FOCUS ON H_2S: PART 3

THE EFFECT OF pH AND COPPER ON THE FORMATION OF H_2S POST-BOTTLING

Dr. Carien Coetzee

Basic Wine

20 May 2020

As described in Part 1 and 2 of this *Focus on H_2S* series, **copper (Cu^{2+}) plays an important role in post-bottling formation of hydrogen sulfide (H_2S)**. Follow-up blog posts will delve deeper into **winemaking parameters** and their role in the accumulation of H_2S (especially in the presence of Cu^{2+}) during storage/ageing of wine. It is recommended to first read through Part 1 and 2 before continuing with the current blog post as it will provide important background information.

Wine pH has the potential to influence many chemical reactions in wine and it is an important parameter in nearly all aspects of winemaking, including protection against microbial spoilage, colour

stability, tartrate precipitation and wine aroma and flavour. A study titled, "The effects of pH and copper on the formation of volatile sulfur compounds in Chardonnay and Shiraz wines post-bottling[1]" aimed to determine whether **wine pH had a significant effect on the formation of reductive aroma** post-bottling. Part 3 of this blog series will report on some of the main findings of this study focussing on how the pH of the wine and the **interaction between the wine pH and Cu^{2+}** influence H_2S accumulation.

MATERIALS AND METHODS

One white and one red wine (produced in Australia) was used in the study. No copper additions were made during the winemaking process. The treatments were as follows:

White wine

1) pH 3.46 unchanged – no Cu^{2+}
2) pH 3.46 unchanged – 0.5 mg/L Cu^{2+}
3) pH adjusted to 3.00 – no Cu^{2+}
4) pH adjusted to 3.00 – 0.5 mg/L Cu^{2+}

Red wine

1) pH 3.72 unchanged – no Cu^{2+}
2) pH 3.72 unchanged – 0.5 mg/L Cu^{2+}
3) pH adjusted to 3.00 – no Cu^{2+}
4) pH adjusted to 3.00 – 0.5 mg/L Cu^{2+}

The H_2S content was analysed at day zero (directly after Cu^{2+} addition) and then after one month, three months and six months. The wines were stored under low oxygen conditions.

RESULTS

WHITE WINE

No Cu^{2+}

- After **six** months' storage, the **"no Cu^{2+}"** treatments showed a slight increase in H_2S (**less than 3 µg/L**). This was seen for **both pH levels** tested.

0.5 mg/L Cu^{2+} added

- The addition of 0.5 mg/L **Cu^{2+} resulted in significant increases in H_2S** after **three** month's storage. An increase of 43 µg/L and 15 µg/L were reported for pH 3.46 and pH 3.00 respectively. Therefore, after three months, the **higher pH wine resulted in much higher H_2S content compared to the lower pH wine.**
- After **six** months, the concentration of H_2S at pH 3.46 decreased from the 43 µg/L (observed after three months) to 27 µg/L. At pH 3.00, the H_2S increased from 15 µg/L (observed after three months) to 19 µg/L.

RED WINE

No Cu^{2+}

- During the entire **six months' storage**, the **"no Cu^{2+}"** treatments only showed a slight increase in H_2S (**less than 3 µg/L**). This was seen for both pH levels tested.

0.5 mg/L Cu^{2+} added

- The addition of 0.5 µg/L **Cu^{2+} resulted in significant increases in H_2S** after three month's storage. An increase of around 23 µg/L was reported for both pH 3.46 and pH 3.00.
- After six months, the variability of the results does not allow meaningful conclusions and will not be considered further.

THE EFFECT OF ADDED COPPER

The **presence of Cu^{2+} in the white and red wine samples (at either pH) clearly had a profound impact on the formation of H_2S** during the storage period. The H_2S concentrations were **consistently significantly higher** in wines with added copper than in wines without copper during the six months

post-treatment. The effect of Cu^{2+} on the formation of post-bottling H_2S has been reported before[2,3] and mechanisms involved are discussed in Part 1 and 2 of this series.

THE EFFECT OF pH

The influence of wine pH on H_2S formation was only observed in samples that were also treated with Cu^{2+}. In samples **without** added Cu^{2+}, the **pH did not affect** the amount of H_2S produced post-bottling.

For the white wine to which Cu^{2+} were added, the **lower pH resulted in lower formation (on average 51% less) of H_2S**.

The effects of pH and copper on H_2S formation in the red wines were not as pronounced as in the white wines, with significant **decreasing effects of lower pH levels only measured directly after treatment and again after a month post-treatment**.

After one month, the H_2S concentration in the **lower pH red wine was slightly lower** (6 µg/L) compared to the higher pH red wine (10 µg/L). After three months, the difference in H_2S concentration between the two red wine pH treatments was negligible.

The different effects observed between the red wines and white wines is likely due to the differing nature of the wines' matrix components.

HOW pH AND Cu^{2+} AFFECT H_2S

The **influence of the interaction between pH and Cu^{2+} are clear**, however, the mechanisms involved are not so simple. Without going into too much detail, some explanation is provided:

The differences in **particle size and concentration of copper-tartrate complexes** (see Part 1) suggests that **various types of copper-tartrate complexes are produced at varying pH levels**. **Lower pH decreased copper-tartrate complex size and lower particle concentrations were measured** when compared to copper-tartrate complexes produced at higher pH. **This may affect the binding sites of Cu^{2+} that are available to either catalyse the formation of H_2S or bind the H_2S produced to form CuS complexes**. This may explain some of the pH-related effects observed in these experiments.

CONCLUSION

In Part 1 and Part 2 of this *Focus on* H_2S series, the role of copper in the formation of H_2S is explained. We now start to look at **winemaking parameters (such as pH) and how they can modulate the formation of H_2S.**

The two **main findings** of this study are

1) **The post-bottling formation of H_2S was significantly affected by elevated copper concentrations**
2) **The effects of added copper on H_2S formation were decreased when the wine pH was lowered**

Wine pH thus significantly affects H_2S formation when elevated residual Cu^{2+} is present. This indicates that less H_2S was produced through copper-catalysed reactions in wines at a lower pH than in wines at a higher pH level.

In a complex matrix such as wine, the ability to control parameters can be an extremely valuable tool. Winemakers can **manage wine pH by adjusting the acid content** and the decision to add copper (through copper sulfate fining) is at their discretion. **These are two controllable parameters which have been proven to significantly influence H_2S formation post-bottling**. It is recommended that winemakers consider the effect of copper and pH in their role in the modulation of H_2S formation.

Part 4 of this *Focus on H_2S* series will look at sulphur dioxide and the interactive effect with copper on the role of post-bottling H_2S accumulation.

REFERENCES

(1) Bekker, M. Z.; Mierczynska-Vasilev, A.; Smith, P. A.; Wilkes, E. N. The Effects of PH and Copper on the Formation of Volatile Sulfur Compounds in Chardonnay and Shiraz Wines Post-Bottling. *Food Chem.* **2016**, *207*, 148–156. https://doi.org/10.1016/j.foodchem.2016.03.060.

(2) Ugliano, M.; Kwiatkowski, M.; Vidal, S.; Capone, D.; Siebert, T.; Dieval, J.-B.; Aagaard, O.; Waters, E. J. Evolution of 3-Mercaptohexanol, Hydrogen Sulfide, and Methyl Mercaptan during Bottle Storage of Sauvignon Blanc Wines. Effect of Glutathione, Copper, Oxygen Exposure, and Closure-Derived Oxygen. *J. Agric. Food Chem.* **2011**, *59* (6), 2564–2572. https://doi.org/10.1021/jf1043585.

(3) Viviers, M. Z.; Smith, M. E.; Wilkes, E.; Smith, P. Effects of Five Metals on the Evolution of Hydrogen Sulfide, Methanethiol, and Dimethyl Sulfide during Anaerobic Storage of Chardonnay and Shiraz Wines. *J. Agric. Food Chem.* **2013**, *61* (50), 12385–12396. https://doi.org/10.1021/jf403422x.