SO₂ & Sorbate Management

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Sulfur in Wine

Reduced  neutral  Oxidized
electron-rich  neutral  electron-poor

$H_2S$  $SO_2$  $SO_4^{2-}$
hydrogen sulfide  sulfur dioxide  sulfate

elemental sulfur  $S^{2-}$  $HSO_3^-$
sulfides  bisulfite
1. Microbial stability
2. Inhibition of browning enzymes
3. Binding of acetaldehyde
4. Antioxidant
History of SO$_2$ in Winemaking

- Regulated in Europe since 1400s
- US labeling since 1988
Health Aspects of SO$_2$

- Problem population: **Steroid-dependent** asthmatics
  - = 20% of asthmatics
  - = 200,000 in US
  - Can be fatal!

- Does it cause headaches?
  - No!
Regulation of SO$_2$

• In Winemaking
  Total SO$_2$ allowed:  350 mg/L
  Labeling required*: ≥ 10 mg/L

• Naturally produced by yeast:
  1 - 14 mg/L

*even if naturally produced
Total $SO_2$ in Commercial Wine

1994-98 BATF analysis of 4,676 wines (mg/L)

- Legal limit: 350
- Average US: 74
- Average CA: 74  OR: 61  WA: 71  NY: 116
- 94% less than 150
- 82% less than 100
- 0.4% more than 350  Maximum: 686!
Forms of SO$_2$

SO$_2$ + H$_2$O ⇄ SO$_{2aq}$

Molecular SO$_2$

SO$_{2aq}$ ⇄ H$^+$ + HSO$_3^-$

pK 1.8

Bisulfite ion

HSO$_3^-$ ⇄ H$^+$ + SO$_3^{2-}$

pK 7.2

Sulfite ion
Forms of SO$_2$ in Wine

- $\text{HSO}_3^-$
- $\text{SO}_2^2$-
- $\text{SO}_3^{3-}$
Forms of SO$_2$ in Wine

- HSO$_3^-$
- SO$_2^{\text{molecular}}$
**Free bisulfite** ion binds with:

- Acetaldehyde
- Pyruvate
- 2-Ketoglutarate
- Malvidin-3-glucoside
- Glucose

=> “Bound $SO_2^-$“ vs. “Free $SO_2^-$“
"Total SO$_2$" = Bound bisulfite ions + Free bisulfite ions + Molecular SO$_2$ (+ Sulfite ions)
Molecular SO$_2$ => Antimicrobial activity
Mousecular $SO_2$
Temperature and Molecular SO$_2$  

=> Wine Serving Temperature

- $32^\circ F$ (0°C)  60%  1.61
- $50^\circ F$ (10°C)  78%  1.72
- $68^\circ F$ (20°C)  100%  1.83
- $77^\circ F$ (25°C)  115%  1.89
- $122^\circ F$ (50°C)  195%  2.12
Microbial Stability and SO2

$\text{SO}_2$ sensitivity:

- Malolactic bacteria? YES!
- Saccharomyces? NO!
- Kloeckera? YES?
- Brettanomyces? YES?
pH and Molecular SO₂

Free SO₂ required

SO₂

HSO₃⁻

SO₃²⁻
Microbial Stability, pH and SO₂

![Graph showing the relationship between pH, % molecular SO₂, and Free SO₂ (mg/L).]
pH and Molecular $\text{SO}_2$

\[
\% \text{ SO}_2^{\text{molecular}} = \frac{100}{1 + 10^{\text{pH} - 1.83}}
\]

$\text{Free SO}_2 = 0.85 \cdot (1 + 10^{\text{pH} - 1.83})$

Decrease pH by 0.1
$\Rightarrow$ use $\approx 20\%$ less Free $\text{SO}_2$

Decrease pH by 0.3
$\Rightarrow$ use $\approx 50\%$ less Free $\text{SO}_2$
pH and Molecular SO$_2$

pK$_1$ in water = 1.77

pK$_1$ in wine = 1.83
### Free SO₂ required at Wine pH (mg/L)

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**Molecular SO₂:** 0.85 mg/L

www.foodsci.purdue.edu/research/labs/enology/FreeSO2(pH)Pro.pdf
SO\textsubscript{2} and Fermentation Lag Phase

Alcohol

Days

mg/L
SO$_2$, EtOH and MLF

*Oenococcus oeni* suppression:

- free SO$_2$ to 0.8$^\text{molecular}$ at 12% EtOH
- free SO$_2$ to 0.5$^\text{molecular}$ at 14% EtOH
SO$_2$, Thiamin and Brett

Thiamin cleavage by HSO$_3^-$

Rate vs pH graph

- Rate on the y-axis
- pH on the x-axis
- The graph shows an increase in rate as pH increases from 3.00 to 4.00
Inhibition of Browning Enzymes

Polyphenol oxidases

• Tyrosinase (from grape)? YES!
• Laccase (from Botrytis rot)? NO!
Binding of Acetaldehyde

Acetaldehyde = "oxidized", "Sherry"
"bruised apple" aroma

\[
\text{CH}_3\text{CHO} + \text{HSO}_3^- \rightleftharpoons \text{CH}_3\text{CHOHHSO}_3^-
\]

Acetaldehyde     Bisulfite     Hydroxyethane sulfonic acid
SO₂ and Oxygen

SO₂ = a weak antioxidant

- Phenol + O₂ = Quinone + H₂O₂
- H₂O₂ + Ethanol = Acetaldehyde
- H₂O₂ + Phenol = Quinone
- H₂O₂ + SO₂ = Sulfate SO₄²⁻
- O₂ + SO₃²⁻ = Sulfate ¹/₂ : 30 days
- O₂ + Ascorbate = DehydroA ¹/₂ : 35 min

Note: Sulfate (oxidized sulfite) doesn’t show in Total SO₂!
SO$_2$ and Oxygen at Bottling

vs.
Normal bottle headspace, *ullage*, is commercially between 4 and 7 mL.

**Example:**
7 mL of air @ 20% oxygen = 2 mg O₂

⇒ 2 mg O₂ + 4 mg SO₂ => Sulfate

⇒ 4 mg SO₂/750 mL bottle ≈ 6 mg/L

*Free SO₂ Loss*
SO\textsubscript{2} and Oxygen at Bottling

If bottling without N\textsubscript{2} sparging, wine receives ca. 1 saturation with air during filling:

Example:
750 mL of wine @ 69 °F = 1.4 mg O\textsubscript{2}

⇒ 1.4 mg O\textsubscript{2} + 2.9 mg SO\textsubscript{2} ⇒ Sulfate
⇒ 2.9 mg SO\textsubscript{2}/750 mL bottle ≈ 4 mg/L

Free SO\textsubscript{2} Loss
Combined Free SO$_2$ loss at bottling:

\[ 6 + 4 \text{ mg/L} \approx 10 \text{ mg/L} \]

+ additional losses

\[ \Rightarrow \text{Add 10 - 25 mg/L SO}_2\text{ EXTRA before bottling} \]
SO$_2$ Application

Burning Sulfur Wicks
SO$_2$ Application

Weighing out Potassium Metabisulfite

Watch cold stability!

RadioShack USB Scale
SO$_2$ Application

Dosing SO$_2$ Gas

Caution!
Sorbic Acid

- Yeast growth inhibitor: 200 mg/L
- Legal limit: 300 mg/L
- Sensory threshold: 135 mg/L

- Some yeasts are resistant!
- NO effect against bacteria

- Added as potassium salt (Sorbate)

=> Watch cold stability!
Geranium Off-Odor

Cause
- Sorbic acid + Malolactic bacteria

Prevention
- Avoid sorbate as preservative
- Use sorbate only with proper SO$_2$
- Add no earlier than day before bottling
- Always bubble test/sterile filter
- NO removal option from wine
Barrel Maintenance

- Physical Cleaning
- Chemical Cleaning
- Sanitation
- Storage
Barrel Maintenance
Physical Cleaning

- Low/high water pressure sprayers
- Steam cleaners (to ca. 7 oz condensate)
- Dry ice (CO$_2$) blasting
- Shaving/re-toasting
Barrel Maintenance
Cleaning/Sanitizing w/Water/Steam

Note:

• No chlorine residues in water + soften

• Solubility of K-bitartrate is 10x higher in hot water than in cold

• Cell kill at 180°F = 10x more effective than at 170°F
Sanitizers
Chlorine
Keep out of the cellar!
Heat Conductivity of Wood

• Conductivity of wood is 1/1000 that of copper

• Conductivity of the wood along the grain is about 3x better than across the grain.
Relative Thermal Conductivity

Cu: 32
Alu: 17
Iron: 4
SS: 1
Water: 0.04
Wood: 0.03
Air: 0.002
BBL Nooks & Crannies!
Barrel Maintenance
Chemical Cleaning

Rinse solutions (averages)

- “Hot” (100-180°F) water optional 3-5 min
- Soda ash Na₂CO₃ optional 2 g/L
- Cold water
- Percarbonate optional 2 g/L
- Citric acid = BOD to neutralize 1.6 g/L
Barrel Preparation
Sanitation

- **Sanitizing agents?**
  - Steam/hot & cold water
  - Soda ash
  - Percarbonate
  - Surfactants
  - SO₂
  - DMDC
  - UV light
  - Accelerated electron beam
  - Chlorine
  - Ozone
Barrel Maintenance
Chemical Sanitation

Experimental/historic rinse solutions:

- Vinegar / Peracetic acid
- CuSO$_4$
- High-proof alcohol
- Salt water
“Sanitizers”
Soda Ash \( \text{Na}_2\text{CO}_3 \)

- Strong alkaline (pH 11.3 at 1%)
- Dissolves proteins, fats, oils, carbohydrates, tartrates
- Neutralizes acidic odors (V.A.)
- Neutral pH best for bacteria
- Sanitizing effect?
“Sanitizers”

Percarbonates

- Per(oxy)carbonate $\text{NaO-O-COONa}$
- Release of oxygen radicals via $\text{H}_2\text{O}_2$
- Application at room temperature
- Effective over wide pH range (1 - 8)
- Alkaline
- Degradation to soda ash, water, $\text{O}_2$
- Sanitation effect via $\text{H}_2\text{O}_2$?
“Sanitizers”

Percarbonates

Common uses:

“Chlorine-free” laundry and wood bleach
Barrel Storage
Sulfur (Dioxide)

Dry:
• 1.7 - 3.4 g S/bbl
• Every 3-4 weeks!

Wet:
• 225 g Citric/bbl
• 45 g KMBS/bbl
Stop and smell the Barrel!
The Wine Grape Task Force is a cooperation between the Indiana Wine Grape Council and Purdue University to serve the State’s vintners and growers and help propel the Indiana wine/grape industry into world-class competitiveness. Its 5-member team is available at any time to trouble-shoot emerging issues in your vineyard and winery: 1-800-832-WINE

- 2006 Spring Grape and Wine Workshop REGISTRATION
  - March 20, 2006 - Host: Chateau Thomas Winery

- 2006 Indiana Horticultural Congress
  - Grape Pest Management (Bruce Bodelson)
  - Wine Quality - The Science of Funk (Christian Butzke)
  - Exploring the Aroma Potential of Traminette (Patty Skidnis)
  - The Joy of Malolactic Fermentation (Elle Butz)
  - EPA Worker Protection Standards Compliance for Wine Growers (Joe Becovitz)
  - Winery Safety - A Crush Course (Christian Butzke)

- 2005 Fall Grape and Wine Workshop
  - Wine Quality Control Basics (Christian Butzke)

- 2005 Spring Grape and Wine Workshop
  - A Fresh Look at the Science and Art of Winemaking (Christian Butzke)

Winery Laboratory Information
- Winery Lab Starter Kit
- Free SO₂/pH Chart
- Residual Sugar Color Chart

Grape Production and Pest Management Information
- Dept. of Horticulture Fruit and Vegetable Connection (Bruce Bodelson)

Workshops and Services for the Food Industry and Food Entrepreneurs
- Dept. of Food Science Extension Classes (Christian Butzke)

Recent Research
- The Science of Closures
- Musty Taint in Wine - TCA as a Special Case (Christian Butzke)

www.indianawines.org

www.foodsci.purdue.edu/research/labs/enology