Bruce Zoecklein

Managing Sulfur-like Off Odors in Wine

This review incorporates the latest research with practical guidelines to help winemakers understand and work with these potent volatile compounds.

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THE PHYSICIST Leo Sziland once announced to a friend that he was thinking of keeping a diary, not to publish, but to record the facts for God. His friend asked, "Don't you think God knows the facts?"

"Yes," Sziland responded. "He knows the facts, but he doesn't know this version of the facts."

Winemakers should use their empirical knowledge of the facts coupled with an understanding of the latest research findings to optimally manage sulfur-like off (SLO) odor compounds. This review provides some winemaking guidelines for understanding factors influencing production of SLO, monitoring strategies and remedial steps important to crafting fine wines.

MANAGING VOLATILE SULFUR COMPOUNDS

Crafting fine wine requires a holistic understanding of winemaking and usually includes the following goals:

- Maintaining a stable and concentrated colloidal matrix
- Ensuring no excess of volatiles contributing to "chemical" and "mineral" aromas
- Ensuring no or limited herbaceous aromas
- Ensuring no excess harsh or "green" tannins
- Managing desirable varietals, including volatile sulfur compounds (VSC)
- Ensuring no excess sulfur-like off odors (SLO) impacting aromas and mouthfeel.

Managing VSC represents a double-edged sword. On the one hand, certain sulfur-containing compounds, like H_2S (hydrogen sulfide), can contribute to SLO and impart negative attributes; on the other hand, some sulfur compounds, like 3-mercaptohexanol and 3-mercaptohexylacetate (3-MHA), impart fruitiness and have a positive aroma impact. Furthermore, VSC compounds can become more or less desirable, depending upon their absolute concentration, their relative concentration and the specific wine matrix. Therefore, the challenge for winemakers is to modulate the concentrations of VSC in accordance with consumer preferences and stylistic goals.

Understanding SLO requires an integration of academic findings, empirical knowledge and practical in-house experimentation. It is hoped that this review will aid in that integration.

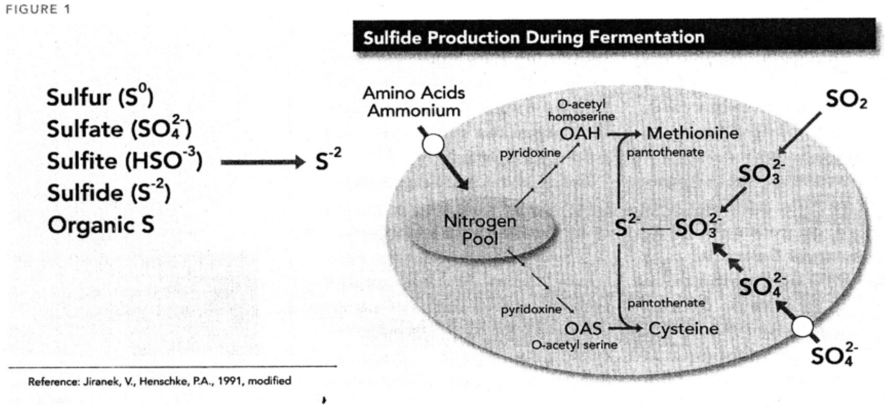
Yeast Production of SLO. Yeasts can utilize elemental sulfur, sulfate, sulfide, sulfite and organic sources of sulfur in grape juice to produce H_2S (see FIGURE 1).

As a product of sulfate reduction, H_2S is an intermediate in the biosynthesis of sulfur-containing compounds required for cell growth and function.

SLO formation in wine is governed by the many factors that influence the yeast sulfide reduction system. As illustrated below, in a series of regulated steps, sulfate is brought into the cell and reduced to sulfide via two ATP-activation steps. At this point, sulfide is combined enzymatically with nitrogen-containing carbon precursors to ultimately form cysteine and methionine, two S-containing amino acids. This sulfate reduction sequence is activated to produce sulfide whenever there is a metabolic demand for cysteine and methionine. All organic sulfur compounds are formed via sulfur-containing amino acids. In the absence of intracellular nitrogen, this reduction sequence can continue, forming excess H_2S, which is not incorporated into amino acids but is liberated into the wine. Therefore, a high rate of sustained H_2S production can be observed in response to N (nitrogen) deficiency.

Sulfite (sulfur dioxide) can diffuse into the yeast cell, bypassing the regulatory mechanisms normally controlling sulfate reduction. This may help to explain why H_2S production can be greater when too much sulfite (more than 80 mg/L, depending upon the yeast strain) is present during fermentation.

FIGURE 1



Reference: Jiranek, V., Henschke, P.A., 1991, modified

TABLE 1

Examples of Sulfur-like Off Odor Compounds in Wines

SLO	Sensory Description	Sensory Threshold (µg/L)	Boiling Point (°C)
Hydrogen Sulfide	Rotten egg	0.5	-61
Carbonyl Sulfide	Ether	3.0	-50
Methyl Mercaptan, Methanethiol	Stagnant water	1.5	6
Ethanethiol	Onion	1.1	35
Dimethyl Sulfide	Quince, truffle	10.0	35
Methionol	Cooked cabbage	1200	90
Diethyl Sulfide	Ether	0.9	92
Dimethyl Disulfide	Quince, asparagus	15.0	109
Diethyl Disulfide	Garlic, rubber	4.3	151
Thioesters			

SLO Compounds Commonly Found in Wines. There are nearly 100 VSC reported in wine, some desirable, others contributing to SLO (see TABLE 1).

As pure compounds, the above have different sensory characteristics and, generally, low sensory thresholds. Sensory thresholds can vary depending on the matrix (water vs. wine and indeed the type of wine). Beyond these differences, SLO can be divided into three categories: light or low-boiling-point compounds (those with a boiling point below 90°C); heavy or high-boiling-point sulfur compounds (those with a boiling point at or above 90°C); and thiol-acetic acid esters. This is not an academic distinction; the light compounds are produced during fermentation and post-fermentation and have unpleasant odor descriptors. Because of their volatility, some attempt to lower the concentration of members of this group by aeration, sparging and/or reaction with copper.

The heavy or high-boiling-point compounds are produced by yeast metabolism during fermentation, not post-fermentation. These remain stable in the wine post-fermentation. High boilers cannot be removed by aeration due to their limited volatility, and they do not react with copper. As such, they represent a large winemaking problem.

The thioesters are odorless, but can undergo hydrolysis, or breakdown, to release thiols, thus contributing to disagreeable odors.

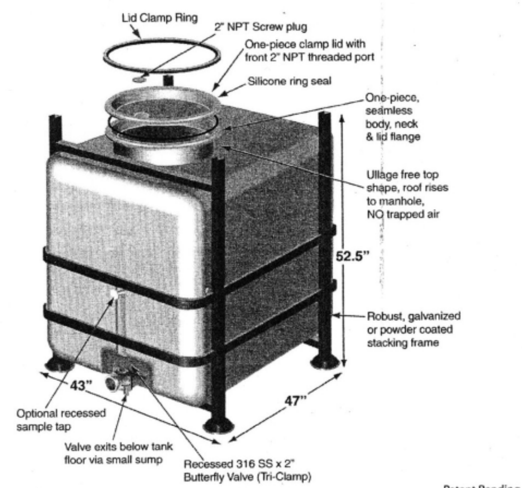
Sensory Features of SLO. The sensory attributes of SLO listed above change as a function of concentration (absolute and relative) and with the nature of the wine matrix. For example, a thiol that has an attribute of peas or vegetal at low concentrations may be described as rotten cabbage, etc., at higher concentrations. Evaluations for SLO in wines should be conducted on all wines pre-bottling.

Most think of SLO in terms of olfactory sensations alone. However, SLO can have an impact on wine mouthfeel, imparting a mineral, bitter, hard and/or astringent aspect. (For additional information on this subject, see *www.vtwines.info*. Under Industry Pubs, click On-line Publications, then Components of Red Wine Mouthfeel.)

It is the quantitative and qualitative nature of SLO, such as those listed in TABLE 1, that provides the sensory impression and dictates remedial winemaking actions.

Factors Impacting SLO Formation. The following is a partial list of the many factors that may contribute to the production of SLO by yeast:

- Elemental sulfur
- High sulfate concentration
- Presence of high levels of sulfur dioxide
- Degradation of sulfur-containing amino acids
- Release and/or metabolism of grape-derived sulfur-containing precursors
- Nutritional deficiency
  - Nitrogen
  - Oxygen
  - Pantothenate
  - High threonine, relative to other amino acids
  - Relative methionine-to-ammonia concentrations
- Yeast stress
- Yeast genetics



Practical SLO Management. The following is a list and discussion of practical winemaking steps to consider in SLO management:

1. Understand yeast performance
2. Measure fermentable nitrogen
3. Understand viticultural and environmental factors impacting assimilable N
4. Understand fruit processing and YAN
5. Control non-soluble solids (NSS)
6. Optimize oxygen management
7. Select appropriate yeast
8. Determine proper concentration and timing of supplements
9. Avoid carbon dioxide toxicity
10. Have a Hazard Analysis and Critical Control Points Plan

1. Understand Yeast Performance. FIGURE 2 illustrates the vast array of factors that influence yeast performance. Many of these contribute to yeast stress, individually or collectively. Stress can change the biochemical machinery, possibly resulting in a reduction in fermentation capacity and premature cell death. Premature cell death results in autolysis, with the release of sulfur-containing amino acids and peptides. Conditions that produce yeast stress and unhealthy cells are more likely to promote autolysis and increase the production of SLO.

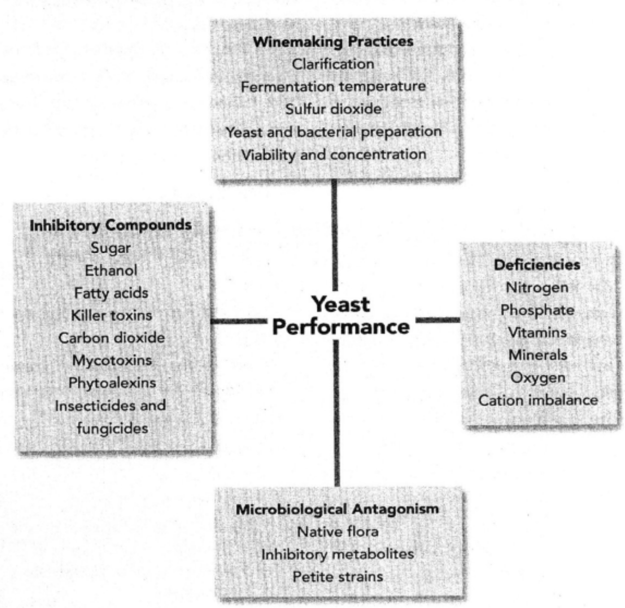
2. Measure Fermentable Nitrogen. Fermentable nitrogen has received considerable attention because it can be a contributor to SLO production, both too high and too low a concentration. Additionally, N is relatively easy to measure.

The nitrogen required by yeasts to conduct a healthy fermentation includes two forms, ammonia N and a group of amino acids referred to as alpha-amino acids, or free amino nitrogen (FAN). Together, both sources contribute the nitrogen utilized by yeast, referred to as yeast-assimilable (YAN) or fermentable nitrogen.

The minimum yeast assimilable nitrogen required is approximately 140 mg/L for a 21-degrees Brix juice and perhaps 250 mg/L for a 23-degrees Brix juice. However, it should be noted that these concentrations are broad-based generalizations for several reasons:

FIGURE 2

Understanding Yeast Performance



Reference: Gump, Zoecklein and Fugelsang (2001)

- The nitrogen level requirement to optimize fermentation is highly yeast-strain specific, governed largely by the genetics of the yeast.
- It may be that the qualitative makeup of FAN amino acids, not simply the total yeast assimilable N, is the most important factor. The significance of the qualitative nature of YAN helps to explain so-called reductive grapes, varieties that have a greater tendency to produce SLO. It also helps to explain seasonal and block differences in SLO production.
- A low concentration of assimilable nitrogen is often coupled with deficiencies in important micronutrients required for optimum yeast performance.

Two common procedures for measurement of fermentable N are the Formol titration and NOPA test. We modified the Formol titration procedure and compared the results with the NOPA method (*Am. J. Enol. Vitic.* 53:325-329). Some features of these two procedures are summarized below:

Formol Titration
- Simple titration procedure
- No instrumentation required
- Precise but not extremely accurate
- Measures both FAN and NH_4 N

NOPA Procedure
- Measures FAN but not NH_4 N
- Must measure NH_4 N separately
- Requires spectrophotometer
- Available in enzyme kit format

The Formol titration has the advantage of measuring both ammonia and FAN amino acids. However, the method titrates proline (which yeast cannot use) and does not react with all the nitrogen in arginine that the yeast may be able to use. Our research suggested that this generally balances out although the arginine /proline ratio can vary significantly. The ratio is usually higher in skins than in the pulp. Arginine accumulation begins well before véraison and continues to maturity, then plateaus. Proline, on the other hand, increases late in the season (four weeks post-véraison). High proline is associated with increased maturity and with vine stress.

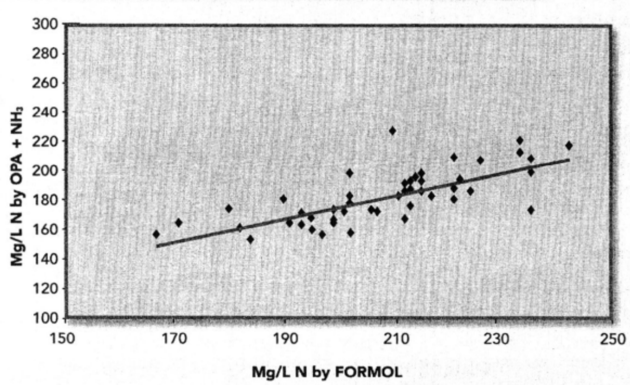
FIGURE 3 shows the relationship between the two tests. As can be seen, the methods are comparable, demonstrating reasonable linearity. Formaldehyde is a carcinogen and must be used with caution. As such, we have developed a low-volume Formol procedure, which is available at *www.vtwines.info* (under Industry Pubs, click On-line Publications, then Reduced Volume Formol Titration, adjacent to Fermentable Nitrogen).

3. Understand Viticultural and Environmental Factors Impacting Assimilable N.
A number of viticultural and environmental factors can impact yeast assimilable N, including the following: cultivar, rot incidence, block, crop load, mulch, moisture stress and maturity level. (For a discussion of these subjects, see *www.vtwines.info*; under Industry Pubs, click Enology Notes, then Subject Index to Enology Notes.)

From véraison onward, the following changes occur in the fruit. NH_3

FIGURE 3

Formol vs. [OPA + NH3]



increases, then declines. FAN amino acids increase, then decline, with the rate of decline different among FAN components. With extended maturity, YAN declines.

There appear to be some correlations between the quantitative changes in YAN and SLO formation, including high threonine, relative to other amino acids, and the relative methionine-to-ammonia concentration. Both situations are reported to contribute to SLO formation. There also appears to be a correlation between ATA (atypical aging) and SLO formation. (See *Enology Notes* #14, 77, 107, 110 and 111 for discussions on ATA.)

Some generalizations regarding cultivars and YAN are as follows: Merlot is usually low in YAN. Syrah is usually somewhat low in YAN; this is coupled with high potential alcohol. Pinot Noir is often sufficient in YAN. Sauvignon Blanc is often sufficient in YAN.

It should be noted, however, that site, season and vineyard management practices can have a very large influence.

4. Understand Fruit Processing and YAN.

There is a relationship between juice extraction methods and fermentable nitrogen. This relationship stems from the fact that arginine, the FAN amino acid in the greatest concentration, is located mainly in the skins. Therefore, winemaking protocols, such as the following contrasts, result in different YAN concentrations:

- Whole cluster pressing vs. crush and drain of whites
- Bleeding vs. non-dejuiced reds
- Short vs. long-vatted reds

For those evaluating the N status of vineyard samples just prior to harvest, which I recommend, the relationship between sample processing methodology and cellar processing must be noted.

5. Control the Non-Soluble Solids (NSS) Level.

Turbidity of white juice should be adjusted with some precision, to attain stylistic goals and the aromatic finesse of the wine. Juice clarity can be measured in nephol units (NTU). The desirable NTU range is between 100 and 250. Low non-soluble solids concentration going into the fermentor can result in a low concentration of YAN and other nutrients, and can increase the likelihood of SLO. High NSS concentration increases the risk of SLO production, including high-boiling compounds.

6. Optimize Oxygen Management.

Yeast produce membrane lipids only when grown aerobically. In the initial growth phase, proper oxygen management leads to proper production and storage of sterols in the yeast cell, which can be shared with subsequent daughter cells. It is possible to increase yeast ethanol tolerance by promoting synthesis of sterols, by adding oxygen (air) in the starter and during fermentation. Yeast lees deplete the oxygen content and can impact the redox potential and formation of SLO.

Additionally, some yeast-derived commercial products aid in sterol synthesis. Oxygen management involves an understanding of the following:

- In general, yeast need 8-10 mg/L oxygen during the initial growth phase for optimum growth.
- Oxidative stress may be a primary cause of early yeast mortality.
- Lees are potent oxygen consumers, even after yeast cell death.
- Lack of oxygen can contribute to SLO.
- Oxygen additions may allow yeast to produce more glutathione, an important white wine antioxidant.

7. Select Appropriate Yeast

Wine yeast play a central role in the production of volatile sulfur compounds, both the good and the bad. Yeasts are responsible for the transformation of non-volatile grape-derived precursors to odor-active volatiles, which can positively contribute to the thiol-based varietal character of a number of cultivars including Sauvignon Blanc, Chenin Blanc, Riesling, Petite Manseng, etc. Wine yeasts vary tremendously with regard to this conversion.

SLO production is controlled more by yeast genetics than winemaking; however, fermentation environment does play a role. For example, the level of H_2S can vary by as much as 2,000-fold for a given strain, simply by changing the environment.

Some strains are less efficient users of nitrogen and have higher nitrogen requirements. Commercial strains can vary by more that 50 percent with regard to their N requirement. Additionally, uninoculated, feral fermentations, with a large population of non-*Saccharomyces* cells (therefore not alcohol tolerant) can cause problems. Non-*Saccharomyces* become inhibited by the increasing alcohol concentration, lose viability and undergo autolysis during the early- to mid-stages of the alcoholic fermentation.

8. Provide Proper Concentration and Timing of Supplements.

Improper concentration and timing of N supplements can result in the following:

- Increased production of SLO
- Increased unwanted flora (if added too early or too late)
- Rapid fermentation
- Loss of volatiles, particularly if the source is DAP
- Decreased complexity.

Too much nitrogen can stimulate the growth of unwanted organisms, increase the biomass and cause too rapid a fermentation. Rapid fermentation can increase aroma compound loss due to increased volatility, resulting in the loss of complexity. Additionally, ammonia (in the form of DAP) can prevent the appearance of aromatic degradation products from amino acids.

Amino acids are an important source of yeast-derived esters, which can add to complexity and wine quality. Thus, the supply of nitrogen must be available to allow a continuous re-synthesis of proteins. If that does not occur, the yeast lose the ability to conduct the fermentation.

Nitrogen addition may be effective in avoiding problem fermentations until about two-thirds of the sugar is utilized. Cells which have passed the point of transcriptional responsiveness will not respond to added nutrients.

It should be noted that there are significant differences between native (fruit-derived YAN) and addition products. Addition of nutrient products may not provide the same results as having an adequate native N concentration. As such, vineyard management which produces adequate fruit YAN may be very important.

Fermentation complements/addition products often contain some of the following:

- inorganic nitrogen (DAP)
- organic nitrogen (alpha-amino acids)
- unsaturated fatty acids
- sterols, thiamine, folic acid, niacin, biotin and calcium pantothenate
- magnesium sulfate
- inactive yeast cell walls
- peptides
- micro-crystalline cellulose
- other yeast autolysis products.

The possible benefits of complex yeast nutrient (CYN) addition include better resistance to oxidation as a result of increases in glutathione, higher levels of free sulfur dioxide, better color and increased protection of aromatic quality. The reader should consult manufacturers' product literature for discussions regarding nutrient additions and timing. There are currently time-release nutrient products available.

9. Avoid Carbon Dioxide Toxicity.
Carbon dioxide is toxic to yeast and can impact cell performance. The release of carbon dioxide helps to minimize toxicity and decreases the lag phase of yeast growth. This is the time in which juice is most sensitive to both enzymatic and chemical oxidation.

Mixing during fermentation keeps the yeast in suspension and helps to drive carbon dioxide out of solution, resulting in a lowering of carbon dioxide saturation. Mixing during fermentation may be important, regardless of the size and shape of the vessel. Some addition products contain inert compounds like micro-crystalline cellulose, the purpose of which is to help release carbon dioxide from solution, presumptively lowering the toxic impact.

10. Have a Hazard Analysis and Critical Control Points (HAACP) Plan.
See www.vtwines.info for details.

POST-FERMENTATION SLO MANAGEMENT OPTIONS

The following is a list and discussion of post-fermentation winery processing options for SLO management. They include:

1. Understanding oxidation-reduction potential
2. SLO monitoring
3. Wine aeration/oxygenation; micro-oxygenation
4. Copper additions
5. Antioxidants (ascorbic acid, sulfur dioxide)
6. Carbons and SLO management
7. Lees management/yeast fining/tannin additions
8. Wine closures and SLO

1. Understanding Oxidation-Reduction Potential.
Oxidation-reduction (redox) reactions describe the general principles and behavior of most wine chemistry. An understanding of redox is key to understanding SLO and their management. Some generalizations regarding redox can be seen in the sidebar on this page. (For additional information on redox potential see *Enology Notes* at *www.vtwines.info*, click Enology Notes Index.)

UNDERSTANDING REDOX

An understanding of oxidation-reduction (redox) reactions is key to understanding and managing SLO. Some generalizations regarding redox include the following:

- Oxidation-reduction (redox) reactions are a series of interlinked reactions involving the oxidation of one compound and the reduction of another.
- Oxidation and reduction are two different chemical processes that complement each other.
- As electrons are transferred, one compound is oxidized while the other reduced.
- Oxidation is the loss of electrons. Reduction is the gain of electrons.
- For every oxidation reaction, there is a reduction reaction.
- Electrons are rearranging themselves into a more favorable order.
- This order is determined by the redox potential of the compounds.
- Oxygen is not required although it is frequently the species that starts the process.
- Redox potential can be measured in the same way that pH is measured.
- Redox potential is a measure of how oxidative or reductive a system is, measured in millivolts (mV).
- The higher the mV, the less reductive, the more oxidative.
- Aerated red wine: redox potential is usually between 400-450 mV.
- Non-aerated stored red wine usual range: 200-250 mV.
- Redox potential changes much more easily in whites.
- Tank wines have a lower redox potential than barrel wines.
- Redox potential is lowest at the bottom of a tank, hence the significance of lees stirring.
- Post-fermentation, a wine could be in a reduced state, but this does not necessarily mean that the wine is displaying SLO.

2. SLO Monitoring.
Wine will always contain sulfide precursors because these are normal constituents of fermentation, with an almost endless array of SLO in various states of oxidation and reduction. As a function of redox potential, these may manifest themselves in various forms post-fermentation.

The nature of the SLO compound(s) must be understood before remedial steps are taken.

A sensory aroma screen should be conducted on all wines prior to bottling. The specific nature of such a screen is discussed in Zoecklein et al. (1999). It allows for the sensory separation of three general, but important, groups of SLO: hydrogen sulfide, thiols and disulfides.

It is essential that winemakers conduct an aroma screen on all wines prior to any remedial SLO adjustments.

Three glasses of the same wine are evaluated: a control, a glass containing copper sulfate and a glass containing cadmium sulfate. The interpretation is given in TABLE 2. Note: This review is solely for odor evaluation; wines treated as described above should not be tasted.

Because of individual perception threshold differences and the difficulty of recognition of SLO compounds, it is a good idea to conduct an aroma screen on all wines prior to bottling.

TABLE 2

Outline of a sensory aroma screen for determining the general nature of some SLO in wine

Control	Copper Sulfate	Cadmium Sulfate	Interpretation
	Odor is gone	Odor is gone	H_2S present
	Odor is gone	No change	Mercaptans
	Odor is gone	Odor is less, but not gone	Both H_2S and mercaptans
	No change	No change	Dimethyl disulfide or other

3. Wine Aeration/Oxygenation.
One misconception is the belief that a wine with SLO can always be fixed by oxidation. This has arisen due to some sensory changes noted on some occasions. If H_2S is present, the oxidation of H_2S to elemental sulfur can occur as below:

$$2H_2S + O_2 \leftrightarrows 2H_2O + 2\,S$$

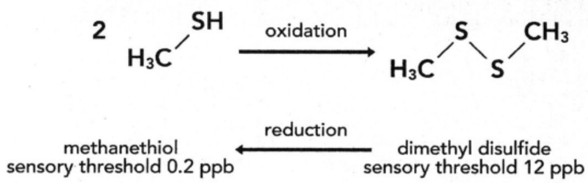
This leaves elemental sulfur present at the bottom of a tank, which must be removed. Otherwise, the reverse reaction would occur. While this reaction can occur, wines contain a host of antioxidants or reducing agents that will compete for any oxygen added.

There is some volatilization of low boilers like H_2S that can occur. How much volatilization is possible depends upon the particular SLO compound(s). What does occur with oxygen exposure is that the form of the sulfide changes, in accordance with the shift in the redox potential.

A good example of redox is the oxidation of methanethiol to dimethyl disulfide. Oxidation of one SLO compound to a slightly less stinky one is sometimes possible. The sensory thresholds for sulfides shift markedly with small changes in molecular structure, ranging from 2 ppb to 12 ppb. Note that no oxygen is involved. One compound, like methanethiol, can be oxidized to form dimethyl disulfide. This reaction is reversible (FIGURE 4).

Oxidation of methanethiol to disulfides can easily take place with wine aeration. Aeration may not remove sulfides, but simply change their form and, therefore, their sensory descriptors and thresholds. Oxidation causes a cascading set of reactions stabilizing the electron shifts. The redox potential would be readjusted to near, but not exactly the same, as the original potential. To help avoid unwanted oxidation, especially in white wines, H_2S may be blown off with inert gases, such as nitrogen. However, this may take a significant quantity of gas and requires an understanding of the specific SLO in the wine, e.g., an aroma screen.

Micro-oxygenation. It has been known for some time that micro-oxygenation can lower the perception of veggie/herbal character in a wine. Originally in our research we presumed this effect was the result of changes in pyrazines. However, that was not confirmed by our



$$2\ R\text{-}S\text{-}H + \tfrac{1}{2}\ O_2 \rightleftharpoons R\text{-}S\text{-}S\text{-}H + H_2O$$

analysis. The odor of thiols complements those of pyrazines, and indeed some thiols contribute to "green"-type odors. Micro-oxygenation results in oxidation of some thiols, resulting in both a change in the perception of SLO and veggy character (FIGURE 5). This highlights the interrelationships of aroma compounds in wines.

4. Copper Additions.

The use of copper poses an interesting dilemma to winemakers. It can be used to treat H_2S and some thios but, at the same time, will reduce the concentration of desirable VSC compounds. It does not discriminate between SLO and VSCs contributing to varietal character. Some of the considerations regarding the use of copper include the following:

- Legality/perception
- Reactivity only with certain SLOs
- Protein haze
- Timing of addition: yeast stress, redox
- Sensory impact on varietal character and intensity
- Impact on longevity.

Copper can react with some SLO, while not others:

- H_2S and thiols react with Cu^{+2}
- Disulfides and thioesters do not react with Cu^{+2}
- Thioesters can degrade to thiols (and esters), which can react with Cu^{+2}.

Copper reacts with hydrogen sulfide according to the following reaction:

$$H_2S + CuSO_4 \rightarrow CuS + H_2SO_4$$

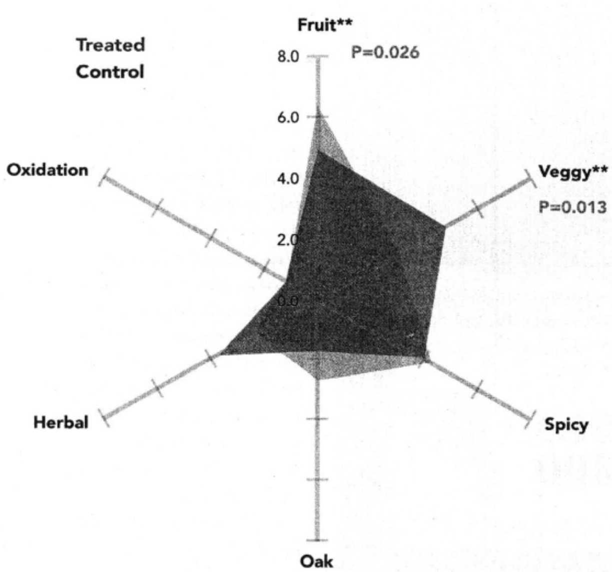
Copper also reacts with some thiols, including methyl mercaptan. However, copper does not react with disulfides (thiol oxidation product).

$$2\ CH_3SH + \tfrac{1}{2}\ O_2 \rightarrow CH_3SSCH_3 + H_2O$$

Methyl mercaptan — Dimethyl disulfide

SO_2
Ascorbic Acid
←

FIGURE 5



Copper sulfide will not react with disulfides or "heavy" sulfur compounds (TABLE 1). However, copper sulfide has been used by some winemakers with sulfur dioxide and ascorbic acid, whereby the SO_2 cleaves the disulfide, resulting in two mercaptans which can then be bound with copper. The ascorbic acid acts as an antioxidant to keep the mercaptan from oxidizing. One of several problems is that this reaction is very slow at wine pHs. The above reaction illustrates the importance of conducting aroma screens.

In addition to only reacting with certain SLO, copper also has the disadvantage of being a strong oxidizer, possibly impacting wine longevity. The potential oxidizing effect is illustrated by the Fenton-type reaction:

$$H_2O_2 + Cu^{+2} \rightarrow Cu^{+3} + OH + OH^*$$

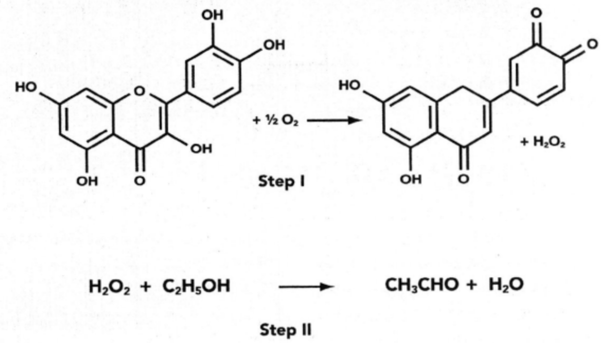
The OH*, or hydroxyl radical, is the most oxidative species. This is a potentially large problem, notably in white wines with relatively lower concentrations of oxidative buffers, such as phenols.

Addition of copper sulfate to the fermentor is a practice used by some in an attempt to limit SLO production. While the majority of the copper (about 60 percent or more) is bound to yeast and precipitates from solution, such additions are not benign. Copper addition, either during or post-fermentation, can have a large negative impact by lowering the varietal intensity of the aromas derived from VSC. As such, the varietal characters of Sauvignon Blanc, Riesling, Gewürztraminer, Petit Manseng and Chenin Blanc are diminished due to copper's ability to bind mercapto- compounds.

> "The challenge for winemakers is to modulate the concentrations of VSC in accordance with consumer preferences and stylistic goals."

FIGURE 6

Coupled Oxidation



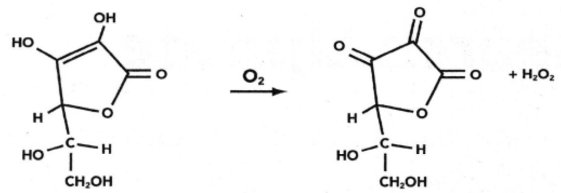
Copper and Glutathione. Copper also impacts wine longevity as a result of oxidation and removal of antioxidants. One of the most important antioxidants in white wines is glutathione. Glutathione is a sulfur-containing polypeptide both found in grapes and produced by yeasts. It is a strong antioxidant. As such, it helps protect labile aroma/flavor compounds from oxidative degradation. Copper additions, in the form of Bordeaux sprays and as a remedial winemaking activity, have the ability to bind and completely inactivate glutathione. Optimizing the production and management of glutathione may be important in winemaking of low phenol whites.

5. Antioxidants (Ascorbic Acid, Sulfur Dioxide).

Understanding the mechanisms of oxidation is important. As illustrated in FIGURE 6 below, wine oxidation can involve the oxidation of a phenol to produce a quinone (oxidation product) and hydrogen peroxide. In the example below, the hydrogen peroxide generated oxidizes ethanol to acetaldehyde (coupled oxidation).

It is important to note that sulfur dioxide additions do not bind the oxygen and, therefore, do not prevent the first step in this coupled oxidation. Some winemakers use ascorbic acid, or vitamin C, as an antioxidant. Ascorbic acid sometimes protects the fruit and acts as an antioxidant while at other times it can act as a protooxidant, or oxidative promoter.

The two roles of ascorbic acid are mainly the result of concentration and the presence of adequate sulfur dioxide.



As illustrated in FIGURE 7 above, when ascorbic acid is added to wine, it binds oxygen rapidly to form two reaction products, dehydroascorbate and hydrogen peroxide. If there is not enough ascorbic acid maintained to react with the oxygen, oxidative degradation, including coupled oxidation, can occur. If there is not adequate sulfur dioxide maintained to bind with the hydrogen peroxide formed by the ascorbic acid, wine oxidation can occur.

Therefore, the keys to optimizing the performance of ascorbic acid as an antioxidant are to maintain a concentration of about 50 mg/L and to have adequate sulfur dioxide. Therefore, the use of ascorbic acid involves the following considerations:

- Reaction between ascorbic acid and oxygen is much more rapid than SO_2.
- SO_2 does not directly react with oxygen but mainly with reaction products, such as H_2O_2.
- Optimum levels of ascorbic acid (50 mg/L or more) and more SO_2 can prolong the antioxidant phase of ascorbic acid.
- For example: If 100 mg/L ascorbic acid in wine reacts completely with oxygen, 62 mg/L SO_2 are required to react with the ascorbic acid oxidation product.
- Because of the problems associated with ascorbic acid, it is not a popular addition agent used in the U.S.

6. Carbons and SLO Management.

Activated carbon adsorbants are used occasionally as a means of modifying the sensory properties of wines. The activation process develops pores of molecular dimensions within the carbon particle, which provides an extremely high internal porosity and surface area. Carbons are relatively non-specific adsorptive agents that tend to bind with weakly polar molecules. Carbons have been suggested as a tool to remove SLO, work originally designed to remove chemical warfare agents like mustard gas from contaminated air. Carbons have been shown to bind some problem SLO in wines such as DES (diethyl sulfide). Such compounds present a significant problem due to their extremely low sensory threshold (see TABLE 1).

While possibly effective in binding some SLO, the addition of carbon may cause carbon-catalyzed oxidation. Because the carbon molecule contains a great deal of air, additions may increase wine oxidation (see Zoecklein et al., 1999). For example, the adsorption of DES onto a carbon particle likely also results in its oxidation to diethyl sulfone resulting in a change in sensory perception. The problems associated with carbon-catalyzed oxidation and the non-specific nature of its binding limited the effectiveness as a remedial tool.

7. Lees Management/Yeast Fining/Tannin Additions.

Each of these topics is discussed in my *Enology Notes* series. (Go to *www.vtwines.info*, click Enology Notes, then Enology Notes Index.)

8. Wine Closures and SLO.

Wine closures can impact post-bottling SLO. The following are important considerations:

- Low or no oxygen ingress screw cap-type closures/liners are more prone to cause accumulation of thiols post-bottling.
- Low oxygen ingress results in a lowering of the redox potential.
- Lack of oxygen to oxidize thiols to disulfides can impact SLO perception.
- To deal with this potential problem some are adding copper at bottling. The desirability of a prophylactic addition of a heavy metal is questionable.
- Cu^{+2} bottling can impact longevity, but can bind H_2S and some thiols.
- Copper addition at bottling has no impact on disulfides and thioesters.

PUTTING SLO IN PERSPECTIVE

The English philosopher **Bertrand Russell** created the logical and semantic paradox that asks the question: Is the set of all sets that are not members of themselves a member of itself? To some, the mechanisms of sulfur-like off odor formation and oxidation-reduction potential are reminiscent of Russell's Paradox. It is hoped that this review is not.

Sulfur-like off odors in wines have been around for the 8,000 years of wine production and will likely remain. However, a practical understanding of the production and management issues governing these very potent and important wine volatiles is essential for premium wine production. **wbm**