Sulfur Dioxide Use in Winemaking

Sulfur dioxide (SO_2) is an essential additive in winemaking. This chemical largely is used as a food and wine preservative for its antimicrobial and antioxidant properties. It inhibits, and in some cases kills, some yeast and bacteria. SO_2 also protects grape must and wine from oxidation by enzymatic and chemical reactions, and therefore from browning and off-odors. With proper additions, SO_2 aids in preserving aromas and provides protection against incidental oxygen and microbial exposure. It must be used in conjunction with sound winemaking practices, which include stringent cleaning and sanitation protocols and use of inert gases. Learn more in the Iowa State University and Outreach publication Use of Inert Gases, FS52, store.extension.iastate.edu/product/16405, and Cleaning and Sanitation in the Winery, FS42, store.extension.iastate.edu/product/15978.

Note: Concentrations of SO_2 are measured and calculated in milligrams per liter (mg/L). Often these are interchangeably displayed in parts per million (ppm); 1 mg/L is equivalent to 1 ppm.

Chemical and Antimicrobial Properties

At room temperature, SO_2 is a hazardous gas with an irritating odor. Risks due to overexposure include burns to the skin and respiratory issues. The gas readily dissolves in water to produce sulfites, and has increased solubility at lower temperatures. Yeast naturally produce SO_2 during fermentation at the rate of 10-20 mg/L; even if no additions are made, wine generally will have some amount of SO_2. In wine production, additions of SO_2 often are made using potassium metabisulfite (KMBS), the water-soluble potassium salt of sulfur dioxide. It is a crystalline powder containing 57.6% SO_2.

In wine, SO_2 exists in three forms in a pH-dependent equilibrium (Figure 1): molecular (SO_2), bisulfite (HSO_3^-), and sulfite (SO_3^{2-}). These forms make up what is known as free SO_2, meaning it is available for antimicrobial and antioxidant protection. Some amount of the bisulfite form (HSO_3^-) will bind to compounds in the wine. Once bound, the SO_2 is no longer available to protect the wine. However, free SO_2 and bound SO_2 are added together to determine the amount of total SO_2 (Figure 2).

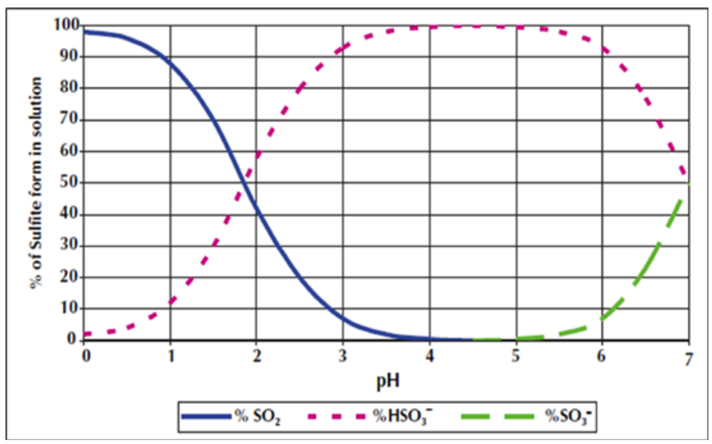

Figure 1. Percentage of forms of SO_2, molecular (SO_2), bisulfite (HSO_3^-), and sulfite (SO_3^{2-}) in wine over pH 0-7. Adapted from: Practical Winery & Vineyard, 2014.

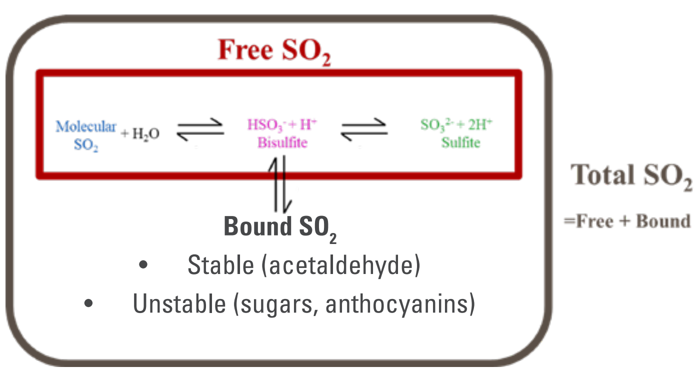

Figure 2. Dissociation of sulfur dioxide into various forms under different pH conditions.

The molecular form of SO_2 accounts for less than 10% of the free SO_2 at wine pH (pH 3.0-4.0) (Figure 1), but has the most effective antimicrobial activity and some antioxidant potential. Only molecular SO_2 can pass through yeast and bacteria cell membranes. Inside the cells, where the pH is higher (pH ~ 6), molecular SO_2 dissociates, i.e. is transformed to bisulfite (HSO_3^-) (Figure 2). This latter form binds readily with other compounds, including proteins, which eventually kills cells. The extent of its activity varies by type of yeast and bacteria. The molecular form is volatile, and can be smelled (approximately 50-100 mg/L free SO_2 or 2 mg/L molecular SO_2). Some also is lost to headspace.

At wine pH, bisulfite is the predominate form, accounting for over 90% of the SO_2. It has some antioxidant activity through its binding action to proteins (e.g. enzymes such as polyphenoloxidase (PPO), responsible for browning) and other compounds. Unstable binding with sugars, anthocyanins, and proteins is somewhat reversible compared to stable binding with acetaldehyde, which is irreversible. Acetaldehyde, a by-product of oxidation, is associated with odors of bruised apple, nuttiness, or sherry. Upon binding with bisulfite, acetaldehyde becomes odorless, and anthocyanin pigments become colorless (bisulfite bleaching).

Sulfite concentration is negligible at wine pH. It has the ability to directly react with oxygen, but is not present in any appreciable amount.

Importance of SO_2 Additions and Monitoring

The most important form of free SO_2 to preserve wine quality is the molecular SO_2 form. Therefore, all calculations to determine additions are based on the target amount of molecular SO_2. Maintaining 0.5-0.8 ppm of molecular SO_2 is considered sufficient to protect *Vitis vinifera* red and white wines, respectively, from yeast and bacterial spoilage. For non-*V. vinifera* wines, it is recommended to use 0.8 ppm of molecular SO_2 as the target amount for additions. The percentage of molecular SO_2 present in wine is directly related to the pH (Table 1); note a 10-fold difference in the amount of molecular SO_2 present at pH 3.0 compared to pH 4.0. The desired free SO_2 needed to reach 0.8 ppm molecular SO_2 at various pH levels is provided in Table 1.

Free SO_2 in wine will decrease over time due to binding of bisulfite form and loss by volatility of molecular SO_2. Decreases should be minimal when wine is carefully handled and protected from spoilage and oxygen exposure. Know the intended purpose of SO_2 additions at every step of the winemaking process, and make a plan for additions and monitoring. Monthly monitoring by measuring free SO_2 and periodic additions of SO_2 ensure that wines are protected, and that free SO_2 is maintained at the desired level according to a wine's pH.

Monitoring also is necessary to ensure compliance with labeling requirements and legal limits for the amount of total SO_2 in a finished wine. Any wine with more than 10 mg/L total SO_2 must have a "contains sulfites" statement. Additionally, the Alcohol and Tobacco Tax and Trade Bureau (TTB) has a legal limit set at 350 mg/L total SO_2. Proper training and caution are important when working with SO_2, as high concentrations and prolonged exposure are acutely toxic.

Table 1. Distribution of free SO_2 at various pH values.

pH	% SO_2 molecular	% HSO_3^- bisulfite	% SO_3^{2-} sulfite	Free SO_2 (mg/L) to obtain 0.8 ppm molecular SO_2
2.9	7.5	92.5	0.009	11
3.0	6.1	93.9	0.012	13
3.1	4.9	95.1	0.015	16
3.2	3.9	96.1	0.019	21
3.3	3.1	96.8	0.024	26
3.4	2.5	97.5	0.030	32
3.5	2.0	98.0	0.038	40
3.6	1.6	98.4	0.048	50
3.7	1.3	98.7	0.061	63
3.8	1.0	98.9	0.077	79
3.9	0.8	99.1	0.097	99
4.0	0.6	99.2	0.122	125

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

Calculating Sulfur Dioxide Additions

Additions of SO_2 often are made to wine using potassium metabisulfite ($K_2S_2O_5$, abbreviated as KMBS), which contains 57.6% SO_2. To make an addition of SO_2 by KMBS, first know the pH of the wine, and check the level of free SO_2 already present.

Next, use Table 1 and the pH of the wine to find the target amount of free SO_2 needed to maintain 0.8 ppm molecular SO_2. Then subtract the current, measured free SO_2 concentration in the wine from the target free SO_2; the difference is the addition to make.

Target free SO_2 (mg/L) - Current free SO_2 (mg/L) = SO_2 addition to make (mg/L)

Once you determine the addition to make, use the equation below to calculate how much KMBS to add to the batch. Note the factor of 1.74 accounts for KMBS containing 57.6% SO_2. To convert wine to liters from gallons, multiply gallons by 3.785. Divide by 1,000 to convert from milligrams (mg) to grams (g) of KMBS to add.

Desired Free SO_2 (mg/L) × 1.74 × L of wine / 1000 = g KMBS to add

Some amount of the calculated free SO_2 addition will bind and be unavailable to protect the wine, resulting in a free SO_2 value lower than the target. It is recommended to increase your calculated addition by 30-50% to account for the portion that will bind. Make the addition by dissolving the KMBS in a small volume of cool chlorine-free water, then mix into the batch. After the addition is made, it is good practice to re-measure free SO_2, particularly at critical points such as pre-bottling.

Example calculation: How many grams of KMBS should be added to a 450 gallon batch of wine with pH 3.5 and current free SO_2 level of 27 ppm? Assume the winemaker wants to achieve 0.8 ppm molecular SO_2.

450 gallons x 3.785 L/gallon = 1703.25 L

Target free SO_2 is 40 mg/L for pH of 3.5 (Table 1)

40 mg/L target free SO_2 – 27 mg/L current free SO_2 = 13 mg/L addition of SO_2

13 mg/L x 1.74 x 1703.25 L / 1000 = 38.5 g KMBS to add

To account for what may bind, an additional 30-50% may be added. For example, to add an extra 40%:

38.5 g KMBS x 0.4 = 15.4 g KMBS

38.5 g KMBS + 15.4 g KMBS = 53.9 g KMBS to add.

Key Points for Sulfur Dioxide Use in Wine

- Know wine pH and free sulfur dioxide concentration of wines in production
- Maintain 0.5 - 0.8 ppm molecular SO_2 to inhibit growth of most yeast and bacteria in wine
- Calculate additions and double check
- KMBS contains 57.6% SO_2
- Use inert gas cover to minimize O_2 in the headspace while making additions
- After making an add, mix the wine, then measure SO_2 (within 24 hours)
- Monitor SO_2 level in wines on a regular schedule; monthly is ideal
- Safety training for proper use and handling of SO_2 is essential

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