PRACTICAL Winery&Vineyard

Managing Free Sulfur Dioxide in Barrels

An improved understanding of the behavior of free SO_2 in barrel ageing wine can help improve wine quality and reduce the risk of costly downgrades

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SULFUR DIOXIDE (SO_2) HAS seen broad use in winemaking for centuries and has been used in its present-day salt form since the 1920s.[1] SO_2 is particularly important in barrel ageing where the surface-area-to-volume ratio, permeability of the vessel, and opportunities for microbial spoilage are all increased relative to tank or bottle.

By acting as both an antioxidant and antimicrobial, SO_2 reduces risk and improves consistency in a barrel program. Because of its participation in multiple chemical and microbiological processes, a mechanistic understanding — and careful management — of free SO_2 reactions is central to controlling risk and maximizing wine quality in a barrel program.[2,3]

Barrel Downgrades and the Role of SO_2

Barrels often contain a winery's most valuable wines, rendering mistakes that potentially lead to lost or downgraded product to be very costly. An example of the potential revenue impacts of barrel downgrades to a winery are illustrated in **FIGURE 1**. Fruit for a top tier wine can be several times more expensive than the fruit destined for lower tiers — whether purchased from a grower, or when considering the impact of farming costs and yields when growing for premium quality compared to lower quality.

After a successful ferment, the homogenous wine batch is split from large tank into many much smaller barrels. Each individual barrel progresses on a unique trajectory throughout the ageing cycle with variations in oxygen exposure, microbiome, oak character, temperature exposure, and a multitude of additional factors.

In preparation for bottling, the winemaking team strives to build the best possible blends that maximize quality, revenue, and market fit. In the example shown in **FIGURE 1**, if one single barrel originally intended for a top-tier blend is relegated to a mid-tier SKU, it would decrease the revenue opportunity of that barrel by $13,800. Similarly, downgrading a lower tier barrel that does not make the quality and stylistic goals of that SKU into a bulk program, could reduce that barrel's revenue opportunity by $3,900. These downgrades are most costly in higher tier wines where each individual barrel holds so much valuable product.

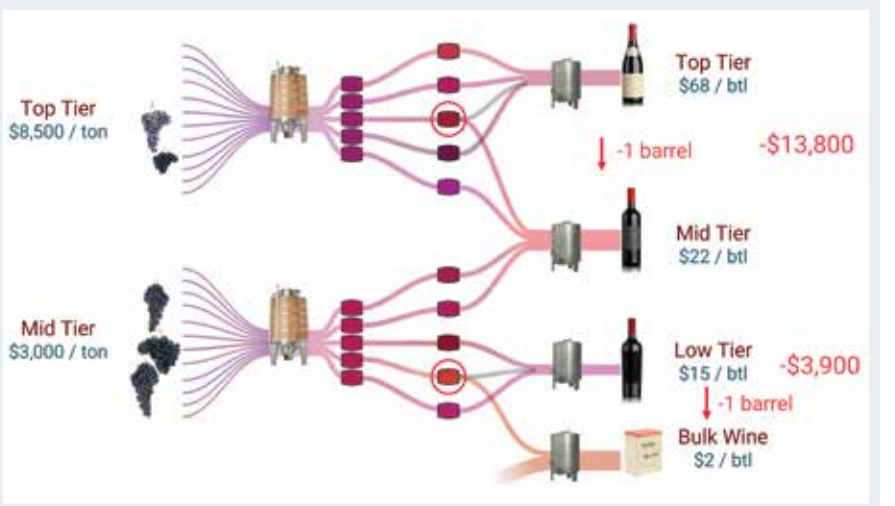

FIGURE 1 Typical process flow of a barrel aged wine program with example prices of fruit and bottle sale prices to highlight the monetary impact a barrel downgrade can have for a winery.

Given its central role in protecting wine from oxidation and microbial impacts, suboptimal free SO_2 concentration is often a contributing cause of wine quality loss during barrel maturation, which result in barrel downgrades. Of course, not all downgrades are directly caused by free SO_2; some may be caused by unexpected oak profiles, stylistic decisions, issues with product-market fit, or other factors. Bearing this in mind, free SO_2 is certainly known by the winemaking community to play a major role in maintaining quality and reducing risk in barrel ageing programs. Appropriate concentrations of free SO_2 mitigate the growth of spoilage bacteria and deleterious yeast strains, such as Brettanomyces, and inhibit oxidation pathways of desirable aromatic compounds.[2,3,4]

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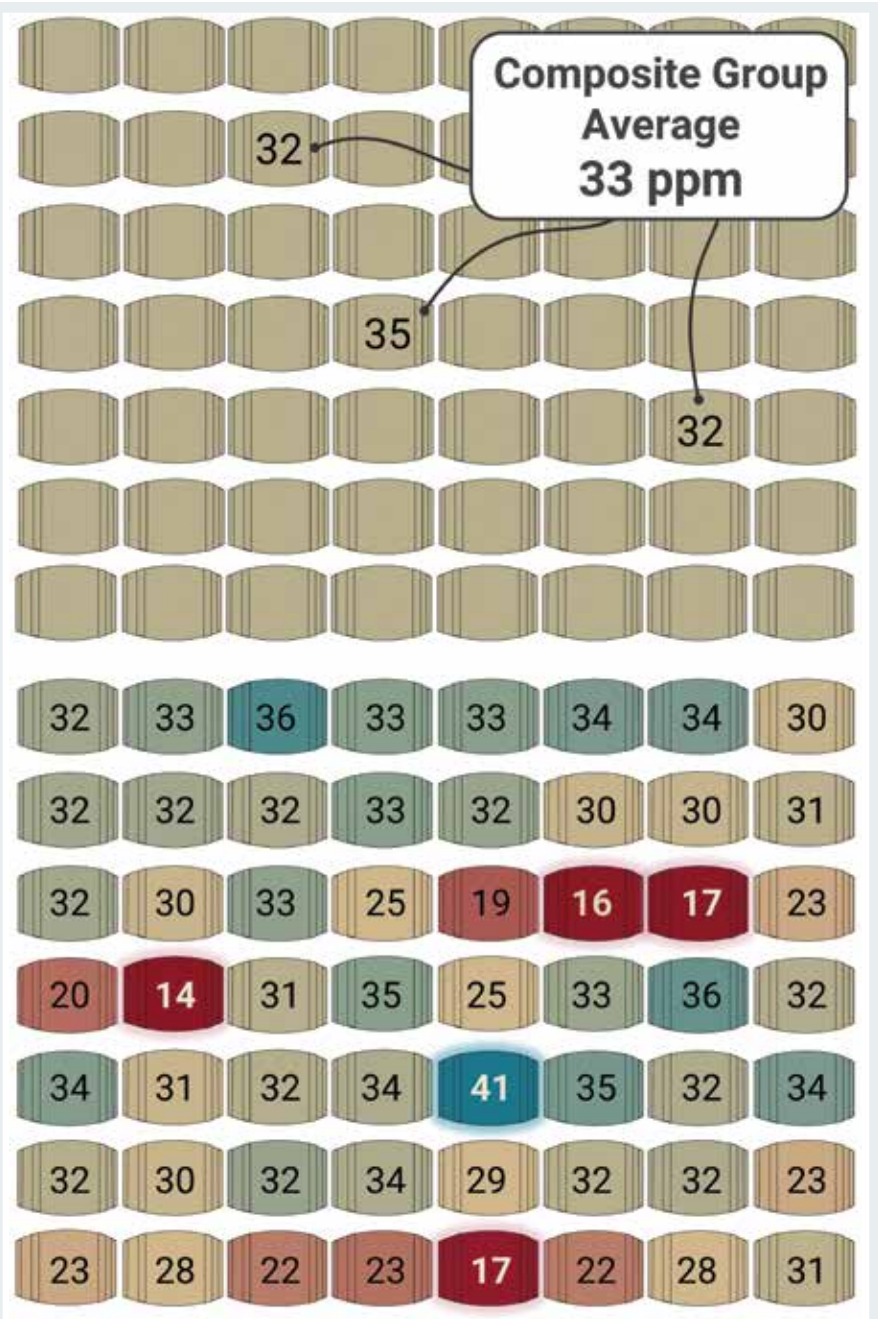

FIGURE 2 Free SO_2 concentrations (ppm) of a 56-barrel group of Merlot. A typical group-level approach to free SO_2 measurement practiced in most wineries (top) as compared to a barrel-by-barrel measurement of the actual free SO_2 concentrations in each individual barrel (bottom).

Free SO_2 Varies from Barrel to Barrel

Despite free SO_2's impact on wine quality in a barrel program, most barrels are never explicitly sampled and measured. Almost all wineries with more than a few dozen barrels only sample free SO_2 from a small subset of barrels within each barrel group. These samples are typically blended to form a composite sample and analyzed for free SO_2 concentration, providing the winemaker with an estimate of the free SO_2 concentration of every barrel within that group.

Making sulfite addition decisions with the measurements obtained from a composite sample of a few barrels in a group tacitly assumes that all barrels in that group contain about the same concentration of free SO_2. The example in **FIGURE 2** shows a 56-barrel group of Merlot, six months into the ageing cycle. Three of the barrels were sampled to form a composite group average, leading the winemaking team to conclude that the group is at 33 ppm free SO_2 concentration. Individual samples were drawn from each barrel in the group and analyzed for free SO_2. The results, shown in the lower panel of **FIGURE 2**, suggest that this assumption of homogeneity is far for from reality, with some of the barrels having less than half of the free SO_2 as others within the same group.

The data from this barrel group showed a significant level of variance in free SO_2 concentration, but is this specific to just this group of barrels? To better understand barrel-by-barrel variance, more than 2,000 barrels were analyzed from 60 different barrel groups, in 16 different wineries. The wineries ranged in size from 100-barrel to 6,000-barrel programs and were located in several different wine regions across Canada and the United States.

FIGURE 3 summarizes the results of all the measured SO_2 data from this study, displayed as distributions of the molecular SO_2 concentration of each barrel in the group. Molecular SO_2 concentration is used in lieu of free SO_2 as it accounts for the difference in pH for each wine. These data suggest that broad variance in free SO_2 concentrations is common, if not ubiquitous.

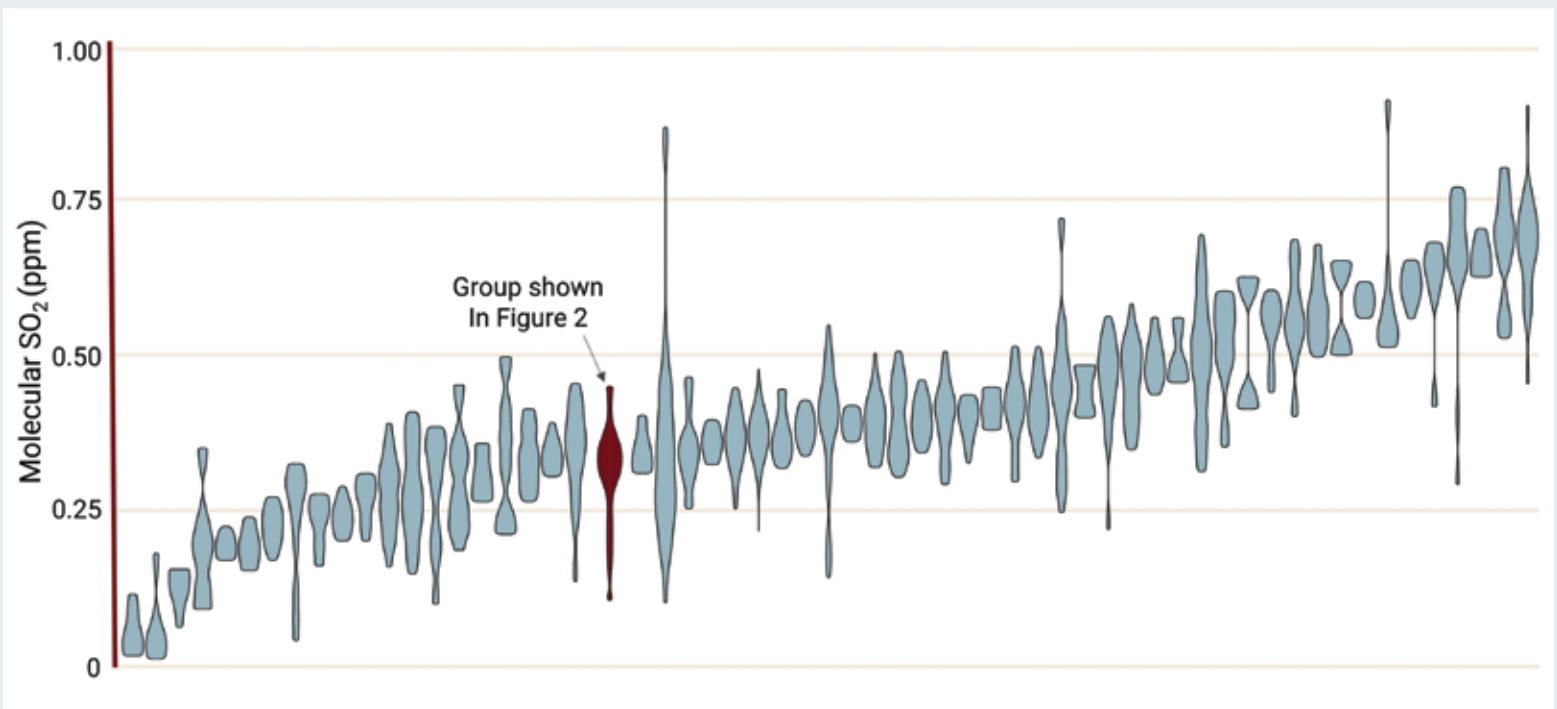

FIGURE 3 Distribution of molecular SO_2 concentration for 60 different barrel groups from 16 different wineries. The width of each distribution corresponds to the number of barrels within that group with a given concentration of molecular SO_2. Note the group shown in red corresponds to the same group of barrels shown in FIGURE 2.

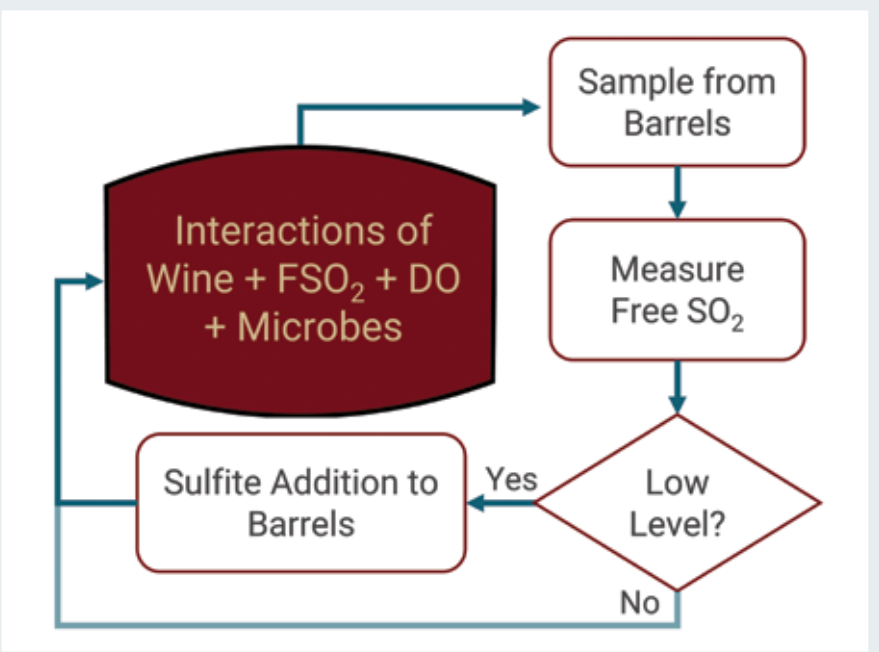

FIGURE 4 Free SO_2 management activities completed by a winemaking team to maintain closed-loop control of free SO_2 levels.

Managing Free SO_2 In-Barrel

What would cause barrels of the same wine, in the same cellar, sitting side-by-side, to have different concentrations of free SO_2? There are many different factors to consider, which can broadly be broken down into two groups: the biochemical interactions within the barrel and the barrel management activities completed by the winemaking team; together, these create a feedback loop for managing free SO_2, shown graphically in **FIGURE 4**. Samples are drawn from barrels, the samples are analyzed for free SO_2 concentration, this information is passed to the winemaking team, and a decision of whether to add sulfites is made. A detailed discussion of each process and the impact on free SO_2 management is discussed below.

Sampling and Measuring Free SO_2

If a winery is only sampling a small number of barrels within a group, the decision of which barrels to select for sampling can impact the information the winemaker has available to make decisions. This can ultimately lead to different actions being taken, depending on which barrels are selected by those performing the cellar work.

FIGURE 5 shows the same 56-barrel group discussed previously. For the example barrel group shown, composite samples taken from three different subsets of barrels lead to concentrations of 20 ppm, 32 ppm, and 36 ppm. If a winemaker receives information from the lab showing the barrel group is at 36 ppm, they may take a different course of action than if they are informed it is at 20 ppm – perhaps no sulfites would be added in the former case, but a significant sulfite addition would be requested in the latter case. This means the very same barrel group could end up having almost twice the sulfite levels depending on which of the barrels happen to be selected for sampling.

It is, of course, understandable why a winemaker would elect to only sample and analyze a subset of barrels within a group. If using aeration-oxidation for SO_2 measurement, each sample requires 15 minutes to analyze in addition to the labor required to access barrels, pull samples, and correctly label and

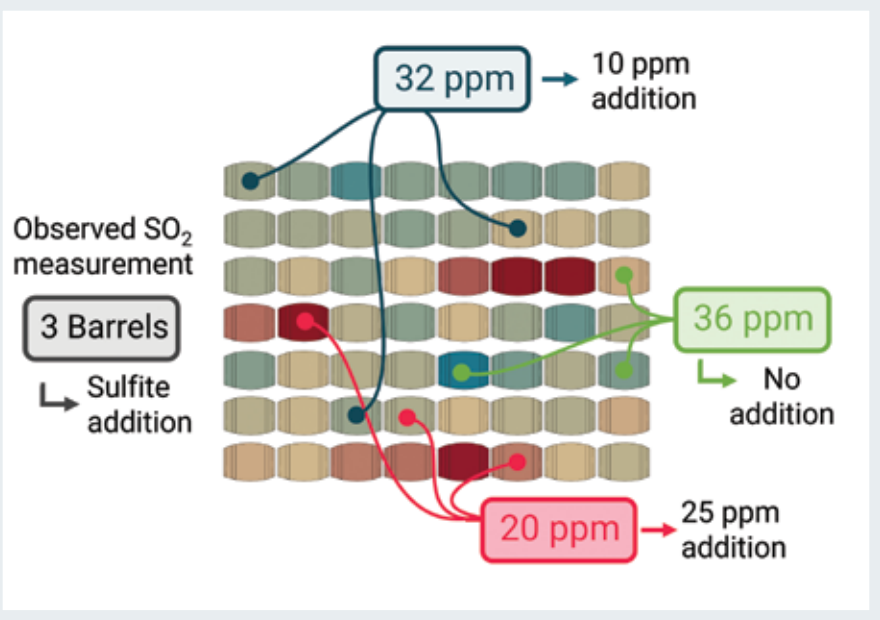

FIGURE 5 Depending on which three barrels are sampled from this group, the winemaking team receives very different information on the SO_2 concentration of the group. Different samples may lead to different sulfite addition decisions being made.

track the resulting measurement data. For any winery with more than a few dozen barrels, this would quickly become both tedious and impractical.

Should a winemaker decide to sample a bigger percentage of barrels in a group, or move to barrel-by-barrel analysis, an appropriate free SO_2 measurement method is needed. There are several free SO_2 measurement methods available that vary in cost, measurement time, precision, and susceptibility to wine matrix effects.

A thorough comparative analysis of free SO_2 measurement methods is beyond the scope of this article but the key factors to consider when choosing a free SO_2 measurement method for barrel management are speed and accuracy. The more samples that can be processed, with sufficient accuracy, the better information the winemaker has available to make decisions and identify issues before wine quality is impacted. No matter what analysis method is selected, careful documentation of free SO_2 readings can allow a winemaker to detect unexpected changes in free SO_2 levels and identify patterns that may indicate an underlying oxidative or microbial issue.

Sulfite Additions to Barrels

Once the winemaker has received the free SO_2 concentration information, they will decide if a sulfite addition is required by comparing the measured concentration to a desired setpoint. The SO_2 setpoint of a group will depend on the grape variety, pH, time of year, goals, and risk-tolerance of the winemaking team. Ideally, each barrel receives the specific sulfite addition required to move the concentration to the setpoint. The variance in free SO_2 concentration within a group can be mitigated by sampling and measuring more barrels and performing customized sulfite additions, particularly to target outliers.

The most common means of adding sulfites to barrels are powdered potassium metabisulfite (KMS) or sodium metabisulfite (SMS) salts, or an aqueous solution made from these salts. The compounds are also available in pre-measured tablets which typically contain a carbonate to release carbon dioxide gas bubbles when dissolved in wine (i.e. effervesce), designed to encourage mixing of the sulfite through the wine.

Stratification of Sulfites in Barrels

When sampling barrels in the winery, we observed it could sometimes take days or weeks for free SO_2 concentrations to rise after a sulfite addition. To investigate this in more detail, an experimental facility was created with oak barrels (228L American Oak) instrumented with taps at seven different locations inside the barrel, allowing for samples to be drawn and analyzed for free SO_2 concentration with the aeration-oxidation method. The goal of this experiment was to measure how sulfite concentrations develop throughout the barrel after an addition is made.

Two common methods of sulfite additions were considered: addition by 10 percent free SO_2 aqueous KMS solution, and addition with pre-dosed effervescent KMS tablets (Campden tablets). In both cases, a 40 mg/L free SO_2 addition was made to each test barrel. An artificial wine matrix was used to reduce sulfite binding with pH = 3.4 and temperature held at a constant 18°C. The barrels were not stirred, topped, or moved during the experiment.

After the sulfite addition was made, samples were drawn (50 mL) from each measurement station at different time intervals to track the development of the free SO_2 concentration distribution. Results for both the aqueous KMS and effervescent tablet additions are shown in **FIGURE 6**, showing the spatial free SO_2 concentration distributions at one hour and six days after the respective additions were made.

Significant stratification of the sulfite addition remained, for both methods, after six days. In the aqueous KMS solution addition, most of the added sulfites remain in the lower quarter of the barrel one hour after addition.

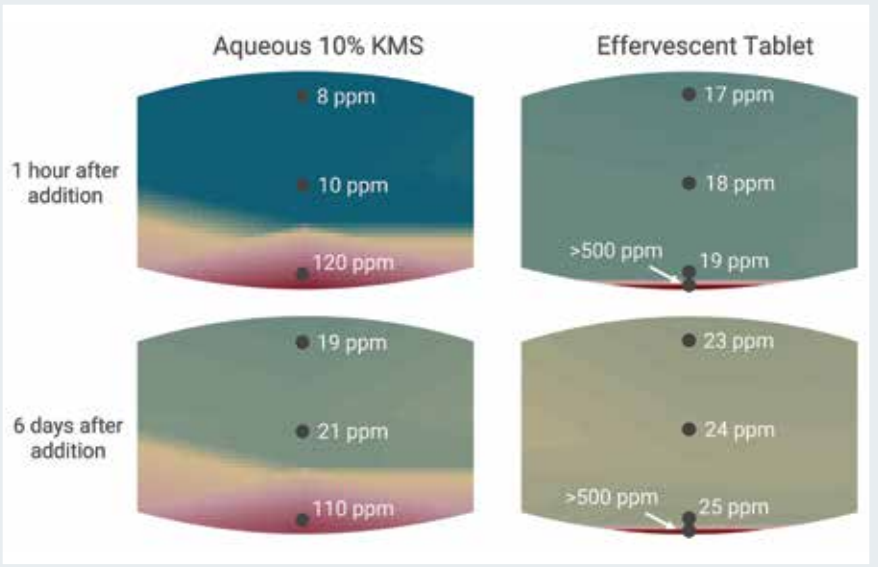

FIGURE 6 Experimental measurement of the distribution of free SO_2 concentration in a 228L barrel one hour after a sulfite addition (top row) and six days after a sulfite addition (bottom row) for 40 ppm additions made with a 10% aqueous KMS solution (left column) and effervescent tablet (right column).

The effervescent tablet distributed about half of the sulfites vertically into the barrel within one hour, driven by the mixing created by the CO_2 bubbling. However, the other half of the 40 mg/L addition remained concentrated at the very bottom surface of the barrel.

After six days of diffusion, 21 mg/L of the 40 mg/L aqueous KMS addition had made it to the centroid of the barrel, while 24 mg/L of the 40 mg/L tablet addition made it to the centroid of the barrel. Most of the remaining sulfite addition was concentrated at the bottom of the barrel in both cases.

The biggest implication of these results, in the context of free SO_2 management, is that the depth at which a sample is drawn from a barrel can have an impact on the measurement. What is the "correct" depth to sample at? There is no definitive answer. Sampling near the center of the barrel, or biased towards the top, captures a more conservative measurement, and considering most of the oxygen and microbial forcing will be biased towards the top surface, this may make sense. It is more important that the sampling depth be consistent between barrels, so that an apples-to-apples comparison can be made.

If a barrel is sampled and measured to have a free SO_2 concentration well outside of the expected level for the barrel group, it may be worth resampling at a different depth to determine if the variance is caused by stratification or if the barrel is a true outlier and needs specific attention.

Stirring the barrel after a sulfite addition can, of course, break up the stratification and lead to a more homogeneous distribution of free SO_2. Stirring also distributes particulate and lees, folds in oxygen, and potentially adds microbial forcing — all of which increase free SO_2 consumption. We have conducted in-winery experiments that show a marked increase in binding rate of free SO_2 in barrels that are opened and stirred as compared to barrels that have an addition only. Because stirring impacts so many parts of barrel ageing, whether to stir or not should be a contextualized decision based on winemaking goals, with free SO_2 stratification being one aspect to consider.

Takeaways to Improve Barrel Sulfite Management

Sulfites are an important tool to control risk in a barrel program and proper SO_2 management helps to prevent barrel downgrades, which can have significant financial impact. Most winemakers rely on composite samples from a small subset of barrels to evaluate the free SO_2 concentrations of an entire barrel group, but the dataset shown suggests that free SO_2 concentrations often vary significantly between barrels within the same barrel group and there are often outliers.

Sampling only a small subset of barrels within a group can exacerbate variance by affecting the information flowing to the winemaker and therefore their barrel management decisions. Sampling a bigger percentage of barrels or transitioning to barrel-by-barrel sampling and customized additions can help to reduce variance by capturing and correcting outliers.

Concentrated sulfite additions can stratify within unstirred barrels which can cause free SO_2 concentrations to vary depending on the depth within the barrel. This impacts the antimicrobial and antioxidant protection at different points in the barrel and can affect how samples are taken from barrels. Sampling from a consistent depth within the barrel and resampling at different depths to investigate anomalies can both help mitigate the impact of stratification on decision-making.

The free SO_2 management cycle implemented by the winemaking team can benefit from better information flow and tracking, ultimately preventing losses in quality and helping winemakers to consistently achieve their stylistic goals. **WBM**

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