat et al., 2004). The combination of premature harvest and high crop load tends to predispose wines strongly to the formation of ATA.

Soluble solids in the juice, however, are an equivocal parameter for evaluating the propensity of a wine to develop ATA. One study showed no relationship between the occurrence of ATA and Brix readings (Linsenmeier, 2007 a), while other authors reported Brix readings and alcohol content to correlate negatively with perceived ATA intensity (Gessner et al., 1995; Köhler et al., 1995). Since ATA may also appear in wines obtained from fruit with high Brix readings grown under hot-climate conditions, traditional Brix figures are considered to reflect only alcoholic ripeness as opposed to aromatic ripeness, the latter precluding the formation of ATA (Schneider and Almeida, 2005).

Yeast assimilable nitrogen (YAN) in the juice showed a weak correlation with the propensity of wine to develop ATA. However, this correlation is not a causal one. While low YAN levels indicate a high propensity for ATA formation, high YAN levels do not exclude it (Amann et al., 2001). Taken as a whole, there are not yet any reliable tools to predict ATA by analysis of the fruit.

Nutrient Deficiencies

Research on the impact of nitrogen (N) status and fertilization has given inconsistent results. Under cool-climate conditions, increased N fertilization was reported to reduce the occurrence and intensity of ATA (Schwab et al., 1996) or to be without any effect (Müller, 1999). Drought-induced low nitrogen status during veraison and early fruit ripening was considered to trigger ATA formation, while both irrigation and foliar N application reduced off-flavors associated with ATA and improved varietal aroma character (Cheng et al., 2004).

In a long-term experiment, variable N fertilization affected AAP concentration in the wine as much as the growing conditions during the year. Generally, AAP concentration and ATA intensity increased with increasing N fertilization. This result is explained by the antioxidant capacity of the wines, which decreased with increasing N fertilization. Antioxidant capacity as measured by chemoluminescence accounted for 13 to 67% of the total variance of ATA. Antioxidants such as phenols were exerting a masking effect on ATA intensity. However, N fertilization regimes are not sufficient to explain ATA. Despite significant effects of the growing conditions and of the fertilization regime accounting for ~20% of the total variance, a high residual variance accounting for more than 50% of the total variance of ATA intensity in wine could not be explained. Grape yield was positively correlated with ATA but accounted for only 10% of the variance. As a conclusion, fertilization with 60 kg/ha N is recommended, while higher N amounts increase the propensity of the wines to produce ATA (Linsenmeier et al., 2007 a; Linsenmeier et al., 2007 b).

Hydric Stress and Irrigation

Since ATA occurs primarily in wines from harvests characterized by dry summers, drought stress during ripening has been shown to be one of the most important causes of ATA. As cover crops compete for water and N, the effect of drought is reinforced under conditions of permanent green cover. Soil treatment (Schwab et al., 1996; Sponholz et al., 1997), irrigation (Cheng et al., 2004), and application of farmyard manure (Schwab and Peternel, 1997) decreased perceived ATA intensity.

UV-Radiation

Under viticultural stress situations, protection from UV-B radiation by repeated spraying of a synthetic UV-B absorption reagent resulted in lower AAP concentrations in the wine. This is explained by the fact that metabolites of tryptophan degradation absorb UV light, inducing a photochemical reaction susceptible to contribute to the formation of compounds involved in ATA (Hühn, 2003).

Enological Measures against ATA

Although ATA is the consequence of a viticultural problem and requires viticultural tools for a long-term solution, enological aspects have to be considered in order to cope with the

numerous wines prone to develop it. Various strategies are available to mitigate ATA, but only one enological treatment is able to prevent it in a reliable way.

Yeast Strain and Yeast Nutrients

After inoculation of an identical juice with two different *S. cerevisiae* yeast strains, AAP in the one year old wine was 0.6 and 1.1 µg/L, respectively (Rauhut et al., 2003). It is not clear whether these amounts resulted directly from yeast metabolism or were produced by the chemical pathway post-fermentation. Other authors reported active dry yeast strains to produce only very low amounts of AAP during fermentation not exceeding 0.4 µg/L and, therefore, below the odor threshold (Gessner et al., 1996). Nevertheless, inoculation with wild yeast strains and spontaneous fermentations were shown to be able to cause higher amounts of AAP (Sponholz et al., 1997; Simat et al., 2004). Yeast strains producing strong fermentation aromatics can delay the sensory appearance of ATA by masking effects, but not prevent it (Köhler et al., 1996).

Likewise, the effect of yeast nutrients is not conclusive. While some authors (Köhler et al., 1996; Hoenicke et al., 2001; Bach, 2005) reported no significant effect of juice supplementation with diammonium hydrogen phosphate (DAP) and inactive yeasts on AAP concentration or ATA intensity, another investigation showed that DAP can decrease the amount of AAP (Rauhut et al., 2003). This effect is ascribed to an interception of oxygen radicals by metabolic products of the yeast such as glutathione.

Obviously, yeast strain and nutrition status have some impact on perceived ATA intensity. Differences between yeast strains in AAP synthesis, release of radical scavengers, and production of masking fruity aroma compounds play a role. However, ATA is not a by-product of alcoholic fermentation, but rather the result of stress in the vineyard. Thus, the choice of an active dry yeast strain cannot be considered an appropriate tool to mitigate ATA. The crucial parameters of wine composition affecting the conversion of IAA into AAP are the consequence of vineyard management.

Pre-Fermentation Strategies

Skin contact has been shown to decrease perceived ATA intensity and AAP concentration by 35% (Bach, 2005). This effect is partially ascribed to an increased extraction of grape phenols able to scavenge oxygen radicals involved in the chemical generation of AAP (Gessner et al., 1996; Linsenmeier et al., 2007 a). Accordingly, wines obtained from free-run juice are more prone to produce ATA due to their lower total phenol content than the wine from pressed juice (Amann et al., 2001). Higher concentrations of varietal fruit aromatics extracted during skin contact and pressing play possibly and additional role in the sensory perception of ATA by masking it.

Although juice oxidation is known to decrease the concentration of phenols by oxidative polymerization and subsequent precipitation, the extent of that effect did not increase ATA intensity (Köhler et al., 1996). However, active oxygenation and hyperoxidation should be

avoided on juices obtained from stressed fruit, and nitrogen instead of air should be used when they are clarified by flotation.

Juice clarification is seen as an important step to reduce ATA potential in the resulting wines (Wohlfahrt, 1993). The residual juice turbidity is far more important than the technical means used to achieve it. The fermentation of juice bottoms is very likely to produce ATA in the resulting wine while the corresponding clarified juices do not, suggesting that a large fraction of the precursor is bound to insoluble solids (Schneider, 2013 b).

Post-Fermentation Strategies

Since flavor intensity of ATA increases with wine age and older wines contain higher concentrations of AAP than younger wines, wine storage at low temperatures can delay the formation of ATA, but cannot prevent it. Storage on the lees had no impact on perceived ATA intensity. Thus, the time point of racking and filtration is not relevant (Köhler et al., 1996).

Additions of inactivated yeast post-fermentation failed to prevent ATA (Bach, 2005). Supplements of tannins (100 mg/L) before and after alcoholic fermentation did not diminish the formation of AAP while supplements of pure glutathione (20 to 150 mg/L) did so in some wines, depending on the yeast strain. Only addition of ascorbic acid (75 and 150 mg/L) prevented the formation of AAP and ATA systematically (Rauhut et al., 2003). Although yeast nutrients and metabolites might improve the antioxidant capacity of the wine, their effect does not equal that of ascorbic acid.

The addition of 100 to 250 mg/L ascorbic acid in a timely manner is the only efficient means to protect wines against ATA over a period of at least three years. It has been successfully implemented under commercial winemaking conditions in wines from vineyards with a history of producing wines prone to develop it (Gessner et al., 1999 a; Schneider, 2013 b). The addition of ascorbic acid is recommended to take place at or before the first addition of sulfur dioxide after alcoholic fermentation. Additions at a subsequent time point are possible and sufficient to prevent intensification of an existing ATA off-flavor. However, such additions are not able to mitigate it since the reactions involved in the formation of ATA are irreversible. During further storage and cellar operations, wines treated in this way must be kept with adequate levels of free SO_2 and carefully protected from oxygen uptake to avoid the autoxidation of ascorbic acid. No fining or any other treatments have been shown capable of remedying spoiled wines.

Evaluation of the Propensity for ATA

Viticultural measures cannot avoid ATA with certainty, and there are not yet any reliable analytical techniques available to predict a wine's propensity for developing ATA (Linsenmeier et al., 2007 a; b). Instead, an accelerated aging test has been proposed and widely introduced into practice (Gessner et al., 1999 b): A clarified sample of wine containing at least 40 mg/L free SO_2 is poured into two flasks, one of them receiving an additional supplementation of 150 mg/L ascorbic acid. Both flasks are stored at 40 to 50°C for three to four days. After cooling down, both samples are evaluated by smell. If the sample without

ascorbic acid addition displays ATA, then the wine is prone to develop it. A wine spiked with AAP is recommended as a reference for less trained evaluators.

This accelerated aging test is also able to reveal the propensity of a wine for other kinds of aging, e.g., petrol flavor or reduction flavor. If reduction flavor is produced in the course of the test, addition of a drop of copper sulfate solution facilitates the identification of AAP. However, this test gives no information about a wine's stability to oxidative aging.

POST-BOTTLING REDUCTION FLAVOR

Reduction flavor is related to the presence of volatile sulfurous compounds (VSC). When they occur above sensory threshold, they impart a stinky, fecal smell to the wine reminiscent of burnt rubber, rotten cabbage, rotten eggs, rotten onions, sewage, garlic, cooked corn, burnt match, etc. It is standard knowledge in enology that this kind of off-flavor is linked to yeast metabolism and to a lack of yeast-assimilable nitrogen causing the yeast to produce detrimentally high amounts of VSC during and after primary fermentation. Therefore, reduction flavor is generally considered as an odor defect typical of young wines, which are carefully screened for its occurrence. Wines affected by VSC in odor-active concentrations are treated either by addition of copper ions in the form of copper sulfate or copper citrate able to precipitate certain VSC, or by oxygen supplementation via racking susceptible to oxidize some VSC to less odor-active VSC compounds.

In contrast to the attention paid to VSC in young wines prior to bottling, the wine industry has been much more indulgent to their appearance during bottle storage over a long time. It has even been excluded to consider them as responsible for a specific kind of aging referred to as post-bottling reduction flavor in this chapter. This attitude has changed since cork as the traditional wine bottle closure has been partially replaced by alternative bottle closures in numerous wine growing countries. The appearance of post-bottling reduction flavor is closely related to redox chemistry that, in turn, is intimately connected to the oxygen transfer rate (OTR) of bottle closures.

Wine can never be bottled completely free of VSC. The fermentation process leaves a sulfidic fingerprint, the composition of which depends upon the yeast strain and the nutrient conditions in the must. During primary fermentation, the most noticeable of the VSC is hydrogen sulfide that undergoes rapid reaction with ethanol and/or acetaldehyde to produce simple thiols such as methanethiol in a first step. VSC are quite reactive, and so there is a myriad of them in any wine. Their detailed enumeration would go beyond any practical interest in this context. The most important of them with relevance to post-bottling reduction flavor, their synonyms, odor descriptors, typical threshold concentrations, and concentration ranges are listed in Table 2. One must bear in mind that threshold data vary enormously, depending on the wine matrix and the source of information. Therefore, they are of limited use.

Table 2. Volatile sulfurous compounds related to post-bottling reduction flavor

Compounds	Odor descriptor	Aroma threshold (µg/L)	Typical concentration range (µg/L)
Hydrogen sulfide	rotten eggs, sewage	1-2	0-370
Methanethiol (methyl sulfide, methyl mercaptan)	burnt rubber, rotten cabbage	1.5	0-11
Ethanethiol (ethyl sulfide, ethyl mercaptan)	rubber, burnt match, rotten onions, garlic	1.5	0-50
Dimethyl disulfide	cooked cabbage	10-30	0-22
Diethyl disulfide	rotten onions, rubber	4-30	0-85
Methyl thioacetate	cheesy, egg, sulfurous	40-50	0-115
Ethyl thioacetate	garlic, onions	10-70	0-180

The Role of Precursors

How can it be explained that clean wines may develop reduction flavor considerable time after they had been bottled under sterile conditions, i.e., in the absence of any yeast cells? Besides the highly odor-active VSC as hydrogen sulfide and simple sulfides (mercaptans), yeast produces also VSC with a low odor activity or a high odor threshold, respectively. These compounds comprise the dialkyldisulfides as dimethyl disulfide and diethyl disulfide, and the thioacetates. They are the precursors of the more odor-active VSC responsible for the formation of post-bottling reduction flavor.

Thioacetates are the methyl and ethyl esters of thioacetic acid. Like many esters in wine, they undergo acidic hydrolysis. The resulting products are methanethiol and ethanethiol with an odor activity approximately one decimal power higher than their parent molecules. The reaction is driven by pH, storage temperature, and the initial concentration of thioacetates. If the latter is high enough, sulfides can be released in concentrations largely above their threshold within a matter of weeks (Rauhut and Kürbel, 1994). No oxygen-related reactions are involved in this hydrolysis.

Disulfides are in a redox equilibrium with their respective sulfides. A common practice in wineries in response to the occurrence of VSC is to oxygenate the wine by means of racking, splashing, or micro-oxygenation with the accompanying observation that the stinky off-odor decreases. The explanation for the disappearance of the odor can be found in the relatively easy oxidation of sulfides to disulfides according to the scheme:

$$2\ CH_3\text{-}SH \rightarrow CH_3\text{-}S\text{-}S\text{-}CH_3$$

methanethiol dimethyl disulfide

A common observation is that some months later, the stink is back and the wine needs oxygenation again. The obvious explanation for the recurrence of the off-flavor is the subsequent reduction of the disulfides under a suitable low redox potential. The reaction is totally reversible. For the couple diethyl disulfide-ethanethiol, the kinetics of disulfide reduction has been shown to be first order with respect to disulfide and sulfite ($SO_3^=$) (Bobet et al., 1990). This means the rate of thiol accumulation is concentration-dependent for both sulfite and disulfides. Thus, it is difficult to recommend a suitable level of SO_2 to mitigate the problem. Yet, low pH and high levels of free SO_2 will foster the process (Limmer, 2005 a).

Since treatment of VSC-tainted white wines by oxygenation is rarely a long-term solution, sparsely specific and wearing for fruity aroma compounds in white wines, removal of reduction flavor by adding copper ions is preferred. It is most effective if made shortly after the end of fermentation, when yeast cells are still available to adsorb residual copper ions. The amounts required are usually determined by bench sensory trials on each wine and generally less than the stability limit of 0.5 mg/L Cu^+ (Cowey, 2008; Schneider, 2008 b). However, their action is limited to removing the simple thiols and hydrogen sulfide. These compounds are among the most prevalent ones in reduction flavor and have a marked sensory impact at low levels. Thus, it is fortuitous that they readily respond to copper and are easily remedied. However, disulfides and thioacetates do not react with copper and can be converted into the more deleterious thiols at a later stage. For that reason, reduction flavor can revert after a wine has been cleaned up with copper. The underlying reactions are the two independent pathways of thiol formation from disulfides and thioacetates referred to above.

When thiols are generated by these pathways in super-threshold concentrations after bottling, post-bottling reduction flavor appears as a specific form of aging. Even at sub-threshold level, many wines are impaired to varying degrees by the presence of VSC. This occurs frequently when there is no overt evidence of reduction. Many ‘terroir’ or ‘minerality’ attributes of wines are in fact confused with bad sulfide management programs, given the ubiquitous nature of sulfides in wines and their significant sensory effects. Actually, most of these flaws go unnoticed as long as one does not check for them by a copper clean-up in the glass. When the wine displays a fresher and more attractive aroma within a couple of seconds after adding a drop of diluted copper sulfate solution, the occurrence of post-bottling reduction flavor is proven (Limmer, 2005 a; Schneider, 2008 b).

The Impact of Bottle Closures and Post-Bottling Oxygen

Since the introduction of screw caps, the prevalence of post-bottling reduction flavor has increased. Numerous long-term storage trials on wines sealed with different bottle closures have shown that in comparison with corks and synthetic closures, lots sealed with near-anoxic screw caps retain more free SO_2, display less browning, higher intensity ratings for sulfurous (flint/rubber) aroma, higher concentrations of methanethiol and hydrogen sulfide but also higher levels of varietal thiols like 3-mercaptohexanol as in Sauvignon blanc wine (Godden et al., 2001; Godden et al., 2005; Lopes et al., 2009; Dimkou et al., 2011; Silva et al., 2011; Ugliano et al., 2011; Ugliano, 2013).

The differences in the appearance of sulfurous off-flavors are ascribed to varying levels of oxygen transmission rate (OTR) of the bottle closures used. Thereby, the rate of oxygen ingress through most corks and synthetic closures exceeds that of the thiol accumulation and shifts the equilibrium between disulfides and thiols towards the less odor-intensive disulfides. In contrast, the almost airtight screw caps generate a lower redox potential favoring the accumulation of thiols produced by disulfide reduction and thioacetate hydrolysis. These thiols smell worse than the original compounds that generated them. Consequently, the otherwise clean wine can become stinky. The same reasoning applies to filtered wines developing reduction flavor when they are stored under anaerobic conditions in stainless steel tanks. However, the pre-bottling 'oxidative' state has no effect on the ability of the wine to form thiols post-bottling. Post-bottling thiol production occurs in all wines irrespective of their history and of bottle closure. It is the extent of thiol accumulation and the sensory effect derived therefrom that varies according to the amount of oxygen ingress, defined by the OTR of the bottle closure (Limmer, 2005 b; Limmer, 2006).

Since certain wines show more susceptibility to develop sulfidic off-odors than other ones, the link between the use of low OTR closures and the occurrence of these off-odors is not systematic. Screw caps are not directly responsible for the occurrence of post-bottling reduction flavor, but they increase its probability and intensity if the wine is prone to develop it. Furthermore, the formation of post-bottling reduction flavor is not limited to wines bottled with screw caps, but can also be observed under corks with a low OTR.

The impact of post-bottling oxygen uptake on the formation of sulfidic off-flavors during bottle storage has only been understood after the more recent development of sufficiently sensitive methods of non-invasive oxygen measurement. They have allowed to exactly quantifying OTR by diffusion and permeation kinetics of the various bottle closure systems. One of the outcomes of these measurements has been that the OTR of screw caps fitted with tin-Saran liner is nil, of those fitted with Saranex liner close to 1 mg O_2/year (Vidal et al., 2011), and of natural corks in the range of 1 to 5 mg O_2/year (Lopes et al., 2006; 2007; Silva et al., 2011; Oliveira et al., 2013).

The most obvious option for dealing with post-bottling reduction flavor would be simply by oxygen ingress through the bottle closure. A benign oxidation at an OTR just enough to mitigate the thiol accumulation is a simple approach corresponding to what has been going on under natural cork stoppers for centuries. However, predicting the minimum OTR for each wine will be impossible in practical terms. It should be slightly more than sensory evaluation

suggests is enough to accommodate the range of thiol production one could expect to encounter. The only way to determine this aspect is to compare the same wine under various closures. For that reason, bottle closure trials are of supreme importance to gather experience.

From the moment a wine is sealed under different closures, one starts to create different wines. The closure, along with other bottling variables, may be seen as part of the winemaking process. The modifications in wine quality that can be attributed to these variables can be of greater magnitude than those derived from many vineyard or winemaking variables. Bottle closure OTR in one of the key drivers in determining how a wine will develop after bottling, especially with longer-term storage periods. White wines are more sensitive to oxygen introduced at bottling and through bottle closures than red wines, resulting in a more pronounced impact on wine style and shelf life. While high levels of oxygen decrease shelf life dramatically via oxidative aging, low oxygen exposure preserves better the fruity aromas of young wine, but also increases the risk of an excessive accumulation of reductive aroma compounds (Godden et al., 2001; Ugliano et al., 2009). Bottle closure trials aim at finding the right balance between the two extremes for a given type of wine. However, they must take into account that natural corks display much less OTR consistency than any alternative closure.

The appearance of branded bottle closures as screw caps, technical corks or synthetic stoppers, with a choice of graduated OTR will facilitate these trials to better adapt the closure to the wine. Although screw caps are often considered as a single closure type, not all screw caps are alike. The basic difference is the nature of their liner. It is the business end of the screw caps and controls their OTR. In the realm of screw caps, different OTR options have already been offered over the past decades according to the liner they are fitted with. There are liners consisting only of a PVC or LDPE (low density polyethylene) compound wadding displaying an OTR of 1.4 mg O_2/year (Müller and Weisser, 2002), usually found in screw caps used for bottles with MCA finish. Liners made of expanded polyethylene overlain by a PVDC (polyvinylidene chloride) film are known as Saranex and provide an OTR of 1.0 mg O_2/year. If these are fitted with an additional tin foil layer, they are commonly designated as tin-Saran liners that display an OTR of 0 mg O_2/year (Vidal et al., 2011).

Metal-lined screw caps are the most popular ones in the wine industry where they serve as a reference other closures are compared with. Consequently, they are in the focus of attention of common closure debates. However, taking into account the liner-dependent OTR, screw caps cannot be considered a single closure type. In a storage trial with Chardonnay and Pinot noir wines over three years, LDPE screw caps gave the highest dissolved oxygen and lowest SO_2, while tin-Saran screw caps yielded lowest dissolved oxygen and highest SO_2. There was a decrease of methanethiol and hydrogen sulfide in both wines, but most markedly in those sealed with LDPE screw caps and synthetic closures. LDPE screw-capped wines showed highest acetaldehyde, highest *ß*-damascenone, and lowest linalool concentrations after three years of bottle aging, while Saranex screw-capped lots took an intermediate position (He et al., 2013). In another storage trial on Sauvignon blanc over two years, closures with a very low OTR such as tin-Saran screw caps showed more favorable to the preservation of varietal aromas and antioxidants (SO_2 and ascorbic acid), but also for the development of VCR. On the other hand, oxygen provided by Saranex screw caps and natural corks revealed to be enough to preserve the fruit aromas and mitigate reduced and oxidized characters at the same time (Lopes et al., 2009). These findings clearly indicate that the difference in OTR between different screw cap

liners is of sensory significance with respect to thiol accumulation during bottle aging, and that screw caps deserve a more detailed consideration of their OTR.

Pre-Bottling Measures Against Post-Bottling Reduction Flavor

As outlined before, copper additions only precipitate thiols and hydrogen sulfide but do not react with disulfides and thioacetates as their precursors during bottle aging. In fact, there is no way to remove the thioacetates; the only option is to bottle them. However, there is a recommended technique for the removal of disulfides. It is based on their reduction to thiols. It involves the addition of ascorbic acid to the wine, concurrently with SO_2, and storage under anaerobic conditions in stainless steel. The role of ascorbic acid is to scavenge any oxygen, decrease the redox potential, and prevent thiols from oxidizing back to disulfides (Cowey, 2008). After several weeks or months, copper fining removing the thiols obtained from disulfide reduction can clean up the wine. This procedure is only applied when pre-bottling disulfides occur at super-threshold concentrations in a way that simple copper additions are not feasible to remove the sulfurous off-flavor. The method is cumbersome, time-consuming and not always successful since only a portion of the disulfides may be reduced. Therefore, it is not used for improving wines' resistance to post-bottling reduction flavor.

Accepting that removal of the thiol precursors is not practical, other options are needed to prevent post-bottling reduction flavor. One possibility is to add a surplus of copper at bottling. It is based on the assumption that low native copper contents in modern wines are one of the reasons that might explain an increased incidence of sulfidic off-flavors during bottle aging. During alcoholic fermentation, yeasts absorb most of the copper contained in the must so that copper levels in young wines are usually less than 0.1 mg/L Cu^+. They remain on this low level since modern winery equipment made of stainless steel does not provide any contamination with 'useful' traces of copper. Thus, copper additions at bottling would overcome a natural copper deficiency and provide a surplus of free copper (Schneider, 2008 b). This surplus must exceed the amounts of copper required for removal of all thiols and hydrogen sulfide present as well as the amounts binding with wine constituents like proteins and polysaccharides. Under these conditions, any formation of post-bottling thiols is quickly and permanently rendered impotent by the residual copper, provided that enough surplus copper is available (Limmer, 2005 c). However, as the concentrations of disulfides and thioacetates in wines are unknown, this amount must be a guess based on experience. In a long-term sensory study, it has been shown that copper additions of as low as 0.25 mg/L Cu^+ and total copper concentrations of $\leq$ 0.3 mg/L Cu^+ at bottling were able to overcome a natural copper deficiency and prevent post-bottling reduction flavor in more than 95% of the wines which developed it without such an addition (Schneider, 2008 b). The underlying concept is that free copper ions intercept any post-bottling thiols as the disulfides and thioacetates degrade. This approach of preventive copper additions has some merit but also some potential disadvantages when too much copper is added.

First, spiked copper concentrations higher than 0.5 mg/L Cu^+ have been shown to decrease hydrogen sulfide and methanethiol concentrations at elevated oxygen concentrations

immediately post-bottling, but to increase them when the wine reached conditions of low dissolved oxygen some months after bottling, thus reverting the initial effect. This finding suggests that chemistry follows a different pathway at high copper concentrations and elevated Cu:Fe ratios (Ugliano et al., 2011; Viviers et al., 2013).

Second, final copper concentration must not exceed 0.5 mg/L Cu^+ which is the legal limit for health standards in many countries. It is also the copper stability limit. In the presence of ascorbic acid, the copper instability issue is more severe and the recommended safe maximum only 0.3 mg/L Cu^+ (Schneider, 2008 b). Observing these limits requires a meticulous copper management and analytical control measurements.

Third, copper is not as specific as it should be. It acts as a transition metal in that it accelerates chemical oxidation. Thus, the best condition for copper additions to occur in is completely anaerobic in order to exclude any oxygen uptake. Furthermore, copper additions are detrimental to the aroma of wines whose varietal character is at least partially driven by 'beneficial' polyfunctional thiols, e.g., Sauvignon Blanc and some other cultivars.

Another option for dealing with post-bottling sulfidic off-odors caused by disulfide and thioacetate degradation would be prevention at the root. Unfortunately, it is still beyond the scope of current knowledge to control alcoholic fermentation in a way to avoid consistently the formation of these precursors. The causes of VSC production are varied. The nutrient status of the must has an influence. There is a negative correlation between yeast-assimilable nitrogen and VSC produced during fermentation, but this correlation does not explain satisfactorily the total sulfide profile left after fermentation. Furthermore, the quantity and profile of these compounds are highly specific to the particular yeast strain (Rauhut et al., 1996). This is to say that a nutrient supply that works well for one yeast will show markedly different results for another yeast strain, even of the same taxonomic species. Different strains of *S. cerevisiae* produce uniquely different VSC patterns during fermentation. Thus, inoculation with yeast strains known for their low VSC production and optimization of nutrient supply would surely be a step towards decreasing disulfide and thioacetate production during fermentation, but in no way a means to prevent it.

PETROL FLAVOR

It is debatable whether petrol flavor should be categorized as a specific kind of aging flavor. Its appearance is limited to a very few varieties, most notably Riesling followed by Alvarinho with some distance behind, which are prone to form the indispensable precursors in the grapes in sufficient amounts. However, when it does occur, its smell can be so overpowering and one-dimensional in a way that all other kinds of aging are masked. It is one of the most precisely defined, exquisitely evocative, and easily recognizable terms in the wine tasting vocabulary. Its acceptance depends on intensity and cultural context.

In Riesling wines grown under cool-climate conditions, petrol flavor can only be perceived after at least two years of aging and is generally accepted by consumers. Under these conditions,

it is also described as reminiscent of 'dry apricots' when terms like petrol or kerosene flavor are considered too difficult to communicate to novice consumers. However, in hot-climate growing regions, it can arise much earlier and in considerably higher intensities overwhelming the highly complex, fruity aromas of young Riesling and disturbing the balance of the wine. In this case, it is considered undesirable and causes the wines to be rejected. Therefore, when Riesling is designed to be released only after some years of bottle aging, there is an understandable interest in limiting the volume of petrol and maximizing its complexity and finesse.

1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) has been identified as the molecule responsible for petrol flavor in aged Riesling wines. TDN is a C_{13} norisoprenoid, which, according to semantic arguments, may be classified as a terpene or not. During aging of Riesling, it is produced in much higher concentrations than in most other white varietal wines where its concentrations remains too low to be sensorially detectable (Simpson and Miller, 1983). Its odor detection threshold has been reported to be 2 µg/L in both model wine and neutral white wine, indicating little masking of TDN due to the odorants in the neutral wine (Sacks et al., 2014). There are few aroma compounds in wine that are more distinctive and polarizing than TDN.

TDN is generated from multiple, non-volatile glycosidic precursors by acidic hydrolysis (Winterhalter et al., 1990). The research on the nature and relative importance of these precursors for TDN production in Riesling is far away from being completed and reveals a complex picture of reaction pathways (Daniel et al., 2009). Carotenoids, more precisely lutein, have been the first identified and most investigated precursors of TDN (Marais, 1992).

Several viticultural means have been studied to reduce TDN concentration in wine by decreasing precursor concentrations in the fruit. Generally, TDN increases with grape maturity. It is higher in wines produced from sun-exposed grapes than in wines made from shaded grapes, indicating that the microclimate within the canopy has an important effect (Marais et al., 1992 a). In a study investigating the effect of berry shading and increased sun exposure on TDN and its precursors, a 75% leave removal in the fruiting zone yielded more than twice as much TDN when carried out 33 days post-berry set, compared to leave removal two and 68 days post-berry set (Kwasniewski et al., 2010). Thus, canopy management is an important tool to influence TDN concentrations in Riesling from a given growing site.

Furthermore, overall climate is important for TDN expression. In fact, TDN can be used as a tool to distinguish whether a given Riesling wine has been made from grapes from warmer or cooler climates. A comparison of Riesling wines of different vintages and different regions in South Africa, Germany, and Northern Italy showed that wines produced in South Africa displayed significantly higher TDN concentrations than those from the cooler European countries. This finding correlated with lower average daily temperatures, fewer daily sunshine hours, and higher average monthly rainfall in the European growing regions (Marais et al., 1992 b). It explains why the classical Riesling wines are produced in relatively cool wine growing regions. Hot-climate growing areas require sophisticated viticultural measures to reduce sun and heat exposure of grapes if Riesling wines with organoleptically acceptable TDN levels are to be produced. Under specific cool-climate conditions, nitrogen fertilization reduced TDN concentrations in both young and aged Riesling wines during a three years field trial (Linsenmeier and Löhnertz, 2007).

In conclusion, the viticultural conditions that promote high TDN levels in Riesling are well documented and include low yields, high temperatures during the growth period, increased fruit-exposure, water stress, and low nitrogen levels. Some of these factors are linked one to another. They involve practices and conditions that encourage the production of high quality Riesling in other respects, but this does not make it impossible to take specific steps to lower the TDN regime in a given vineyard. Attention to berry shading appears the most effective tool.

There is only limited research on how to reduce TDN formation by enological means. In fermentation trials using nine different yeast strains, it has been shown that only half of the carotenoid precursors remained after alcoholic fermentation, while formation of TDN took already place during fermentation. TDN content of the young wines correlated with ß-glucosidase activity and cell number of the yeast strains. Lutein was identified as the main TDN precursor (Periadnadi, 2003). These observations confirm that precursors are, at least to some extent, glycosidically bound and accessible to microbiological degradation with release of TDN. They might open the way to further research on selected yeast strains with regard to managing TDN content in Riesling wines.

An effective means to influence wines' TDN concentrations makes use of one of the usually less appreciated properties of certain bottle closures, more precisely their flavor scalping capacity. After two years of bottle storage in a horizontal position, natural cork had adsorbed approximately 50% of the TDN found in any wine, while the technical corks had removed as much as 70% and the most adsorptive of the synthetic closures nothing less than 98%. Screw caps preserved TDN at its initial concentration (Capone et al., 2003). Thus, the use of screw caps might lead Riesling wines to intensify significantly their petrol flavor when they are prone to develop it.

As one would expect and in line with the kinetics of other kinds of wine aging, the effect of temperature has been stressed. The development of petrol flavor in Riesling wines was reported to be restricted to sensorially acceptable levels by storage at 15°C (Marais et al., 1992 c). Although older vintages tend to display higher levels of TDN, its generation can be slowed down by adequate storage temperature.

CONCLUSION

Premature aging of fruity white wines is a frequent phenomenon causing serious economic and reputational losses to the global wine industry. However, white wine aging has not a uniform appearance and requires a multifaceted approach in sensory, chemical, and winemaking terms. This paper is an innovative attempt to categorize the different kinds of aging according to sensory criteria as they are used by wine industry professionals. For each of four categories, characteristic sensory attributes, sensory impact compounds, and their formation pathways are given.

Typical aging, commonly referred to as aging per se, is largely driven by oxygen uptake pre- and post-bottling, but can also occur under anaerobic conditions at elevated storage

temperatures. In the presence of oxygen, it is characterized by the synthesis of a large array of carbonyl compounds including phenylacetaldehyde, benzaldehyde, methional, and sotolon that are not responsive to binding with sulfur dioxide. Oxygen uptake also accelerates the inevitable degradation of yeast-derived aroma esters and grape-derived terpernols and norisoprenoids responsible for fruity-floral aroma attributes. Regardless of oxygen ingress, reactions of caramelization and those of the Maillard type involving sugars, amino acids, and dicarbonyls produce further odor-active compounds. Attributes of typical aging comprise hay, straw, black tea, nuts, honey, cooked vegetables, and boiled potatoes. However, it is difficult to reconstruct by sensory means to what extent oxygen has contributed to their generation. The most important enological means to limit typical aging comprise cool storage and restricting oxygen uptake post-fermentation including the use of bottle closures with low oxygen ingress, as well as not too reductive a juice treatment and a thorough juice clarification pre-fermentation. Additions of ascorbic acid or free SO_2 levels above average are not suitable to mitigate oxygen-derived reactions in a significant way. Typical aging can arise in conjunction with atypical aging and petrol flavor.

Atypical aging is related to viticultural stress caused by drought, soil nutrient deficiencies, excessive UV radiation, overcropping, permanent green cover, and harvest before aromatic ripeness. Its most important sensory impact compound is 2-aminoacetophenone whose odor is reminiscent of mothballs, naphthalene, floor polish, soap, dry linen, and acacia blossom, sometimes superimposed by a fecal odor compound reminding reduction flavor. It can appear as a defect in relatively young wines after SO_2 is added the first time post-fermentation. Thereby, oxygen radicals are generated leading to the oxidative degradation of indole-2-acetic acid into 2-aminoacetophenone and further compounds when the wine lacks antioxidants such as phenols with sufficient radical scavenging activity. Oxygen is only required in trace amounts not susceptible to generate any oxidative aging, thus explaining the different sets of attributes for both forms of aging. The only enological means to prevent it in wines prone to produce it is the timely addition of ascorbic acid acting as a radical scavenger. Long-term solutions to cope with atypical aging have to be sought in the vineyard. The propensity for atypical aging can be predicted by a specific accelerated aging test. It can occur along with typical aging and reduction flavor. Most frequently, however, it is confounded with these kinds of odor defects.

Post-bottling reduction flavor is due to the hydrolysis of thioacetates and reduction of disulfides to more odor-active, stinky mercaptans (thiols) and their accumulation to super-threshold concentrations under conditions of restricted oxygen ingress. Thiol production by the aforementioned precursors occurs in all wines, but it is the extent of their accumulation and the sensory effect derived therefrom that varies according to the amount of oxygen ingress. When the rate of oxygen ingress exceeds that of the thiol accumulation, the equilibrium between disulfides and thiols shifts towards the less odor-intensive disulfides. In contrast, bottle closures with a low oxygen transmission rate favor thiol accumulation. These dynamics are in accordance with those in filtered wines developing reduction flavor when they are stored under anaerobic conditions in stainless steel containers. Counter-measures comprise bottling with preventive additions of copper ions in concentrations not exceeding a total of 0.5 mg/L Cu^+ when bottles are sealed with airtight screw caps, or the use of bottle closures with a higher oxygen transmission rate. In this context, the choice of the bottle closure constrains finding the right balance between reduction flavor and oxidative aging. Post-bottling reduction flavor can unequivocally be identified by attributes like burnt rubber, garlic, rotten cabbage, rotten onions,

and rotten eggs. However, it is frequently blandished as an expression of minerality or terroir. It might occur simultaneously with atypical aging and petrol flavor.

Petrol flavor is easily recognized by the unmistakable odor profile reminiscent of petrol, kerosene, and dry apricots. It is caused by 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) resulting from acidic hydrolysis of non-volatile, glycosidic precursors like carotenoids. Only a few grape varieties, predominantly Riesling, display precursor concentrations sufficiently elevated for petrol flavor formation. Its intensity correlates with grape maturity, sun exposure, and average daily temperature, while berry shading by adequate canopy management is the most effective viticultural tool to decrease it. TDN concentration in wine increases with storage temperature and is impacted by bottle closures, with natural cork and synthetic stoppers adsorbing more than 50% of it and screw caps maintaining the initial concentration. Petrol flavor is not necessarily considered detrimental at intensity levels occurring under cool-climate conditions, but it is undesirable when high intensities disturb the aroma balance of Riesling wines grown in hot-climate regions. No redox-related reactions are involved in its formation. Given its link to elevated grape ripeness as a prerequisite, it never occurs in conjunction with atypical aging, but may appear mixed with attributes of typical aging and post-bottling reduction flavor.

All white wines undergo a process of aging that is mostly undesired. When dealing with young wines, the only question is which form of aging a given wine is prone to develop, and at which rate. Atypical aging, post-bottling reduction flavor, and petrol flavor are characterized by specific impact odor compounds that can be identified and quantified with some analytical expense, but typical aging lacks an analytically unequivocal definition. Thus, a better sensory discrimination of the aforementioned forms of white wine aging is an indispensable presupposition for improving wines' shelf live. Accelerated aging tests may be further developed and used to help predict the kind of aging a given wine will be subject to. Otherwise, viticultural or enological countermeasure might miss the mark since each form of aging is governed by its own set of precursors and chemical pathways. The only common factor accelerating all kinds of white wine aging is storage temperature.

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