

ENARTIS NEWS

REDUCTION: HOW TO PREVENT IT AND HOW TO TREAT IT

Reduction is one of the most common problems in winemaking. Hydrogen sulphide and other volatile sulphur-containing compounds (VSC) are generally produced during alcoholic fermentation, but can also develop during wine storage, ageing, and post bottling. The aromas generated by these sulphur 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 character. Their presence, when close to or above the sensory threshold, decreases wine aromatic quality. For this reason, it is important to know how to prevent or treat this defect during the different stages of winemaking.

ORIGIN OF REDUCTION

Alcoholic fermentation: the beginning of reduction

Production of sulphur off-aromas begins during alcoholic fermentation.

The first mechanism is related to the **synthesis of amino acids**. Yeast produces hydrogen sulphide (H_2S) as a normal step in the synthesis of sulphur-containing amino acids. This explains why accumulation of H_2S often occurs in cases of nutrient deficiency 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 sulphur to H_2S** . Elemental sulphur is commonly sprayed in the vineyard to control powdery mildew. Formation of H_2S from S-residues cannot be corrected by nutrient addition and is much less dependent on yeast genetic. H_2S is usually formed from S-residues in the second half of the fermentation, when carbon dioxide stripping effect is weaker. As a result, H_2S persist in the wine.

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

Another often overlooked cause of H_2S formation is the early addition of sulphur dioxide at the end of alcoholic fermentation. The enzymatic activities of the fermenting yeast remain active for at least 10-15 days after the end of alcoholic fermentation. An addition of SO_2 in this phase activates the sulphite reductase pathway, a protective mechanism for yeast

to transform toxic compound 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 sulphites.

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

COMPOUNDS RESPONSIBLE OF SULPHUR OFF-AROMAS

Hydrogen sulphide (H_2S)

Of the sulphur compounds, H_2S is the most common and infamous sulphur off-aroma. H_2S has a low sensory threshold and an odour reminiscent of rotten eggs. While appropriate nutrition management is the best way to prevent excessive H_2S formation during fermentation, in addition, 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 oxidised, so aeration may also be used. However, oxidation can cause a loss of desirable S-containing compounds if done to 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 formation of the more problematic sulphur containing compounds, mercaptans.

Mercaptans

This is a large group of very pungent sulphur 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 oxidised to form other less-potent compounds, e.g. to their corresponding disulphides, 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 the wine (see further).

Disulphides

Mercaptans can oxidise to form disulphides 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 disulphides increases their sensory threshold and changes their ability to bind to copper. Therefore, while mercaptans react with copper, their oxidised form cannot react with copper sulphate.

Disulphides can be reduced back to mercaptans, and

then can be removed by copper. This is the main concept of using ascorbic acid in combination with copper sulphate or copper citrate as a treatment. Disulphides 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 to make sure that free SO₂ levels are adequate before adding ascorbic acid, which can increase the potential for wine oxidation.

Main sulphur off-aroma compounds in wine

Sulphur compound		Aroma	Threshold
Hydrogen sulphide (H ₂ S)		Rotten eggs, sewer gas	0,5 ppb
Mercaptans	Methyl mercaptan	Rotten cabbage	1 ppb
	Ethyl mercaptan	Burnt match, earthy	0.02 - 2 ppb
Disulphides	Dimethyl disulphide (DMDS)	Onions, cooked cabbage	15 - 30 ppb
	Diethyl Disulphide (DEDS)	Burnt rubber, garlic	4 ppb

How to recognise the cause of sulphur off-aroma

The best way to assess the problem is to run an aroma screen before deciding on further treatment.

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

is the control, copper sulphate 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. The interpretation of the results is given in the table here below.

Control	Copper sulphate (2 g/hL of copper)	Enartis Tan Elevage 2 g/hL	Ascorbic acid (5 g/hL) + Enartis Tan Elevage (2 g/hL)	Interpretation
Sulphur off-aroma	Off-odour disappears	Off-odour is still there	Off-odour is still there	H ₂ S
	Off-odour disappears	Off-odour disappears		Mercaptans
	Off-odour is still there	Off-odour is still there	Off-odour disappears	Disulphides

WHAT TREATMENTS ARE AVAILABLE?

Aeration

Aeration can contribute to the volatilization of H₂S. Furthermore, exposure to oxygen will lead to the transformation of low sensory threshold mercaptans to less pungent disulphides. This might initially appear to improve organoleptic qualities, but as mentioned before, disulphides can be hard to remove and still impart off aroma. To avoid oxidation of these sulphur compounds when attempting to remove H₂S 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 H₂S and certain mercaptans but does not react with disulphides. 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 catalyse oxidation reactions, leading to premature ageing, as well as the formation of cupric haze.

Recent studies pointed out that, contrary to conventional wisdom, copper-sulphide complexes are not readily removed by racking and can even pass through some types of filtration. Moreover, these complexes can recycle bound sulphur compounds over time, revealing sulphur off-aromas post bottling. To minimize the risk of residual copper, it is recommended to use a fining mixture containing copper like Revelarom as a curative and preventive for sulphur aroma. The special 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 a high residual copper, there are several options for removal. Among them:

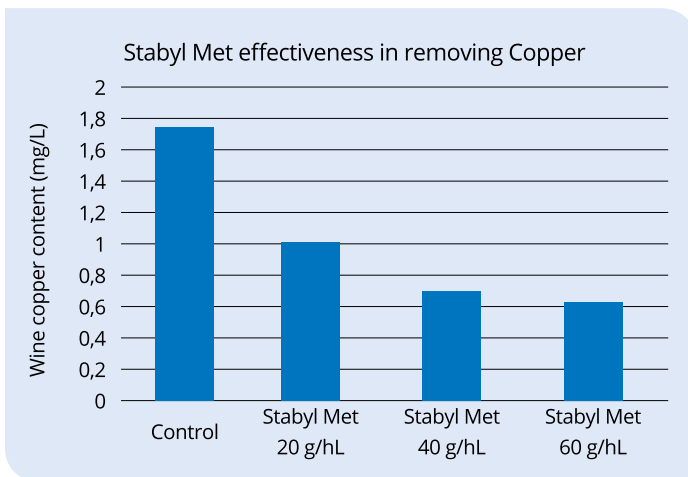
Bentonite fining (**Pluxcompact**) and yeast hulls (**Surli Natural**) can help remove small amounts of copper between 0.1-0.2 mg/L

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 eliminate from wine, as it is not soluble and settles very fast.

Tannin Addition

The addition of tannins, especially ellagic and condensed tannins, can bind and react with mercaptans to form odourless complexes. These complexes are very stable over time and do not entail the risk post bottling sulphur 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.



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