

Managing pH and TA in wine

Wine is an acidic substance, and there are ranges of acidity that are appropriate to each varietal. In general a wine that is too acidic will taste sharp or sour, while one that is not acidic enough will taste flat and insipid. It's no surprise to those of you on the quest for great achievements in winemaking that pH and acidity (TA) are important aspects that are key to know and control. In the previous issue of The Wine Analyst's Blog ([April pH Blog](#)), we discussed pH and how it's measured. In this issue of The Wine Analyst's Blog, we'll learn more about pH, TA, and how to understand and manage them in winemaking. We'll also look at yeast assimilable nitrogen (YAN) which uses the TA system.

Titrateable acidity (TA) and pH

The first lesson here is: these are related but not in a simple way. As we saw in the previous blog, pH is a measure of the acidity of a wine based on its instantaneous hydrogen ion concentration (or its *activity*, to be precise). TA is the total amount of possible hydrogen ions that can contribute to acidity (but don't until "called upon", as it were). Let me explain.

You may recall that if we dissolve a "strong" acid like hydrochloric acid, HCl, in water, it makes the water acidic in proportion to the amount we add, and the pH of that solution is a simple log calculation. So if you add 3.6 grams (1/10 of a "mole" or mol) of HCl to a liter of water, you'll have 1/10 or 0.1 mol/L (mole per liter) of HCl that dissociates to 0.1 mol/L each of hydrogen ion and chloride ion. If you add 3.6 *milligrams* (1/10000 of a mol) of HCl to a liter, you'll have 0.0001 mol per liter of each ion. This means that the pH of these two solutions will be 1.0 and 4.0, respectively (the higher the pH, the less the hydrogen ion and instantaneous acidity).

The fruit acids in wine (like tartaric, malic, lactic acids) are different from the strong acids like HCl. They are called "weak" acids because, when dissolved in water, they don't release every possible hydrogen ion; in fact only a small percentage of the hydrogen ions are released. If you dissolve 7.5 grams of tartaric acid in 1 L water, you will have 0.1 mol/L of *potential* hydrogen ions, but the pH will not be 1.0, as it was in the case of the hydrochloric acid. Rather the pH will be about 2.0, or 0.01 mol/L hydrogen ion concentration, about 1/10 of the value we get for HCl at the same concentration.

On the other hand, if we were to analyze these two solutions for Titrateable Acidity (TA), we would get the same number. That's because the total amount of possible hydrogen ions is the same in both cases.

Let's review how to do a TA test:

Measuring titrateable acidity

Titrateable acidity is determined by titrating a sample with the TA Titrant that has a standard known concentration (0.133 N) of sodium hydroxide (NaOH). We add the TA Titrant slowly with stirring until the pH meter tells we have hit the target pH of 8.2. From the volume of Titrant used, we calculate the TA value. The following steps are from the more complete instructions in the Manual.

1. Prepare sample
 - a. If you are working with must from a red varietal, take 100 mL or more and put it in a blender on high for 30 seconds. This is optional for whites (see below). Allow to settle, or strain to remove solids.
 - b. Degas the sample by repeated shaking, then venting, in a closed small tube or sample bottle

until no more gas evolves.

2. Fill the syringe or burette with TA Titrant (0.133N NaOH) and set it to 0.0, or note starting value.
3. Place 5.0 mL wine or must in the titration vessel (100 mL polypropylene beaker). Add about 15 mL of deionized (DI) water (distilled water).
4. Put the instrument in TA mode, insert the pH electrode and maintain stirring or swirling.
5. Add TA Titrant slowly, watching the pH rise. When the pH reaches 6.5 or so, slow down to dropwise. Stop when the pH reaches 8.2. Determine V , the mL of TA Titrant required to get there.
6. Calculate the TA value as: $TA = 2 * V$ (*i. e. 2 times V*). This gives g/L as tartaric acid.

Tips and provisos:

1. The idea of homogenizing the must is to promote the extraction of acids from the grape skins, imitating the effect of prolonged fermentation on the skins, as done for most reds. Since whites and rosés are not fermented in this way, it is probably more predictive to not homogenize these.
2. Degassing a wine or must is important to remove excess dissolved CO₂. Otherwise it shows up in the TA result, which you don't want.
3. In Europe and some other places, it is customary to titrate to pH 7.0. You can set the SC-200 or -300 to signal at this pH rather than the default of 8.2; see below for a discussion of this.
4. If you take 10.0 mL of wine instead of 5, your calculation is just $TA = V$ and you get a little more precision. The drawback is that it will take more than 5 mL of TA Titrant so if you use a syringe rather than a buret, you'll have to fill it twice, offsetting the gain in precision. And you are using more reagents.
5. The complete equation for TA is

$$TA (g/L Tartaric) = \frac{V * 0.133 * 75}{S} \quad \text{Eq. 1}$$

where V = mL Titrant needed to reach the endpoint; 0.133 = normality of the Titrant, S = mL sample. The value 75 is the *equivalent weight* of tartaric acid.

- a. To report your values as percent, divide the g/L value by 10; e.g. if your wine comes out as 6.6 g/L that is 0.66%.
- b. To report your values as some other acid, substitute that acid's equivalent weight in the above equation for the 75 figure. For example, cider makers prefer to report TA values as malic acid, whose equivalent weight is 67.
- c. Another way to report TA is in units of milliequivalents of acid per liter, meq/L, as is often done in Europe. This is technically more correct in my view, because you don't have to assume the identity of any particular acid in reporting the value. To calculate your results in meq/L, replace the '75' figure in Eq. 1 above with 1000.

pH 7.0 vs pH 8.2?

As mentioned above, many TA titrations, as in Europe, are done by stopping the titration at pH 7.0 instead of 8.2, as usually done in the USA. Obviously you should get a higher value for TA when you titrate to pH 8.2 rather than 7.0. Typically the value will be 5 to 10% higher. So which is correct?

This is an almost "philosophical" question. The major fruit acids in wine are tartaric, malic, lactic, acetic, and a few others. All of these are completely titrated by the time you reach pH 7.0, so

this would argue in favor of using the pH 7.0 endpoint. On the other hand, that 5 to 10% higher TA value shows us that there is still *some kind of acid* being titrated when you go past pH 7.0 to 8.2, arguing in favor of *that* endpoint.

In truth, both of these are arbitrary. The neutral point of water is pH 7.0, and most common acids are indeed titrated by that point, as we mentioned, but others aren't. The reason that pH 8.2 was adopted in the USA is that it is the pH at which the acid-base indicator *phenolphthalein* changes from colorless to pink, a convenient and decades-old alternative to using a pH meter (but hard to use with red wines!). In our winery, we continue to use pH 8.2 out of habit, but whichever you use, be aware that other labs may be determining TA using the other endpoint.

If you want to use pH 7.0 as your endpoint in TA mode on your SC-200 or-300, you can change the default from 8.2 in Test Mode. (See Appendix A in the manual):

1. Enter Test Mode by turning on the instrument while holding down the POWER button for ~ 2 seconds, then releasing it. You should see the firmware number, usually 3.1.2 or 3.2.d.
2. Press the POWER button briefly 14 times. You should see the message “Set tA Pt” scrolling, then the current value will be displayed (8.2 by default).
3. Press the ENTER button to toggle the endpoint between 8.2 and 7.0.
4. Exit Test Mode by holding down the POWER button until the unit shuts off.

Adjusting pH and TA in wine

At some point in your life as a winemaker, you're going to encounter a batch of wine or must whose pH and/or TA are out of whack, “unbalanced”. What do we mean by that? First and foremost, it's how the wine *tastes*. So to a certain extent it's up to you to decide when a wine meets your sensory objectives. Some people really don't like their Big Cabernet to have a pH down at 3.2. Others may be fine with it. And I know of more than a few chardonnays with a pH of 3.6 that are, well, different, to be sure, but some people like it that way. Consider also the TA: a wine at pH 3.0 and TA of 11 probably would benefit from reducing acidity, while a white wine with pH 3.0 and TA 6 may be perfectly acceptable.

However, it's hard to predict taste when looking at *must* before, or in the early stages of, fermentation. That's why it's important to make any needed adjustments as early as possible in the winemaking process.

Normal ranges of pH and TA vary for the varietal, but I would say that anything below pH 2.9 or above pH 4.0 is likely to need adjustment. In addition, any TA values below 5 g/L (0.5%) or above 10 g/L (1.0%) should be *considered* candidates for adjustment. Table 1 below gives some rough guidelines to decision-making. Remember, taste is ultimately what counts.

Table 1. Guidelines for pH and TA adjustment. “Trouble” is encountered when a wine has high pH/high TA or low pH/low TA (the latter is rare); these are hard to adjust by normal means of reducing or adding acid.

		TA, g/L		
		<5	6-9	>10
pH	< 2.9	low pH trouble	reduce acidity	reduce acidity alot
	2.9-3.4	add acidity	OK	reduce acidity
	3.4-3.9	add acidity	OK	reduce acidity
	>4.0	add acidity alot	add acidity	high pH trouble

Making adjustments of your wine's pH

If your data (and don't forget, tasting!) suggest an adjustment of your wine's pH, then proceed carefully. I recommend always adding *half the amount* of adjustment chemicals that you think you need, because it's always easy to add more later, but correcting an over-adjustment is not usually going to turn out well! So here are the main scenarios:

Lowering pH

In general, as you increase TA you decrease pH, and vice versa. An old rule of thumb is that the pH drops 0.1 unit for every 1 g/L of tartaric acid added, but under extreme conditions ("high pH trouble" in Table 1 above) this relationship falters. The weak acids in wines cause them to be what we call "buffers" (see below for a discussion) that resist changes in pH compared to less- or non-buffered systems. In general, the higher the TA value, the more buffer character and more resistance to changing the pH.

High pH, Low TA.

Here you can add tartaric acid, and the rule of thumb will probably hold: the pH will drop about 0.1 pH unit for every gram of tartaric acid added per liter. The TA will of course go up 1 g/L at the same time. So if your pH was 4.0 and your TA was 5, you could add 4 g/L of tartaric acid and perhaps see the pH drop to about 3.6, while the TA should rise to 9. Adding more tartaric may lower the pH more, but you will start to see some resistance to further pH changes as the TA value now goes above 9. And usually going above 9 g/L in TA is to be avoided.

High pH, high TA.

You can add tartaric acid here as well, but the buffer level will be higher. If you have a pH 4.0 wine whose TA is already 9, you are going to encounter more resistance to pH change. You might find that adding 4 g/L of tartaric only brings the pH down less than 0.2 units, while your TA soars to 13 g/L.

High pH trouble

Things get hard when TA and pH are both way high. You'll have very high buffer resistance to lowering pH, and TA is already way high. Probably best to make the wine into a style that doesn't need to age very long.

Raising pH

Low pH, high TA.

Here you can try any number of things. First, if you're doing malolactic fermentation, keep in mind that you can expect an increase in pH of about 0.1 to 0.2 units upon completion of MLF. If you want to raise pH chemically you can try food grade potassium bicarbonate (KHCO_3) or calcium carbonate (CaCO_3). For both, 0.67 g/L reduces TA by 1 g/L and generally raises pH by 0.1 unit. Avoid adding too much calcium carbonate as high calcium levels can lead to tartrate instability. There are also commercial products like Acidex that can be used to raise pH. I don't have experience with these, but they are said to work well where appropriate.

Low pH, low TA.

Here you could add tartaric acid and then adjust the pH up with carbonates as above.

Wines are buffers - what that means for pH adjusting.

Wine is a “buffer”, i.e., a solution of weak acids and their salts that can absorb changes in acidity (TA) without major changes in pH. If you add 1 g/L of tartaric acid to very pure water, its pH will drop from around 7 to about 2.5. But if you add this to a typical wine at pH 3.5, the pH will drop maybe to only 3.4; this is due to the buffering effect.

In wine, the major weak acid and salt species are tartaric acid (represented as H₂T because two acid hydrogens are available per molecule of tartaric acid) and hydrogen tartrate ion (HT⁻), the latter usually associated with potassium. (The other wine acids and their salts behave similarly so for simplicity I’m just talking about the tartaric system). When we put tartaric acid (H₂T) into water, it partly dissociates into a hydrogen ion (H⁺) and its salt form, the bitartrate ion (HT⁻):



There’s a pretty simple relationship between the pH of any buffer system and the concentration of its components

$$\text{pH} = \text{pKa} + \log [\text{S}/\text{A}] \quad \text{Eq. 2}$$

where pKa is the negative logarithm of the acid’s dissociation constant (a known constant that reflects the ability, or strength, of the acid to dissociate as in Reaction 1 above), and S and A are the concentrations of the salt and acid forms, which for tartaric acid are HT⁻ and H₂T, respectively. The pKa for tartaric acid’s dissociating into H⁺ and HT⁻ is 2.89. So equation 2 becomes

$$\text{pH} = 2.89 + \log [\text{HT}^-/\text{H}_2\text{T}] \quad \text{Eq. 3}$$

The full mathematical treatment of tartaric acid’s pH behavior is a little more complicated because tartaric acid can release two hydrogen ions (the HT⁻ in Reaction 1 can further dissociate into H⁺ and T⁻² with a pKa of 4.4, i.e. a weaker acid), but equation 3 describes the situation pretty well especially at pH 3.5 and below.

From equation 2 or 3, there are three points I’d like to make. First, the ability of a buffer to resist changes in pH has to do with the log term, a ratio of the salt and acid forms. If you add acid or alkali (e.g. tartaric or carbonate, resp.), the change in pH is moderated by the ratio. Second, the higher the amount of S and A, the more the resistance to change in pH by adding acid or alkali. Higher S and A are precisely what you have in a higher TA wine, hence the infamous resistance to lowering pH exhibited by high TA wines. Finally, you can see that when you *dilute* your wine (or any buffer solution) with pure water, the pH won’t change! That’s because the ratio of S/A will be the same; even though both S and A have been diluted, it’s been by the same amount. (You would have to dilute wine by several *thousand* fold before you might expect to see any increase in its pH; under these conditions, Eq 2 becomes more complicated and the acidity of the water itself comes into play). See below in the FAQs for a little more on this, but, take note: *you can’t practically raise your wine’s or must’s pH by diluting it with water.*

Yeast assimilable nitrogen (YAN)

I thought I would briefly mention YAN here because it is essentially a TA test. At the beginning of fermentation, as long as you are doing TA anyway, why not include the extra step to do the YAN test?

Yeast assimilable nitrogen is an important nutrient in fermentation of wine. If levels are too

low, fermentation may stop prematurely, and/or off odors can develop (mostly from generation of hydrogen sulfide – “rotten egg” smell). In this case you may want to add supplements like DAP or other yeast nutrients before and/or during fermentation. Many yeast and nutrient manufacturers follow a study by the UC Davis Department of Viticulture and Enology relating optimal nitrogen levels (in milligrams of nitrogen per liter, mg N/L) to brix level at harvest:

21°Bx = 200 mg N/L	25°Bx = 300 mg N/L
23°Bx = 250 mg N/L	27°Bx = 350 mg N/L

A wine sample is titrated to pH 8.2 with TA Titrant (this gives the TA value as a bonus). Then the YAN reagent (formaldehyde) is added. This causes any amino groups or ammonia to become formylated, releasing one proton per amine/ammonia and lowering the pH. The sample is then titrated back to 8.2 as before. The YAN value is calculated from the volume of TA Titrant used in the second titration. For more information on the YAN test, check out the manual here: [Vinmetrica YAN Manual](#)

pH and TA FAQs

- Q. If pH is related to hydrogen ion concentration, can't you just dilute the wine or must with water to raise the pH (i.e. lower the hydrogen ion concentration)?

A. No, you really can't, as just mentioned above. If we had a simple strong acid solution, like hydrochloric acid, then yes, we could raise pH by diluting it. But the weak acids in wine just release more of their bound hydrogen ions as you dilute them, countering the expected decrease in hydrogen ion concentration. And as we saw above, wine is a kind of buffer that resists changes in pH by dilution. All you achieve by diluting is reduced alcohol and a watered-down taste.

In fact most wines will show a measurable *drop* in pH with as much as *a ten-fold dilution by pure water*. This is because, as you may remember from the last blog, the pH meter responds to the *activity* of the hydrogen ion, rather than its concentration. The activity coefficient increases closer to 1.0 as any solution is diluted, and since the hydrogen ion concentration is not changing (due to the buffering ability of the acids and their salts), the measured activity becomes closer to the concentration; hence the pH decreases.

- Q. What's the best way to add acidity, and how will that change the TA?

A. The best way to add acidity is: slowly and carefully! As discussed above, add half the amount you think you need, then re-check pH and TA to see where you are.

When you add acidity with tartaric acid (as we recommend) then the TA just goes up by the amount you added (in g/L). As we've seen above, the decrease in pH that this effects depends on the TA (buffering) ability of the wine.

- Q. My water is made by reverse osmosis (RO) and comes out with a pH of 8.5; won't it affect the pH of my wine if I use this water to dissolve nutrients or tartaric acid to adjust my wine's parameters?

A. Unless your water (whether it be distilled, deionized, RO, or even tap water) is very impure, its pH is not significant in terms of what effect it might have on your wine's pH. Think of it this way: most city water straight out of the tap is around 600 mg/L total dissolved solids (TDS); RO water is around 1/10 of this, while distilled or deionized water is essentially zero TDS. Only a small fraction of TDS is acidic or basic enough (almost always basic, represented as CaCO₃) to add or subtract from titratable acidity. Worst case scenario: you

are using *tap* water to adjust your wine. Even if its basic fraction of TDS were unusually high, say 100 mg/L equivalent of CaCO₃, then there'd be only about 2 mmol/L of acid neutralizing ability. Your wine has, let's say, 6 g/L as tartaric acid; that is 6 g/L divided by 75mmol H⁺/g tartaric acid = 0.080 mol/L or 80 mmol/L acid. So even if you mixed 1 whole liter of an unusually alkaline *tap* water with one liter of your wine (which I hope you would never do!), you would only neutralize at most 1/40 of the wine's acidity. Since your wine is buffered, this would have a negligible effect on its pH, even accounting for the fact that you diluted the wine by 100% (though this dilution might *lower* the pH as we saw in FAQ 1 above!).

Try the experiment. Measure out 20 mL of wine and add 20 mL of *tap, RO, or purified* water. Measure the pH of the water, the wine, and the mixture. Reports are due on Friday.

4. Q. I measured the pH of distilled water, expecting it to be 7.0, but instead it came out way different! Is something wrong with my equipment?
- A. No. Don't frustrate yourself trying to interpret the pH of pure water. In principle, very pure water should indeed have a pH of 7.0, but usually it is 5 to 6 because atmospheric CO₂ dissolves readily into the water to produce carbonic acid. Some deionizers will produce perfectly pure water that is nevertheless slightly alkaline, pH 7.5 - 8. Check your pH calibration instead with cream of tartar (see previous blog).