This Article Contains Sulfites

Grapes 101

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

By Chris Gerling

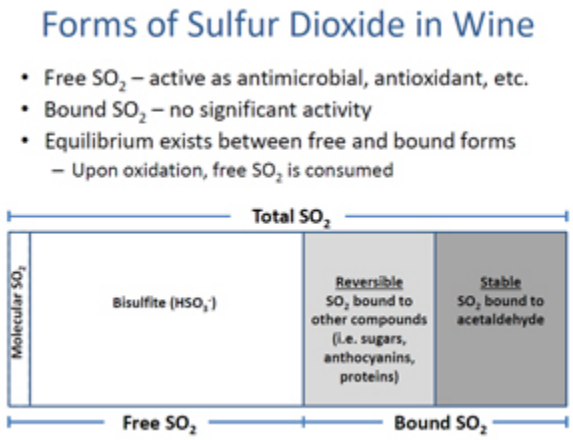
Iodine is used in the titrametric 'Ripper' method for measuring SO2

Somewhere below the notes about peach, jasmine and honeysuckle and possibly off to the right of the Government Warning about not operating motor vehicles, on most wine back-labels you are likely to find the two-word phrase "Contains Sulfites." What are these sulfites? How and why did they get into the wine? Are they necessary? Are they dangerous? While these seem like fairly simple questions, the theory and practice behind the use of sulfites is not so simple. At the New York Wine Analytical Lab, the vast majority of problems we see stem from problems with SO_2 management. In other words, getting a handle on SO_2 is one of the least enjoyable but most important facets of the winemaker's job.

Why sulfites?

“Sulfite” describes any compound that contains the sulfite ion (SO_3^{2-}). In practical winemaking terms we are almost always referring to sulfur dioxide (SO_2) or one of the compounds by which SO_2 is delivered to the wine. The “Contains Sulfites” warning must be placed on any bottle of wine that contains 10 or more parts per million (ppm). SO_2 is added to juice, wine and other foods because it is a powerful and flexible preservative—so effective, in fact, that many yeast strains actually produce a small amount of it to deter competing microbes.

While alcohol will protect people from pathogens, from a quality standpoint there are still a number of ways wine can be ruined. Able to counteract both microbial and oxidative challenges, SO_2 protects wines from these two major routes of spoilage and can even disable enzymes that lead to browning. SO_2 may be added as solid, liquid or gas, but only the gaseous form is 100% SO_2. When adding tablets or powders (or liquids in which these solids have been dissolved), the actual compound is likely to be potassium metabisulfite ($K_2S_2O_5$ or "KMBS") or an analog, and SO_2 is only a portion of what is added. KMBS is roughly 57% SO_2.



Free vs. bound SO_2

If you spend any time around a winemaker, you will inevitably hear the phrase "free SO_2." Just like all of the KMBS that gets added is not SO_2, not all of the SO_2 added to wine remains active. Some portion will become bound by various wine components and will no longer be available to serve as a protectant–hence the need to distinguish between total and free SO_2. Free SO_2 represents the portion that has not been bound and can therefore react with anything new that might threaten the wine. How much SO_2 is bound depends on the quantity of binding compounds in the wine, of which there are two major classes: those that bind reversibly and those that bind irreversibly. Acetaldehyde, a product of yeast metabolism and also alcoholic oxidation, is the primary binding compound, and it binds more or less permanently. Glucose (sugar), however, is an example of a compound that bonds weakly and possibly reversibly. Still with me? There's another twist, and that involves pH.

In solution, SO_2 can dissociate into three species: sulfite, bisulfite and what we call molecular SO_2. These different species help explain the antioxidant and antimicrobial properties. The proportion of each species is largely determined by the pH of the solution–juice and wine being in the range of 3 to 4. At wine pH, sulfite is not present in meaningful amounts, so what is left is the antioxidant bisulfite (roughly 95% by proportion) and antimicrobial molecular SO_2 (5% or less). The proportion of molecular SO_2 is also determined by pH, with lower pH providing

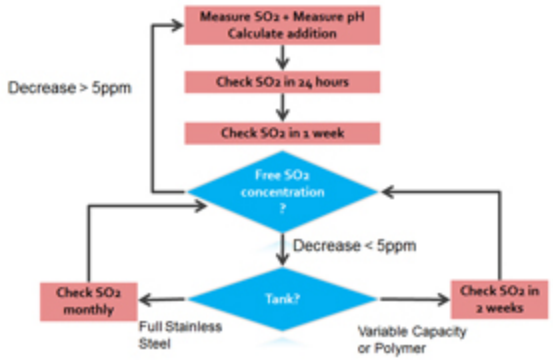
more molecular SO_2 (and less bisulfite) and higher pH giving less. The key idea is that molecular SO_2, and the antimicrobial assistance it provides, is present in small amounts but is very important in role, and so a higher pH means requires more SO_2 to do the same job. Here's an example: a measurement determines that the free SO_2 in a given wine is 30 parts per million (ppm). Is this enough to get molecular protection? It depends. If the pH of the wine is 3.4 or less, we have enough. If the pH is 3.5 or higher, the SO_2 level is probably low.

Measuring sulfites

So, to summarize: All of that powder you added is not SO_2, a subset of the SO_2 in the powder is bound rather than free, and most of the SO_2 that is free is not the part that is providing antimicrobial protection. It turns out that winemakers are most interested in a fraction of a fraction of a fraction of something that is quantified in parts per million. As you might expect, measurement is important– and tricky. There are a few ways to measure SO_2, but the two primary methods available to small wineries are titration (i.e., "ripper") and aeration/ oxidation (i.e., "A/O" or "aspiration"). The titrimetric method is plagued by sources of interference and the fact that color changes can be very difficult to spot in red wine. A/O is much more accurate but involves a semi-elaborate laboratory set-up and then requires 10-15 minutes per sample. Neither of these methods is a particularly appealing way to spend an afternoon.

Frequent measurements are necessary, however, because SO_2 concentrations in wine can be far from static. If there is oxygen ingress or microbial activity, more binding compounds will be formed and more SO_2 will become bound. It is almost impossible to stop the slow consumption of free SO_2, especially in a container that is not completely full. Once there is no (or not enough) free SO_2 remaining, the wine is now vulnerable to damage.

SO_2 is like a castle gate, repelling barbarian invaders. If the gate is removed for any length of time while invaders are present, it won't do much good to replace it later. Once microbial spoilage or oxidative character has taken hold, bringing the SO_2 level back up won't fix the problem; SO_2 is prevention, not cure. When you combine the relative difficulty and importance of measurement, you begin to see why effective management is not necessarily simple.



There are a few ways that measurement is becoming easier, however. One place to start is our action chart (see Figure at right) that provides a decision sequence based on tank material. A/O setups that are stripped to the bare essentials have become relatively cheap and easy to get. Gavin Sacks and his students have also developed a new method that combines ease of analysis with similar accuracy to A/O. We will provide details of the method in coming publications when testing and publication are further along.

Too much of a good thing?

With all of the dangers of too little SO_2 and the relative difficulty of measurement, you may be wondering why people don't just dump some in and then some more for good measure. There are plenty of reasons why that's not such a good idea, however. The maximum amount of SO_2 a wine may contain is regulated by governments around the world, so having too much is, first and foremost, illegal. Large doses are considered unhealthy, and even smaller doses may be dangerous to people with asthma and those who are allergic. SO_2 can also be smelled, tasted, and actually "felt" when it is present in wine in too great a concentration. Needless to say, people don't appreciate smelling struck match, tasting something metallic or feeling like their sinuses are being drilled when they pour a glass of wine. For all of these reasons and more, winemakers want to use as little SO_2 as possible while still achieving protection.

There you have it. We don't want too little SO_2, and we don't want too much. Calculations aren't easy (fraction of a fraction of a fraction, remember), and exact measurement is also difficult. Even when none has been added to a wine, the yeast may have produced enough to require labeling. The good news is that while the process can be onerous, it is still relatively straightforward, and those with patience and perseverance can manage SO_2 without too much trouble. And mastering SO_2 is what separates winemakers from people who like to make wine. For more on binding compounds, regulations and more, check out the Research Focus article from Appellation Cornell in 2011.

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