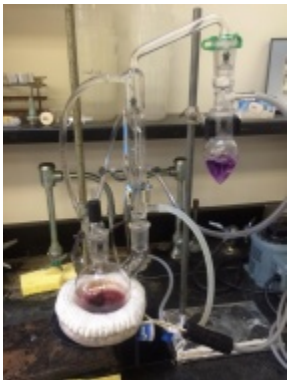
Grapes 101

This Article Contains Sulfites - Part II

Grapes 101 is a series of brief articles highlighting the fundamentals of cool climate grape and wine production.
By Chris Gerling

Editor's Note: *See previous article, also entitled* *This Article Contains Sulfites* *in Issue 12 of Appellation Cornell, published in 2012*.



Measuring sulfur dioxide (SO2) using the "Ripper Method" apparatus in the lab. Photo by Chris Gerling.

Sulfur dioxide (SO_2) is basically *the* wine preservative. There are a few other compounds to choose from, but across centuries and continents, when winemakers have reached for a way to keep their wines clean and fresh, they have almost always employed SO_2. I have compiled a list of our current thinking about SO_2, starting with basics and moving to more recent (or recently remembered) items that may even surprise people who work with it every day. If you're new to wine and SO_2, take it from the top; if you have some experience with wine chemistry, you may want to start at the bottom and move upward until you're no longer surprised.

1. **SO_2 is not new, nor is its use limited to wine.** The ancient Greeks knew of the efficacy of burning sulfur compounds for decontamination, and supposedly Ulysses called for this treatment in his house when he finally returned from Troy. To this day, sulfur wicks are often burned in barrels that will be stored empty for any length of time. And it's not just wine: sulfites are also used to preserve dried fruit, deli meats, certain vegetables and even seafood. These days, SO_2 gets into most wines through the addition of a solution of powdered potassium or sodium metabisulfite in water (small and mid-size wineries) or by adding the gas directly (larger operations). Effervescent tablets are also available.

2. **SO_2 multitasks like a champ.** The primary reason SO_2 has been and continues to be the preferred preservative is because it offers two kinds of protection to wine- inhibiting: both spoilage and oxidation. This part can get tricky, because the multiple actions rely on multiple personalities. When added to wine, SO_2 dissociates and becomes two different

chemical species, one antimicrobial (molecular SO_2) and one antioxidant (bisulfite), as shown in **Figure 1**. But wait, there's more. Some bisulfite will be bound by acetaldehyde and other compounds, effectively removing it from action. Only the "free" SO_2 that has not been bound has significant protective properties, so it is the free portion that most interests winemakers. No other single compound we're aware of can offer both of these benefits as effectively and as safely. Speaking of safety…

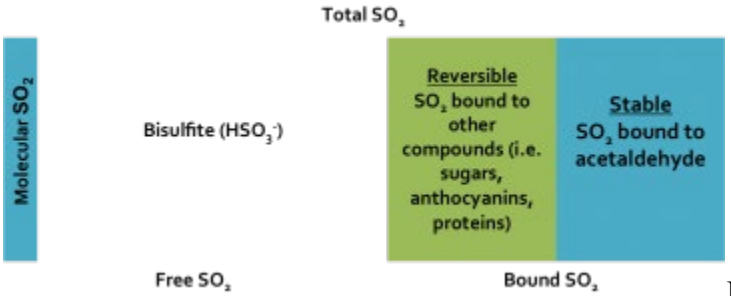


Figure 1. The distribution of SO_2 species. At wine pH values 3.2-3.5, sulfite is not present in significant concentrations.

3. **Wine headaches and SO_2**. As far as we can tell, those wine headaches are not about SO_2. We all know the stories and may have friends or family members who complain of headaches after drinking wine (especially red wine). There are definitely some possible adverse reactions from SO_2 exposure, mostly relating to sinus irritation and/or difficulty breathing, especially among those with asthma or asthma-related conditions. But the headache issue may be related to other factors, and controlled studies have yet to establish a clear link. SO_2 is also generally present in lower doses in red wines, especially free SO_2. The current prime suspects are biogenic amines (amino acid derivatives that may have biochemical activity-histamine being a prime example) and/or good old alcohol and the dehydration it brings along.

4. **How much is enough?** There's no "right" amount of SO_2 at bottling, especially if you don't know the pH of the wine. Back in point #2, I mentioned that SO_2 is actually two chemical species in wine, and that some is bound and some is free. Species distribution is determined by pH, with lower pH resulting in more molecular SO_2 at a given free SO_2 concentration. Many winemakers have a standard amount of free SO_2 (remember point #2?) at which they prefer to bottle the wine. While this might make sense from an oxidation standpoint, from an antimicrobial perspective, we see that we really also need to know the pH. As **Figure 2** shows, a given amount of free SO_2 may provide too little, the right amount or too much molecular SO_2. How can there be too much, you say? Once the sensory threshold is reached, the irritating qualities become much more apparent.

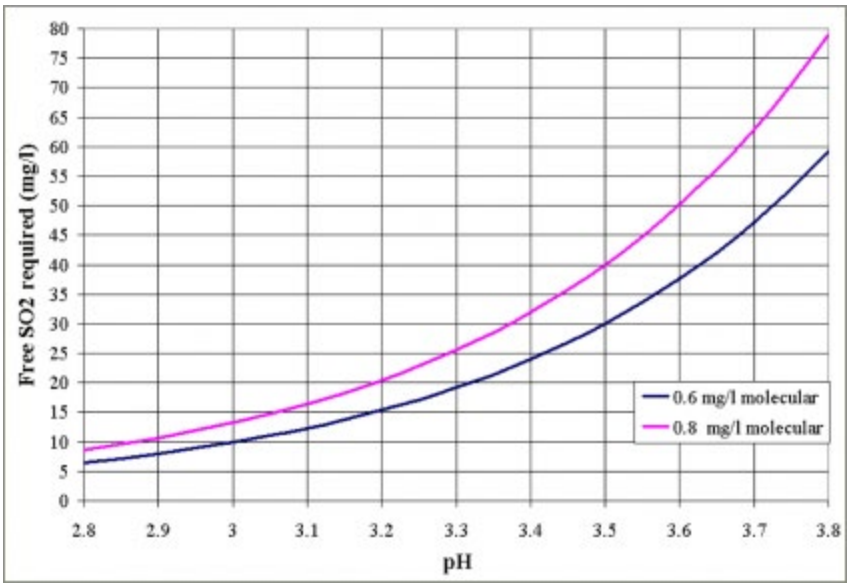


Figure 2. The amount of free SO2 required to protect against microbial spoilage depends on the pH of the wine.

5. **Sulfite-free?** Just because you didn't add any SO_2, or because you bought an organic wine, doesn't mean that your wine is sulfite-free. The secrets of SO_2 are known to more than just the human winemaking community. Yeast, our partners in fermentation, have also evolved to produce SO_2 in order to inhibit competing microbes. During the course of fermentation, some strains can produce much more than 10 parts per million (ppm, equivalent to mg/L) of total SO_2, the minimum concentration requiring "Contains Sulfites" on the label. A wine that is certified organic may not have any added sulfites, but still may need to mention sulfites on the label. A wine that is sold as "made with organic grapes" may have up to 100 ppm of total SO_2 from the yeast and/or additions. The bottom line is that any wine that does not have the sulfite acknowledgement on the label must undergo analysis to prove it is indeed below 10 ppm.

6. **Measuring free $S0_2$.** You don't have as much free SO_2 in your red wine as you thought. If you think that understanding all the forms and phases of SO_2 is complicated, try measuring it. We need to know the amount of free SO_2 to know how much protection the wine has, and the total amount (free plus bound) is the amount that most regulatory bodies are concerned with. In order to separate the SO_2 in a way that facilitates quantification, most methods call for acidifying the sample. Research has shown (for decades, actually) that such a change distorts the wine system and, particularly in the case of red wine, causes a lot of weakly bound SO_2 to be quantified as free. There is no free lunch, and there is a lot less free SO_2 in red wines than we think. This finding poses two big questions: 1) If we don't have "enough" SO_2 in red wine, why are they mostly spoilage and oxidation-free? And 2) how do I actually measure red wine accurately? The first question is a stumper, and preliminary trials have shown that the weakly bound SO_2 is not really useful for inhibiting microbes. The second question is a little easier, since Dlubac and Sacks have recently developed a method using gas detection tubes to

measure molecular SO_2 directly.

7. **SO_2 and water quality.** Preparing SO_2 solutions in plain water is a riskier proposition than you think. When the Sacks lab was working on the new measurement method and set out to evaluate and compare the existing methods, they made another "new" discovery that was also previously known but largely forgotten. Back to point #1, we remember that many winemakers make a powder in water solution to add SO_2. Water quality can be incredibly important while making this addition. In the presence- or absence- of certain impurities, SO_2 may react with itself and dissipate very rapidly. The insidious part is that sometimes a questionable water source may work fine, and other times problems can arise with "good" water. To see for ourselves, we made up some standard solutions using tap water, distilled water, and a 10% ethanol/water blend. I should note that we have pretty terrible water (pipes in our building, not the local water quality), but we were still surprised to see what happened, as can be seen in **Figure 3**. The tap water lost 40 ppm from both standards almost instantly, meaning that the 40 ppm standard had basically nothing and the 100 ppm standard had 60. Twenty-four hours later, the 100 ppm standard was all gone as well. The scary thing is that sometimes the same problem can happen with very pure water. The solution is to stabilize with 10% ethanol (or methanol if you're making a standard solution and not planning to add to the wine), but we can work to find a stabilizing agent that's more readily available. For now, if you're storing SO_2 for any time at all, it might be a good idea to do a check before and/or after adding it to a tank.

		After Add		24 Hours	
		Free	Total	Free	Total
Tap Water	40	5	2	0	0
Tap Water	100	64	65	0	0
Distilled Water	40	39	36	37	39
Distilled Water	100	98	98	94	100
10% Ethanol	40	41	40	39	42
10% Ethanol	100	102	105	99	110
Wine	40	19	37	11	38
Wine	100	72	105	59	103

Figure 3. Free and total SO2 concentrations in four liquids, measured right after making the solution and then 24 hours later.

As described above, SO_2 is an amazing and complicated preservative. It provides multi-faceted protection for wine, but also comes with plenty of challenges. People are wary of SO_2, and not without reason. Personally, I don't find it pleasant and would not add it to a cookie recipe to make them tastier. Yet, we can't find anything that combines the

relative safety and efficacy of SO_2, or we would have replaced it. And it's always a game of lesser evils and relative odds. For example, when used judiciously, SO_2 can limit acetaldehyde production. Acetaldehyde is a by-product of fermentation processes and is also thought to be carcinogenic. Which would you rather consume? In general, winemakers continue to use less SO_2 and government limits continue to drop. Perhaps a replacement preservative will be found soon. I, for one, just hope that it's easier to measure.

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