

CornellCALS

College of Agriculture and Life Sciences

SO₂ and You: Understanding the 'When', 'Why', and 'How' of SO₂ Management in Your Winery

NGP Webinar Tuesday, May 8, 2018



• Claim: I get headaches from drinking wine, so I know I am sensitive to sulfur. Maybe that explains why I am allergic to eggs.

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<u>Sulfur</u> is an **element**, found in many protein-rich food sources (eggs, meat) in the form of amino acids or methylsulfonylmethane (MSM) associated with leafy greens and cruciferous vegetables.

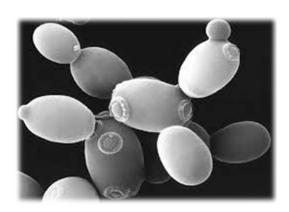


<u>Sulfite</u> is a sulfur-containing **molecule**, found in dried fruit, processed foods, and alcoholic beverages like wine.

• Claim: I haven't added any external sources of sulfur to my wine, so I can label my wine as "sulfite-free."

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Perhaps not...

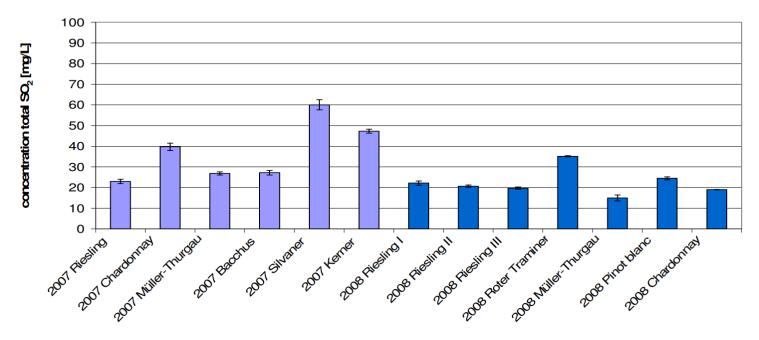


"low SO₂ producers": (0-10, 10-20) mg/L

"high SO₂ producers": up to **80** mg/L

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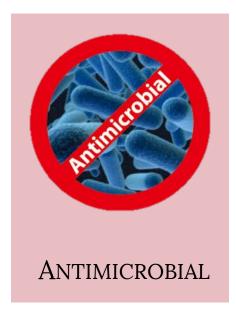


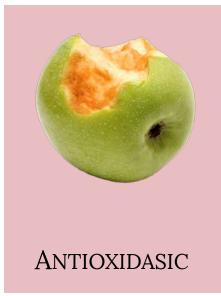


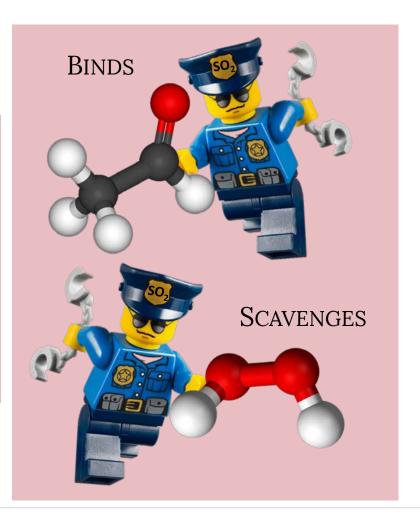
Source: Werner, M. et al., InfoWine (2009)



Why add sulfur dioxide?



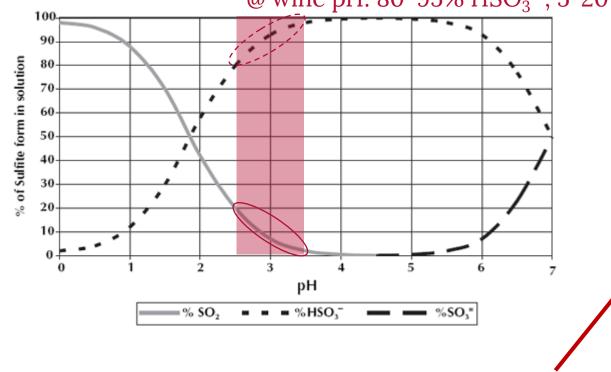




The Many Forms of Sulfur Dioxide

$$H_2O + SO_2 \leftrightarrow H^+ + HSO_3^- \leftrightarrow 2H^+ + SO_3^{2-}$$

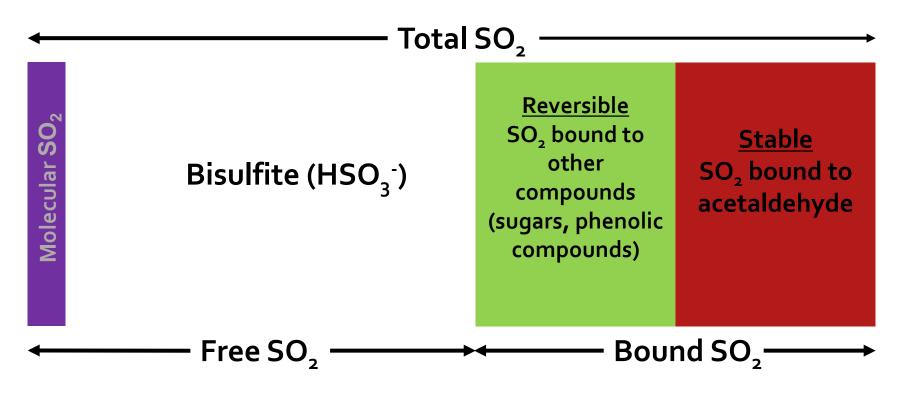
@ wine pH: 80-95% HSO₃⁻, 5-20% SO₂





"CONTAINS **BI**SULFITES"

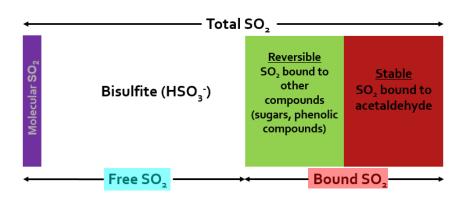
What do you mean when you talk about "sulfur"?



Adapted from A.K. Mansfield



What do you mean when you talk about "sulfur"?



Effective antimicrobial agent

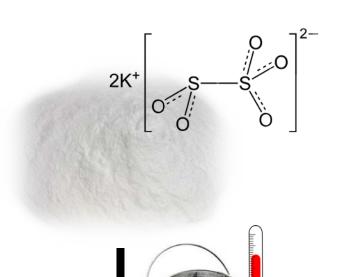
Volatile = odorous

"Buffer zone" against oxidation

Already done its job



How is sulfur added to wine?



~57% available SO₂

57.6% KMBS converts to SO_2 3.785 gallons in a liter

So, after some math...

Volume of Wine (gallons)

 \mathcal{X}

Desired SO₂ addition (ppm)

 χ

0.0066

= Mass of KMBS (*g*) to add to wine

How else is sulfur added to wine?

- Liquid SO₂ solution made from bubbling gaseous sulfur dioxide into the water
 - Drawbacks: gaseous SO₂ is rather volatile and dangerous to inhale, so it imposes a considerable safety risk
- Sodium metabisulfite (67.4% conversion instead of 57.6%!)...alas, health implications for sodium intake, so this is used more often as a sanitizing agent
- Barrels often cleaned with 5 g elemental sulfur tablets
 - Must be VERY careful not to leave un-burned sulfur or ashes behind in the barrel, as it will reduce to form hydrogen sulfide (rotten egg smelling H₂S)
 - Can contribute up to additional 10 ppm total SO₂ for 225 L barrel



"More is better-dump it on in!"

NO! Not advised.

Too much will lead to:





While too little can lead to:

- Oxidation (acetaldehyde production, oxidative browning)
- Spoilage microorganisms

Legal Limits: The Upper End

Country	Wine Type, RS	Limit (ppm)	Legal Reference
USA	All	350	27 CFR 4.22(b)(1)
Canada	All	350	Canadian Food & Drug Reg. B.02.100
Australia	< 35 g/L (3.5% RS)	250	ANZFSC 4.5.1: Clause
	> 35 g/L	300	5(5)(a)
European Union	White, $< 5 \text{ g/L}$	200	
	Red, $< 5 \text{ g/L}$	150	EC No 606/2009,
	White, $> 5 \text{ g/L}$	250	Annex I B
	Red, $> 5 \text{ g/L}$	200	

Adapted from Appellation Cornell 2011-3



Eliminating Excess SO₂: A Fool's Errand

- Bubble wine with excess nitrogen gas to try to volatilize molecular SO₂
 - Remember molecular SO₂ and free bisulfite is in dynamic equilibrium
- Add hydrogen peroxide to bind with the molecular SO₂ to form sulfuric acid
 - NOT advised as this is often illegal in many winemaking regions, as well as from federally regulated food and beverage laws
- Best advice: don't add too much SO₂ to begin with

Know Your pH!

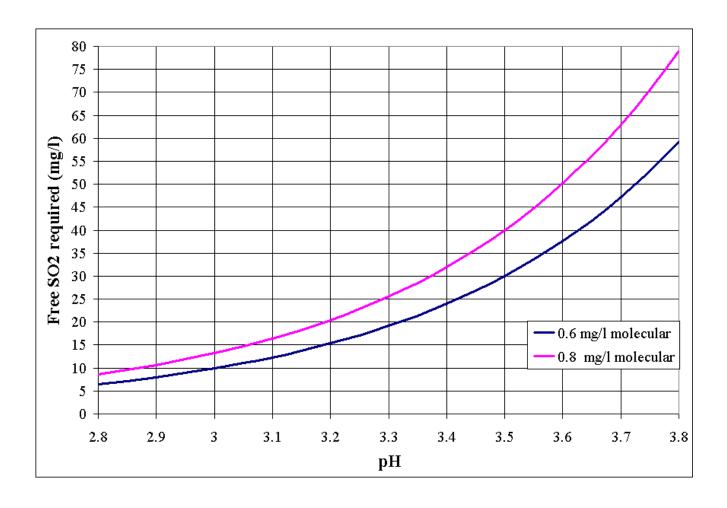
100 90 80 70 60 50 40 30 20 10 0 1 2 3 4 PH

Remember: Free SO₂ is a function of pH.

What exactly is their relation? I am glad you asked!

$$[molecular SO_2] = \frac{[Free SO_2]}{1 + 10^{pH-1.81}}$$

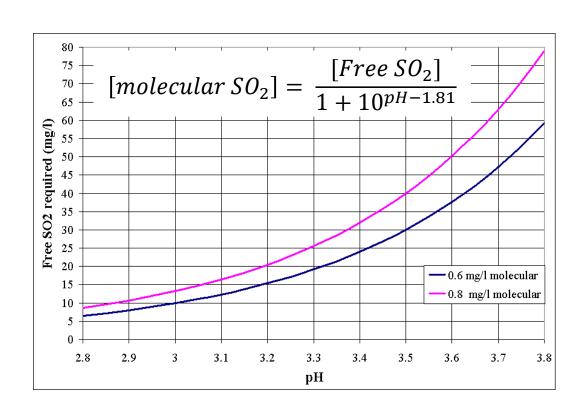
Know Your Wine





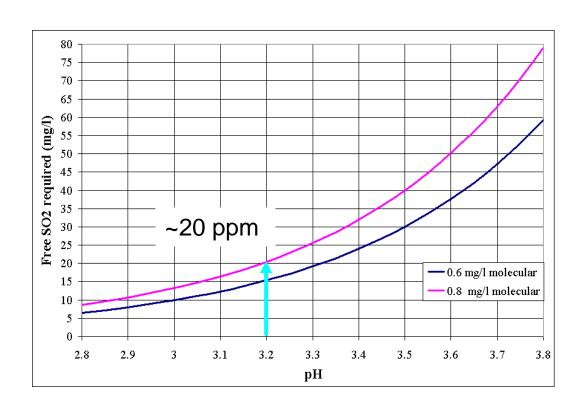
Practice Problem 1

A white wine with pH 3.2 is soon to be bottled. How much free SO₂ is required for a [molecular SO₂] of 0.8 ppm?



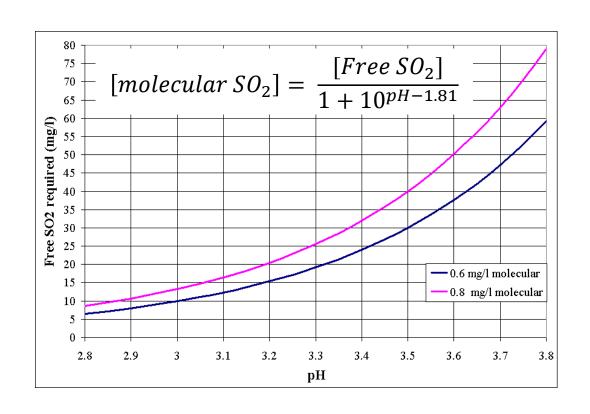
Practice Problem 1: Solution

A white wine with pH 3.2 is soon to be bottled. How much free SO₂ is required for a [molecular SO₂] of 0.8 ppm?



Practice Problem 2

A dry red wine with pH 3.60 is soon to be bottled. How much free SO₂ is required for a [molecular SO₂] of 0.5 ppm?



Practice Problem 2: Solution

A dry red wine with pH 3.60 is soon to be bottled. How much free SO₂ is required for a [molecular SO₂] of 0.5 ppm?

$$[molecular SO_2] = \frac{[Free SO_2]}{1 + 10^{pH-1.81}}$$

$$[0.5] = \frac{[x]}{1 + 10^{3.6 - 1.81}}$$

$$(0.5) \times 62.66 = [x]$$

$$[free SO_2] = 31.3 ppm$$

Questions so far?





Free SO₂ Requirements: Less Math

Minimum Free SO₂ Required (ppm)

	<u> </u>	\1 1 /
	Target: 0.5 ppm	Target: 0.8 ppm
<u>Wine pH</u>	<u>molecular SO₂</u>	$\underline{\text{molecular SO}_2}$
2.90	6.7	10.6
3.00	8.2	13.2
3.10	10.2	16.4
3.20	12.8	20.4
3.30	16.0	25.5
3.40	20.0	31.9
3.50	25.0	40.0
3.60	31.3	50.1



HARVEST/PRE-FERMENTATION

Maybe add here

FERMENTATION

Don't add here

POST-FERMENTATION

Add here

PRE-BOTTLING

Add here

HARVEST/PRE-FERMENTATION

Maybe add here

Factors to Consider:

- How clean is the fruit?
- Do you want to prevent any spontaneous or wild fermentations?
- Do you want to prevent oxidative browning?
- Do you want to prevent MLF?

Rule of thumb: 30-50 ppm after crush for whites 25-50 ppm after crush for reds



Photo credit: Denise Gardner

HARVEST/PRE-FERMENTATION

Maybe add here

FERMENTATION

Don't add here

POST-FERMENTATION

Add here

PRE-BOTTLING

Add here

POST-FERMENTATION Add here

Factors to Consider:

- Will the wine undergo MLF? Do you want it to?
- Whites: generally you want to prevent microbial issues and oxidation/browning at this point
- Reds: less oxidation protection generally needed

Rule of thumb: $0.8 \text{ PPM Mol. } So_2 \text{ whites}$ $0.5 \text{ PPM Mol. } So_2 \text{ reds}$

HARVEST/PRE-FERMENTATION

Maybe add here

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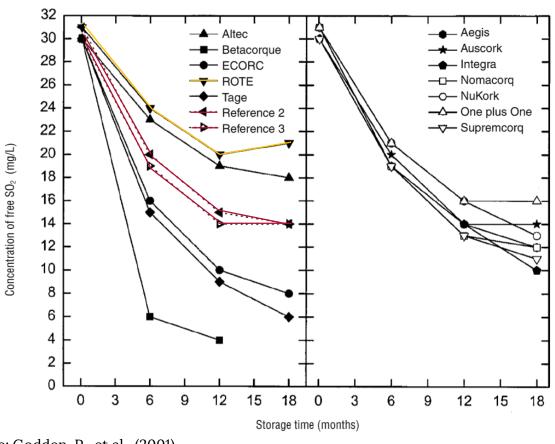
PRE-BOTTLING Add here

Factors to Consider:

- Does your wine have significant residual sugar?
- What kind of bottle enclosure are you using?
- How long will this be in the bottle before release?
- What is the final pH of the wine?
- How much oxygen exposure will the wine having during bottling?

RULE OF THUMB: MEASURE FREE SO₂ LEVELS PRE-BOTTLING; ADD ENOUGH FOR ~30 PPM FREE SO₂

Post-Bottling [SO₂] Decay



- Natural cork
- Screw cap

Source: Godden, P., et al. (2001)



Methods of Analysis

- Ripper Method-iodine titration to endpoint (color change subjective)
- Titrets (simplified and portable Ripper method)
- Aeration-Oxidation (AO)
- Segmented Flow Analysis (Foss FiaStar)





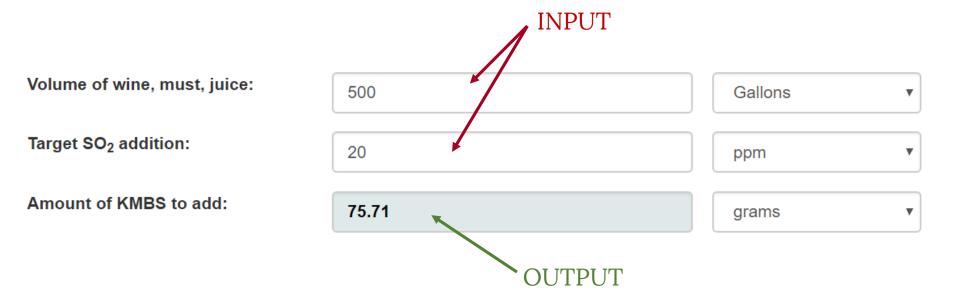
Comparing Methods: Which is right for you?

METHOD	PROS	CONS
RIPPER	 Simple titration setup Quick Measures free and total SO₂ 	 Red wine endpoint difficult to determine Time sensitive- easy to underestimate of total SO₂ Non-selective titration (i.e. ascorbic acid)
TITRETS	 No setup Quick No cleanup - disposable 	 Relatively expensive (\$1/sample) Only measures free SO₂ Same caveats as Ripper Method but even less accurate
A-O	 Most accurate and precise Measures free and bound SO₂ 	 Interference from volatile acids or bases Initial investment of specialized equipment Time-intensive distillation step



Calculation Resources

• https://vinoenology.com/calculators/SO2-addition/



Content Resources

- https://grapesandwine.cals.co rnell.edu/sites/grapesandwine.cals.co rnell.edu/sites/grapesandwine.cals.co rnell.edu/sites/grapesandwine.cals.co rnell.edu/sites/grapesandwine.cals.co rnell.edu/files/shared/documents/Research-Focus-2011-3.pdf
- Godden, P., Francis, L, et al. (2001). Wine bottle closures: physical characteristics and effect on composition and sensory properties of a Semillon wine. Australian Journal of Grape and Wine Research, 7, 64-105.
- Werner, M., Rauhut, D., Cottereau, P. (2009). Yeasts and Natural Production of Sulphites. Internet Journal of Enology and Viticulture, N 12/3.

Many thanks to Anna K. Mansfield for allowing me to adapt some of the information and slides from Cornell Enology Extension.

If you remember anything about this talk:

- Molecular SO₂ at 0.5-0.8 ppm is going to act as antimicrobial agent
- Free SO₂ is pH dependent but aim for 20-40 ppm additions during crush/harvest, post-fermentation, storage
- Wine style (pH, sugar) will affect free:bound SO₂ ratio—only free SO₂ is available to help as an antioxidant
- Know your wine! pH, free SO₂ levels-measure and calculate carefully
- Aim to get SO₂ levels just right-too much or too little can lead to serious wine defects

You Be the Judge

"Sulphur dioxide contributes significantly to hangovers. Heavy drinkers who also have to get up in the morning would be advised to stick to natural wine."

-a random online blogger

Questions?

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