Sulfur and “reduced sulfur” compounds

*The good, bad and ugly...*

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Elemental sulfur in the vineyard

**Antimicrobial** and protect from oxidation

Sulfur dioxide in the winery

Can also end up with Sulfur from S containing amino acids in yeast: cysteine and methionine
Sulfur Dioxide

Not all sulfur is created equal
| Molecular Form | SO$_2$ | Active form, antimicrobial  
|               |       | Binds H$_2$O$_2$ (*hydrogen peroxide*)  
|               |       | Inhibits oxidation through interacting with precursors  
| Bisulfite Form | HSO$_3^-$ | Least effective form; can bind with sugars, phenolics and anthocyanins (*bleaching*)  
|               |       | Will bind with acetaldehyde  
|               |       | Can reduce browning in white wines; enzyme inhibition (PPO)  
| Sulfite Ion Form | SO$_3^-$ | *Can react directly with Oxygen but levels are very low at wine pH*  

How Much Sulfur Do we Need?

pH dependent equilibrium

Molecular Form  Bisulfite Form  Sulfite Ion Form

$\text{SO}_2 \leftrightarrow \text{HSO}_3^- \leftrightarrow \text{SO}_3^{2-}$

pH meter and this chart

Table 1: Table of molecular SO$_2$ concentrations over pH

<table>
<thead>
<tr>
<th>pH</th>
<th>% of Free Sulfur Molecular SO$_2$</th>
<th>ppm free for 0.8 Molecular</th>
<th>ppm free for 0.5 Molecular</th>
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<tr>
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<td>7.5</td>
<td>11</td>
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<td>6.6</td>
<td>12</td>
<td>7</td>
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<tr>
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<td>0.7</td>
<td>125</td>
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</tr>
</tbody>
</table>

Adapted from: Enology Briefs I (1), Feb/Mar 1982. University of California Cooperative Extension
*Saccharomyces cerevisiae*: semi-tolerant ≈0.825mg/L molecular to eliminate viability

*Acetobacter/Gluconobacter*: obligate anaerobe; 0.7 to 1.0 mg/L molecular

*Oenococcus oeni*: ≈0.8 mg/L molecular; 0.4 to 0.6mg/L to inhibit Malic acid fermentation

*Lactobacillus*: > 0.8 mg/L molecular; *L. Pantarum* ≈ 4.0mg/L for elimination

*Pediococcus*: ≈0.8 mg/L molecular, more tolerant than *Lactobacillus*

*Brettanomyces/Dekera* ≈0.4 to 0.6 mg/L molecular; “viable but not culturable”
Aeration / oxidation:

1) Sample is acidified to maintain SO₂ in free form; drawn through H₂O₂

\[ \text{SO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_4 \]

Titrate against NaOH to get **FREE** SO₂

2) Same sample is HEATED; liberated BOUND SO₂

Aspirate sample into H₂O₂

Titrated against NaOH to get **BOUND** SO₂

**Total = Free + Bound (mg/L)***
Ripper Method: Based on Titration of HSO$_3^-$ with Iodine

$$\text{HSO}_3^- + \text{I}_3^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 3\text{H}^+ + 3\text{I}^-$$

Less glassware (flask only); iodine reacts with other compounds (reducing agents; phenolics, aldehydes, ascorbate); temperature sensitive.

1) Add starch to ~ 50 ml wine (Iodine indicator) 
   Acidify with 5ml Sulfuric acid (25%) 
   *Add Sodium bicarbonate (NaHCO$_3$)*
   Titrate against iodine until indicator = blue
   **Calculate FREE SO$_2$**

2) Add 25ml 1M NaOH to 20 ml sample, sit for 10 min. 
   Add starch indicator 
   Acidify with H$_2$SO$_4$
   *Add NaHCO$_3 and titrate with iodine as before*
   **Calculate TOTAL SO$_2$**
At higher levels we can smell SO₂

Struck match, nose-burn, taste in back of throat

Threshold of sensitivity: **10ppm in air; 15-40ppm in wine**

Legal limit at 350 mg/L (ppm) total

Check pH, consult SO₂ chart, and make appropriate additions for wine

Excessive sulfur can result in *presence of reduced sulfur compounds*:

\[ \text{H}_2\text{S} \rightarrow \text{mercaptans / thiols} \rightarrow \text{disulfides} \]
Hydrogen Sulfide (H$_2$S)

$H_2S$ is the ‘reduced’ form of sulfur
In general – H$_2$S is produced by yeast during primary fermentation; can develop during secondary fermentation (*gross lees*)

Yeast require S to build amino acids $\rightarrow$ more yeast cells (cysteine / methionine)
If stressed, yeast may produce H$_2$S

Excessive S (and SO2)
Proper nitrogen levels / nutrients
Temperature
Rate of fermentation
Yeast strain
Gross lees
Hydrogen Sulfide (H₂S)

*Inevitable to encounter H₂S during fermentations*
- Rotten egg, skunky aroma; very pungent and distinct (volatile)

**Generally very sensitive:** *Threshold ~ 10 ppb in water, 5-80 ppb in wine*

- **Red wines:** Pump-over, drain-and-return, some gentle aeration
- **White wines:** Gentle aeration, sparge with Nitrogen or Argon gas

- Limit sulfur, proper nitrogen during ferment (YAN), watch temperatures
- Try to deal with H₂S at onset and check regularly afterwards
Thiols or Mercaptans
‘reduced sulfur compounds’

If H$_2$S is not managed properly it can be stabilized through oxidation into *thiols / mercaptans*

**Intense aroma:** sweaty, rotten, cabbage/garlic, putrid, rubber stopper, burning brakes

*Threshold in wine can be 2-10 ppb*

-Can be removed via copper fining (copper sulfate)
-Best if avoided through management of H$_2$S
-Excessive oxidation, especially with white wines, can contribute to formation
-At *sub-threshold* levels can ‘scalp’ aroma character of wine
Sulfides and Disulfides

If thiols are further oxidized they can form sulfides / disulfides

\[
\text{H}_3\text{C} \equiv \text{S} - \text{CH}_3
\]

**Dimethyl sulfide (DMS)** – canned corn, radish, cabbage, sweet/musty

*Threshold in wine: 25-60 ppb*

\[
\text{H}_3\text{C} \equiv \text{S} - \text{S} - \text{CH}_3
\]

**Dimethyl disulfide (DMDS)** – Onion, garlic, cabbage, burnt rubber

*Threshold in wine: 30+ ppb*
Sulfides and Disulfides

Thresholds are considerably higher than precursors

Harder to eliminate:
→ Ascorbic acid + copper sulfate + SO$_2$
  - Have to force sulfides back to thiols (reduction) to remove them
  - If not managed precisely in red wines you can promote oxidation due to ascorbic acid reactions (browning)
  - Not as problematic in white wine (no anthocyanins / tannins)

While sensory threshold is lower, sub-threshold levels can also ‘scalp’ aroma of wine

Essential to properly manage S in wine from start of fermentation
Sulfur and “reduced sulfur” compounds

*The good, bad and ugly...*

The objective is to **be familiar** with the aroma / character associated with specific faults in your own mind- *how you think they smell* - understand your sensitivity to various compounds

Utilize the nose of everyone in your team to screen wines from start to finish

If you identify a problem at onset you can can take proper steps to eliminate or reduce the negative impacts

Smell your wines often and keep your nose in practice

Don’t fall in the habit of treating all wines the same; convince yourself why you are making certain additions.
Good Management Practices

- Make SO2 additions based on pH and condition of grapes / wine
- Select low H₂S producing yeast strains
- Check N levels before fermentation and supplement as needed
- Keep your nose to ferments and address issues as they arise
- Proper lees management
- Measure free and total SO₂ by some method on a regular basis
- Understand your sensory limitations and those on your team
- Know your options:
  - Aeration / sparging
  - Racking / lees removal
  - Copper / Copper sulfate / Ascorbate + SO₂
  - Yeast hulls
  - Blending?
  - Call a friend
- Bench Trials
Happy Smelling