Penn State **Extension**

PQA Clark Smith Wrap Up

August 2011

First and foremost, I think it's important to recognize the efforts by the PQA in getting Clark Smith to visit our exciting industry. I'd like to send a very special thank you to Dominic Strohlein for organizing this event and all of his effort in making Clark's trip quite successful. Additionally, thank you to all of those who tasted wines with Clark and showed him what Pennsylvania wines are all about.

Clark quickly recognized the talent of our winemakers and was very enthusiastic about where many were going in terms of quality. He was very excited about our wines, and found that many of those he tasted were showing characters of "mineralty." The wine literature is a bit conflicting when it comes to the term mineralty, but Clark emphasized that this character showed a freshness in structure, especially in the finish of many white wines.

Clark's class, *Fundamentals of Wine Chemistry*, was very well attended and he touched on 6 main points:

1. Basics About Acids
2. Understanding Sulfur Dioxide
3. Crush Chemistry
4. Fining
5. Spoilage and Membrane Technology

I thought Clark had several positive messages to share with our industry. One of the main quotes that I pulled from his talk: "To make wine in this state, you have to understand two fundamental concepts: one of them is **acid control** and the other is **reduction**." By the end of his talk, I concluded that many of his discussions and lessons circled around these topics. From these lessons, I pulled a few key points that I think are essential for everyone to hear and read.

What's the Difference Between pH and TA? And why should I care?

Clark gave two standard definitions:

- pH – the amount of free hydrogen ions (protons) in a solution
- titratable acidity (TA) – all disassociated protons of a solution; titratable acidity is *not* total acidity

When it comes to acidity, Clark emphasized that titratable acidity (TA) is directly related to what we taste on the palate. In theory, TA is an analytical procedure that mimics how we taste acids in our mouth. When we take a sip of wine, our mouth produces saliva continuously until all the acid is neutralized. We perceive this as "sourness," "tartness," or "acidity." A titration is essentially an analytical mouth where one is pulling all of the acid out of a solution until it is neutralized, which is visualized with an endpoint.

Unlike TA, pH is not related to what we actually taste. However, pH manages all of our chemistry and microbiology decisions in the winemaking process. Therefore, all chemical reactions and microbiological stability in the wine is related to pH. Clark emphasized that many of our winemaking decisions cannot be made without making a reference to the wine's pH. I came to think of pH as our direction. In order to make decisions during winemaking, knowing the pH of that wine can often help direct which decision to make. An example of pH's importance includes knowing how much SO2 to add to the wine to ensure the appropriate amount of molecular SO2 is in solution.

SO_2 – Know the Basics

I think some of the discussions on SO2 additions were some of the important that we had during Clark's two day course. Clark started out this section by stating:

"I would love it if you never use the world "sulfur" as a wine descriptor ever again. The truth is, sulfur can refer to a lot of different things. Let's try to more finely divide those distinctions and not use it as a general term. Another one is "oak." When someone says, 'There's too much oak!' Well, there's like 12 different aromas we could be talking about."

I tend to agree with this statement. When Clark asked for an aroma descriptor, someone in the audience shouted out "rotten eggs." SO2, however, does not smell like rotten eggs at all. Hydrogen sulfide, H2S, smells like rotten eggs. But it is so often that many people within the industry say, "That rotten egg smell is sulfur." The term *sulfur*, as Clark stated, is too general. There are various forms of sulfur compounds in wine. Sulfur dioxide (SO2) in its molecular form, smells like a burnt match or elicits a painful sensation in one's nose. Hydrogen sulfide smells like rotten eggs. And then there are several sulfur compounds that are classified as mercaptans or thiols that are reminiscent of many other aromas.

The chemical reactions related to sulfur dioxide are as follows:

$$\mathbf{SO_2(m) + H_20 \leftrightarrow H+ + HSO^{3-} \leftrightarrow 2H+ + SO_3^{2-}}$$

The three forms of SO2 [SO_2(m), HSO^{3-}, and SO_3^{2-}] make up the free SO2 concentration.

- SO2 (m) stands for *molecular*. This form of SO2 has antimicrobial properties. The general rule of thumb is to retain 0.8 g/L (0.8 ppm) of molecular SO2 in your wine for microbial stability, but this concentration is well above threshold (meaning that the average consumer can sense/smell the SO2 in the wine). Therefore, most winemakers shoot for a concentration of 0.5 g/L (0.5 ppm) of molecular SO2. Remember the concentration of molecular SO2 is directly related to the wine's pH.

- HSO^{3-} is the bisulfite form of SO2. It is this form of sulfur dioxide that will precipitate out of the wine during cold stabilization. Bisulfite also inhibits browning of wines by inhibiting polyphenoloxidase (PPO) and combining with oxidative intermediate compounds. Bisulfite is also responsible for combining with anthocyanins, forming colorless pigment compounds. It is the cause of red wine bleaching.
- SO_3^{2-} is the sulfite form of SO2. Sulfite exists in a 3-way equilibrium with bisulfite and molecular SO2 at any given time during a wine's existence, as shown in the above equation. The equilibrium is directly related to pH.
- Clark emphasized that titrettes are not an appropriate way to analyze SO2 concentration.

Clark's explanation on the sulfur dioxide equilibrium was one of the best I've ever heard. I very much encourage you to read further about pKa's and how they relate to the SO2 equilibrium. If anyone needs more information on this topic, please email me.

When to use Micro-Oxygenation (Micro-Ox)

Clark is a master and firm believer in micro-ox. Micro-ox is the direct and controlled application of oxygen into the wine. The application of micro-ox can occur in three phases of the winemaking process:

- Phase 1 (Color Stability Phase): Occurs post alcoholic fermentation and pre-SO2 treatment with an application of about 10 – 100 mL/L per month for about a month.
- Phase 2 (Structuring Refinement Phase): Occurs post SO2 treatment and pre-barrel aging with an application rate of 2 – 10 mL/L/month.
- Phase 3 (Harmonization Phase): Occurs post barrel aging at an application rate of 0.25 – 0.5 mL/L per month for maybe for a couple of months to soften the pithiness of the wine.

Tannins – Unwrapped

There are several classifications of phenols that is often very confusing to winemakers and enologists. Clark gave the following definitions for clarification purposes:

Compound Name	Definition
Phenol (Phenolic)	Any compound containing a benzene ring with an –OH (hydroxyl) functional group attached.
Flavonoid	Any class of three-ringed phenolics extractable from [grape] skins.
Anthocyanin	Any of the five red-colored flavonoid monomers.
Flavilium Ion	Low pH red-colored form of an anthocyanin.
Anthocyanin Monomers	Subjective to bisulfite bleaching. This form of anthocyanins is also capable of structural improvement. They are also vulnerable to oxidation.
Monomer	A discrete small molecule which can serve as the building block for a

	macromolecule (polymer).
Polymer	A macromolecule created by linking monomers together.
Tannin	A polyphenol with an affinity for protein.
Polymeric Pigment	Stable, unbleachable color which is the basis for refined texture.

Phenols (monomer units) can bond together to polymerize and form poly-phenols (or long-chained phenol units linked together). These poly-phenols can strip the proteins off of your saliva and give you a grainy feeling that we designate as "astringency." Polymers can form into linear formations. This is referred to as non-oxidative polymerization of phenols. Oxidative polymerization forms daisy-chain, crooked chains of phenols, which interact more strongly with salivary protein because they are not as compact as linear poly-phenols. It is important to note that anthocyanins act as "end units" for poly-phenol chains, meaning that they stop the structure from building further. This anthocyanin bonding inhibits daisy-chaining.

"Bitterness," however, is related to the concentration of monomeric phenols in the wine. In this form, the phenols are not as soluble in wine, and we perceive this as "bitterness."

The following is a brief table that emphasizes when to use certain fining agents in wine, and how they relate to monomeric (bitter) and oxidative-polymeric (astringent) phenols.

Fining Agent	Source	Reason to Use…
Gelatin	Bones/Meat Products	Polyphenol Astringency (Make sure you fine for astringency early. Fine for bitterness later on in production.)
Casein	Milk	Polyphenol Astringency
Albumin	Eggs	Polyphenol Astringency
Isinglass	Fish Bladder	Polyphenol Astringency
Yeast Biolees	Yeast	Bring in softness.
PVPP		Monomeric Phenol Bitterness (Fine for it late if the bitterness is going to persist; don't fine a red wine early because you'll take out anthocyanins.)

Clark talked a lot about how essential *color* is needed in red wines, simply because anthocyanins will minimize the oxidative polymerization of phenols. Therefore, a higher concentration of anthocyanins will minimize harsh astringency of red wines. Theoretically, this should mean that in juice that comes in with poor color, the wines softness would be minimized while its harshness, or astringency, increased. A darker red wine would lead to shorter-chained polymers and therefore softer wines with less dryness or astringency. Clark emphasized that micro-oxygenation helps proliferate the reaction of stabilizing color (application after alcoholic fermentation). Why? Because the integration of oxygen helps speed up the reaction of color stabilization: forming polymeric pigments and increasing non-oxidative polymerization of phenols.

Let's Talk about Sulfides

Clark emphasized that we need to stop using the word "sulfur" generically. The truth is, there are many forms of sulfur-based compounds in wine, and each form has a specific smell or flavor. The following table is a summary of the most common forms of stinky sulfur-based compounds in wine:

Compound	Abbreviation	Aroma	Threshold	Sparge Treatment?	Copper Treatment?
Hydrogen Sulfide	H_2S	Rotten Egg	50 ppb	Yes	Yes
Ethyl Mercaptan	EtSH	Diesel, Onion	5 ppb	No	Yes
Diethyl Mercaptan (Oxidative product of EtSH)	EtS-SEt	Canned Asparagus	25 ppb	No	No
Ethyl-Methyl Mercaptan	EtS-SMe	Wet Wool		No	No
Dimethyl Sulfide (DMS)	CH_3-S-CH_3	Canned Corn	50 ppb	Yes	No

[Please note that SO_2 (sulfur dioxide) is not on this list. SO_2 can smell like "a freshly burnt match" to some people, but it usually irritates the nasal passageways in a painful way. It does **NOT** smell like rotten eggs.]

Where do these sulfur-based compounds come from?

a. Dusting sulfur – This is typically the source of H_2S when you see a lot of H_2S in the fermentation tank, unless you are not using nutrients appropriately during alcoholic fermentation.
b. Proteins – some contain a lot of S as their side groups, which can be utilized by yeast or bacteria and end up in the wine.
c. DAP attends to accelerate fermentation to a point where we won't get the yeast to utilize the other nutrients in the tank (if you give someone Twinkies, they won't eat their oatmeal). This often causes H_2S formation during fermentation.
d. Light exposure, especially in white wines – This is often referred to as "light struck" and occurs when a bottle is left sitting in the sun or heated to high temperatures ("cooked").