The ins and outs of a copper fining trial

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In the past few weeks, Vinlab has received quite a few enquiries regarding **copper fining trials** and recommendations. A *blog post* explaining sulphur off-odours has been published and further information is available in the *Vinlab manual* on page 72 and 125.

It is important to understand that **several** different compounds can produce a **reductive character** in wine, and that not all of them can react with and subsequently be removed by, copper. The best way to assess the problem is to do a step by step procedure to establish the **source of the problem** then determine the appropriate method to **fix** it.

Determine and treat the problem

To establish which of the reductive compounds are responsible for the off-odour, an experimental procedure needs to be followed that includes the use of chemical reagents such as **copper**, **cadmium** and **ascorbic acid**. This procedure can be found in the *Vinlab manual* on page 72.

If the problem is only H_2S:

- H_2S development **during fermentation** can usually be remedied by **aeration** and the addition of **nitrogen**-containing compounds. A small amount of **$CuSO_4$** can also be added at the very end of fermentation instead of DAP.
- If H_2S is present **after fermentation**, the wine should be racked to lightly aerate the wine. If the problem persists then the wine needs to be **fined with $CuSO_4$**.

If the problem is mono-mercaptans:

- The wine needs to be **fined with $CuSO_4$**. The reaction forms an insoluble copper mercaptide salt that can be filtered from the wine.
- Aeration should not be attempted under any circumstances. Mercaptans are readily oxidized to form disulfides, which are significantly harder to remove.

If the problem is disulphides:

- Ensure a **free SO_2** concentration of at least 20 mg/L, add 5 mg/L **ascorbic acid**, and allow to react for one day before fining with **$CuSO_4$.**

If wine fining with **$CuSO_4$** is proven to be the **solution to the problem**, then a **fining trial** must be performed to determine the **minimum concentration** at which the off-odour can be effectively **removed** without significantly increasing the **copper concentration** in the wine.

This blog post aims to aid the industry in conducting **small scale copper fining tests** in-house at the winery. Results from this test will determine whether the off-odour can be removed successfully using

$CuSO_4$ and if so, what the **optimum dosage** would be. *Vinlab* also offers these fining and testing services for the time-deprived producer!

Procedure for conducting a copper fining trial

1. For the copper fining trial, you need a 0.04% copper sulphate ($CuSO_4.5H_2O$) solution. This ready-made solution can be obtained from Vinlab. Please *contact us* to place an order.
2. Label five 100 mL volumetric flasks as shown in Table 1 (green).
3. Add the corresponding amount of 0.04% copper sulphate solution to the volumetric flasks (Table 1; blue). Note that *no* addition is made to the Control (flask 1).

Table 1. Labels and volume of 0.04% copper sulphate solution to add

Labels	1. Control	2. 0.25 mg/L Cu ions	3. 0.50 mg/L Cu ions	4. 0.75 mg/L Cu ions	5. 1.00 mg/L Cu ions
Volume of 0.04% $CuSO_4.5H_2O$ to add	0.00 mL	0.25 mL	0.50 mL	0.75 mL	1.00 mL

4. Add wine to all the flasks and bring to the 100 mL mark and mix well
5. Leave the flasks at room temperature for 24 hours. Be sure to properly close the container to limit air exposure.

⇨ If you do not have volumetric flasks, then you can use an alternative container. Be sure to leave as little as possible headspace and avoid using cling wrap which is porous and could result in the escape of the reductive aroma.

6. Evaluate the wine samples to test for improved aroma.
    - Only open the flasks when you are ready for the evaluation
        - The reductive aroma may volatilise from the wine sample if exposed to air for too long. This could lead to inaccurate (false positive) results. You can test this by sniffing the control first to be sure the reductive aroma is still present.
    - If possible, let an objective person also evaluate the wines without them knowing what the trial is about (blind tasting)
    - Be sure to mark your glasses with codes so not to get confused
    - Make notes

⇒ If **all** the experimental samples **still have the sulphur-related off-odours** this can mean one or more of the following:

- the odour is due to the presence of disulphides or poly-mercaptans which will not react with the copper (in this case the addition of ascorbic acid before copper could be considered with caution as there are some risks involved in this treatment)
- the odour is due to dimethyl sulphide which will not react with copper
- the odour is due to something other than the general reductive S-containing compounds (perhaps methoxypyrazines adding to the vegetative character)
- not enough copper was added to react with all the sulphides present in the wine (this is highly unlikely and would indicate extremely high levels of H_2S)

⇨ If one or more of the experimental glasses are **odour free** it means that the odour is probably caused by H_2S and mono-mercaptans. In this case, proceed to Step 7

7. Select the sample with the best combination of reduced off-odour and least amount of copper added
8. Write down the chosen sample as well as the copper ion concentration in that sample (Table 2). This is the concentration of **copper ions** that needs to be administered to the larger wine volume.
   ***Please note this is not the concentration of copper sulphate that needs to be administered. See explanation below*

Table 2. Concentration of copper ions in the sample

Labels	1. Control	2. 0.25 mg/L Cu ions	3. 0.50 mg/L Cu ions	4. 0.75 mg/L Cu ions	5. 1.00 mg/L Cu ions
Cu ion concentration	0.00 mg/L	0.25 mg/L	0.50 mg/L	0.75 mg/L	1.00 mg/L

Copper addition to large volume

After careful evaluation of the experimental samples the chosen dosage can be applied to the bigger wine volume. Take care that results from lab-scale trials do not always transfer directly to larger volumes of wine, so you will need to re-evaluate the wines after treatment and before conducting further cellar activities. Keep in mind that reactions may take longer to occur in the cellar than in the lab set-up, so allow extra time before determining whether sufficient copper has been added or whether additional additions should be made.
For larger scale copper additions, a 1% copper sulphate solution can be used or the correct weight of $CuSO_4.5H_2O$ can be dissolved into a smaller volume of wine before mixing into the larger volume. The correct amount copper sulphate to be added can be seen in the table below. This table uses the addition of 0.5 mg/L copper ions and two wine volumes as examples. The correct addition can be calculated from this table depending on the specific needs.
***it is important to note that 3.93 mg/L $CuSO_4.5H_2O$ results in 1 mg/L Cu^{2+} ions*

Table 2. Example of two different wine volumes to be treated using two different mediums (powder and solution) for a final copper ion concentration of 0.5 mg/L

Volume of wine to be treated (L)	**Weight of $CuSO_4.5H_2O$ powder added (g)**	**Volume of 1% $CuSO_4.5H_2O$ added (mL)**	**Cu^{2+} ion concentration in the final treated wine (mg/L)**
1000	1.965	196.5	0.5
10000	19.65	1965	0.5

The copper sulphate solution should be added while **gently stirring** the wine. After a couple of days, the wine can be evaluated for aroma improvement. It is a good idea to keep a few samples of the **untreated wine** (before copper addition) so you have the Control wine to compare the treated wine to. If the wine has improved sufficiently the wine can be **filtered** to remove the residual copper.

The copper content in the treated wines needs to be **tested again** to ensure that the wine complies with regulations. Please be aware that the acceptable concentration of copper in commercially available wine varies with jurisdiction.

A few things to keep in consideration

- ⇨ The best time to add copper is at the end of fermentation and could eliminate potential precursors before off-odour formation. At this stage a minimum concentration of copper can be added. Earlier addition is not advised as yeast cells can bind with copper and reduce effectiveness. Also, addition of copper during fermentation may promote H_2S production by yeast.

- ⇨ The reacted copper will be removed from the wine during racking. A small portion can remain in the wine and it is the producer's responsibility to test the chosen sample to ensure the copper concentration does not exceed 1.0 mg/L. The quickest and most effective means of analysis is measurement with an ICP (Inductively Coupled Plasma), which can be performed at *Vinlab*.

- ⇨ Other than human health risks, **excessive copper additions can lead to wine quality problems**. These problems include **haziness** due to copper casse formation, and is greatly increased if copper sulfate is added immediately prior to bottling, without allowing adequate time for the wine to stabilize during storage. Copper can also act as an **oxidation catalyst**, so excessive additions beyond that which can react with unwanted sulfur compounds can increase the risk of oxidation (and a loss in SO_2), especially in white wines. Copper will also not only react with the unwanted reductive aromas, but will **remove other positive aromas** such as the fruity volatile thiols especially when present in excess. For this reason, adding copper as a preventative (a practice observed increasingly with wines sealed under screwcaps) without probable cause is not advised.

References

Vinlab Manual
http://www.fruit.cornell.edu/shared/pdfs/SulfurOffOdor.pdf
https://www.extension.iastate.edu/wine/sites/www.extension.iastate.edu/files/wine/coppersulfatetrial1.pdf