Copper, the good, the bad, the ugly

Dr Eric Wilkes
Commercial Services
Why do we use copper at all?

- To get rid of the bad smells of course.
- Copper has a long history of use in beverage production to remove unpleasant sulfur related smells.
## What are these smells?

<table>
<thead>
<tr>
<th>Low MW Sulfur Compound</th>
<th>Odour Descriptor</th>
<th>Aroma Threshold (ug/L)</th>
<th>Detected (ug/L)</th>
<th>Literature Review</th>
<th>AWRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfide</td>
<td>rotten egg, sewage like</td>
<td>1</td>
<td>nd - 370</td>
<td>nd - 56</td>
<td></td>
</tr>
<tr>
<td>Methanethiol</td>
<td>rotten cabbage, burnt rubber, putrefacation</td>
<td>1.5</td>
<td>nd - 16</td>
<td>nd - 11</td>
<td></td>
</tr>
<tr>
<td>Ethanethiol</td>
<td>onion, rubbery, burnt match, sulfidy, earthy</td>
<td>1.5</td>
<td>nd - 50</td>
<td>nd - 3</td>
<td></td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td><em>blackcurrant</em>, cooked cabbage, asparagus, canned corn, molasses</td>
<td>25</td>
<td>nd - 474</td>
<td>nd - 980</td>
<td></td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td><em>sweet, ethereal, slight green</em>, rubber, sulfidy, chokingly repulsive</td>
<td>5</td>
<td>nd - 18</td>
<td>nd - 140</td>
<td></td>
</tr>
<tr>
<td>Diethyl sulfide</td>
<td>garlic, rubbery</td>
<td>1</td>
<td>nd - 10</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Methyl thioacetate</td>
<td>sulfurous, cheesy, egg</td>
<td>40</td>
<td>nd - 115</td>
<td>nd - 53</td>
<td></td>
</tr>
<tr>
<td>Dimethyl disulfide</td>
<td>vegetal, cabbage, intense onion-like (at high levels)</td>
<td>10</td>
<td>nd - 22</td>
<td>nd - 2</td>
<td></td>
</tr>
<tr>
<td>Ethyl thioacetate</td>
<td>sulfurous, garlic, onion</td>
<td>70</td>
<td>nd - 180</td>
<td>nd - 32</td>
<td></td>
</tr>
<tr>
<td>Diethyl disulfide</td>
<td>bad smelling, onion</td>
<td>4</td>
<td>nd - 85</td>
<td>nd - 1.5</td>
<td></td>
</tr>
</tbody>
</table>
It can be very effective.

\[
\begin{align*}
\text{H}_2\text{S} & \quad \text{H}_2\text{S} + \text{Cu}^{2+} \rightarrow \text{CuS} \\
\text{mercaptan} & \quad \text{CH}_3\text{CH}_2\text{SH} + \text{Cu}^{2+} \rightarrow \text{Cu(CH}_3\text{CH}_2\text{S)}_2 \\
\text{DMDS} & \quad \text{CH}_3\text{S-SCH}_3 + \text{Cu}^{2+} \rightarrow \text{unreactive} \\
\text{DMS} & \quad \text{CH}_3\text{SCH}_3 + \text{Cu}^{2+} \rightarrow \text{unreactive}
\end{align*}
\]
But why doesn’t it always work?

- Why does my wine go stinky again after it is treated in tank?
- Why don’t the bench trials always reflect what I see in tank?

It is all a question of *equilibrium*!
Its not quite as simple as you may think!

$$3\text{H}_2\text{S} + \text{CH}_3\text{C} = \text{O} \rightarrow 2 \text{CH}_3\text{CH} = \text{SH}$$

1-hydroxy-ethanethiol

Too Hard

intense rubbery or苏联y odour

cis/trans-4,7-dimethyl-1,2,3,5,6-pentathiepane
meat like aroma

cis/trans-3,6-dimethyl-1,2,4,5-tetrathiane
rubbery chemical aroma

bis(1-mercaptoethyl)sulfide

spicy meat, meat like or allium aroma
If only it was that simple!

**H₂S**
hydrogen sulfide
1 µg/L

Wine components

(CH₃OH or CH₃CHO)

methanethiol (mercaptan)
1.5 µg/L

Oxidised Sulfur compounds >10 µg/L

Methyl thioacetate
40 µg/L

 OSC

reduction oxidation acetylation hydrolysis
Myth busting!

All the copper I add drops out as insoluble sulfide!

Sulfide

1-2 μg/l
0.000002 g/l

Copper Sulfate

0.5ppm
0.0005 g/l

It is not unusual to see copper values increase at exactly the same rate as addition.
Downsides of residual copper

- Hazes
- Increased loss of 3-MH and 3-MHA
- More rapid loss of SO₂
- Increases in sulfides
Increased copper levels in bottled wine are well known to increase protein instability.

Generally recommended to keep levels below 0.5 ppm, but limit depends on the wine.
Increased loss of 3-MH and 3-MHA

3-MH (3-Mercaptohexan-1-ol)  3-MHA (3-Mercaptohexan-1-ol acetate)

Dr. Mandy Herbst-Johnstone
School of Chemical Sciences
The University of Auckland
More rapid loss of \( \text{SO}_2 \)

\( \text{SO}_2 \) cannot interact with \( \text{O}_2 \) directly. It requires the presence of metals such as copper and iron.

Increases in sulfides

After just 2 months this chardonnay was already showing the impact of increased copper.
While the MeSH has gone down, we don’t know where!
The H₂S seems to be maxing at typical copper levels.
Fining with Bentonite took the wine from 0.2 to 0.5 mg/L of Iron.

**Relationship between Cu/Fe and H$_2$S**

$R^2 = 0.9204$

Cu/Fe ratio critical to H$_2$S levels.

At really high copper levels other stuff happens.
Isn’t this just driven by the closure?

MeSH with time

For at least the first 2 years the differences are no greater than impact of metals in other trials

Average results for 9 different closures.

Final level does not correlate with closure OTR!

Pattern typical of what we see as the available O₂ / SO₂ environment changes.
How bad could it get??????

Clare Valley Riesling after 8 months.

Remember, the threshold for is about 1 for most people!
Why the differences between wines?

- No such thing as free copper in wine.
- It is all interacting in some way with the different species in wine.

- Some of these prevent copper getting involved in the oxidation/reduction chemistry.

- Others don’t!

- Incredibly important to tailor copper additions to the wine in question.

Never just make a standard addition!
The wines in front of you.

<table>
<thead>
<tr>
<th></th>
<th>Red Control</th>
<th>Wine 1</th>
<th>Wine 2</th>
<th>Wine 3</th>
<th>Wine 4</th>
<th>Wine 5</th>
<th>Wine 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon disulfide</td>
<td>2.0</td>
<td>2.0</td>
<td>2.3</td>
<td>1.6</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>73.7</td>
<td>87.0</td>
<td>65.7</td>
<td>21.0</td>
<td>21.0</td>
<td>21.0</td>
<td>21.0</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1.7</td>
<td>1.4</td>
<td>0.9</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>Methanethiol</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1.1</td>
<td>4.5</td>
<td>4.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Methyl thioacetate</td>
<td>6.4</td>
<td>7.4</td>
<td>6.7</td>
<td>7.4</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

**Graphs:**

**Red Wines**
- Carbon disulfide, Hydrogen sulfide, Methanethiol

**White Wines**
- Carbon disulfide, Hydrogen sulfide, Methanethiol
When is it ok to use copper?

- Best time to add is at the end of fermentation
  - Eliminate the potential precursors as early as possible
  - Use the solids to remove as much of the excess copper as possible

- If you have to do it later
  - Know what sulfur compounds you are treating (copper/cadmium test)
  - Add the minimum amount of copper.
  - Give it time to stabilize before bottling.
  - Test the copper levels before and after addition.

Never add on the day of bottling.
Copper can be incredibly effective in preventing the development of off sulfur characters.

However if excess is left in the wine it can lead to:
- the development of the same undesirable characters
- hazes
- degradation of SO$_2$ levels and desirable sulfur compounds

Copper is best added early in the wines life when fermentation solids can help to remove it.

Later additions can lead to a build up of available copper.

Not all copper is striped from wine post addition as sulfides.

Careful trials can lead to successful management of copper levels.
Acknowledgements

- Paul Smith
- Marlize Viviers
- Mark Smith
- Martin Day
- Mandy Herbst-Johnstone (Uni of Auckland)
- Treasury Wine Estates
- The rest of the AWRI team.
Thankyou

Questions?