

SULFUR DIOXIDE

The science behind this anti-microbial, anti-oxidant wine additive

BY Pat Henderson, Senior Winemaker, Kenwood Vineyards, Kenwood, Calif., Author of *About Wine*

Sulfur dioxide was first used in winemaking when the Romans discovered that if you burn candles made of sulfur inside empty wine vessels it would keep them fresh and prevent them gaining a vinegar smell. 2,000 years later sulfur dioxide, or SO₂, still remains without a doubt the most important additive that is used in winemaking.

Used as both an antimicrobial agent and antioxidant, winemakers find it indispensable to preserve wine quality and freshness. However, if used improperly, the effects can be just as adverse as they can be beneficial.

All wines benefit from tender care, whether one is crushing, racking, or bottling, the gentlest method of accomplishing a task is usually the most successful. Just as it is with any of the other tools and techniques a vintner may use, the addition of sulfur dioxide works best when enough is added at the proper time to accomplish the desired result without adding too much and adversely affecting wine quality.

The amount and timing of sulfur dioxide additions depends on the style of wine that is being made and the composition of the wine to which it is being added. While it is possible to make wine without adding sulfur dioxide, you cannot make wine that contains no sulfur dioxide at all. This is because yeast produce a small amount, about 10 parts per million, during fermentation.

When adding sulfur dioxide to must or wine it is important to consider the stage of winemaking that it is in, such as fermentation, ageing or prebottling. You should also consider what the status of the malolactic fermentation is and whether you want to encourage or discourage it, and how turbid or clean the wine is, and how long it will be before the wine is consumed.

Because of these variables and the variation in winemaking styles, every winemaker or winemaking text is likely to have a different answer to the question: “how much sulfur dioxide should be added?” This confusion can be frustrating to novice vintners but it illustrates one important point; there are few absolute rules of winemaking and depending on the situation and the type of wine that is being made there are many options.

Every winemaker or winemaking text is likely to have a different answer to the question: “How much sulfur dioxide should be added?”

Additionally, since there is no “one size fits all” answer on the use of sulfur dioxide in wine, it is important to have an understanding of the chemistry of sulfur dioxide and how it reacts in a given wine before it can be used properly.

The subject of chemistry can be daunting for those who have not studied it since high school and the chemistry of sulfur dioxide in wine is no exception. Because of this, some winemakers have only a basic knowledge of how sulfur dioxide reacts in wine and the different forms that it takes.

Chemistry of sulfur dioxide

Sulfur is an element found on the periodic table. In its pure form, it can be dusted or sprayed on grapevines during the growing season to prevent rot and mildew from developing. If sulfur is **oxidized**, it forms sulfur dioxide or SO₂.

Oxidation is the term used by chemists to describe when an element or compound, such as sulfur, loses electrons. While oxidation reactions do not necessarily have to have the presence of oxygen to occur, they often do because when oxygen reacts with an element or compound it readily accepts electrons.

The burning of sulfur in the air oxidizes it and produces SO₂ in the chemical reac-

tion: S + O₂ = SO₂.

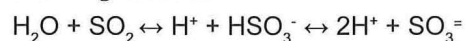
Sulfur dioxide gas has a sharp pungent aroma that smells like a burnt match, this is hardly surprising because match heads contain sulfur and when they ignite, they release SO₂.

In a chemical reaction where sulfur gains electrons it is said to be reduced. Compounds that are made up of reduced sulfur are called **sulfides**. Sulfide compounds are characterized by a strong unpleasant odor.

Hydrogen disulfide (H₂S), is a wine spoilage compound that has an aroma that smells like rotten eggs. It can have several causes, but it is most frequently a result of residual sulfur dust present on grapes when they are harvested, being reduced by yeast to H₂S during fermentation.

Hydrogen disulfide can also be caused by a shortage of yeast nutrients during fermentation. H₂S can undergo further chemical reaction to form compounds called mercaptans. Mercaptans also have strong unpleasant aromas that are reminiscent of cabbage, garlic, and skunk. Although sulfur dioxide and sulfides both contain the element sulfur, there is no danger of added SO₂ forming H₂S.

Sulfur dioxide itself is a gas that readily dissolves in water, once dissolved it reacts with the water to form new compounds called **sulfites** as shown in the following reaction:



In solution with H₂O (water), SO₂ is called **molecular SO₂**, HSO₃⁻ is called **bisulfite** and SO₃⁼ is called **sulfite**. The negative signs (- and =) denote the negative charge of the bisulfite and sulfite ions (molecules with a charge are called ions). The double arrows (↔) of the equation denote that the reaction is at equilibrium. At equilibrium, the rate at which bisulfite ions become sulfite is the same as the rate sulfite ions become bisulfite. The reaction between the different types of sulfite is going both ways at a steady state so the concentration of the sulfite compounds remains constant.

While the concentration of the different forms of sulfites may be steady, it does not mean there are equal amounts of the compounds in solution; the acidity or pH of the water has a huge affect on their concentration. The more acidic or the lower the pH of the water, the more heavily the reaction is weighted to the molecular SO₂ side. The more basic or higher the pH is, the more sulfite that is present as illustrated in Figure I.

How does it differ when SO₂ dissolves in wine? Since wine is more than 80%

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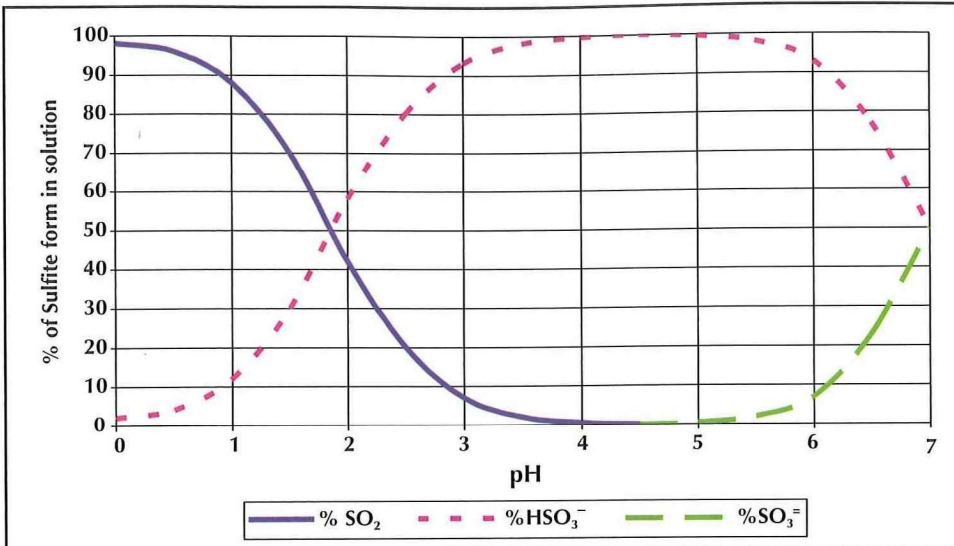


Figure I. The percentage of the different forms of free sulfite over the pH range (0 to 7). Wines usually range from pH 3 to 4, so bisulfite (HSO₃⁻) is the dominant form of free sulfite in wine.

Total sulfur dioxide		
Free sulfur dioxide		Bound sulfur dioxide
Molecular SO ₂	Bisulfite HSO ₃ ⁻	Sulfite SO ₃ ⁼
		Sulfites attached to sugars, acetaldehyde and phenolic compounds

Figure II. Different forms of SO₂.

water, the reaction, or **disassociation**, of molecular SO₂ into sulfites happens in much the same manner. Since wine is acidic (between 3 and 4 pH), molecular SO₂ and bisulfite make up the vast majority (99.99% at pH 3.4) of the sulfite compounds present in wine.

Sulfites will also react with other chemical constituents found in wine such as sugars, acetaldehyde, and phenolic compounds. When a sulfite reacts with

another molecule and becomes part of its structure it no longer takes part in the equilibrium reaction and it is called **bound**. Sulfites that still are part of the equilibrium reaction are called **free**. The combined amounts of free and bound sulfites are called **Total SO₂**.

The more compounds that are available in a wine for sulfites to bind to, the higher the ratio of bound to total sulfites there will be. Therefore, wines that are sweet or

have high solids because they have not been settled or filtered will have a lower ratio of free to total SO₂.

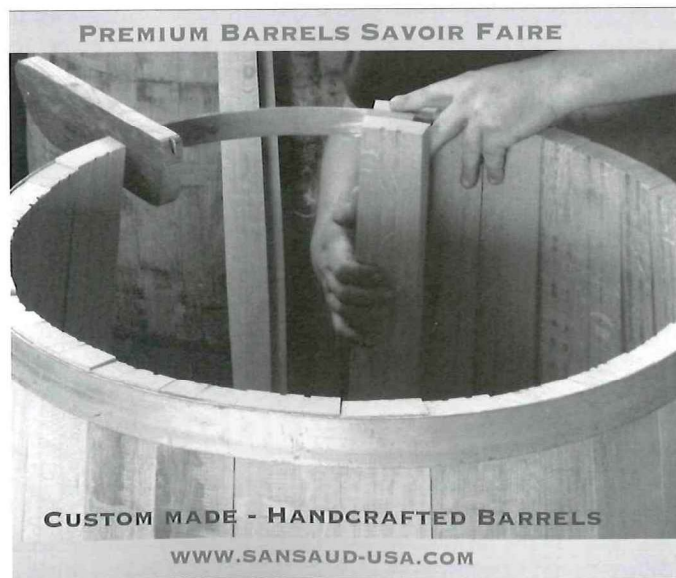
When sulfite binds to anthocyanins (the phenolic molecule that gives red wines their color), the anthocyanins go from a colored to a colorless form. Red wines that receive an SO₂ addition will have a slightly less intense color. This effect is particularly noticeable in light colored reds or rosé wines.

Knowing both the amount of free and total sulfites is very important because only the free forms of sulfites are available for providing a preservative role in wine. This is often expressed as ppm free SO₂/ppm total SO₂ to denote which number is free and which is total; these numbers can readily be determined by chemical analysis.

Sulfur dioxide concentration is measured in parts per million (ppm) or as milligrams per liter (mg/L). A wine with 19 ppm free SO₂ and 51 ppm total SO₂ would be noted with 19/51. The amount of bound sulfites would be equal to the total SO₂ minus the free SO₂, (51 - 19 = 32). For dry table wines the level of free sulfur is usually somewhere around 35% to 75% of the level of total SO₂.

Anti-oxidation role of sulfur dioxide

Oxidative reactions can occur in both red and white wines but are particularly noticeable in the latter. Dissolved oxygen in wine can react with phenolic compounds giving the wine a brownish hue. Another product of this oxidation is the compound acetaldehyde, which has a nutty, sherry-like aroma. Sulfur dioxide is used by winemakers to prevent this oxi-



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Table I: Table of molecular SO₂ concentrations over pH

pH	% of Free Sulfur Molecular SO ₂	ppm free for 0.8 Molecular	ppm free for 0.5 Molecular
2.90	7.5	11	7
2.95	6.6	12	7
3.00	6.1	13	8
3.05	5.3	15	9
3.10	4.9	16	10
3.15	4.3	19	12
3.20	3.9	21	13
3.25	3.4	23	15
3.30	3.1	26	16
3.35	2.7	29	18
3.40	2.5	32	20
3.45	2.2	37	23
3.50	2.0	40	25
3.55	1.8	46	29
3.60	1.6	50	31
3.65	1.4	57	36
3.70	1.3	63	39
3.75	1.1	72	45
3.80	1.0	79	49
3.85	0.9	91	57
3.90	0.8	99	62
3.95	0.7	114	71
4.00	0.7	125	78

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

dition; however it does not act by directly removing oxygen from wines and musts.

Although the sulfite ion (SO₃²⁻) can bind with oxygen, there is very little sulfite ion present in solution at the pH range found in wine (see Figure I). Rather sulfur dioxide prevents oxidation by binding with the precursors involved in oxidative reactions preventing them from reacting with oxygen or by binding with compounds already oxidized to reverse oxygen's effect. Sulfur dioxide also acts by reducing the activity of the degenerative enzyme tyrosinase (polyphenol oxidase), which is present in juice.

Because of sulfur dioxide's ability to bind with the precursors and the products of oxidation, it can be used as both a preventative and a treatment. For example, an oxidized white wine with a brown tint and a nutty smell can be improved with an addition of sulfur dioxide that bleaches out some of the dark color and binds with the acetaldehyde to reduce the nutty smell.

Antimicrobial role of sulfur dioxide

Sulfur dioxide is a broad-spectrum antimicrobial agent that has an inhibitory effect on a wide variety of microorganisms. The level of sulfur dioxide at which the microbe, either yeast or bacteria, is affected varies widely by species. This

Figure III: Formula for potassium metabisulfite addition

$$\frac{(\text{gallons of wine}) \times 3.785 \times (\text{ppm of addition})}{(1000) \times (0.576)} = \text{grams of KMB to add}$$

3.785 is the conversion from gallons to liters

1000 converts mg/L (ppm) to g/L

0.576 is the fraction of SO₂ in KMB

This formula can be simplified to:

$$(\text{gallons of wine}) \times (\text{ppm of addition}) \times (0.0066) = \text{grams of KMB to add}$$

variation allows winemakers to use sulfur dioxide to treat microbes in the wine or must selectively and inhibit or kill undesirable microbes without harming the desirable ones.

It has been understood since the early 1900s that only the free forms of sulfur dioxide (and not the bound) have an antimicrobial effect. It was further discovered in the 1960s that molecular SO₂ was several hundred times more effective than bisulfite.

The mechanism for sulfur dioxide's antimicrobial effect works by the sulfur dioxide entering the microbe and disrupting the activity of the enzymes and proteins of the cell. Since only the molecular form of sulfur dioxide can enter through the cell membrane, it is the concentration of molecular sulfur dioxide that controls microbial growth.

Although there is some evidence that a high concentration of acetaldehyde-bound bisulfite inhibits the growth of some species of malolactic bacteria, this effect is eclipsed by the role of molecular SO₂. Since the percentage of free SO₂ that is in the molecular form is dependent on pH, the importance of pH in the effectiveness of sulfur dioxide and the microbial stability of wine in general cannot be overstated.

Effect of sulfur dioxide on yeast and malolactic bacteria

Sulfur dioxide has some degree of inhibitory effect on all yeast; however, the *Saccharomyces* yeast strains that are used by winemakers for alcoholic fermentation are much more resistant to it than "wild" yeasts are. Wild yeast is the term used for a number of non-*Saccharomyces* species of ambient yeast that are present on grapes and in the winery cellar. Wild yeasts are sensitive to both sulfur dioxide and alcohol.

Wild yeast can begin a spontaneous fermentation in juice but soon are killed by the alcohol that they produce. At this point, the *Saccharomyces* that is present, either indigenous to the grapes or added by the winemaker, which is more resistant to alcohol takes over to complete the fermentation.

Wild yeast can sometimes be the

source of off-flavors therefore most winemakers elect to control them with a small dose of sulfur dioxide and then inoculate the must with a commercial wine strain of *Saccharomyces*. A molecular SO₂ level of 0.4 ppm (equivalent to a free SO₂ level of 20 ppm at 3.50 pH) will kill wild yeast without adversely affecting *Saccharomyces*.

The inhibitory effect of sulfur dioxide on malolactic fermentation is much greater than it is for the alcoholic fermentation that is performed by *Saccharomyces* yeast. Malolactic fermentation (often abbreviated to ML fermentation or MLF), is the secondary fermentation by bacteria that converts malic acid found in grape juice to lactic acid, which is less acidic.

There are several species of bacteria that are capable of MLF in wine, some more desirable than others. *Oenococcus oeni*, the most commonly used species of malolactic bacteria, is very sensitive to sulfur dioxide and has difficulty growing at levels above 25 ppm total SO₂.

The sensitivity of malolactic bacteria to sulfur dioxide can be used by winemakers to influence the flavor of a wine. MLF has several effects on the flavor of a wine, it lowers the acidity and it can produce a "buttery" aroma, particularly in white wines. In addition to these sensory qualities, it makes a wine more microbiologically stable.

If the MLF is completed in the cellar prior to bottling, you do not have to worry about it occurring after bottling and spoiling the wine. If you wish to make a more tart, fruit forward wine such as a Riesling or Sauvignon Blanc, MLF would not be as appropriate and MLF can be prevented by an early dose of sulfur dioxide.

In a wine that will be aged for a longer period in barrels, or if you desire a softer less acidic character, MLF is more appropriate. Chardonnay and red wines often are put through MLF either prior to or during ageing.

Effect of sulfur dioxide on wine spoilage microorganisms

Although there are no human pathogens that can grow in wine, there are a number

of spoilage bacteria and yeast that can adversely affect a wine's flavor. The most common of these are *Acetobacter*, *Lactobacillus*, *Pediococcus*, and *Brettanomyces*. All of these are sensitive to some degree to sulfur dioxide but the best results come from a combination of sulfur dioxide and good cellar practices.

Acetobacter is also known as acetic acid or vinegar bacteria. As the name implies, it can grow in wine and produce vinegar (acetic acid). *Acetobacter* can only develop in the presence of oxygen and often becomes a problem in wines that are being aged in un-topped containers. It can be controlled with a combination of sulfur dioxide and keeping tanks and barrels topped and full after fermentation.

Lactobacillus and *Pediococcus* are both forms of undesirable malolactic bacteria. *Lactobacillus* typically grows in high pH red wines that have a stuck fermentation. It grows on the sugar present from the incomplete alcoholic fermentation and produces large quantities of acetic acid. Because it usually grows in high pH musts (greater than 3.75), sulfur dioxide is less effective. The best treatment is prevention, adding acid to a high pH must, and maintaining a healthy fermentation

that completes to dryness.

If *Lactobacillus* has already become established, lysozyme (an antimicrobial enzyme that is effective at high pH), can be added to control growth. *Pediococcus* produces an off-aroma that is described as "vegetal" or "dirty socks" and often comes from cooperage that has not been kept clean. Like all spoilage microbes, it can be prevented by a combination of proper sanitation of winery equipment and cooperage, adding pure inoculums of yeast and malolactic bacteria for fermentation, and the addition of sulfur dioxide.

Brettanomyces is yeast that can grow in wine without the presence of oxygen or sugar. It usually shows up in high pH red wines while they are being aged and it produces an aroma that is described as "barnyard" or "horse sweat." *Brettanomyces* grows very slowly and some winemakers feel that a small amount of its aroma can add complexity to a wine. However, too much of this character can be seen as a flaw and most winemakers avoid it.

Sulfur dioxide usually does not kill *Brettanomyces* but prevents it from growing. As a wine ages, the level of free SO₂ diminishes, and a wine that has

been adjusted with sulfur dioxide prior to being placed in barrels may require supplementary additions as it is being aged to prevent *Brettanomyces* from developing.

When to add sulfur dioxide

The flavor of white wines always benefits from the preservative nature of sulfur dioxide. The timing of the addition, whether it is added before or after alcoholic fermentation, has a huge affect on a wine's ultimate character. If sulfur dioxide is added prior to alcoholic fermentation, the enzyme polyphenol oxidase is inhibited and less oxidative browning of the juice occurs. This helps to preserve the fruity and floral aromas found in the juice.

The presence of sulfur dioxide will also inhibit malolactic bacteria and help to prevent malolactic fermentation (MLF) from occurring, leaving more of the natural acidity in the final wine. This method is preferred for fruit-forward wines with crisp acidity that will not receive a great deal of barrel ageing.

If sulfur dioxide is not added prior to alcoholic fermentation, more oxidative browning will occur and, within a few days of pressing, the juice will take on a

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Figure IV: Example of a sulfur dioxide addition calculation

A Zinfandel has just finished aging in a barrel for one year and needs its sulfur dioxide level adjusted before it is ready to be bottled. It is dry and has completed malolactic fermentation and has very good clarity from setting during ageing. The analysis before the addition is pH 3.45, and the sulfur dioxide is 16/35 and there are 6,000 gallons of wine.

Q: How many grams of KMB should be added to protect the wine after it has been bottled?

A: Since the wine has completed both the alcoholic and malolactic fermentations a molecular SO₂ level of 0.5 ppm should be adequate to preserve the wine. By looking at the chart in figure 3 you can see the free SO₂ must be 23 ppm to have a molecular SO₂ level of 0.5ppm. With the free SO₂ currently at 16 ppm it must increase by 7 ppm to attain the desired amount.

$$23 \text{ ppm} - 16 \text{ ppm} = 7 \text{ ppm}$$

Since only a portion of the KMB that is added will be free SO₂, it is necessary to estimate what the percentage that will become free SO₂. Since the wine is clean and dry, we can assume that the ratio will be on the high side of the 35 to 75% range and for this example we will use 70%.

$$7 \text{ ppm} \div 0.7 = 10 \text{ ppm}$$

To determine the amount of KMB when adding 10 ppm:

$$(10 \text{ ppm}) \times (6,000 \text{ gallons}) \times (0.0066) = 396 \text{ grams of KMB}$$

If you wish to convert this to pounds (one pound is approximately 454 grams):

$$396 \text{ grams} \div 454 \text{ grams per pound} = .872 \text{ pounds}$$

For an aqueous solution of sulfur dioxide:

$$\text{volume of aqueous SO}_2 \text{ in mL} = \frac{\text{PPM addition}}{2.6} \times \frac{\text{gallons wine}}{\% \text{ SO}_2 \text{ solution}}$$

For the wine used in the KMB example using 5% aqueous SO₂.

$$10/2.6 \times 6,000/5 = 4,615 \text{ mL}$$

There is a certain amount of guesswork in estimating just how much of a sulfur dioxide addition will be available as free SO₂ and it is always best to be conservative—you can always add more, but you cannot add less.

brownish hue. While this dark color may cause alarm, you should not be overly concerned because after fermentation the dark, oxidized phenols will settle out, leaving a wine that is much brighter and more appropriate in color for a white wine.

Since the phenols that can oxidize have been removed from settling and racking, there is less of a potential for the wine to oxidize after fermentation and the wine will be more color-stable and better able to age. This method of pre-fermentation oxidation does diminish some of the fruity and floral aromas in the final wine.

The absence of sulfur dioxide allows MLF to commence after primary fermentation is complete, lowering the acidity of the wine, and making it more microbiologically stable. After MLF is finished, sulfur dioxide should be added to protect the wine. If MLF is not desired, the wine should be adjusted with sulfur dioxide after primary fermentation is complete.

For red wines, it is a good idea to add a small amount (about 30 to 40 ppm), of sulfur dioxide immediately after the grapes have been crushed. While not absolutely necessary, this will discourage the growth of spoilage organisms such as Lactobacillus and allow the yeast to get a good start on the fermentation without competition from other microbes.

By the end of primary fermentation, the majority of SO₂ will be bound up and there will not be so much residual SO₂ that the growth of malolactic bacteria is inhibited. After MLF is complete, sulfur dioxide should be added to protect the wine during ageing.

For both red and white wines, as they age, free sulfites are bound by other compounds or are oxidized to sulfate anion resulting in a gradual lowering of the effective amount of sulfur dioxide in wine. For this reason, it is always a good idea to monitor the SO₂ level during ageing and to add more as needed.

How much sulfur dioxide to add?

Since it is the molecular form (SO₂) of sulfur dioxide that has the most potent antimicrobial effect, and the percentage of sulfite that is in the molecular form is directly dependent on the pH, one must always consider both the pH and the free SO₂ when deciding how much sulfur dioxide to add to a wine.

By knowing the pH, you can determine the percentage of free sulfur that is in the molecular (SO₂) form by using Table I.

For white wines, a level of 0.8 ppm molecular SO₂ will slow down the growth of yeast and will prevent the growth of most other microbes. This level of sulfur dioxide will bind up most of the acetalde-

hyde in a wine and reduce any oxidation aroma considerably. Therefore, 0.8 ppm is a good target level for molecular SO₂ immediately prior to bottling and will provide the maximum protection for the finished wine.

However, sensitive tasters will be able to detect a slight burnt match aroma at 0.8 ppm SO₂. This is usually not a problem however because few consumers will be able to detect it. Additionally if the wine is bottle-aged for a few months before consumption, the SO₂ will decrease as more sulfites react with other chemical constituents in the wine and become bound. Thus, a wine bottled at 0.8 ppm will decrease to a lower level fairly quickly and there would be no detectable sulfur dioxide aroma.

Winemakers who seal their wine with screw caps know that the sulfur levels diminish more slowly after bottling than wines sealed with corks. In this case, 0.7 ppm would be a better target for molecular SO₂ at bottling. During storage, after all fermentations have completed, white wines should be adjusted to between 0.5 and 0.8 ppm molecular. If the wine is sweet or if you wish to prevent MLF, the wine should be kept at the high side of this range.

Total SO₂ should be kept below 110 ppm for table wines because, at higher levels, the wine can acquire off-flavors. For dessert and fortified wines, that are very sweet, it may be necessary to exceed this limit to obtain adequate free SO₂.

For red wines, a level of 0.5 ppm molecular SO₂ at bottling is an appropriate target. You do not need to keep the molecular SO₂ as high on red wines as you do white wines for several reasons:

First, in most cases, MLF is complete in reds so there is no need to try to discourage it.

Second, red wines are less sensitive to oxidation and their flavor is less dependent on fresh fruity aromas so sulfur dioxide's preservative effects are not as critical.

Third, red wines usually have a higher pH than whites and often it is not possible to adjust the sulfur dioxide to a level that reached 0.8 ppm molecular SO₂ without having too much total SO₂.

By knowing the pH of the wine and using the chart in Table I, it is easy to see what level of free SO₂ is necessary to obtain a given level of molecular SO₂. However, it is more difficult to determine precisely what the ratio of free to bound sulfur dioxide level will be.

When adding sulfur dioxide, the amount in ppm that you add should change the total SO₂ by the same ppm. However, because some of the sulfur

dioxide that you add will become bound, the level of free SO_2 will change by a fraction of the amount that is added.

Free SO_2 in wine ranges from about 35% to 75% of the total SO_2 depending on the amount of compounds that are available in the wine to which the sulfite molecules can bind. To approximate what the ratio will be, use the 35% level for wines that are turbid or sweet and the 75% level for clean, dry wines.

The higher the level of total SO_2 in the wine, the higher the ratio will be, because there are fewer unbound compounds available for reacting with additional sulfur dioxide as it is added. Sulfur dioxide is also more effective if it is added less often and in greater quantities because it will be more of a shock to the microbes. For example, one addition of 30 ppm is more effective at killing microbes than two additions of 15 ppm spread several weeks apart.

Forms of sulfur dioxide to add

Sulfur dioxide is available in its pure form as a compressed gas that can be made into an aqueous solution for wine additions. Most wineries use a stable, powdered form of sulfur dioxide called potassium metabisulfite. Potassium metabisulfite has the molecular formula of $\text{K}_2\text{S}_2\text{O}_5$ and is 57.6% available SO_2 by weight. Potassium metabisulfite is often abbreviated as KMB or sometimes PMBS or KMBS (K is the chemical symbol for potassium). It should be noted that KMB, PMBS and KMBS are abbreviations and not chemical formulas.

The formula and calculations for determining how many grams of KMB you need to add for a given rise in ppm of SO_2 is shown in Figures III and IV. For convenience, pre-weighed effervescent tablets are also available for additions to barrels.

Some wineries prefer to use a premixed aqueous solution of sulfur dioxide rather than KMB. The liquid is typically 5% to 10% SO_2 by weight and it can be purchased or made up at the winery by dissolving SO_2 gas or KMB into distilled water. The liquid can be directly added to wine without mixing and the proper amount is measured volumetrically instead of weighed on a scale. There is an example of the calculation for a sulfur dioxide addition to wine in Figure IV.

Sulfur dioxide is also available in another powdered form, sodium metabisulfite. Solutions of sodium metabisulfite in water make an excellent sanitizing agent for winemaking equipment but it should **not** be used for making additions to wine. Although it is not toxic, the sodium in sodium metabisulfite is not healthful and it is best left out of wine.

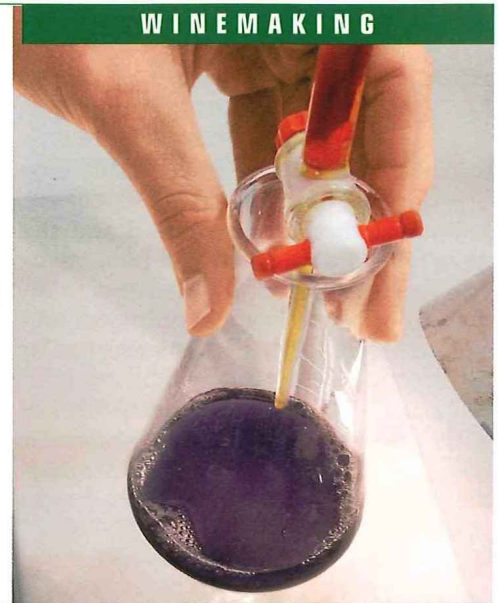
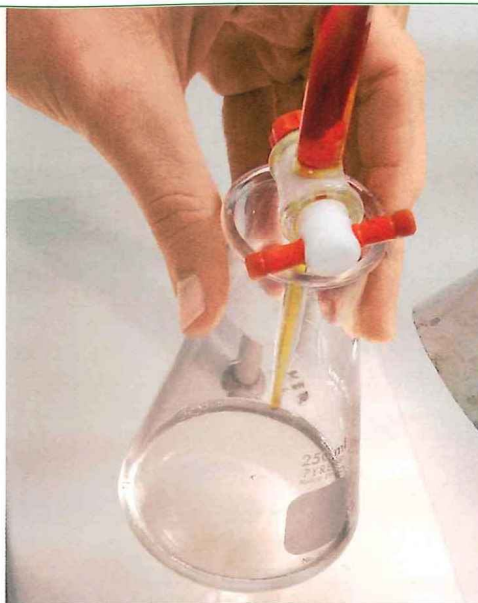


Figure V-a and V-b: At the endpoint of the Ripper titration, the indicator goes from colorless to blue. This is easy to see in white wines as demonstrated in the before, V-a (left) and after, V-b (right).

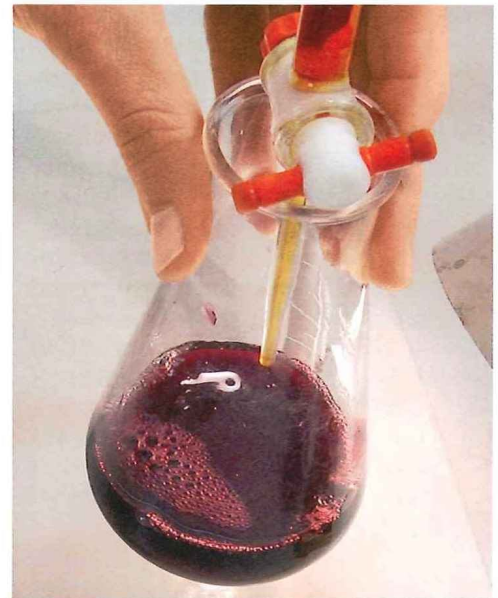
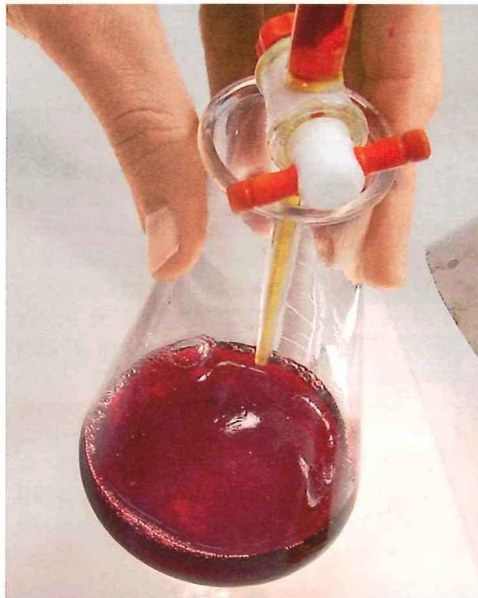


Figure V-c and V-d: For red wines, the blue color of the endpoint is obscured by the red color of the wine and is less obvious, as shown in the before, V-c (left) and after, V-d (right).

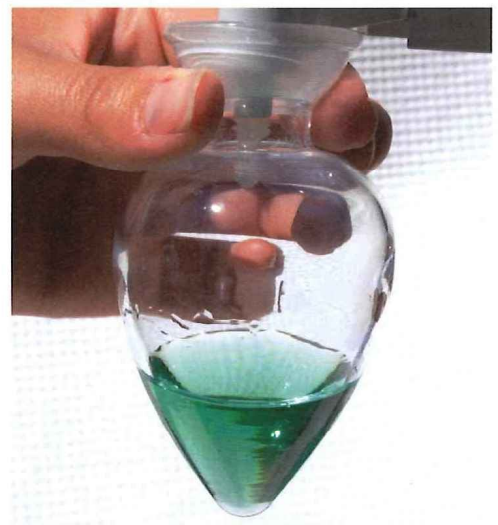


Figure V-e and V-f: In the aeration/oxidation method the sulfur dioxide is aspirated out of the wine sample before titration so the endpoint is not affected by the color of the wine. Before and after the endpoint are shown in figures V-e (left) and V-f (right).

Measuring sulfur dioxide

The exact amount of both free and total sulfur dioxide in a wine or must can only be determined by chemical analysis. Two primary methods that are used are known as the Ripper method and the Aeration-Oxidation method. Both methods have limitations and require an investment in laboratory equipment and chemicals and a degree of expertise in laboratory practices.

The Ripper method works much better with white wines than it does for red wines. At the endpoint of the ripper reaction, the indicator goes from colorless to

indigo blue as seen in a white wine in Figures V-a and V-b. The blue color of the endpoint in the reaction is much more difficult to determine in deeply colored red wines as seen in Figures V-c and V-d.

In the Aeration-Oxidation method the endpoint of the titration is not affected by a wine's color and goes from purple to light green, as seen in Figures V-e and V-f. For this reason, the Aeration-Oxidation method is preferred for red wines.

If the Ripper method is the only method available, red wines can be diluted 50% before analysis to lower the intensity of the color. Just be sure to double the

results to make up for the dilution. Additionally for red wines, the free sulfur dioxide by ripper usually runs slightly higher than the actual amount. After adding sulfur dioxide, wait 24 hours before performing analysis to allow the free SO₂ to stabilize.

Working with sulfur dioxide

Working with the powdered forms of sulfur dioxide is not a dangerous activity but there are certain precautions that should be taken. Sulfur dioxide at the levels that are found in wine are not high enough to cause for concern however winemakers are exposed to greater levels when they are working with sulfur dioxide solutions.

Fumes of sulfur dioxide gas can irritate the throat and eyes so it is always best to work in a well-ventilated place and to use a respirator when mixing sulfur dioxide solutions. When adding KMB, first mix the powder in a small amount of cold water (about 50 g per Liter, [7 ounce per gal]), then after it has dissolved, mix the solution into the wine.

Additionally, under highly acidic conditions, the concentration of the more volatile molecular form SO₂ is higher, so you should never mix both acid and sulfites together in the same container when they are being added to wine. A better method is when adding both acid and KMB is to first mix and add the acid to the wine and then add sulfur dioxide. A very small portion of the population can have an intense asthmatic reaction when exposed to the fumes of sulfur dioxide, so extra care should be taken for anyone with a history of asthma when working with sulfites.

Summary

Sulfur dioxide is one of the most effective tools that a winemaker has to protect a wine's quality and influence what it will taste like. Deciding when and how much sulfur dioxide to add depends on what stage of winemaking the wine is in and what you are trying to accomplish with the addition. Furthermore, to determine the proper quantity of potassium metabisulfite to use for the addition, you need to know the pH and free and total sulfur of the wine.

With any technique used by a winemaker, it is important to have knowledge of the science behind the skill. By understanding the chemistry of sulfur dioxide and what reactions that occur when it is added to wine, you can make decisions that are based on your goals for what you want the wine to ultimately taste like rather than just following a "one size fits all" recipe. **PWV**

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