PREVENTION AND TREATMENT OF REDUCTIVE AROMAS

Reduction in wines is one of the most common problems in winemaking. Hydrogen sulfide and other volatile sulfur-containing compounds are commonly produced during alcoholic fermentation, but they can also develop during storage and ageing, as well as after bottling. The aromas generated by these sulfur compounds are usually described as rotten egg, burnt rubber, skunky, burnt match, asparagus, onion and garlic. These compounds have low sensory thresholds. At times, when found below their sensory thresholds, they tend to mask and decrease aromatic qualities, without pointing to an obvious reduction flaw. Additionally, sulfur-containing compounds can impact mouthfeel and intensify other negative wine attributes such as bitterness and herbaceous characters.

It is essential to note that not all sulfur compounds in wine produce off-aromas. There is a group of sulfur compounds that contribute positively to wine aroma. These compounds, known as volatile thiols, have a fruity smell and are the source of varietal character in certain wines. Treatments designed to remove and eliminate negative sulfur compounds are not selective, therefore they can also affect the positive compounds. It is important to remember that prevention is crucial in avoiding sulfur off-aromas.

What is the Source of Sulfur in Wine and How does it Become an Off-Aroma?
The presence of sulfur in juice originates from diverse sources:

- Elemental sulfur from spray residue
- Inorganic forms: sulfates (SO_4) and sulfites (SO_2)
- Organic forms: sulfur-containing aminoacids present in grapes (cysteine, methionine)

There are several factors that affect the production of sulfur off-aromas. With all of them, reduction of the above sources of sulfur during yeast biosynthesis leads to the formation of H_2S; yeast produce sulfites and hydrogen sulfide as a normal step in the synthesis of sulfur containing aminoacids to form a new cell. When sulfur is not incorporated into aminoacids, it gets expelled out of the cell because of its toxicity. This can occur when sulfur is in excess as well as when there is a shortage of nitrogen. Additionally, yeast genetics is a factor that causes yeast to produce excessive amounts of H_2S.

The Formation of Hydrogen Sulfide and Other Sulfur Compounds
Hydrogen sulfide has a low sensory threshold and an odor similar to rotten eggs. Environmental factors including temperature and alcohol can influence its detection level. H_2S is highly volatile, thus the reason aeration sometimes works for its elimination. If H_2S is not removed from wine, it can react to form ethyl mercaptan (ethanethiol) which is known to have a burnt match, earthy smell. Copper sulfate can be used to eliminate H_2S and some mercaptans, but it requires the addition of copper which, in excess, can lead to various other reactions including oxidation and haze formation.

Once converted into ethyl mercaptan this compound becomes harder to remove from wine because of its higher boiling point. It also has a low sensory threshold of 0.02-2.0 ppb which makes it one of the smelliest substances that exist. Ethyl mercaptan (ethanethiol) is commonly used as an odorant in natural gas to help detect and warn of gas leaks. Copper sulfate can be used to bind mercaptans and reduce their presence, but is not clear if this treatment removes these sulfur compounds from the wine.

Mercaptans can oxidize to form disulfides when exposed to oxygen. These new compounds smell like, garlic, canned asparagus, burnt rubber, and onion and are almost impossible to eliminate. The chemical change induced by the oxidation from mercaptan to disulfides impacts their sensory attributes and changes their ability to bind to copper sulfate. Therefore, while mercaptans react with copper, their oxidized form doesn't.

Furthermore, disulfides can be reduced back to mercaptans, then bind with copper sulfate. This is the main concept of using ascorbic acid in combination with copper sulfate as a treatment. But these reactions could take a considerable amount of time. Ascorbic acid acts only as an antioxidant to prevent the mercaptan form oxidizing back into disulfides and requires the presence of SO_2 as the means to cleave the disulfide back into a mercaptan.

Another type of defect also caused by sulfur off-aromas is known as light-struck defect. This defect is triggered by light exposure after bottling. The source of the off-aroma is degradation of sulfur-containing aminoacids present in wine. Their breakdown is catalyzed by light and the presence of residual vitamin riboflavin. This issue can be avoided by using glass that prevents the passage of UV-light or using bentonites that have the ability to remove riboflavin (Pluxbenton N).

There are close to 100 different sulfur compounds in wine and they can all exist at the same time. This is the reason why, when using copper sulfate as a treatment, some of these off-aromas might appear to be removed, but in some wines there isn't complete elimination.

Table 1. Sulfide Sensory Thresholds and Aroma Descriptors

Compound	Aroma	Threshold	Copper Treatment?
Hydrogen Sulfide	Rotten Egg	0.5 ppb	Yes
Ethyl Mercaptan (ethanethiol)	Burnt Match, Earthy	0.02- 2.0ppb	Yes
Methyl Mercaptan (methanethiol)	Rotten Cabbage, Stagnant Water	1 ppb	Yes
Dimethyl Sulfide (DMS)	Canned Corn, Cooked Cabbage, Asparagus	10-25 ppb	No
Diethyl Sulfide	Rubbery	1 ppb	No
Dimethyl Disulfide	Garlic Burnt Rubber	15-30 ppb	No
Diethyl Disulfide	Onion, Cabbage, Vegetal	4 ppb	No

Table 2. How to Prevent the Formation of Negative Sulfur Compounds during Fermentation, Storage and Ageing

	Cause	Solution
Harvesting and Juice Settling	Presence of residual elemental sulfur from fungicides	Be aware of vineyard sprays. Settling white must before fermentation might help remove some elemental sulfur. In addition, the use of bentonite and yeast hulls can improve the elimination of pesticides during settling.
	Presence of copper from vineyard sprays	High concentration of copper in juice can cause sluggish and stuck fermentations as it can be toxic to yeast. The use of yeast derivative products containing PVI-PVP can help eliminate excessive copper during fermentation and prevent premature oxidation. **(Pro XP, Pro FT** and **Stabyl PVI-PVP)**
	High levels of non-soluble solids	Low solid levels can cause nitrogen deficiency, while high levels can create a reductive environment increasing the risk of sulfur off-aroma production. Settling and clarifying juice to turbidity levels between 100-250 NTU is ideal for a healthy fermentation.

	Cause	Solution
Fermentation	Yeast strain (genetics)	Enzymatic regulation variations between yeast strains are known to impact the production of fermentative aromas. At the same time, these variations will also impact the production of H_2S. Selecting yeast strains that produce low levels of H_2S is an important step in preventing the formation of sulfur off-aromas. **The following are some of Enartis yeast strains that produce low levels of H_2S: AMR-1, Q5, ES 454, Primitivo, Vintage Red, WS, EZ Ferm 44, Top 15, VQ10, VQ15, VQ Assmanshausen, Aroma White, Q Citrus, ES 123, ES 181, Top Essence, Vintage White**
	Unbalanced nutrition (high or low levels of nitrogen and vitamin deficiency)	Deficient or high levels of nitrogen can cause yeast to produced H_2S. It is important to measure yeast available nitrogen (YAN), and provide a balanced source of nutrients in the form of organic and inorganic nitrogen, vitamins and minerals during the period with the highest demand for nutrients (growth phase). **Nutriferm Energy, Nutriferm Special** and **Nutriferm Advance.**
	Lack of oxygen during yeast growth	Provide 8-10 mg/L of oxygen during the growth phase of yeast. Oxygen is necessary for the creation of sterols by yeast – an important component of the yeast cell wall. Providing oxygen during this stage will contribute to the ability of yeast to tolerate harsh environmental conditions, including high alcohol and high temperatures.
Storage and Ageing	Reductive environment towards the end of fermentation and during ageing	Remove heavy lees as they form: Wines stored on heavy lees can lead to the release of sulfur compounds by yeast enzymatic activity, particularly if a wine displayed reductive odors during alcoholic fermentation. The risk remains even when yeast cells are dead, as their enzymatic activity remains active. During storage of reductive wines, employ additives that increase the reductive strength of wine such as **Tan Max Nature** and **Tan Elevage**. These tannins have the ability to increase wine reductive potential, as well as eliminate the perception of some mercaptans.
Bottling	Presence of Riboflavin	Use anti-UV glass to bottle wine. Reduce the amount of riboflavin in wine with **Pluxbenton N**.
	Wine closures	Closures that limit the transfer of oxygen can cause a decrease in the redox potential that leads to the release of reductive off-aromas.

What Treatments are Available?

Aeration

Aeration can contribute to the volatilization of low boiling point sulfur compounds like H_2S, however, exposure to oxygen will lead to the transformation of low sensory threshold sulfur compounds (mercaptans) to ones with higher sensory thresholds such as disulfides. This might initially appear to improve organoleptic qualities, but as mentioned before, disulfides can be hard to remove and they are able to convert back to mercaptans under the right conditions. To avoid oxidation of these sulfur compounds when attempting to remove H_2S with aeration, use an inert gas like nitrogen and be aware of the volatilization of other positive volatile aromas.

Copper Sulfate

Copper sulfate is commonly used in the treatment of reductive characters. It reacts with hydrogen sulfide (H_2S) and certain mercaptans but doesn't have an effect on disulfides or heavy sulfur compounds. Furthermore, these reactions may require the addition of copper in excess, which can also affect fruity volatile thiols, causing a decrease in aromatic complexity. The other issue with excess copper is its ability to catalyze reactions of oxidation leading to premature ageing, as well as the formation of copper haze (excess copper reacting with proteins).

Some winemakers adopt the use of copper sulfate as curative and preventive for the formation of sulfur compounds. This strategy might lead to residual Cu+ that exceeds the legal limit (0.5 ppm).

In the event of a high residual copper, there are several options for removal:

- Bentonite fining, as well as yeast hulls, can help remove small amounts of copper between 0.1-0.2 mg/L.
- Potassium Ferrocyanide: This treatment, also referred as blue fining, can be dangerous. Due to a very complex redox system it's nearly impossible to recommend a dosage, which can lead to an overdose and the production of cyanide.
- PVI-PVP: Another option currently available and approved for the use by the TTB is PVI-PVP. This polymer has high selectivity for metals. It can remove up to 50% of CU+ and up to 30% of Fe+. PVI-PVP is easy to handle and remove from wine as it is not soluble and settles very fast.

Copper Citrate

Copper citrate reacts with the same compounds as copper sulfate but leaves 50% less residual CU^+, allowing for higher addition rates while limiting side effects. This form of copper is *not* approved to use in the United States by the TTB to treat wines.

Carbon

Steam-activated carbon can be effective in removing aromas from wine, however it is not a selective treatment and can decrease aromatic potential. Carbon is used on wines where other treatments do not work. It is effective at removing Diethyl Sulfide which cannot be removed with any form of copper. Additionally, carbon is difficult to settle by gravity and requires a flocculating agent to facilitate clarification. The addition of PVPP, gelatin and bentonite can improve its settling.

Tannin Additions

The addition of tannins, especially Ellagic tannins, from untoasted oak can provide reductive strength and increase redox potential. Ellagic tannins also have the ability to bind with mercaptans and remove them. The addition of **Tan Elevage or Tan Max Nature** can help improve organoleptic characteristics of a reduced wine.

If you have any questions or would like product samples, please give us a call at (707) 838-6312.

This document is a compilation from information obtain in several publications.

References

Bobet, R. A., Noble, A. C., Boulton, R. B., Kinetics of the Ethanethiol and Diethyl Disulfide Interconversion in Wine-Like Solutions. *Journal of Agricultural and Food Chemistry* 1990, *38*, 449-452.

Zoecklein, B., Managing Sulfur-like Off Odors in Wine. *Wine Business Monthly 2008, Feb, 106-115*

A.C. Clark, E.N. Wilkes, G.R. Scollary, Chemistry of Copper in White Wine. *Australian Journal of Grape and Wine Research Volume 21 (3): 339-347*