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ENARTIS NEWS

PREVENTION AND TREATMENT OF REDUCTIVE AROMAS

Reduction is one of the most common problems in winemaking. Hydrogen sulfide and other volatile sulfur-containing compounds are generally produced during alcoholic fermentation, but they can also develop during wine 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. 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 and treat this defect during the different stages of winemaking.

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 as a normal step in the synthesis of sulfur-containing amino acids. This explains why accumulation of H₂S often occurs in cases of nutrient deficiency associated with amino acid production, such as low available nitrogen or shortage of pantothenic acid and pyridoxine, cofactors in the synthesis of methionine. Genetic differences associated with amino acid production explain why some yeast

strains are reported to be low, medium or high H₂S producers.

A second mechanism is the **transformation of elemental sulfur (S) to H₂S**. Elemental sulfur is commonly sprayed in vineyards to control powdery mildew. Formation of H₂S from S-residues cannot be corrected by nutrient additions and is much less dependent on yeast genetics. H₂S is usually formed from S-residues in the second half of fermentation when the carbon dioxide stripping effect is weaker. As a result, H₂S is stuck in wine.

SO₂ MANAGEMENT AT THE END OF ALCOHOLIC FERMENTATION: UNDERESTIMATED CRITICAL POINT

Another often underestimated cause of hydrogen sulfide formation is the early addition of sulfur 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 SO₂ in this phase activates the sulfite reductase activity that turns the toxic compound into the more harmless H₂S. This is the reason why, in presence of lees, it is

recommended to wait at least two weeks before proceeding with sulfiting.

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 SO₂ for protecting wine from spoilage organisms. **EnartisTan SLI** (ellagic tannin from untoasted American oak) can replace the SO₂ antioxidant effect.

COMPOUNDS RESPONSIBLE OF SULFUR OFF-AROMAS

H₂S

Of the sulfur compounds, H₂S is the most common and probably the most familiar. Hydrogen sulfide has a low sensory threshold and an odor similar to rotten eggs. While appropriate nutrition management is the best way to prevent excessive H₂S formation during fermentation, in addition, there are several approaches to removing H₂S:

- H₂S is highly volatile and can be readily removed through sparging with inert gas.
- H₂S is easily oxidized, 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 H₂S since the complexation of copper with this compound causes it to precipitate.

If H₂S is not removed quickly, it can result in mercaptan production.

Mercaptans

This is a large group of very smelly sulfur compounds among which ethyl mercaptan 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 H₂S removal. The reaction should form an insoluble copper salt that can be filtered from the 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 doesn't.

Disulfides can be reduced back to mercaptans, then bound with copper. This is the main concept of using ascorbic acid in combination with copper sulphate 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 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 SULFUR OFF-AROMA COMPOUNDS IN WINE

Sulfur compound		Aroma	Threshold
Hydrogen sulfide (H ₂ S)		Rotten eggs, sewer gas	0.5 ppb
Mercaptans	Methyl mercaptan	Rotten cabbage	1 ppb
	Ethyl mercaptan	Burnt match, earthy	0.02 - 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 to run an aroma screen 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 sulphate is added to the second

glass, EnartisTan SLI is added to the third glass and the fourth glass is treated with ascorbic acid and EnartisTan SLI. The interpretation of the results is given in the table here below.

Control	Copper sulphate 0.2 g/hL	Enartis Tan SLI 2 g/hL	Ascorbic acid (5 g/hL) + Enartis Tan SLI (2 g/hL)	Interpretation
Stinky wine	Off-odor disappears	Off-odor is still present	Off-odor is still present	H ₂ S
	Off-odor disappears	Off-odor disappears	Off-odor is still present	Mercaptans
	Off-odor is still present	Off-odor is still present	Off-odor disappears	Disulfides

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 higher sensory disulfides. This might initially appear to improve organoleptic qualities, but as mentioned before, disulfides can be hard to remove. To avoid oxidation of these sulfur 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 hydrogen sulfide (H₂S) and certain mercaptans but doesn't have an effect on 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 reactions of oxidation leading to premature ageing, as well as the formation of copper haze.

Recent studies pointed out that, contrary to conventional wisdom, copper-mercaptan complexes are not readily removed by racking or filtration and remain in the wine. Moreover these complexes are reversible and may be responsible for sulfur off-aroma appearance after bottling.

In order to minimize the risk of copper residue, it is recommended to use a fining mixture containing copper like **Revelarom** as a curative and preventive for sulfur aroma. The special combination of organic and inorganic fining agents present in its formulation helps to effectively remove the copper-mercaptan complex and prevent wine enrichment in copper. 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.

Adsorption

Disulfides can be partially removed by steam-activated carbon. Despite carbon has been shown to bind diethyl sulfide, it is a non-specific adsorptive agent that can remove also positive aromatic compounds and negatively affect over-all wine quality. Moreover, its addition can cause oxidation because its pores contain a great quantity of air.



Better results can be obtained by using adsorptive compounds more respectful of wine quality like yeast hulls and activated chitosan. The yeast derivative contained in **Surli Natural** has a good adsorbing ability with disulfides. It eliminates these compounds over time and for this reason is suggested for treating wines that will be aged for at least one month more. Activated chitosan **EnartisStab Micro M** seems to have an immediate effect and can be used as a fining agent in wines that need to be treated prior to bottling.

Tannin addition

The addition of tannins, especially ellagic tannins, has the ability to bind with mercaptans and form odorless complexes. These complexes are very stable over time and do not entail the risk of a later sulfur off-aroma appearance. **EnartisTan SLI** (ellagic tannin from untoasted American oak) and **TanCoeur de Chêne** (ellagic tannin from toasted French oak) are very effective in scavenging mercaptans and can successfully replace the addition of copper also before bottling.

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