# ENARTIS NEWS

## PREVENTION AND TREATMENT OF REDUCTIVE AROMAS

Reduction is one of the most common problems in winemaking. Hydrogen sulphide and other volatile sulphur-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 sulphur 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 or treat this defect during the different stages of winemaking.

## 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 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 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 or high $H_2S$ producers.

A second mechanism is the ***transformation of elemental sulphur (S) 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, $H_2S$ is stuck in the wine.

## $SO_2$ MANAGEMENT AT THE END OF ALCOHOLIC FERMENTATION: UNDERESTIMATED CRITICAL POINT

Another often underestimated cause of hydrogen sulphide 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 activity that turns the 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 the sulphitation.

**Enartis Stab 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. **Enartis Tan SLI** (ellagic tannin from untoasted American oak) can replace the $SO_2$ antioxidant effect.

## COMPOUNDS RESPONSIBLE OF SULPHUR OFF-AROMAS

### $H_2S$

Of the sulphur compounds, $H_2S$ is the most common and probably the most familiar. Hydrogen sulphide has a low sensory threshold and an odour similar to 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 removing $H_2S$:

- $H_2S$ 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 mercaptan production.

### Mercaptans

This is a large group of very smelly sulphur 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 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 doesn't.

Disulphides 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. Disulphides are first reduced with the addition of 50mg/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 $SO_2$ 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 ($H_2S$) | | Rotten eggs, sewer gas | 0,5 ppb |
| Mercaptans | Methyl mercaptan | Rotten cabbage | 1 ppb |
| | Ethyl mercaptan | Burnt match, earthy | 0,02 - ppb |
| Disulphides | Dimethyl disulphide (DMDS) | Onions, cooked cabbage | 15-30 ppb |
| | Diethyl disulphide (DEDS) | Burnet 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, Enartis Tan Elevage is added to the third glass and the fourth glass is treated with ascorbic acid and Enartis Tan 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** |
|---|---|---|---|---|
| Stinky wine | **Off-odour dissappears** | Off-odour is still here | Off-odour is still here | H2S |
| | **Off-odour disappears** | **Off-odour disappe-ars** | | Mercaptans |
| | Off-odour is still here | Off-odour is still here | **Off-odour disappears** | Disulphides |

## WHAT TREATMENTS ARE AVAILABLE?

### Aeration

Aeration can contribute to the volatilisation of $H_2S$. Furthermore, exposure to oxygen will lead to the transformation of low sensory threshold mercaptans to higher sensory disulphides. This might initially appear to improve organoleptic qualities, but as mentioned before, disulphides can be hard to remove. To avoid oxidation of these sulphur compounds when attempting to remove $H_2S$ with aeration, use an inert gas like nitrogen and be aware of the volatilisation of other positive volatile aromas.

### Copper

Copper is commonly used in the treatment of reductive characters. It reacts with hydrogen sulphide ($H_2S$) and certain mercaptans but doesn't have an effect on 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 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 sulphur off-aroma appearance after bottling.
In order to minimise the risk of copper residue, 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 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 (**Surlì One**) 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, has the ability to bind with mercaptans and form odourless complexes. These complexes are very stable over time and do not entail the risk of a later sulphur off-aroma appearance. **Enartis Tan Elevage** (ellagic tannin obtained from light-toasted French oak), **Tan SLI** (ellagic tannin from untoasted American oak) and **Tan Cœur 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. Enartis **Tan Max Nature** (condensed tannin extracted from exotic wood) is another option particularly recommended for treating easy-to-drink, light wines.