

MIDWEST WINE PRESS

SPECIAL REPORT

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THE ART AND BUSINESS OF WINEMAKING IN THE HEARTLAND.

Conquering Acidity in American Wines

By Clark Smith



Time was, you simply could not grow grapes in many regions now proving their excellent potential for delicious wines of all styles. New varieties from pioneer heroes like Elmer Swenson at the University of Minnesota and the innovative genius of a thousand growers have brought us to an uneasy truce with winter kill. Done deal. The new enemy is pucker power.

East of the Rockies, acid balance is the primary challenge for thousands of wineries seeking respect, particularly for dry wines competing for space at table with traditional offerings from more established regions.

That said, it's important to avoid the mindset that less is more. Low acid wines pose their own set of problems, and I urge you to place a high priority on preserving the character for which Midwestern wines are known. I, for one, treasure these wines for their freshness, varietal purity, and yes, their crispness, so difficult to obtain in California where I reside. Midwestern winemakers are well advised to protect this style, taking care to avoid emulating Groucho Marx, who said "I wouldn't want to belong to any club that would have somebody like me as a member."

Deacidification choices are best made by considering all available solutions and a firm grasp of acid-base chemistry. My goal in this article is to explain in plain English the way acidity works in wine, to present the options for its diagnosis and adjustment approaches from low tech to high.

Most wineries outside California have very limited resources, but this is no reason for even the tiniest mom-and-pop winery to pass up the chance to get smart on high tech. Because you are plowing new ground in challenging conditions, a spirit of cooperation exists throughout the Midwest that hasn't been present in California for decades.

Everywhere I see local winery groups banding together to share resources, and because wineries are one of the country's few economic bright spots, strong and growing statewide support is increasingly available. Wineries, even small ones, are agricultural rock stars, chick-magnets for the press, and helping them can make politicians look pretty good. Sometimes facilitating general access to a shiny new toy is the most effective way for a State agency to leverage limited resources to do the most good for the largest number.

The best time to solve any winemaking problem is before you have it. Centralized analytical capabilities can bring sophisticated diagnostic tools to bear when harvest comes, and service providers working in tandem with State bureaucracies have proven that given adequate time, equipment which would otherwise be pointless to contemplate can be put in place.

The Devil is in the details. I hope that by laying out the options, this article will help local factions sort out what they really want and strengthen the support for cooperative initiatives aimed at the 2012 harvest and beyond.

The Basics About Acids

Acids are dissolved compounds which have the property of being able to detach a hydrogen ion which can then exist on its own in solution. We're talking about a proton, because a hydrogen atom is simply a one-proton nucleus with one electron orbiting it, so when you strip away the electron, you've just got a proton. So an acid is just a compound that can slough off a proton.

The density of these free protons is measured by pH. Free protons kick butt. They have strong effects on wine chemistry and microbiology, impacting the rate of ageing, oxidation, browning, and microbial spoilage, as well as on its color and aroma. Wines with high concentrations of protons tend to have brighter color and cleaner, fresher aromas. Beyond these effects, however, pH has no direct taste.

If our wine is tart, then, what do we call that? Short answer is "titratable acidity" (TA). But before explaining more about TA, let's nail down a more solid understanding of pH. When we go to fix our TA, the resulting pH is going to be our main challenge. In managing wine balance, the TA is its public image and the pH is its police force.

The concentration of free protons is expressed as their ratio relative to water molecules present. The small "p" in pH is an abbreviation that denotes an inverse power of ten. In other words, pH 3 means one proton for every 1,000 water molecules ($1/10^3$), while pH 4 means one in 10,000 ($1/10^4$). This is the range for most wines, and although 3.0 to 4.0 doesn't sound like much, it's really a ten-fold difference.

Did I say plain English? Hey, I'm doing my best. You can think of pH as the gas pedal of ageing -- pH 3.0 is like driving 10 MPH, and pH 4.0 is like driving 100 MPH. Just like in driving, both these extremes are usually bad ideas.

Another conceptual challenge is that pH is logically topsy-turvy. I think chemists like it this way, because confusing jargon helps them to feel superior and keep their high-paying jobs. Don't let the bums get you down. Just get used to it: high pH means low free acidity and low numbers mean high acidity.

The mineral acids you encountered in high school chemistry lab -- hydrochloric, nitric, phosphoric and sulfuric -- are "strong" acids which dissolved in water separate entirely from their protons. But the acids we have in wine are "weak," being organic in composition and assembled by living organisms from carbon, oxygen and hydrogen atoms. They can't make up

their minds whether they're acids or not, so they exist in both forms: the original protonated (undissociated) as well as the de-protonated (dissociated) species, co-existing in equilibrium:



All this says is that the acid can pop off a proton. HA (left side) represents the intact molecule containing the proton (H) attached to the rest of the acid (A). The right side shows the two pieces it can split into: the proton (H^+) and A^- representing the remaining molecule, whatever it may be, and carrying a negative charge left behind by the hydrogen when it ionized. Those H^+ guys on the right are the free protons I was talking about – the pH.

In any solution, we will find some of each of these two states, and when we taste wine, the tartness we perceive is from both types. This is called titratable acidity because we can measure it in the lab using a titration which resembles what happens in our mouths. When we taste a sip of wine, exactly enough saliva flows into the mouth to neutralize the acid. Once all the free protons (H^+) are neutralized, the equilibrium readjusts, and the bound ones (HA) dissociate and are also neutralized. That's called "mass action."

If we have a lot of tartness in a wine, we might expect a nice low pH. A lot of Master Sommeliers think that tart wines age longer. 'Taint necessarily so. The wrong mix of acids can give you very tart wines which go straight down the drain in your cellar. That's because some acids are weaker than others, so most of their TA is in the undissociated form. Unfortunately, malic acid, the main acid in underripe grapes, is a pretty weak acid.

The strength of an acid is determined by the pH at which it will ionize. We call that the acid's pKa ("a" is for acid and K is German for "constant"). An acid's pKa is quite simply the pH at which half of the acid is ionized. Take lactic acid for example. Its pKa is 3.8. Above pH 3.8, it's mostly ionized. Below 3.8, it's mostly undissociated.

Pause and take a deep breath. Maybe grab a sandwich.

Acids don't always have just one spot on the molecule where protons can jump off. Grape juice contains a couple of acids which contain two acidic groups. We call them "diprotic" acids. Such acids of course have two pKa's. Yeah, I knew that.

Grape juice has two such acids, tartaric and malic. The relatively stronger tartaric acid (symbolized as H_2Ta), has pKa's of 3.0 and 4.2, while the weaker malic acid (H_2Ma), has pKa's that run to 3.5 and 5.0. That's a lot higher. Wines pHs are usually in the range of 3.0 to 4.0, so you can see that tartaric acid is always a lot more ionized than malic acid is.

Now I want you to recognize how nice I am being for not elaborating the structures of these acids. We're going to stick with the abbreviations Ta and Ma. I'm guessing this works for you. You're welcome.

These acids can pop off one proton, and then the other. A little jargon here. We use the “bi-“ prefix for the intermediate form. So if they lose one proton, they form bitartrate (HTa-) and bimalate (HMa-). The second dissociation gives us tartrate (Ta²⁻) and malate (Ma²⁻).

Let me say that again. Tartaric acid pops off one proton at pH 3.0 and a second at pH 4.2. If I write that out as two chemical equilibria, it looks like this:



Same deal for malic acid. The first proton dissociates at pH 3.5, and the second at 5.0:



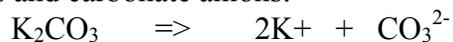
Okay, good work. Now you can get a beer.

For winemakers, a lovely characteristic of tartaric acid is that in the presence of alcohol, bitartrate precipitates with potassium to form crystals. This removes titratable acidity from the wine. Could be good.

The higher the proportion of bitartrate is, the more of this effect we see. The maximum bitartrate concentration occurs exactly halfway between the two pKa's of 3.0 and 4.2. This turns out to be a Big Deal. Listen up: pH 3.6 forms the natural Great Divide for winemaking.

Here's a weird situation. Above 3.6, KHTa precipitation lowers TA and raises pH, just as you'd expect. However, below 3.6, TA is lowered but *pH is also lowered*. The acid goes down but it also goes up. Softer taste, but more stability and freshness. Not too shabby.

Because of this effect, it often works to de-acidify low pH wines by adding potassium carbonate (K₂CO₃). Here's how it works. First, as the compound dissolves, it ionizes into potassium cations and carbonate anions:



Next, the carbonate neutralizes some protons, benignly turning that nasty acid taste into carbon dioxide bubbles and water:



Since it removes free protons, this reaction does raise the pH. But the K⁺ ions will enhance bitartrate precipitation. As long as this happens below pH 3.6, this precipitation will lower both TA and pH, which is a really good outcome. A wine with a TA of 10 gm/L and a pH of 3.1 can emerge with a TA of 7.5 gm/L and a pH of 3.4. Hot stuff. Easy money.

Hi pH / Hi TA Diagnosis

Since malic is such a weak acid, juices with a high proportion of malic can have a high TA but also a high pH because most of the acid is in the undissociated form, so there are only small amounts of free protons.

How can a juice have high pH and high TA? Think about a city police force. You've got your cops on the beat, out there fighting crime, and your cops on the payroll who are not on the street. Where are they? Why, they're in the donut shops. So malic acid is like a really good donut shop where the proton cops like to hang out instead of patrolling the wine. In geek speak, we say that the solution is heavily buffered.

In a typical case, a juice may have a TA of 10 gm/L and a pH of 3.9. The culprit may be high malic acid, but not necessarily. This condition is all too often the case in the Midwest, but rare in warm areas like California, where we still see hi pH/hi TA. Since malic acid is not easily removed, the first step is to determine whether it's our problem at all.

The other way a must can have high pH and high TA is that there is a high amount of potassium and tartrate. Tartrate is not a very good donut shop, but it will do the job if there are enough of them around. Lab analysis for high potassium, which happens under stress conditions in well ripened fruit, can indicate the source of the problem, but there's a simpler way.

In such a wine, we have lots of K^+ and lots of tartrate, so we might expect a big precipitation. But if the pH is too far above 3.6, there won't be very much bitartrate and KHTa will not readily form. To test for this condition in the lab (or that rundown kitchen you call your lab), dissolve some tartaric acid in a small amount of warm water and simply acidify a sample of the juice to exactly pH 3.6. This addition will raise the TA to a very high level, but not to worry.

Now freeze the sample overnight (allowing for ice expansion), then thaw it out in the morning. Hopefully you'll see lots of white crystalline powder in the bottle. Either centrifuge, filter or let it settle out in the fridge, then run a TA. If the problem was high potassium, the resulting juice will have a big drop in TA to maybe around 8.5 gm/L and a pH still at 3.6.

Bad Acid Trips

The rest of this article is about what to do if these two approaches don't work. In other words, how do we get rid of malic acid without getting into even deeper trouble, or spending ourselves into the poor house? There are four approaches to correcting excessive buffer capacity: amelioration, biologicals, double salt, and high tech membranes.

Let's start with the easy, time-honored and perfectly legal practice of watering down the must. Oh, excuse me; I meant "amelioration." Yeah, right. Water is pretty cheap, and the obvious advantage of this method is that it results in lots more wine, up to a legal maximum of 35%. The problem is, it results in lots more wine, which is no fun if you can't sell it because it's thin and joyless.

If you do decide to go this way, you'll be amazed to observe that diluted juice does not change pH. That's the magic of buffers. When you dilute the TA from 10 gm/L to 7, the juice pH will remain right where it was. If it's, say, pH 3.9, what to do? Well, you have to acidify, but this time with tartaric. To end up with a reasonable alcohol content, you'll also probably have to correct your brix with concentrate, or whatever sugar sources are legal in your state. So all that free wine isn't really so free. Most wineries avoid amelioration if they can.

Getting the bugs out

Biological solutions, organisms that eat acid, have great appeal to our inner cheapskate. I will only speak generally here, because yearly advances in our knowledge promise to invalidate any specific information I might offer in this area.

Historically, biological deacidification has been fraught with hidden costs and dangers. Competition during fermentation can cause an organism either to perish or shut down alcoholic fermentation, a tricky balancing act requiring intimate knowledge of the organism's behavior in all circumstances. Sometimes intricate and expensive monitoring and process equipment becomes necessary, coupled with a sophisticated understanding of fermentation kinetics and optima. Scary stuff.

There's no free lunch. The main problem is that the carbon has to go somewhere. Metabolic side products almost always have an impact on wine style. This can vary according to conditions and must competition.

Malolactic fermentation is the best known method, first becoming understood and induced in the early 1960s. It's a big success story, and today few winemakers are daunted by the prospect of pushing a wine through ML. There has even grown up, thanks to the late Jess Jackson, an enthusiastic following for the rich, heavy butter-bomb chardonnays California churns out by the carload. Yet apart from a few specialized products, this method is rarely resorted to because it interferes with clean varietal fruit and obscures the freshness and purity Midwestern wine lovers have come to expect.

Restricted as its use has become, malolactic can, with skill, be used effectively to reduce acidity without harming fruit aromas. This is the common case in French Chablis, and has even been used on aromatic varieties, for example in the Rieslings of Ohio's Markko Vineyards in cool years. The key is prompt fermentation in the presence of yeasts, which have been shown to consume diacetyl, most effectively during primary fermentation, followed by prolonged lees contact.

Less success has so far been seen with *Saccharomyces pombe*, a fastidious and persnickety yeast which consumes much or all malic acid in its often incomplete primary fermentation, but at the expense of peculiar flavors resembling marigolds and pond scum.

Saccharomyces cerevisiae yeasts all consume some malic acid (generally around 10%) during primary fermentation, generally without production of undesirable characters. Recently, strains

like Lallemand's 71B have received favorable marks in reducing as much as one third of malic acid.

My jury is still out. Someday my prince will come. Until he does, biological deacidification methods need to be evaluated with extreme care.

Pass the Double Salt

Were it not for the fuss and bother it entails, double salt deacidification would be the standard treatment to reduce malic acid. It takes advantage of the precipitation of calcium malate that occurs at high pH. A portion of the juice, usually 20 – 30%, is drawn off and treated with an excess of CaCO_3 . The carbonate reacts with 100% of available protons (both free and, by mass action, also the bound), completely neutralizing the juice to pH 6 or 7. The TA drops to zero. Under these conditions, calcium precipitates both tartrate (CaTa) and malate (CaMa) as well as the namesake double salt (Ca_2TaMa). These reactions occur in proportion to what is present.

When recombined, a wine with a TA of 10 gm/L will be reduced to 7, with also 30% of its buffer capacity removed. If needed, the wine can then be re-acidified with tartaric, restoring acid balance. The process does not create calcium instability because the final wine has only 30% of a calcium saturation.

Sounds good. Only trouble is, before recombining the treated portion, it is essential to filter it to remove all crystals and excess CaCO_3 , to say nothing of pulp solids, a very slow and messy process.

To the rescue, crossflow clarification. The new tangential flow filters making appearances all over the country to replace DE filtration seem tailor-made for double-salt filtration. Time to start sucking up to your neighbor who has one.

Double salt must be done prior to malolactic, and preferably at the juice stage, due to the oxidative hazards of taking a fermented wine to such a high pH even for a short time.

Welcome to the Future

Crossflow clarification is emblematic of a dizzying array of new membrane technologies which is sweeping the wine world.

Back in the days of Vinovation, I pioneered the use of tight reverse osmosis. This exceedingly tight filtration, with molecular weight cut-offs of 80 daltons, passes only acetic acid into the permeate, then to be trapped by a resin prior to recombining the permeate. By employing looser RO membranes (erroneously sometimes called nanofiltration) at the legal limit of 150 daltons, the precisely identical method may be used to pass malic acid (134 daltons). Obviously, some flavor will be lost at this porosity but may be less injurious to flavors if run on juice. The method is most easily employed post-fermentation (but prior to malolactic). This trade-off has yet to be sufficiently tested.

Electrodialysis (marketed in the US as STARS), a method perfected some twenty years ago in France for economical and gentle cold stabilization, has been increasingly employed to great advantage for deacidification, lowering TA without any impact on pH. In essence, it runs an electric current through the wine to propel ions out of the wine and through special membranes that can only pass positive (H⁺ and K⁺) or negative (tartrate and malate) ions. The beauty of this method is that unlike conventional cold stabilization, it protects the colloidal structure of the wine, and also saves a lot of energy. In the hands of a skilled operator, ED can give you any pH and TA you want, and runs on finished wine, even post-ML.

Plan A

Of course, the main method winemakers use to prevent high acidity is to wait to pick until the acid comes down. Huge amounts of energy and vineyard planning go into this goal, and the remedial methods I have discussed here are considered merely Plan B. While I am all for ripeness, I often encounter Midwestern wines (I'd include half the Marechal Foch I've tried) which suffer from excessive hang time. These wines have a lot of problems with dry tannins, raisiny aromas and poor longevity.

Assessing true ripeness is going to have to wait for another full column. Meantime, bear in mind that a well chosen acid adjustment capability is part of Plan A. Count on the smart money to maintain an open mind and a clear understanding of the options.

Clark Smith (winemaking411.com) is winemaker for WineSmith, founder of the wine technology firm, Vinovation, and Director of the Best-of-Appellation project for AppellationAmerica.com. He writes and lectures widely on postmodern winemaking, an ancient yet innovative view of American winemaking.