

# Sulfur Dioxide

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## Any Thoughts?



Let's be clear:

Potassium Metabisulfite = PMS =  
Sulfur Dioxide = SO<sub>2</sub> = Sulfur

## Sulfur Dioxide Overview

- Purpose of SO<sub>2</sub>
- Forms of SO<sub>2</sub>
- Sulfur Dioxide Additions
- Evaluating SO<sub>2</sub>
- Calculating SO<sub>2</sub> Addition
- Protecting Wine in Bottle

Think of it like this:



## Purpose of Sulfur dioxide

- Antioxidant benefits
  - Inhibits enzymatic action
    - Polyphenol oxidase prior to fermentation
    - Laccase (botrytis) more harmful than polyphenol (less sensitive to SO<sub>2</sub> and more stable at wine pH)



## Purpose of Sulfur dioxide

- Antioxidant benefits
  - Oxidation causes browning, loss of fruit, aldehydic character
  - SO<sub>2</sub> competes with O<sub>2</sub> for susceptible groups
  - Oxygen and sulfur co-exist for short times
    - Oxygen consumes 4X sulfur (16mg O<sub>2</sub> uses 64 mg SO<sub>2</sub>)
  - Prevents aldehydic aromas, unless sherry!

## Purpose of Sulfur dioxide

- Antiseptic benefits
  - Prevents wild yeast, bacteria, and mold
  - Yeasts more tolerant than bacteria
  - Inhibits acetic acid and lactic acid bacteria

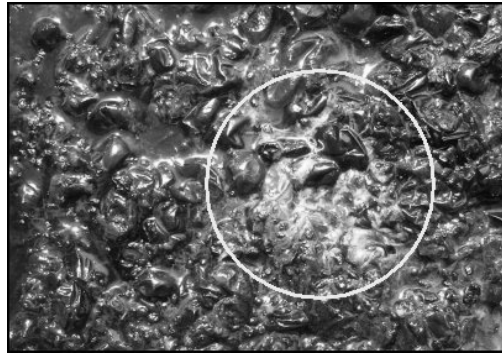
## Forms of Sulfur Dioxide

- Bound SO<sub>2</sub>
- Free SO<sub>2</sub>
- Total SO<sub>2</sub> = (Bound SO<sub>2</sub> + Free SO<sub>2</sub>)

## Forms of Sulfur Dioxide

- Bound SO<sub>2</sub>
  - Worthless!
  - 50x less antiseptic properties than SO<sub>2</sub>
  - Becomes reversibly bound
  - Binds to carbonyl compounds, phenols, and pigments
  - Needs to be accounted for in additions (115—125%)
  - Indicative of oxidation
  - As little as 6 mg/L acetaldehyde-bound-SO<sub>2</sub> can inhibit lactic acid bacteria

## Forms of Sulfur Dioxide



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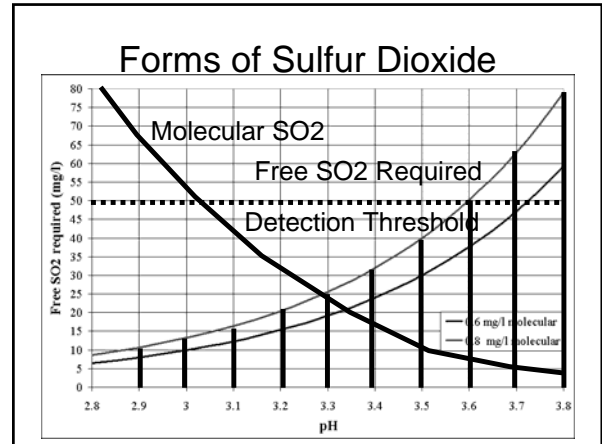
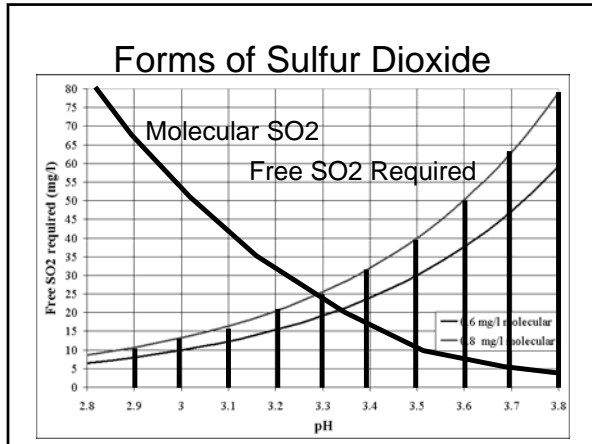
- Free SO<sub>2</sub>—Molecular
  - Volatile and smelly
  - Responsible for antioxidant and antiseptic
  - Toxic to microbes—transported into cells
  - Proportion increases at low pH

## Forms of Sulfur Dioxide

- Free SO<sub>2</sub>
  - Takes 3 forms:

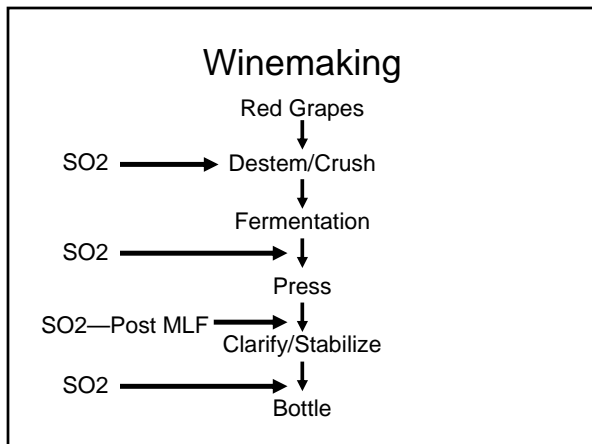






pH	Free SO2 for .8 molecular SO2
2.9	11 ppm
3.0	13 ppm
3.1	16 ppm
3.2	21 ppm
3.3	26 ppm
3.4	32 ppm
3.5	40 ppm
3.6	50 ppm
3.7	63 ppm
3.8	79 ppm
3.9	99 ppm

When do you add Sulfur Dioxide?



- ### Sulfur Dioxide Additions
- Crush
    - Clean fruit; 30-50ppm
    - Mold and rot; 75-100ppm
    - Below 50ppm doesn't delay fermentation, larger dosages may delay (up to 4 days)
    - May delay lag phase
  - Postfermentation and MLF considerations
    - Brettanomyces inhibited by 25 ppm
  - Maintained throughout storage

## Sulfur Dioxide Additions

- Bottling
  - One study, showed 20-30% SO<sub>2</sub> drop over 5 years
  - Faster in red wines
  - Causes:
    - Loss of vapor pressure past cork
    - Oxidation of sulfite within the bottle
    - Slow oxidation by previously oxidized phenols

## Evaluating SO<sub>2</sub>

- Methods:
  - Aeration Oxidation
  - Ripper (Iodine titration)
  - Titrates
- Evaluate 2 hours after addition to allow free and bound to equilibrate.
- Side note: evaluating normality of known base

## Evaluating SO<sub>2</sub>

- Aeration Oxidation



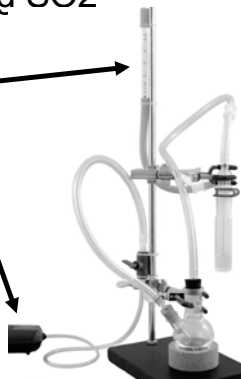
## Evaluating SO<sub>2</sub>

- Blows air through sample
- Releases SO<sub>2</sub>
- Gets caught in solution
- Titrate solution



## Evaluating SO<sub>2</sub>

- Air pump
- Flow meter
  - 1.5 L/min.



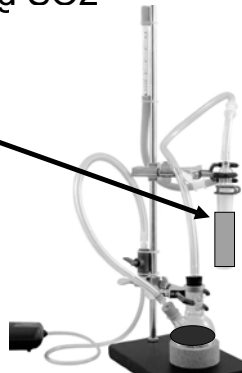
## Evaluating SO<sub>2</sub>

- Acidified wine solution



## Evaluating SO<sub>2</sub>

- Hydrogen peroxide catching solution and indicator solution



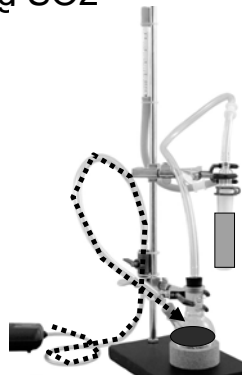
## Evaluating SO<sub>2</sub>

- Turn on the pump



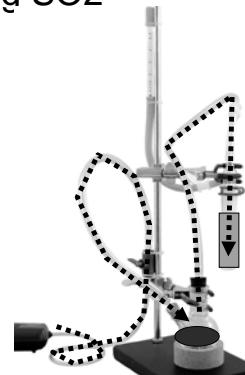
## Evaluating SO<sub>2</sub>

- Aerate the sample



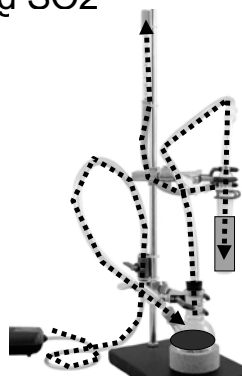
## Evaluating SO<sub>2</sub>

- Air runs through the catching solution



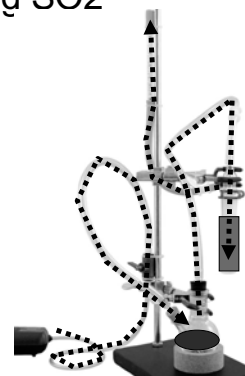
## Evaluating SO<sub>2</sub>

- Run the pump for 10 minutes
- Wait for the color change



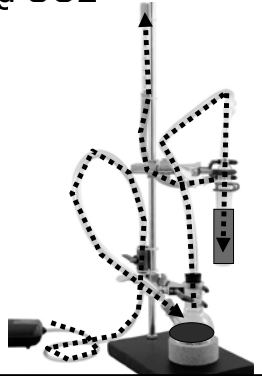
## Evaluating SO<sub>2</sub>

- Color changes



## Evaluating SO2

- Titrate the catching solution back to the original green color



## Evaluating SO2

- Titrate the catching solution back to the original green color



## Evaluating SO2

- Color change indicates fixed end point
- Note the amount of base used



## Evaluating SO2

$$\text{SO}_2 \text{ mg/L} = \frac{\text{Vol} \times \text{Normality} \times 32 \times 1,000}{v_1}$$

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1. Vol = Volume of NaOH in ml
2. N = normality of NaOH
3. V1 = volume of sample
4. CONFUSING!

## Evaluating SO2

$$\text{SO}_2 \text{ mg/L} = \frac{\text{Vol} \times \text{Normality} \times 32 \times 1,000}{v_1}$$

- MI of NaOH x 16 = ppm FSO2

## Evaluating SO2

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2.4 ml x 16 = 38.4 ppm

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5.0 ml x 16 = 80 ppm

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- MI of NaOH x 16 = ppm FSO2  
2.4 ml x 16 = 38.4 ppm  
5.0 ml x 16 = 80 ppm  
0.1 ml x 16 = 1.6 ppm

## Evaluating SO2

- Iodine Titration
  - High variance
  - One drop can make a large difference
  - Auto-titrators

## Evaluating SO2

- Titrates
- To good to be true!
- My recommendation for an even easier method!



## Calculating SO2 Addition

- Calculated as ppm
  - ppm is equivalent to mg/L
  - Proof:
    - 1,000mg/g
    - 1,000g/L
    - 1000mg/g x 1,000 g/L = 1,000,000

## Calculating SO2 Addition

- In a nutshell...

$$\text{Vol.} \times \text{SO}_2 \text{ addition} \div .57 \times 115\% = \text{Addition}$$

## Calculating SO2 Addition

- Potassium Metabisulfite
  - Form to add sulfur to wine
  - Considerations:
    - 57% sulfur
    - Portion goes bound
- Campden tablets
  - 1 tablet weighs ~.55 grams
  - 48% SO<sub>2</sub>

## Calculating SO2 Addition

1. We have 1 Liter of wine with a pH of 3.6. How much Potassium Metabisulfite needs to be added to reach .8 molecular free SO<sub>2</sub>?

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$$1\text{L} \times 50 \text{ ppm} = 50 \text{ ppm}$$

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$$1\text{L} \times 50 \text{ ppm} = 50 \text{ ppm}$$

$$50 \text{ ppm} \div .57 = 87.7 \text{ ppm}$$

## Calculating SO2 Addition

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$$1\text{L} \times 50 \text{ ppm} = 50 \text{ ppm}$$

$$50 \text{ ppm} \div .57 = 87.7 \text{ ppm}$$

$$87.7 \text{ ppm} \times 115\% = 100.9 \text{ ppm}$$

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2. This time, we are working with 1,100 liters of wine. It has a pH of 3.6 and 24 ppm. How many grams of potassium metabisulfite need to be added?

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Target SO2 is 26ppm (50ppm-24ppm)  
 $1,100L \times 26 \text{ ppm} = 28,600 \text{ mg}$

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Target SO2 is 26ppm (50ppm-24ppm)  
 $1,100L \times 26 \text{ ppm} = 28,600 \text{ mg}$   
 $28,600 \text{ mg} \div .57 = 50,175 \text{ mg}$

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Target SO2 is 26ppm (50ppm-24ppm)  
 $1,100L \times 26 \text{ ppm} = 28,600 \text{ mg}$   
 $28,600 \text{ mg} \div .57 = 50,175 \text{ mg}$   
 $50,175 \text{ mg} \times 115\% = 57,702 \text{ mg}$

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 $1,100L \times 26 \text{ ppm} = 28,600 \text{ mg}$   
 $28,600 \text{ mg} \div .57 = 50,175 \text{ mg}$   
 $50,175 \text{ mg} \times 115\% = 57,702 \text{ mg}$   
 $57,702 \text{ mg} \div 1,000 \text{ mg/g} = 57.7 \text{ grams!}$

## Calculating SO2 Addition

- In a nutshell...again...

Vol. x SO2 addition ÷ .57 x 115% = Addition

## Protecting Wine in Bottle

- SO2 used in conjunction:
  - SO2
  - Sorbic acid
  - Lysozyme

## Protecting Wine in Bottle

- Potassium Sorbate
  - Inhibits yeast reproduction
  - Potassium sorbate is 74% sorbic acid
  - Legal limit is 300 ppm
  - Downfall—lactic acid bacteria can produce a geranium odor

## Protecting Wine in Bottle

- Lysozyme
  - Prevents lactic acid bacterial growth
  - Prevents geranium odor
  - ‘Safety net’ for wines that do not go through MLF

## Works Cited

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