

Watching the wine pH, TA and SO₂.

it is important to analyze and adjust the pH, because it affects everything from color intensity to spoilage organisms, most of which like a pH higher than 3.7. So, keep pH at 3.3 to 3.6 for consistently spoilage-free fermentations. Microorganisms such as yeast cells spend a lot of their energy pumping out protons to keep their insides at a higher pH than their environment. Think of it like fishing in Baja from an old, leaky boat. Sure, you spend most of the day bailing out water (protons), which cuts into your fishing time, but life is great. What could possibly go wrong? Well, it could rain. All bailing and no fishing make a microbe starve. This is the moral of the story. Here's how it works: The pH inside the cell drops as protons flow in more quickly than the cell can bail them out. Yeast cells can't function at such a low internal pH. They are like machines made out of yarn that keep a cell running by doing everything from patching membranes to processing food. When intricately knitted and twined perfectly they work better than any mechanical machine, but a low pH makes them fall apart. Fortunately for winemakers, yeast have strong hulls, so they don't leak as easily as other microorganisms. This means they can handle a lower pH outside the cell. Keep it around 3.3 (heavy rain, choppy water) and while most microorganisms couldn't survive, yeast would call it balmy. The higher the pH, the better for microorganisms. Once you move above 3.6 or so, your sanitation practices must be excellent to make a good wine. Again, keeping the pH adjusted is the most important thing.

TA, Sulfur Dioxide, and pH

The second most important condition to track, after pH, is the titratable acidity (TA). TA affects the pH and although that is why it's so important, the two are distinctly different. Think of TA as a "potential pH" that, when a wine is tweaked, influences the final pH. You could adjust the pH perfectly, but if the TA is too low, the pH won't stay there. Any little factor, from a change in temperature to the beginning of fermentation, can result in a drastic pH change. If you've adjusted the TA properly, however, the pH will be buffered. That makes the pH difficult to change, and your wine will be protected. Too much TA can result in a tart wine or one with lots of crystal tartrate precipitation. High TA is often from huge amounts of malic acid, which is later converted to lactic acid during malolactic fermentation. This conversion mellows acidic flavors; lactic acid is technically half as acidic as malic acid, and some people say it tastes different, too. Lactic acid then buffers the wine at a much higher pH, which helps keep spoilage microbes in check.

The third most important influence to keep an eye on is sulfur dioxide, which is used to inhibit oxidative enzymes and microorganisms. Oxidation can slow fermentation, darken the color, and change the aroma of your wine. But the real problem is that sulfur dioxide quickly robs oxygen from yeast, and this can result in a weak or stuck fermentation and subsequent yeast-revenge odors. Yeast must have oxygen in the first few hours of fermentation to produce unsaturated fatty acids for their membranes. Think of unsaturated fatty acids as planks for the boat. Without them the yeast leaks more than they should. Bailing gets slower as alcohol increases, so the yeast will have trouble toward the end of fermentation and may not actually finish to dryness.

Tools of the Trade

You can follow the progress of a fermentation and know whether or not the yeast are thriving. If they're not thriving, you might be able to figure out why. Hydrometers measure the density of a solution, which increases with more dissolved material. Sugars make up most of the dissolved

material. As yeast convert sugar to alcohol, the density of the must decreases, both from the loss of sugar and from the increase in alcohol, which is less dense than water. The goal is to have a healthy fermentation that proceeds the way you want it to. If your fermentation is slower than you would like it might mean the must is too cold, the acidity is too high or too low, you've added too much sulfur dioxide, or you've got a lot of different organisms competing for food and living space. A slow fermentation is indicated by little change in density over the first few days. If the maximum fermentation rate is lower than usual, it may mean that the yeast are inhibited by a residual fungicide from the vineyard or another microbe. A fermentation that slows at the end and doesn't quite finish could mean that your yeast were undernourished from a lack of initial oxygen or another nutrient such as nitrogen. Because density equals mass divided by volume, the density of wine logically should be expressed in grams per liter. However, in the United States winemakers use a Brix scale where 20 grams of sucrose in 100 grams of water at 20° C (68° F) is defined to be 20° Brix. Pure water is 0° Brix. The Baume scale is used in much of Europe. Baume = 0.55 Brix, if you ever need to convert. The scale from Germany is called Oechsle and is simply the three numbers to the right of the decimal point of a density reading in grams per liter. For example a wine at 1.085 grams per liter equals 85 Oechsle. You can use a hydrometer throughout fermentation, but be aware that lots of dissolved solids or pulp will make the hydrometer float higher and give a false high reading. Similarly, the presence of lots of alcohol at the end of fermentation will give an artificially low reading by 1° or 2° Brix. When measuring an active fermentation, spin the hydrometer in the liquid with your thumb and forefinger. This will temporarily spin off any CO₂ bubbles that could keep the hydrometer afloat and skew the reading higher.

Ties That Bind: TA, pH, and Sulfites

There is a lot of unnecessary confusion about the relationship between pH and TA, and it must be understood to make sense of the TA-buffer issue and to understand the titration used to test for TA. As a bonus, understanding this relationship makes understanding sulfite chemistry easier. Wine is full of weak acids, which collect and throw out protons to maintain a certain proportion of free vs. bonded protons. Consider the following example. Let's say 30 protons are collected and 10 are free. That means your acids like to keep a ratio of 3 to 1. If you get some tweezers and pluck out five free protons, the ratio becomes 6 to 1 (30 collected and five free), but the acids panic and fix the ratio by throwing off three collected protons and adding them to the free ones. Now we have 27 collected and 8 free protons, which is about a 3-to-1 ratio again. Here's the important part: pH is a measure of just the free protons, whereas TA measures both collected and free protons. It's that simple. Each acid has a preferred ratio, and what we see is a compromise; the acids constantly work toward equilibrium. As the types and numbers of acids, such as malic and tartaric, change, the compromise is renegotiated and the ratio might change. Acids are only good at keeping this ratio near their buffering range, though. As you keep pulling out protons, the acids fall behind and aren't able to maintain their desired ratio. In practical terms, because pH measures only the free protons, it takes into account only the ones that are kicking around in solution and that can interact with our palate so that the acidity can be tasted. These free protons also can interact with and affect, for example, sulfur dioxide equilibrium and wine color equilibrium. The pH is what really matters when it comes to keeping microorganisms in check, too. If the pH is too high (there aren't enough free protons hanging around to do some damage), then a lot of spoilage organisms

are able to survive. If the pH is lower so that there are a lot of free protons, the cell walls of microorganisms are compromised. Many microorganisms are unable to survive in such an acidic environment. Titratable acidity is total acidity. Titrating involves adding base to a wine and kicking out all of the collected protons that have been hanging back inactive in weak acid equilibria. There is no place for protons to hide when base is added to a wine. One base unit neutralizes one proton, no matter whether the proton is available in solution free and measurable by pH or whether it's hiding, being "inactive" in a weak acid equilibrium. The reason to measure both TA and pH is because one can't necessarily give a good indication of the other, and together they provide a better picture of what's going on in the wine. There are so many different kinds of acids in wine that can contribute to total acidity, yet at any given time only a portion of them can be tasted. Having a lower TA intuitively goes hand in hand with a higher pH (low TA = few free protons = high pH). But keeping track of both numbers gives a realistic picture of the acids that are available now (pH) and those that are both available now and potentially available later (TA) to participate in chemical equilibria that might be further down the line, such as aging reactions. The problem is that pH and TA are expressed differently. TA is the measurement of the concentration of acidity, expressed as a ratio of weight to volume. In the United States the acidity of wine is expressed as tartaric acid equivalence, as if all of the acid in the wine were tartaric. The unit is generally grams per liter. In France the TA is expressed as a sulfuric acid equivalent. The other problem is that you can titrate all day long unless you call it done at some point. In the United States the chosen end point is a pH of 8.2. This is convenient because there is a sharp rise in the titration curve here. So you can make a small error in reading the pH and still get the correct answer. The titration that is used to investigate TA essentially involves removing protons up to a pH of 8.2 and then counting them. Because winemakers can't actually pluck protons out, they add hydroxides to soak them up. They know how many hydroxides it takes to do this by adding a specific volume of a standardized solution. Remember, pH just counts the free protons without messing with the acid's precious ratio. For TA, on the other hand, you keep changing the ratio and the acids keep adjusting it until they can't keep up and you've finally exhausted them. That's where the pH jumps sharply on the titration graph. Acids hold a lot more protons than they allow being free, so the actual number of free protons is much smaller than held. You'd be able to compare this easily, but the units of TA and pH are different.

Sulfites and pH

Sulfites and pH are related, too. When sulfites are added to wine, about half the amount binds with other wine compounds and about half exists free in solution. The bound sulfur dioxide doesn't inhibit microbes. Many winemakers therefore talk about "free" sulfur dioxide levels and keep their wines within certain ranges. The problem with only considering free sulfur dioxide is that there are three different forms with ratios that depend on pH. Sulfur dioxide in the molecular form is the one that inhibits microbes and is most prevalent at lower pH values. Fortunately yeast can handle pH levels that inhibit spoilage microbes. A guideline is to keep molecular sulfur dioxide — which is more important than free sulfur dioxide — around 0.5 to 0.8 grams per liter for whites and 0.5 to 0.6 grams per liter for reds. Remember also that sulfur dioxide is used to inhibit oxidative enzymes, so how much does that take? Well, you can add 30 milligrams per liter at crush, and the enzymes will be inhibited. Under the right circumstances, this might not be necessary. But your fruit must be in good condition, and your sanitation must be excellent.

There is one more consideration. Molecular sulfur dioxide is volatile and will slowly be depleted, especially when racking, barreling, testing, or tasting. Always taste and analyze before making any addition. Analyze after making the addition, too, to make sure it was done correctly.

Measuring Sulfites

The titration for sulfites is not precise, especially for red wine because phenolic compounds interfere. Despite better methods, it is still commonly used in wineries because it doesn't require much equipment and works well enough for estimates. It works sort of like the acidity titration except the sulfite titration is based on oxidation/reduction chemistry, so electrons are being thrown around instead of protons. We'll use iodine to soak them up for counting. As soon as we run out of sulfites, there will be extra iodine, which will interact with a starch indicator and turn dark blue, indicating the end point. It is crucial to do this titration, called the Ripper Analysis, quickly; around 30 seconds from start to finish is fine. Any longer will allow time for bound sulfur dioxide to unbind, and it will look like you have more unbound than you really do. Because most people overshoot the end point during the first run, do a second one knowing what to expect. After a while the color will fade, but the titration is finished, so don't add more iodine. This end point is not always easy to see, but here is some advice that might help: Keep a reference of the untitrated wine nearby for comparison. Use a white paper underneath the titration, use a bright light, and keep the wine cold to make the indicator color brighter.

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