Winemaking and Sulfur Dioxide

Prepared and Presented by:
Frank Schieber, Amateur Winemaker
MoundTop MicroVinification
Vermillion, SD
www.moundtop.com schieber@usd.edu

Outline:

Sulfur Dioxide (Free SO_2)

Protective benefits (antimicrobial; antioxidant).
Free versus Bound SO_2 .
Critical role of wine pH. Molecular SO_2 vs. ionized HSO_3 (Bisulfite)
Calculation of SO_2 additions – Need for empirical measurement.
Accurate measurement of free SO_2 using Aeration-Oxidation (AO) Method.

Critical Role of SO_2 for Winemaking

- Antimicrobial
  Inhibits many types of bacteria/wild yeast.
- Antioxidant
  Prevents browning (pre/post fermentation).
  Inhibits formation of acetaldehyde (and binds-up any that does form); minimizing "Sherry-like" aromas.
- Preserves fruitiness (Varietal character).
- Well tolerated by commercial yeast strains.

Factors Complicating SO_2 Management

- Understanding "Free" vs. "Bound" SO_2. Only "Free" SO_2 provides "insurance" against future wine damage.
- Estimation of Free SO_2 can't be done by formula alone. Quantitative measurement is necessary.
- Free SO_2 ionizes into two separate components: Molecular SO_2 vs. Bisulfite.
- Molecular SO_2 level is highly pH dependent.

Free vs. Bound SO_2

Total SO_2 = **Bound SO_2** + **Free SO_2**

Amount of SO_2 added by the winemaker (plus trace amounts produces by yeast)

Proportion of SO_2 that has interacted with "bad actors" and prevented them from damaging the wine. Hence, this portion of the SO_2 is no longer available to protect against future insults.

"Unused" SO_2 that is still available to inhibit microbes and oxidizing agents that can potentially damage the wine.

("Insurance Policy")

Several Varieties of Free SO_2

- **Molecular** SO_2 (non-ionized)
  Responsible for antimicrobial properties

- **Bisulfite** (ionized form)
  Responsible for antioxidant properties

- **Sulfite** (doubly ionized form)
  Virtually non-existent at wine pH

Ionization of Sulfur Dioxide in Water

(Reaction responsible for various forms of Free SO_2)

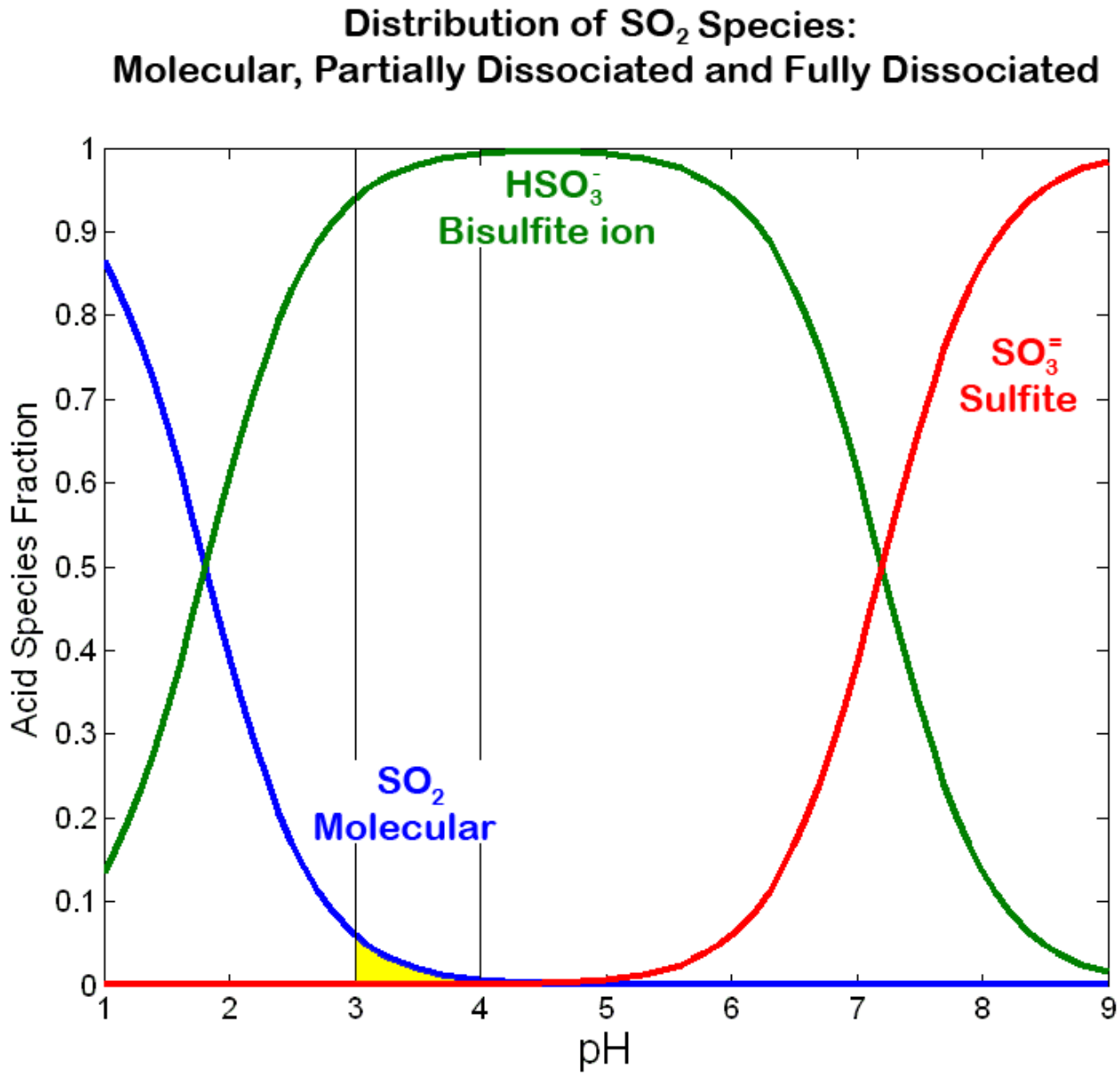
$$H_2O + SO_2 \underset{}{\overset{pKa = 1.81}{\rightleftharpoons}} HSO_3^- \overset{pKa = 7.2}{\rightleftharpoons} SO_3^=$$

Molecular (dissolved gas)	Bisulfite ion	Sulfite ion

The heck you say?

Ionization of Free SO_2

(Let's describe it with a picture)



Notes about Free SO_2

%Molecular SO_2 is tiny and drops dramatically as wine pH increases (see yellow area)

%Bisulfite is huge and relatively stable across Wine pH

Sulfite ion levels (SO_3) are irrelevant.

Wine pH between 3-4

Research shows that the Molecular fraction of Free SO_2 must be maintained at 0.8 mg/L (PPM) in order to provide adequate antimicrobial protection.

Distribution of Free SO_2 "Species" as a function of Wine pH (also shown: mg/L of Free SO_2 Required to yield 0.8 mg/L Molecular SO_2)

pH	%Bisulfite	%Molecular	Free SO_2 Required for 0.8 mg/L Molecular
3.0	93.9	6.1	13 mg/L (PPM)
3.1	95.1	4.9	16
3.2	96.1	3.9	21
3.3	96.9	3.1	26
3.4	97.5	2.5	32
3.5	98.0	2.0	40
3.6	98.4	1.6	50
3.7	98.7	1.3	62
3.8	98.9	1.0	80
3.9	99.1	0.8	100
4.0	99.3	0.6	133

Free SO_2 Req'd (mg/L) = 0.013534 * exp(2.2867 * pH)
($R^2 = 0.999$)

Maintaining 0.8 mg/L Molecular SO_2 is the key to managing sulfite additions to wine.

How do we achieve this?

Case Study #1

Red wine with pH=3.6 has just finished MLF.

Reference to Table/Equation indicates that 50 PPM of free SO_2 is required to achieve the target concentration of 0.8 PPM molecular SO_2

Since about HALF of the first 60 PPM of SO_2 added to a wine immediately becomes bound-up, we need to add approximately:

(0.5)(60 PPM) + 20 PPM = 80 PPM SO_2 addition to achieve goal level of 50 PPM free SO_2

Add 80 PPM SO_2 to the wine.

Test free SO_2 to verify (e.g., Aeration-Oxidation test demonstrated below).

Case Study #2

At the second racking, a wine has a pH of 3.4 and a previous SO_2 addition history of 90 PPM.

Reference to the appropriate table reveals that a wine with a pH=3.4 requires 32 PPM to achieve the target level of 0.8 PPM molecular SO_2.

Laboratory test of the wine reveals a current free SO_2 level of 20 PPM.

Compute the required SO_2 addition as follows:

addition = SO_2 req'd for 0.8 molecular – current free SO_2 level
addition = 32 – 20 = 12 PPM

12 mg/L of SO_2 must be added to the wine to achieve ideal level.

How do we make the physical adjustment to the wine once we know the size of the free SO_2 addition required to achieve a concentration 0.8 mg/L molecular?

Forms of SO_2 Used in Winemaking

- Liquified SO_2 gas (under high pressure)
- 5% Sulfurous acid (H_2SO_3) solution

  (The above are not practical for the amateur)

- Potassium metabisulfite (KMeta) powder
  (57% SO_2 by weight when dissolved in water)

Case Study #3
40 PPM SO_2 Addition using KMeta

Problem:
How much KMeta powder must be added to 10 gallons of wine to raise the current free SO_2 level by 40 PPM?

Solution:
Remember…1 PPM = 1 mg/L

(40 mg/L SO_2 Req'd * 10 gal. of wine * 3.785 L/gal) / 0.57 KMeta concentration

(40 * 10 * 3.785) / 0.57 = 1414/0.57 = 2656 mg of KMeta required

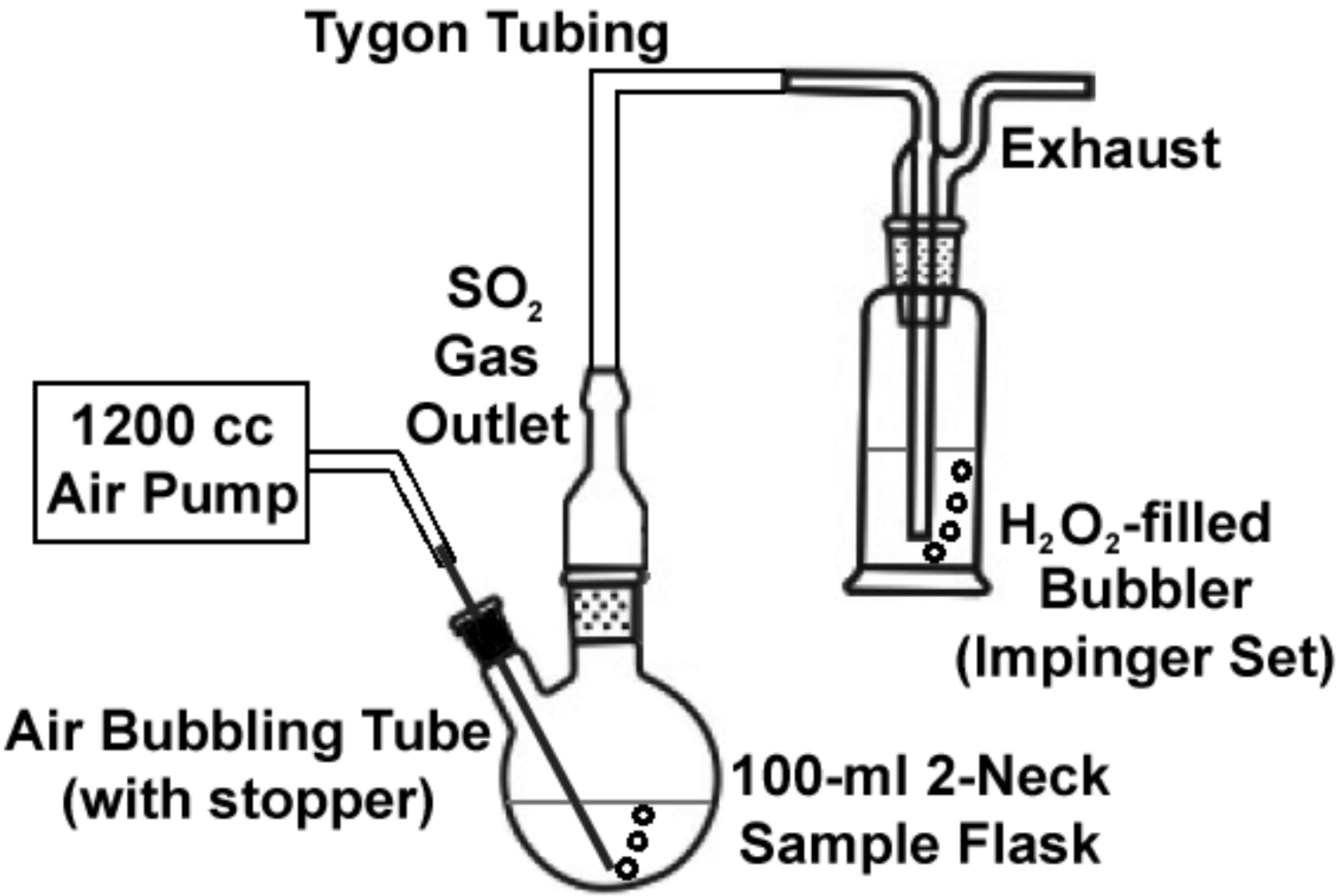
Accurate yet inexpensive 100 g scales
with 0.01 gram precision are readily available.

Downsides of SO_2

- Not effective against bacteria at high pH (Consider Lysozyme treatment)
- Disagreeable taste/aroma at higher levels
- Some individuals are hypersensitive to sulfites (headaches; allergic reactions)
- Legal limit for Total SO_2 (350 mg/L USA) (350 PPM?…A seriously oxidized wine!!!)

Aeration-Oxidation Apparatus

(Determination of Free SO_2)



Logic of A-O Procedure

Add 20 ml (volumetric) wine sample to a 2-neck flask.

Add 10 ml (nominal) of phosphoric acid (25%) to the wine sample. This reduces the pH and converts the free SO_2 to the molecular form.

Purge acidified wine sample of its SO_2 gas by bubbling air through it.

Capture the air used to collect the SO_2 gas and bubble it through a 0.3% hydrogen peroxide (H_2O_2) solution.

The SO_2 entering the H_2O_2 is immediately converted to sulfuric acid:

$$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O \rightarrow H_2SO_4 \text{ (i.e., sulfuric acid)}$$

After 15 min. all of the SO_2 has been volatized from the wine sample.

The amount of SO_2 in the original wine sample can be quantified by measuring the volume of 0.01 N sodium hydroxide (NaOH) required to neutralize the sulfuric acid now in the H_2O_2 trap. This is a achieved using titration techniques and a special dual-color indicator.

Step-by-Step
Aeration-Oxidation (Aspiration) Procedure

- See handout detailing A-O Procedure

- Download from:
  http://www.moundtop.com/so2/SO2-Aspiration-Procedure2.pdf
- Video Demo of A-O Procedure
  http://www.valleyvintner.com/Merchant2/Videos/S02_InstructionVideo.wmv