Sulfur and "reduced sulfur" compounds

The good, bad and ugly…

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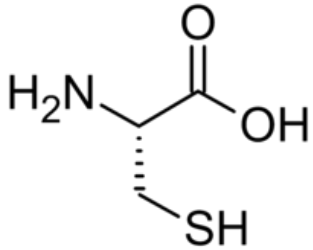
Elemental sulfur in the vineyard

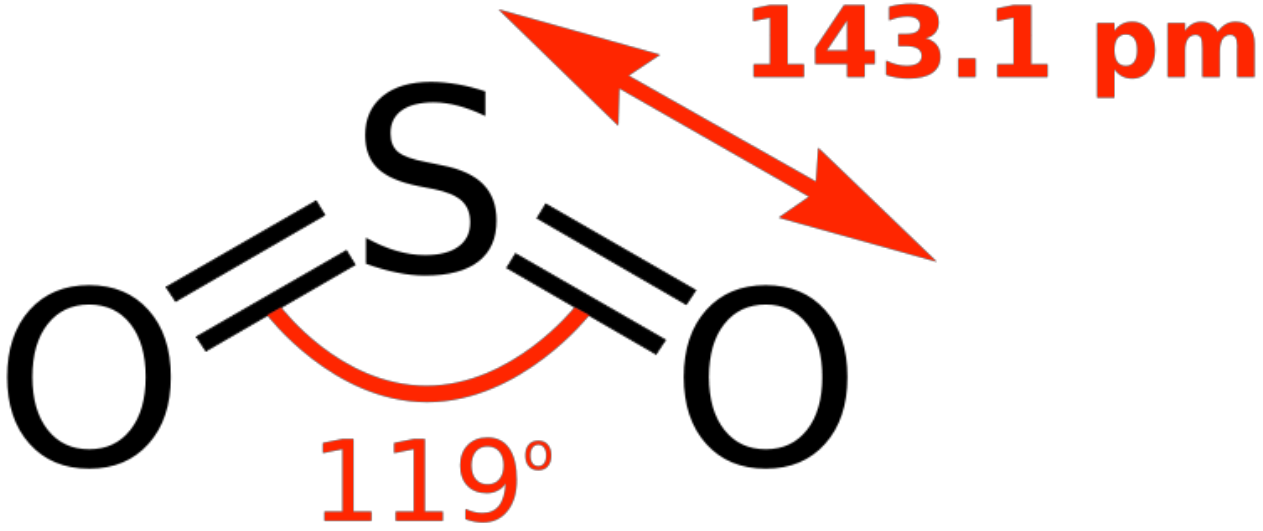
Sulfur dioxide in the winery

Antimicrobial *and protect from oxidation*

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



Sulfur Dioxide

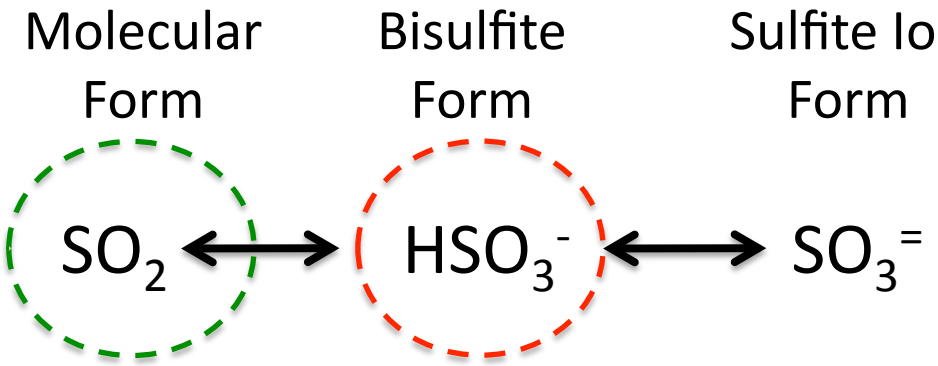


Not all sulfur is created equal

Molecular Form	SO_2	Active form, antimicrobial Binds H_2O_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



pH meter and this chart → →

Table I: Table of molecular SO_2 concentrations over pH

pH	% of Free Sulfur Molecular SO_2	ppm free for 0.8 Molecular	ppm free for 0.5 Molecular
2.90	7.5	11	7
2.95	6.6	12	7
3.00	6.1	13	8
3.05	5.3	15	9
3.10	4.9	16	10
3.15	4.3	19	12
3.20	3.9	21	13
3.25	3.4	23	15
3.30	3.1	26	16
3.35	2.7	29	18
3.40	2.5	32	20
3.45	2.2	37	23
3.50	2.0	40	25
3.55	1.8	46	29
3.60	1.6	50	31
3.65	1.4	57	36
3.70	1.3	63	39
3.75	1.1	72	45
3.80	1.0	79	49
3.85	0.9	91	57
3.90	0.8	99	62
3.95	0.7	114	71
4.00	0.7	125	78

Adapted from: Enology Briefs I (#1), Feb/Mar 1982. University of California Cooperative Extension

***Saccharomyces cerevisiae**: **semi-tolerant** ≈**0.825mg/L moleuclar** 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 SO_2 in free form; drawn through H_2O_2

$SO_2 + H_2O_2 = H_2SO_4$

Titrate against NaOH to get **FREE** SO_2

2) Same sample is HEATED; liberated BOUND SO_2

Aspirate sample into H_2O_2

Titrated against NaOH to get **BOUND** SO_2

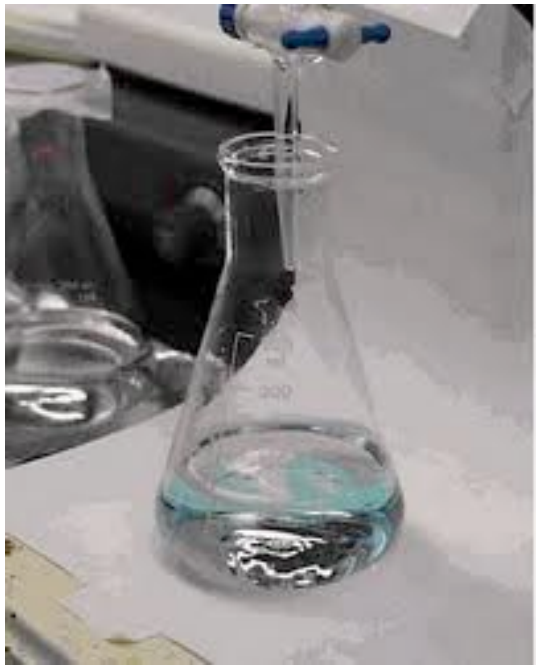
<u>Total = Free + Bound (mg/L)</u>

Ripper Method: Based on Titration of HSO_3^- with Iodine

$$HSO_3^- + I_3^- + H_20 \rightarrow SO_4^= + 3H^+ + 3I^-$$

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_2SO_4
Add $NaHCO_3$ and titrate with Iodine as before
Calculate TOTAL SO_2

At higher levels we can smell SO_2

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

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

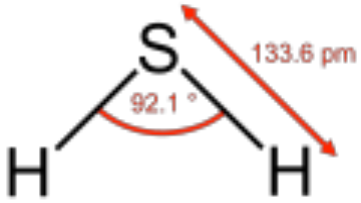
Legal limit at 350 mg/L (ppm) total

Check pH, consult SO_2 chart, and make appropriate additions for wine

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

H_2S → mercaptans / thiols → disulfides

Hydrogen Sulfide (H_2S)



H_2S is the 'reduced' form of sulfur

In general – H_2S is produced by yeast during primary fermentation; can develop during secondary fermentation (*gross lees*)

Yeast require S to build amino acids → more yeast cells (cysteine / methionine)
If stressed, yeast may produce H_2S

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

Hydrogen Sulfide (H_2S)

Inevitable to encounter H_2S during fermentations

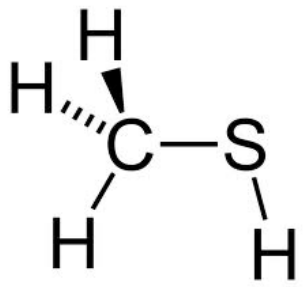
- Rotten egg, skunky aroma; very pungent and distinct (volatile)

Generally very sensitive: *Threshold ~ 10ppb 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

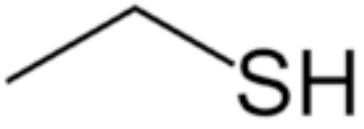
- Limit sulfur, proper nitrogen during ferment (YAN), watch temperatures
- Try to deal with H_2S at onset and check regularly afterwards



Methanethiol

Thiols or Mercaptans

'reduced sulfur compounds'



Ethanethiol

If H_2S is not managed properly it can be stabilized through oxidation into ***thiols / mercaptans***

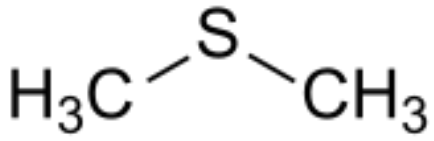
Intense aroma: sweaty, rotten, cabbage/garlic, putrid, rubber stopper, burning brakes

Threshold in wine can be 2-10 ppb

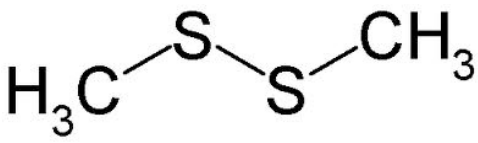
-Can be removed via copper fining (copper sulfate)
-Best if avoided through management of H_2S
-Excessive oxidation, especially with white wines, can contribute to formation
-At *sub-threshold* levels can 'scalp' aroma character of wine

Sulfides and Disulfides

If thiols are further oxidized they can form sulfides / disulfides



Dimethyl sulfide (DMS) – canned corn, radish, cabbage, sweet/musty
Threshold in wine: 25-60 ppb



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*** - <u>understand your sensitivity to various compounds</u>

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 H_2S 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* SO_2 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 + SO_2
    - -Yeast hulls
    - -Blending?
    - -Call a friend
    - -**Bench Trials**

Happy Smelling

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