FOCUS ON H_2S: PART 4

COPPER AND SO_2 USED TOGETHER – EFFECT ON H_2S

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The mechanisms involved in the formation of hydrogen sulfide (H_2S) post-bottling are not yet as well defined as those involved during fermentation. However, recently researchers have been investigating **key factors affecting H_2S concentration** after fermentation and many of the findings are summarised and presented in this blog series (see Part 1, 2 and 3) covering post-bottling H_2S formation.

The use of **copper (Cu^{2+}) and sulphur dioxide (SO_2)** as wine additives are not uncommon in the wine industry and can often be found to be present in the wine at the same time. The **interactive effects between these two compounds are not something that is often considered** and it is of critical

importance that the winemaker understands the **potential outcomes when the additives are used together.**

In the current blog post, the **interactive effects of Cu^{2+} and SO_2 and the effect on H_2S concentration** will be addressed. The original research paper titled "Formation of Hydrogen Sulfide in Wine: Interactions between Copper and Sulfur Dioxide", is published in an open-access journal and can be viewed here.

MATERIALS AND METHODS

Two wines, one white and one red were obtained from an Australian winery. Neither of these wines was treated with SO_2 or Cu^{2+} during the winemaking process.

The wines were placed in 20 mL crimp top vials and the following additions were made "at bottling":

1) **Control**
   - no additions
2) **Cu^{2+}**
   - 1 mg/L Cu^{2+} added
3) **SO_2**
   - 100 mg/L SO_2 added
4) **Cu^{2+} and SO_2**
   - 1 mg/L Cu^{2+} and 100 mg/L SO_2 added

The samples were stored at 20°C under nitrogen to prevent any oxygen exposure.

RESULTS

H_2S formation in the Control samples (blue line)

- For both the white and red wine control samples, there was **no significant increase** in H_2S concentration (Figure 1). The largest increase observed was for the white wine where an increase of 0.9 µg/L (which is quite low) was observed after six months of storage.

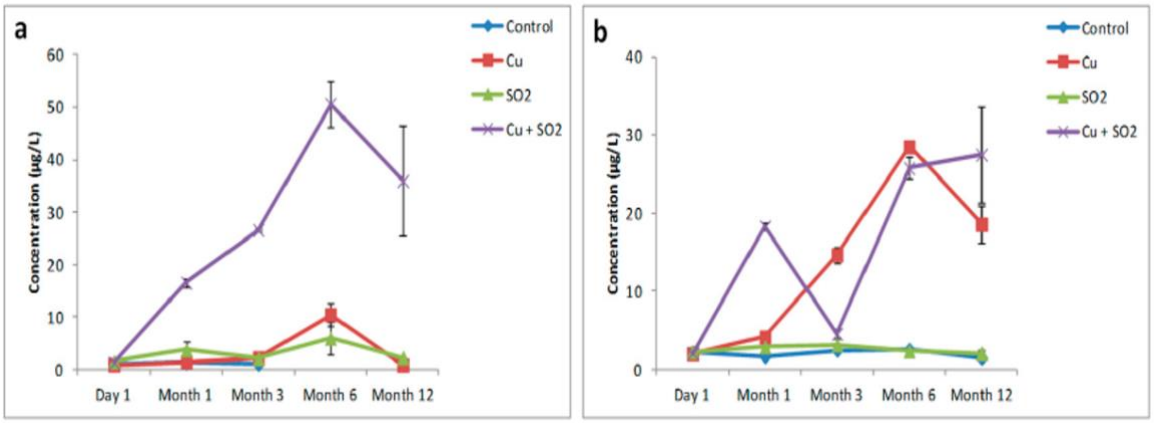

Figure 1. The effects of the treatments on the formation of H_2S over 12 months in (a) white wine and (b) red wine. Adjusted from Bekker *et al.,* 2016[1]. View permissions.

The effect of Cu^{2+} addition on H_2S formation (pink line)

- For the white wine sample, an **increase in H_2S concentration was observed after six months** of storage (from 1 µg/L to 11 µg/L) (Figure 1(a)). However, the concentration decreased again after 12 months of storage ending in a concentration similar to the starting concentration of 1 µg/L. For the most part, the presence of Cu^{2+} alone in the white wine sample did not result in the accumulation of H_2S.

- In the red wine sample, a **significant constant increase in H_2S formation was observed from zero to six months** (from 2 µg/L to 29 µg/L) followed by a decrease in H_2S concentration from six to 12 months ending at 12 µg/L (Figure 1(b)).
  In this case, the **addition of Cu^{2+} alone had a significant effect on the formation of H_2S.**

The effect of SO_2 addition on H_2S formation (green line)

- For both the white and red wine samples, the **addition of SO_2 alone had no significant effect** on the formation of H_2S after 12 months of storage (Figure 1).

The effect of simultaneous addition of Cu^{2+} and SO_2 on H_2S formation (purple line)

- In the white wine sample, the **combination of Cu^{2+} and SO_2 resulted in a significant and large increase in H_2S content**. After one month's storage, the concentration already increased from

1 µg/L to 17 µg/L (Figure 1 (a)). The concentration then increased further to 27 µg/L and 51 µg/L after three and six months, respectively. After 12 months, the concentration decreased to 36 µg/L which is still a significant concentration likely to alter the aroma perception of the wine.

- In the red wine sample, an **increase in H_2S was also observed**. **The concentration increased relatively quickly compared to when Cu^{2+} was added alone**, already reaching 18 µg/L after one month's storage (Figure 1 (b)). After six and 12 months, the concentration increased further to 26 µg/L and 27 µg/L, respectively.

It is clear that the **addition of a combination of Cu^{2+} and SO_2 "at bottling" resulted in significant H_2S increases** for both the white and red wines tested. The increase observed in these samples was also much faster with a large increase of H_2S already after one month of storage.

INTERACTIVE EFFECTS EXPLAINED

The question is: **why is H_2S formed post-bottling, and how does Cu^{2+} and SO_2 influence this formation**? Unfortunately, the answer is not simple and the exact mechanisms involved in the formation of latent H_2S formation is still unclear, however, some possible mechanisms are explained in Part 2 of this series.

However, what we do know is that **oxygen exposure limits the formation of H_2S post-bottling**[2–4]. The basic reaction involves the oxidation of certain wine compounds, such as phenolics, leading to the formation of reactive compounds such as *o*-quinones. These *o*-quinones react readily to various wine constituents, but **especially to sulphur containing compounds such as SO_2, H_2S and even the fruity volatile thiols.**

Through reacting with the *o*-quinone, the inherent properties of the compounds are changed often accompanied by the **removal of the aroma**. For instance, when an *o*-quinone reacts with SO_2, it will result in the formation of a hydroxysulphonate and form part of the total SO_2 content. The ***o*-quinone will also react readily to H_2S, binding the stinky compound and therefore effectively removing it (and the accompanying aroma) from the wine.**

The researchers delved deeper into the study by **investigating the reaction speed of SO_2 with *o*-quinones and comparing that to the reaction speed of H_2S** with *o*-quinones. They found that both

compounds technically react at the same speed. However, in a wine medium, **the concentration of the SO_2 present is much higher compared to H_2S**, therefore, there are **far more SO_2 molecules present which will quickly react with the *o*-quinones, leaving the H_2S unreacted and the aroma unchanged**.

Now let's consider the results found in the current study.

In the samples (both white and red wines) to **which Cu^{2+} and SO_2 were added "at bottling", latent H_2S formation took place** leading to an increase in the concentration. The fact that **SO_2 was present, means that any *o*-quinones formed at this stage immediately reacted with the abundance of available SO_2**. Therefore, **none of the *o*-quinones molecules was available for the reaction with H_2S resulting in the accumulation thereof. The presence of SO_2 thus *indirectly* caused an increase of H_2S.**

In **the absence of SO_2, the *o*-quinones formed, reacted with the H_2S in the wine medium** (perhaps even as H_2S is formed), **therefore reducing the concentration and preventing the accumulation of post-bottling H_2S. There might have been more *o*-quinones forming in the white wine which could explain the difference observed between the white and red wines.**

In principle, the **H_2S is preserved and protected by SO_2** (in the same way that it protects other positive aroma compounds). The **presence of SO_2 thus allows the accumulation of H_2S** and is thus not directly involved in the formation. It seems that Cu^{2+} and SO_2 operate independently on separate pathways, but the **effects of the additives are cumulative**, leading to increased H_2S concentration. It is important to note that in the samples to which only SO_2 were added, there was no H_2S accumulation. Therefore, as mentioned in the previous blogs in this series, the presence of Cu^{2+} is an integral part of the formation of post-bottling H_2S.

CAN SO_2 AND CU^{2+} FORM H_2S DIRECTLY?

Other than the **preservation of H_2S by SO_2**, another mechanism has been proposed previously[5,6] based on the *direct* formation of H_2S. This pathway involves the **formation of H_2S through the reduction of SO_2 by Cu^{2+}, however, the existence of this pathway in a real wine needs to be confirmed**.

A simple test was done to establish if this direct reaction is a realistic possibility[1]. The researchers of the study **added both Cu^{2+} and SO_2 to a model wine medium** and monitored the formation of H_2S. Results showed that **no H_2S was formed**. This could either mean that the reaction does not take place

in wine, or it could indicate the necessity of other wine constituents (absent in the model wine) needed for this reaction to occur.

CONCLUSION

The results reported in the study **suggests that when wines are produced without early Cu^{2+} and SO_2 additions but treated with these additives before bottling, an increase in H_2S may be observed post-bottling.**

The antioxidant and antimicrobial **benefits of SO_2 offsets the risk of developing reduced aromas**. And this study showed that even **late SO_2 additions close to bottling did not pose a risk of increased H_2S unless there was a high concentration of residual Cu^{2+} present in the wines.**

It is therefore critical that the winemaker limits the residual Cu^{2+} to a minimum in the finished wine.

REFERENCES AND PERMISSIONS

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