

ENARTIS NEWS

REDUCTION: HOW TO PREVENT AND TREAT IT

Reduction is one of the most common problems in winemaking. Hydrogen sulfide and other volatile sulfur-containing compounds (VSC) are generally produced during alcoholic fermentation but can also develop during storage, ageing and post-bottling. The aromas generated by these sulfur compounds are described as rotten egg, burnt rubber, skunky, burnt match, asparagus, onion and garlic. Additionally, they can impact mouthfeel and intensify other negative wine attributes such as bitterness and herbaceous characters. Their presence, when close to or above the sensory threshold, decreases wine aroma quality. For this reason, it is important to know how to prevent and treat this defect during the different stages of winemaking.

ORIGIN OF REDUCTION

Alcoholic fermentation: the beginning of reduction

Production of sulfur off-aromas begins during alcoholic fermentation.

The first mechanism is related to the **synthesis of amino acids**. Yeast produce hydrogen sulfide (H_2S) as a normal step in the synthesis of sulfur-containing amino acids. This explains why accumulation of H_2S often occurs in cases of nutrient deficiencies associated with amino acid production, such as low assimilable nitrogen or vitamin deficiencies, which are important cofactors in the synthesis of methionine. Genetic differences associated with amino acid production explain why some yeast strains are reported to be low or high H_2S producers.

A second mechanism is the **transformation of elemental sulfur to H_2S** . Elemental sulfur is commonly sprayed in vineyards to control powdery mildew. Formation of H_2S from S-residues cannot be corrected by nutrient addition and is much less dependent on yeast genetics. H_2S is usually formed from S-residues during the second half of fermentation when carbon dioxide stripping effect is weaker. As a result, H_2S persists in the wine.

SO_2 management at the end of alcoholic fermentation: an underestimated critical point

An often overlooked cause of H_2S formation is the early addition of sulfur dioxide at the end of alcoholic fermentation. The enzymatic activities of fermenting yeast remain active for at least 10-15 days after the end of alcoholic fermentation. An addition of SO_2 during this phase activates the sulfite reductase pathway, a protective mechanism for yeast to transform toxic compounds into the more harmless H_2S .

This is the reason why, in presence of lees, it is recommended to wait at least two weeks before proceeding with adding sulfites.

EnartisStab MICRO M (antimicrobial preparation of specially activated chitosan designed for the treatment of cloudy wine) is an effective alternative to the early addition of SO_2 for protecting wine from spoilage microorganisms. **EnartisTan SLI** (ellagic tannin from untoasted American oak) can replace the antioxidant effect of SO_2 .

COMPOUNDS RESPONSIBLE FOR SULFUR OFF-AROMAS

Hydrogen sulfide (H_2S)

Among the sulfur compounds, H_2S is the most common and infamous sulfur off-aroma. H_2S has a low sensory threshold and an odor reminiscent of rotten eggs. While appropriate nutrition management is the best way to prevent excessive H_2S formation during fermentation, there are several approaches to remediating H_2S :

- H_2S is highly volatile and can be readily removed through sparging with inert gas.
- H_2S is easily oxidized, so aeration may also be used. However, oxidation can cause a loss of desirable S-containing compounds if done in excess, such as thiols critical to Sauvignon Blanc for example.
- Copper addition is a common practice for the removal of H_2S since the complexation of copper with this compound causes it to precipitate.

If H_2S is not removed quickly, it can result in the formation of more problematic sulfur containing compounds, mercaptans.

Mercaptans

This is a large group of very pungent sulfur compounds among which ethyl and methyl mercaptan are the most well-known. In the presence of methyl and ethyl mercaptan, aeration should not be attempted.

Mercaptans are readily oxidized to form other less-potent compounds, e.g. to their corresponding disulfides, which are significantly harder to remove. Mercaptans can be removed to some extent with appropriate copper additions, though this operation has been found to be only about half as efficient as H_2S removal. The reaction should form an insoluble copper salt that can be filtered from wine (see further).

Disulfides

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 increases their sensory threshold and changes their ability to bind to copper. Therefore, while mercaptans react with copper, their oxidized form cannot react with copper sulfate.

Disulfides can be reduced back to mercaptans, then can be removed by copper. This is the main concept of using ascorbic acid in combination with copper sulfate or copper citrate as a treatment. Disulfides are first reduced with the addition of 50 mg/L or more of ascorbic acid, immediately followed by an appropriate addition of copper. This reaction can take a couple of months and it is important that free SO_2 levels are adequate before adding ascorbic acid, which can increase the potential for wine oxidation.

Main sulfur off-aroma compounds in wine

Sulfur compound		Aroma	Threshold
Hydrogen sulfide (H_2S)		Rotten eggs, sewer gas	0.5 ppb
Mercaptans	Methyl mercaptan	Rotten cabbage	1 ppb
	Ethyl mercaptan	Burnt match, earthy	0.02 - 2 ppb
Disulfides	Dimethyl disulfide (DMDS)	Onions, cooked cabbage	15 - 30 ppb
	Diethyl Disulfide (DEDS)	Burnt rubber, garlic	4 ppb

How to recognize the cause of sulfur off-aromas

The best way to assess the problem is sensory screening before deciding on further treatment.

A simple trial consists of taking a wine with sulfur off-aroma, pouring it into 4 glasses where one glass is the

control, copper sulfate is added to the second glass, EnartisTan ELEVAGE is added to the third glass and the fourth glass is treated with ascorbic acid and EnartisTan ELEVAGE. Interpretation of the results is given in the table here below.

Control	Copper sulfate (2 g/hL of copper)	EnartisTan ELEVAGE 2 g/hL	Ascorbic acid (5 g/hL) + EnartisTan ELEVAGE (2 g/hL)	Interpretation
Sulfur off-aroma	Off-odor disappears	Off-odor is still there	Off-odor is still there	H_2S
	Off-odor disappears	Off-odor disappears	Off-odor is still there	Mercaptans
	Off-odor is still there	Off-odor is still there	Off-odor disappears	Disulfides

WHAT TREATMENTS ARE AVAILABLE?

Aeration

Aeration can contribute to the volatilization of H_2S . Furthermore, exposure to oxygen will lead to the transformation of low sensory threshold mercaptans to less pungent disulfides. This might initially appear to improve organoleptic qualities, but as mentioned before, disulfides can be hard to remove and still impart off aromas. 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

Copper is commonly used in the treatment of reductive characters. It reacts with H_2S and certain mercaptans but does not react with disulfides. 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 oxidation reactions, leading to premature ageing, as well as the formation of cupric haze.

Recent studies have shown that, contrary to conventional wisdom, copper-sulfide complexes are not readily removed by racking and can even pass through some types of filtration. Moreover, these complexes can recycle bound sulfur compounds over time, revealing sulfur off-aromas post bottling.

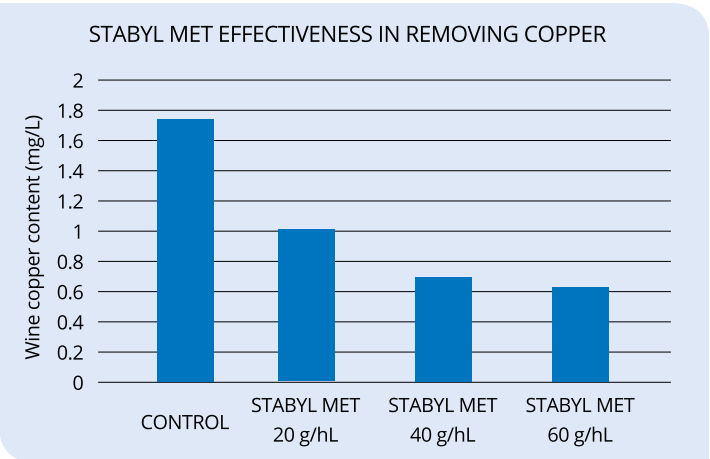
In order to minimize the risk of residual copper, it is recommended to use a fining mixture containing copper like **REVELAROM** as a corrective and preventive for sulfur aromas. The specific combination of organic and inorganic fining agents present in its formulation helps to effectively remove the copper-mercaptan complex and prevent residual copper accumulation in finished wines.

In the event of high residual copper, there are several options for removal. Among them:

Bentonite fining (**PLUXCOMPACT**) and yeast hulls (**SURLI ONE**) can help remove small amounts of copper, between 0.1-0.2 mg/L.

CLARIL HM is a product made of co-polymer of polyvinylimidazole and polyvinylpyrrolidone (PVI/PVP) and chitosan. PVI/PVP is an adsorbent with high selectivity for metals. Its application in winemaking is mainly due to its ability to remove copper and iron. Chitosan reinforces PVI/PVP's effect, especially towards copper.

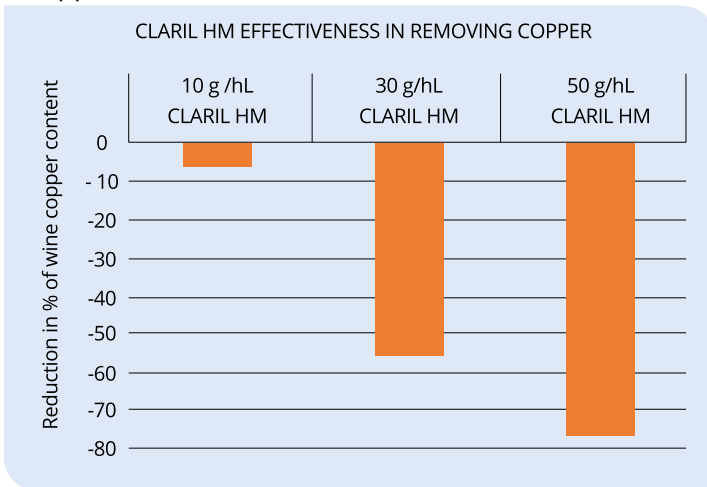
STABYL MET is a product made of co-polymer of polyvinylimidazole and polyvinylpyrrolidone (PVI/PVP) and silica. PVI/PVP is an adsorbent with high selectivity for metals. It can remove up to 50% of Cu^+ and up to 30% of Fe^+ . STABYL MET is easy to handle and remove from wine, as it is not soluble and settles quickly.



Tannin Addition

The addition of tannins, especially ellagic and condensed tannins, can bind and react with mercaptans to form odorless complexes. These complexes are very stable over time and do not entail the post-bottling risk of sulfur off-aroma appearance.

EnartisTan ELEVAGE (ellagic tannin obtained from light-toasted French oak), **EnartisTan SLI** (ellagic tannin from untoasted American oak) and **EnartisTan CŒUR DE CHÊNE** (ellagic tannin from toasted French oak) are very effective in scavenging mercaptans and can successfully replace the addition of copper prior to bottling. **EnartisTan MAX NATURE** (condensed tannin extracted from exotic species wood) is another option particularly recommended for treating easy-to-drink, light wines.



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