From Vine to Bottle, the Chemistry of Wine
Fall Term, 2020
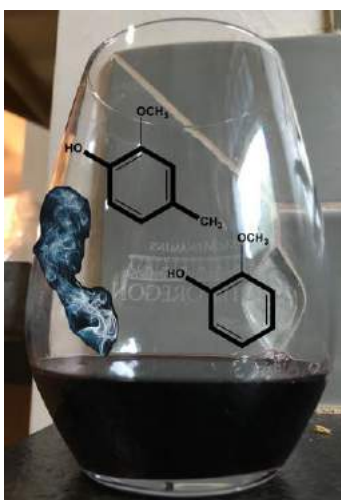**Brooke Taylor**

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Sabbatical Report:

The purpose of my sabbatical was to learn more about the chemistry involved in making and analyzing wine. During the summer of 2020, prior to harvest, I completed a six-week online course titled World of Wine from University of Adelaide and edX. Weekly topics were wine styles and sensory evaluation, the grape vine, the vineyard, wine production, wine making and lastly, grape and wine science. Beginning on the Tuesday after Labor Day, 2020, I began working at Benton-Lane Winery in Monroe, OR. During that time, I sampled grapes throughout the vineyard, analyzed the grape samples for pH (acid levels), TA (titratable acidity) and Brix (sugar concentration). Once the grapes were picked, I assisted with lab analysis, including more pH, TA and Brix for multiple tanks of Pinot Noir, Pinot Gris, and Chardonnay. I analyzed wines for nitrogen levels (nutrients for yeast), as well as glucose-fructose levels to determine when fermentation was complete. For wines harvested previously and aging in barrels, I analyzed free sulfur dioxide levels and alcohol levels. Once the harvest was complete, I interviewed several winemakers, some local, some in Napa, to learn about their path to becoming winemakers, the analysis they use to make wine and their experiences with chemistry in making wine. I also had the opportunity (twice) to blend Cabernet Sauvignon in Napa. Blending wine involves adding small amounts of Bordeaux grapes (Petit Verdot, Malbec, Merlot, Cabernet Franc) to Cabernet Sauvignon to achieve desired characteristics of structure and texture. A final goal of my sabbatical was to learn more about the impacts of climate change on winemaking. Ultimately, I didn't really need to ask about the impacts, as we all lived through it. The first day of work for the harvest was the last time the Willamette Valley saw the sun for two weeks, as the entire Pinot Noir growing region of Oregon was covered with a thick layer of smoke. Additionally, around the 2020 harvest, Napa Valley in California experienced three different smoke events. As a

result, a variety of webinars about testing for smoke compounds and the potential impacts of the smoke on the 2020 harvest were quickly organized and made available on the web for me to view. The smoke caused many Oregon wineries, such as King Estate, to leave the grapes on the vines. Other local wineries such as Antiquum and Territorial picked their grapes, made the wine, and dumped the wine. Benton-Lane completed the process of making wine and the smoke-impacted 2020 Pinot Noir is currently sitting in tanks. The long-term impacts of smoke compounds on wine won't be understood for years to come, however, the 2020 harvest, unfortunately, provided a solid start to gathering baseline data on a very large scale.

My sabbatical turned out to be so much more than expected, and also, somewhat less than what I hoped for. Working at the winery was an amazing experience, and exactly what I hoped to get out of it. There is much more general chemistry in winemaking than I thought and it was really fun to work in the lab again. Some general chemistry concepts have been worked out in the design and manufacture of equipment, such as heat of fermentation and tank design, some aspects are part of the lab work, and other significant concepts of chemistry including pH, TA and Brix are used to make decisions on when to pick specific blocks of the vineyard. All employees from the head winemaker, assistant winemaker, cellar manager and vineyard manager know what the values mean in terms of "the grapes are ready to pick" or the "grapes need more time to ripen on the vines". In addition to these concepts being relevant to the general chemistry classes I teach, the fact that laboratory results are used to make real-life, impactful decisions provides an amazing opportunity to demonstrate and share the value of careful, precise lab techniques with general chemistry students.

Taking my sabbatical in 2020 created other challenges. COVID-19 did not impact the 8-week harvest however three weeks of post-harvest analysis were not possible because each of the

three full-time employees at the winery were exposed to someone who tested positive for COVID and were required to work from home (this was in November, well before the vaccine was available to the general public). COVID also caused many wineries to close their tasting rooms. This made touring the wineries and interviewing the winemakers challenging. Additionally, many winemakers did not respond to calls and emails so some of the folks I mentioned in my proposal were not included in the interviews. I was fortunate however to be able to interview, via Zoom, two California winemakers not included in my original proposal.

My reading materials expanded to a list I couldn't have predicted. I read and took notes from two texts: Concepts of Wine Chemistry by Yair Margalit and based on the recommendation of the winemaker at Abacela winery in Southern Oregon, Andrew Wenzl, I read Post-Modern Winemaking by Clark Smith. So much analytical work has been done on wine and Margalit summarized and explained a variety of research papers published at the time of writing. The academic side is interesting but, in many ways, separate from the practice of making and consuming wine. Smith focused instead on describing a different process for making wine, one that focuses more on the structure of the wine to increase the potential to age the wine. Ultimately, the postmodern view is "wine's chemical composition does not determine its sensory properties, structure does". Margalit focused on the chemical composition, Smith focused on developing structure, both are important and interesting. Knowing the thousands of chemicals in wine, and in many cases their quantities, is fascinating, especially as a chemist, but not really relevant to enjoying (or not) a particular wine. Context is everything. The type of grape, the terroir, the weather, the climate, the soil, the winemaking details, your senses, your environment, your company, so much goes into a wine experience that can't be analyzed by a chemist. Additionally, it was interesting from a basic academic perspective of chemistry to read books

describing the chemistry of wine. Some of the descriptions the authors chose to use made my head hurt, and some were incorrect. In Concepts of Wine Chemistry, the discussion of weak acids in wine and pH, main topics in the third term of general chemistry, were presented in a manner that, in my opinion and experience, made the calculations much more complicated than they need to be. I reworked the examples of calculating the pH of wine and the impact of salts on the pH of the wine using the method we teach at LCC. Other common errors appeared in line structures (drawings) of complex molecules in wine. These structures include conjugated six-carbon rings (shaped like a hexagon). Carbon can only form four bonds but it was not uncommon to see structures in wine chemistry texts with five bonds.

Then there was the smoke, so much smoke, and so many unknowns. If 2020 wine is bottled, what will it taste like in 2022? The combination of lab analysis and sensory characteristics really show through with smoke impacts. Knowing the concentration of a variety of smoke compounds such as guaiacol and 4-methyl guaiacol in grape juice, young wine and eventually aged wine is important but equally important are the sensory characteristics of the sample, and everyone tastes wine or grape juice differently. It's possible for smoke compounds to be present in a sample but not at levels that can be tasted, and it's also possible to have relatively low concentrations of smoke compounds and have the sample be described as "licking an ashtray". Having many people taste the wine is just as important, if not more so, than knowing the micrograms per liter of each smoke compound in the wine. So far, I have been unable to taste the smoke compounds. The commercial labs were unable to keep up with demand for smoke analysis because the entire Willamette Valley and much of Napa Valley experienced smoke events at the same time. Winemakers wanted (and needed) the analysis of the smoke compounds completed in grape juice prior to harvesting their grapes, most likely sometime in

early October. The commercial lab wasn't able to return results until at least November, well past the time the grapes would be picked. To meet the local demand, a lab group at Oregon State University in Agricultural Sciences, stepped in to accept and analyze grape juice and wine samples for smoke compounds using an acid hydrolysis test and equipment not readily found in wine labs. Ultimately, the 2020 harvest threw winemakers into an experiment they didn't sign up for. Smoke compounds can't be tasted in grape juice prior to fermentation because the compounds are bonded to sugars in the juice. The process of fermentation breaks many of the bonds and releases the smoke compounds into the young wine. As the wine ages, more smoke compounds are released. The result? Maybe a wine with a smoke flavor, maybe a pleasant sense, or maybe it tastes like licking an ashtray, or maybe nothing? No one knows for sure, and no one can really speed up the process, so the results really won't be available for a few more years.

I included the summary of the lab work in the main report, as it was the main focus of my sabbatical. Attached to the end of this report are more detailed summaries about each of the other components of my sabbatical, including those I always planned on, as well as the surprises. Topics include a summary of the World of Wine online class, my experience blending wine in Napa, my summary of the two texts I read, a more thorough description of the challenges I experienced working in the lab. I also summarized the impact of the smoke on the 2020 harvest and the two infographics I developed, one on the impact of smoke on wine, the other about the specific smoke compounds. More details about my interviews with winemakers, a brief presentation I gave to third term general chemistry students during spring 2021 about my experience working in the lab during the harvest, a description of the wine related outcomes in general chemistry, and reworked pH examples from the text Concepts of Wine Chemistry by

Yair Margalit and lastly a list of all the resources (print and online) I reviewed during my sabbatical are also included.

Most of my classroom time at LCC is spent teaching general chemistry. The experiences I had during my sabbatical overlap with a variety of topics in each section of the general chemistry sequence. It warmed my heart to look around the lab at work-orders and see dimensional analysis work to calculate how many pounds of yeast to add to a tank of freshly pressed Pinot Noir grapes, or how much KMBS (potassium metabisulfite, a sulfur preservative) to add to a tank to ensure bacteria won't spoil the wine. Collecting data using appropriate techniques and equipment is a goal throughout the lab components of general chemistry. To measure pH and TA a precise volume of juice or wine must first be measured using a volumetric pipet, a standard piece of lab equipment and one used frequently in general chemistry labs. While general chemistry students at LCC don't get to use an automatic titrator like I did in the lab, each term of general chemistry lab includes titration. In the middle term of general chemistry, solutions are discussed. Wine is often thought to be a solution composed of many, many solute components such as weak acids and phenolics including anthocyanins and tannins giving wines color and flavor, structural compounds including alcohol (a product of fermentation where sugars are chemically converted into ethanol by yeast), and so many more in compounds in varying concentrations. According the to the author of Modern-Day Winemaking, Clark Smith, wine is not a solution, but a mixture of tannins, anthocyanins and other insoluble compounds that aggregate into colloids and the colloidal structure allows for interaction between soluble and phenolics to blend aromatic properties that provide structure to the wine. Structure, not composition determines flavor. Who knew? Many of the chemical concepts discussed in the texts I reviewed relate to topics in the general chemistry sequence, specifically, the variety of

weak acids in wine are major topics of discussion in the third term of the sequence, as is acids and bases, pH, and more titrations. In fact, I started the first day of CH 223 sharing with students some of my experiences working in the wine lab. While one doesn't need to have a strong chemistry background to make wine, after completing my sabbatical, I found it very satisfying to understand the chemistry as different processes to make wine were discussed. Other things I discovered during my sabbatical: just because an analytic technique (or many) exist doesn't mean the results of the analysis tell the entire story. Sensory characteristics are just as, if not, more important. Understanding science helps winemakers make decisions, and numbers may tell part of the story but not all of the story. In addition to the limitations of a technique, there is a limit to the usefulness of the analysis. Working in the lab in 2020, given the smoke, was an experience of living through the benefits and challenges of the scientific method. Science is thoughtful, and time consuming, and fascinating and satisfying and frustrating. Wine is artistic, not just scientific. We may know the quantities of smoke compounds in the 2020 wines, but we really won't know how they will impact the wine for years to come. In the meantime, we have lots of other vintages to sip and savor and enjoy. Cheers.

Wine Harvest: Lab Analysis

Two weeks before any grapes are picked, grape sampling occurs. The winery has thirty different blocks, labelled with letters, and of varying sizes. Some blocks are almost four acres, and others are less than an acre. Three blocks contain Chardonnay grapes, and the rest are different clones of Pinot Noir. The winery used to grow Pinot Blanc and Viognier, but those vines have been grafted with Pinot Noir. Grape sampling involves filling a one-gallon Ziploc bag with grapes clusters randomly picked within the block sampling in different rows and from different parts of the vine (top, middle, bottom). Basically, we drive out into the vineyard and walk down the rows cutting grape bunches. Back in the lab, the grapes are hand crushed and the Brix level is tested using a refractometer (figure 1). Three samples are taken and the average recorded. For the Pinot Noir samples, the juice is then stored in the fridge until the next day.

Figure 1: Refractometer for testing Brix (grams of sugar per 100g solution)

Day 1 of working at Benton-Lane started at 7:00 in some of the fastest forming smoky air ever. We probably should not have been outside, but I joined Chuck to collect samples from several blocks of the vineyard. Smoke taint became a major focus of the day. The

smoke came in Monday evening and got worse throughout Tuesday. The skins of the grapes will absorb the smoke. Currently, juice samples take more than two months for ETS, the commercial lab, to analyze because there is such a back log from all the fires in CA. This afternoon, Chuck needed to return outside and collect 250 individual berries to mail in Tupperware containers to the lab. He also had to pick grapes to run a mini fermentation in 5-gallon buckets so the wine can be sent to the lab to be analyzed for smoke taint (using GC-MS). Apparently, juice is delayed but wine tests are complete in a few days. It's entirely possible the harvest could be lost this year because of smoke taint. The chemical, guaiacol, also gets worse as the wine ages. The tests Chuck collected samples for today may be used in an insurance claim. Ideally, a test prior to the smoke would have been completed but the smoky conditions came on rather unexpectedly.

After chilling overnight for the Pinot, or after being crushed (Chardonnay), the titratable acidity (TA) is measured using an automatic titrator (figure 2). TA is a measure of tartaric acid in the grape juice. Prior to the test, the juice is poured into two 100-mL plastic centrifuge tubes and spun. 10.00 mL of juice (measured with a volumetric pipet) is titrated with 0.10 M standardized NaOH to an endpoint set at a pH of 8.2. The machine automatically calculates the grams of tartaric acid in one liter of juice. The NaOH is standardized with 0.10 M HCl, and a 6 g/L tartaric acid standard is also run. The standard of 6 g/L represents a desired acid level in wine.

Figure 2a   Figure 2b

Figure 2a: Automatic titrator for measuring titratable acidity (TA). The clear sample is a 6 g/L tartaric acid standard. Figure 2b: on the right 10.00 mL juice diluted with water (pink) prior to being titrated. On the left, the blue solution has been titrated to the endpoint of pH 8.2.

According to ETS labs 2020 Harvest guide, tartaric acid accumulates in grape tissue during development and declines during ripening as berries grow; the acid is diluted. Higher levels and the wine will be too acidic, lower levels indicate the grapes are shutting down and need to be picked. Acid can be added to the wine later on in this case. The pH of the juice is also measured. A higher TA indicates a lower pH and a lower TA indicates a higher pH. All pH values however are in the range of 3 to 3.3 (figure 3). The Brix level is again measured for the juice and often goes down a few tenths. A Brix level of 23 or higher indicates good sugar levels. Lower than that and it's another indicator that the grapes are shutting down or that they aren't ripe yet. In a "normal" year, the grapes wouldn't be harvested until the Brix levels were above 23. This year because of the smoke, many of the blocks had Brix levels less than ideal. Pallets of sugar were purchased in the expectation of boosting the sugar to ensure adequate alcohol levels in the wine. Thankfully, no sugar needed to be added to any of the tanks, the Brix levels

were high enough. Sampling the entire 30 blocks can be completed in 3 or 4 days. Once

done, we start again.

Figure 3: pH meter is part of the automatic titrator

The results of Brix, TA, and pH measurements on the juice are used to inform the

winemaker of which blocks to pick first. Everyone involved in the harvest, from the

winemakers, the general manager, and the vineyard manager, know how to interpret the

values and use the data to make decisions. It also stressed to me the importance of

providing reliable analysis. The machine needed to be calibrated and the standards run.

Proper lab technique was critical. I have never, and will likely never, pipet so much

again. Proper technique included rinsing the pipet with each juice sample, ensuring the

bottom of the meniscus was at the 10.00 mL TD line, rinsing the probes with distilled

water and rerunning a result when it contained too much error. Titration is a key activity

in general chemistry lab, as is pipetting. Rest assured future LCC students will hear

stories about my time working in the wine lab. "Back in my day, I had to walk uphill

both ways to school…. Oops wrong story. Back when I spent my sabbatical at the wine lab ….”

The first grapes were picked on September 21st, 2020, the same tests, Brix, pH, TA, are run on the juice. The grapes are picked, sorted, and put into tanks with analysis the following day. The tanks varied in size and usually contained a combination of blocks picked on the same day. Because of the ash, the juice collected prior to sorting and destemming was dumped because of greater skin contact. In a non-smoke harvest, this juice would be collected. In addition to running Brix, pH, and TA on the juice, three enzymatic tests are also run. Those tests are for malic acid, primary amino acids, and ammonia (figure 4). For each test, a reagent is combined with the sample (grape juice, wine or standard) and a base wavelength recorded one minute later. Then a second reagent is added, and the wavelength recorded a set time later (somewhere between 5 and 10 minutes). The machine calculates the results on the display. Each test includes a known standard to run for comparison with the set value listed in the literature provided with each test. The primary amino acid and ammonia tests help determine if additional nitrogen nutrients will need to be added to the tank. If primary amino acids are too low, the yeast will start to use amino acids containing sulfur and this will produce sulfur compounds (think rotten egg smell) and is an indication of a stuck fermentation. Two days after picking, the tank would be inoculated with yeast. The winery uses a variety of different types of yeast that do not produce hydrogen sulfide during fermentation. To inoculate a tank, the tonnage of grapes in the tank is used to calculate the quantity of yeast needed in a classis unit conversion, dimensional analysis set up.

A 1:1 ratio of nitrogen nutrients is dissolved in 120F water first. For example, if 2.1 lbs of yeast are needed, 2.1 lbs of nutrient (called Prime) are first added to the hot water. Once the nutrients are mixed with the water, yeast is added, and gently submerged in the water, then left to sit for 30 minutes in order to acclimate. Rough stirring will harm the yeast and dumping the yeast into the cold juice in the tank would kill them, so slowly,

Figure 4: Enzymatic test for ammonia.

the temperature of the yeast slurry is lowered by adding juice from the tank (figure 5). The goal is to have the temperature of the yeast/nutrient mixture within 25F (or 10C) of the temperature of the juice in the tank. Once that temperature difference is achieved the yeast are dumped in the tank and the magic begins.

Figure 5: Lowering the temperature of the yeast slurry by adding tank juice.

Several days later, the temperature and Brix are recorded for the tank. Because fermentation produces carbon dioxide, the refractometer can no longer be used to measure the Brix. Instead, the Anton Palmer device is used. If the Brix value is positive, fermentation is continuing. Once the Brix value is negative, the yeast have converted the sugars to alcohol (this is what is referred to as dry wine). The following day, a glucose-fructose (affectionally called glu-fru) enzymatic test is run to ensure fermentation is complete. A glu-fru result of less than 1 indicates fermentation is complete. Generally, a negative Brix level of 1.5 or more corresponds to a glu-fru level of less than 1. For wine that has a Brix level of 0 to -1, the glu-fru levels generally were greater than 1 and the tank needed to ferment a few more days.

Most of the analysis occurred on samples from the 2020 harvest. The 2019 First Class however was still in barrels. All other 2019 had been bottled. Most wine labels will have the statement "contains sulfites". Sulfites are added in the form of potassium metabisulfite (KMS) as a preservative. In the form of sulfur dioxide, the wine will be protected from bad yeast and from oxygen. The test to measure free sulfur dioxide in the 2019 First Class was my favorite. First, I had to collect a 10-mL sample of wine from each barrel and combine them. After preparing the reagents by dilution, a sample of 3% hydrogen peroxide has three drops of indicator added and turns purple. To that mixture, 0.01 M prepared sodium hydroxide is added dropwise until the mixture becomes green (color changes are the best). 20-mL of wine is pipetted into a round-bottom flask and 10-mL of phosphoric acid, measured with a graduated cylinder, is added. Air is then bubbled into the wine to free the sulfur dioxide (figure 6). The SO_2 dissolves in the hydrogen peroxide solution with the indicator and that solution changes back to purple.

After 10-minutes, the sample is titrated with 0.01 M NaOH in a buret until the color goes

back to green (figure 7). The volume of NaOH is then multiplied by 16 to determine the

parts per million (ppm) of sulfur dioxide in the wine. Based on the pH of the wine, a

table indicates appropriate levels of SO_2 so the winemaker can determine if more sulfur

in the form of KMS needs to be added. As a chemistry teacher, I was curious why the

number 16. The value had no units and the textbook didn't explain where the value came

from.

Figure 6: Aerating the 2019 First Class Pinot Noir to measure free sulfur dioxide.

Turns out, it's the combination of all the stoichiometry steps to calculate the mg of SO_2 in

1-L of wine (ppm). And here we have another example of general chemistry concepts in

wine making. This makes my nerdy chemistry self so happy.

Figure 7a: start of titration   Figure 7b: end of titration

An additional analysis completed on wine was measuring the alcohol percent by volume with an ebulliometer (figure 8a). Ice water is added to the top of the ebulliometer to condense the alcohol and the sample is boiled. Alcohol has a lower boiling point than water and as it vaporizes, the composition of the solution changes and so does the boiling point. A thermometer measures the temperature of boiling of the water after the alcohol has vaporized. During a phase change (melting or in this case boiling), the temperature remains constant so as the alcohol vaporizes the temperature changes. Once the temperature is constant, its value is recorded. The ebulliometer includes a dial with corresponding boiling temperatures and percent alcohol by volume (abv) at 20°C on a dial (figure 8b). The boiling temperature is set to a particular location on the dial and lines up with the corresponding abv. Three trials of pure water are run first, followed by three trials with the wine. I tested the 2019 First Class Pinot Noir and measured boiling points of 90.80°C, 90.70°C for two trials corresponding to abv of 13.3% and 13.5% respectively. This value is printed (and required by law) on the bottle label.

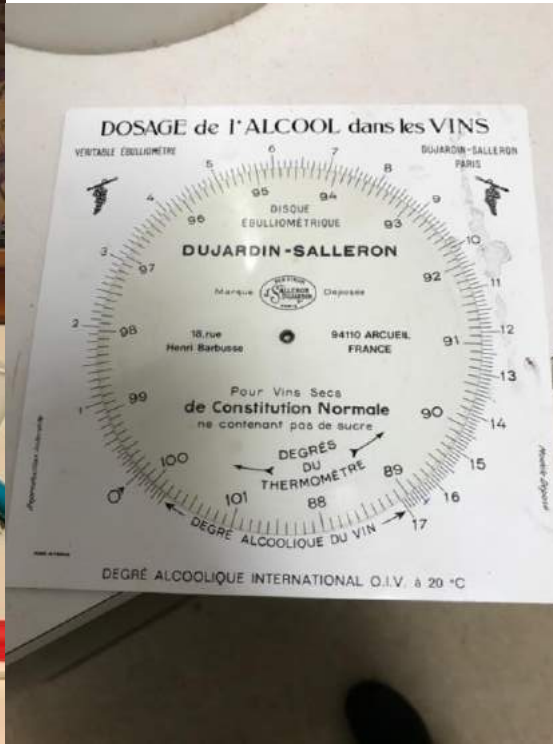Figure 8a: An ebulliometer.   Figure 8b: Dial to determine abv

The lab completes additional tests, such as bentonite, however I was not working

in the lab when the analysis was completed. Bentonite is used to fine (or clear/clarify)

wine. Red wines also undergo malolactic fermentation (MLF) to reduce acidity, alter

flavors and provide microbial stability. MLF is completed by malolactic bacteria. Sulfur

dioxide inhibits MLF so sulfur would not be added until MLF is complete. I completed

the enzymatic tests for malic acid but did not observe MLF, though the process is the

same as the initial fermentation.

The 2020 Pinot Noir was eventually combined into three blends and underwent

reverse osmosis (RO) to remove the smoke compounds. Analysis from ETS labs shows

lower levels of the tested smoke compounds. Unfortunately, RO also removes many of

the compounds giving wine its structure, especially in the mid-palate. I was able to taste

the two blends and without having anything to compare them to, they are fine. However,

I think a side-by-side tasting with a 2019 would really demonstrate all that's lacking in the 2020 vintages. The winery, as of early August 2021, is planning to leave blends 1 and 2 in tanks and not make any decisions about bottling it for at least a year, maybe two years. Prior to RO, some of the wine was stored in neutral oak barrels. Blend 3 has been sold on the bulk market where it will be mixed with wine from a different vineyard and winery. Additionally, the head winemaker is no longer with the company and the new winemaker will not begin working full-time until after the 2021 harvest. The new winemaker will be responsible for determining the future of the 2020 Pinot Noir. Benton-Lane owners are requesting a certain number of cases of 2020 wine to be bottled so it's likely, as a wine-club member, I will be able to eventually purchase and taste the smoke impacted wine.

Smoke Taint in Wine

Lignin is found in the cell walls of wood and bark. The complex polymer breaks down into volatile phenols when burned.
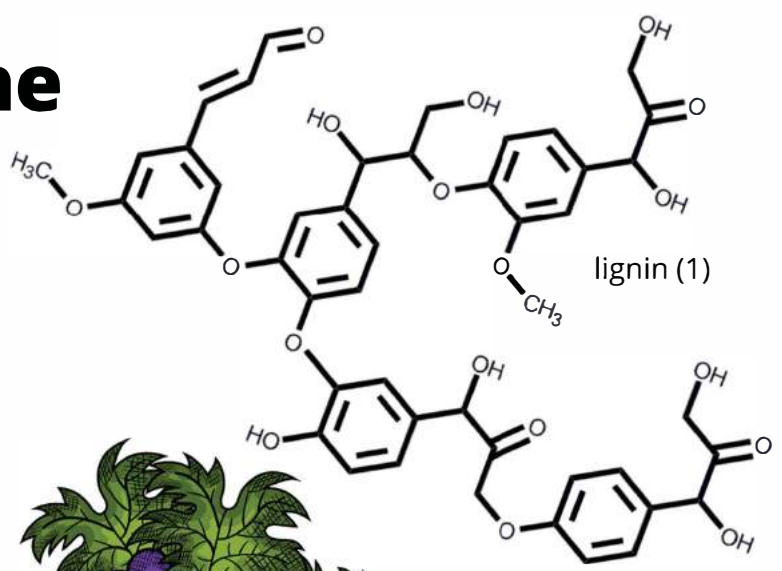
*Volatile phenols in smoke include guaiacol, 4-methyl guaiacol and cresols that may impart ashy flavors on wine.*
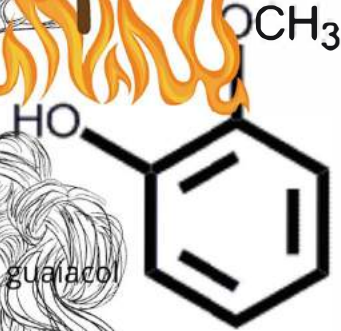
The nontoxic volatile phenols bind to sugars in the grape skins and berries forming nonvolatile glycoconjugates with no smoke flavor or aroma.
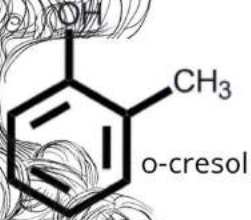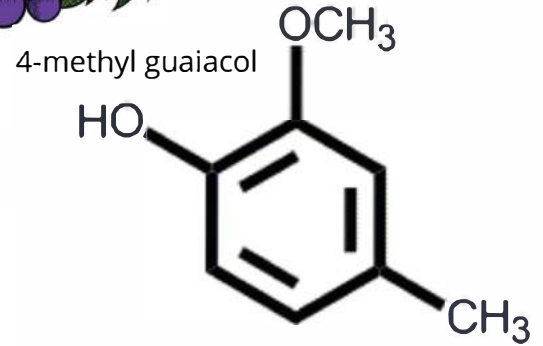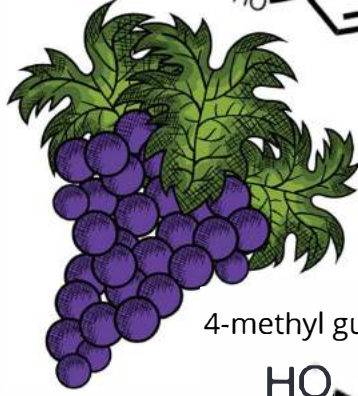
During fermentation, yeast enzymes break the glycosidic bond separating the sugar and volatile phenols. Smoke sensory characteristics can now be detected.
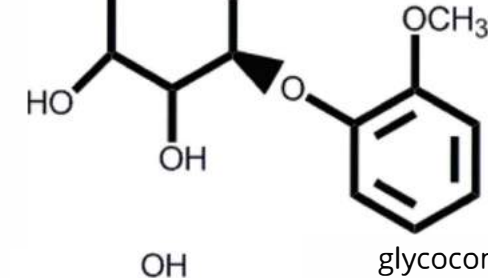
The glycoside bond will continue to break during bottle aging. Enzymes in saliva will also break the bond and may cause a lingering ashy taste.

lignin (1)

guaiacol

o-cresol

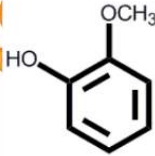4-methyl guaiacol

glycoconjugates (2)

21
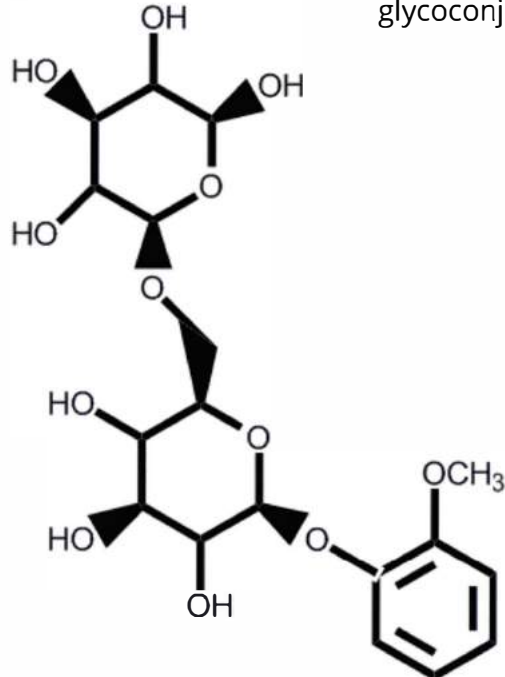
COMPONENTS OF WOOD SMOKE IMPACTING WINE

Over 400 different compounds have been identified in wood smoke. Commercial labs can analyze berry and wine samples to measure the micrograms of each volatile phenol in one liter of juice or wine. At temperatures over 400F, these compounds vaporize and then condense onto smoke particles or ash and are carried by the wind where they come in contact with grapes. The compounds are transported through skins and bind to sugars in grapes.

guaiacol

A common component of wood smoke. Used medically as an expectorant, antiseptic or local anesthetic. A precursor to synthetic sandalwood. Present in the smoke of burning oak trees and oak barrels.
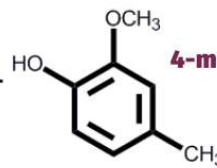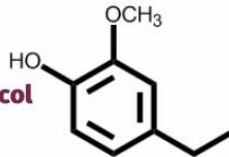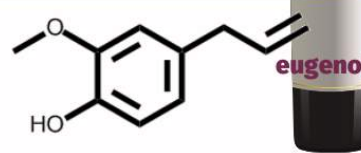
4-methyl guaiacol

Another common component of wood smoke. Also used as a flavoring agent. The odor is described as sweet, woody, smoky, burnt, leathery, spicy with hints of vanilla.
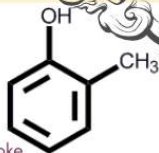
4-ethylguaiacol

Produced by spoilage bacteria Brettanoynces in beer and wine. Described as a woody, smokey, spicy , bacon aromas witha sweet vanilla background.

eugenol

The fragrance of cloves. Used in perfumes and mouthwash, and as an insect attractant and dental analgesic. Can be oxidized to form vanillin.

ortho-cresol

A component of tobacco smoke, extracted from coal tar and used as an intermediate for synthesis other molecules. Found in castoreum gathered from beavers who consume white cedar trees. Described as musty, medicinal, plastic when used as a flavoring or perfume agent.

meta-cresol
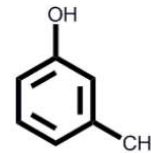
Also a component of tobacco smoke and extracted from coal tar. Used as an antiseptic and disinfectant. Described as musty, medicinal, plastic when used as a flavoring or perfume agent.

para-cresol

A component of tobacco as well as human swea odor is an attractant to mosquitos. Also a major component of pig odor. Described as animalic when used as a flavoring or perfume agent.

phenol
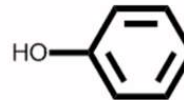
Present in small quantities in mouthwash, spray cleaners, diaper rash ointment, and lip balm. Has a mild sugary scent. Used as a disinfectant and to treat minor sore throat pain.

syringol
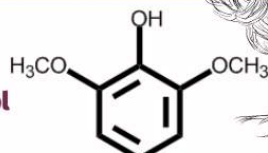
The main aroma of smoked and grilled foods. Used as a synthetic smoke flavoring agent. Suggested to be more common in the smoke of burning hardwoods.

4- methylsyringol
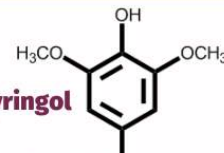
A food additive. Described as smokey, rooty, spicy with a carmellic nuance. The only compound of the ten listed without a reference page on Wikipedia.

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World of Wine online class

The online course was taught by professors from the University of Adelaide (Australia) and made available online by edX. Weekly topics were wine styles and sensory evaluation, the grape vine, the vineyard, wine production, wine making and lastly, grape and wine science. In week 1, we learned the different ways wine is evaluated and described, including color, and sugar content. In formally assessing a wine, appearance, aroma, flavor, taste, color and clarity are all considered. The course shared a variety of documents posted on winefolly.com about wine color and aromas. Only a small number of volatile compounds influence the aroma and flavor of wine, and those compounds can be measured by calculating the odor activity value (OAV). OAV is equal to the concentration of the compound in wine divided by the detection threshold of the compound. A value greater than 1 will influence the wine. A few specific compounds contributing specific aromas to wine were used as examples. Additionally, this week included a taste experiment to understand acidity and astringency using lemon water and black tea. A suggested activity included making tasting notes on an available wine. I learned it's very difficult for me to describe a wine without have descriptors in front of me to select from.

Weeks 2 and 3 were less applicable to my interests because they focused on the anatomy of the grape vine and planting a vineyard. These two weeks of the course would be vital for those who have invested in land and grapes in the hopes to make wine. So many decisions need to be made prior to planting grapes, including what grape variety is best suited for the land, how should the grapes be pruned and trellised, how will the grapes be picked (and when). Cooler temperatures help retain fruit acidity and this

increases the color stability of wines and helps develop the aroma compounds. Higher temperatures increase sugar levels and reduce acidity. Once grapes are planted and growing, their sugar and acid content, titratable acidity, soluble solids content, and pH must be assessed prior to harvest. These are all tasks I look forward to experiencing working at the wine lab. Grapes have hundreds to thousands of chemical compounds that change as the grapes ripen, and the pattern is different each year.

Week 4 started with a virtual wine making activity. After a couple of attempts, changing one variable at a time, I was able to make a gold medal Cabernet Sauvignon. The next week I attempted to make a virtual Chardonnay but was only able to make bronze or silver. White wines spend very little time in their skins once picked and must be chilled. Grape skins contain a class of compounds called phenolics. These are the chemicals that give red wines their color and astringency (mouthfeel). Red wine grapes are harvested, crushed (destemmed first), mixed with tartaric acid and SO_2, fermented, pressed, clarified, MLF, blended, bottled and matured. MLF refers to malolactic fermentation and occurs for red wines only to reduce the acidity. Much of the general process described above impacts flavor and aromas of the wine based on the desired attributes of the winemaker. The red color is the result of a group of chemicals called anthocyanins found in skins. pH, SO_2 presence, and the formation of new pigments as the wine ferments all contribute to the stability of the wine. So many different chemical compounds contribute to the sensory evaluation of a wine. Wine aromas comes from the grapes (primary aromas), fermentation (secondary aromas), and maturation and storage (tertiary aromas). Many of these compounds are bonded to sugars in the grapes. As fermentation occurs, and the sugar is converted to alcohol in a multi-step process, the

volatile compounds are released; others are formed during fermentation. Once fermentation is complete, the wine is stored in steel tanks or oak barrels to mature. This process can both improve flavor and aroma aspects of the wine. Sometimes however, compounds causing taint are only detectable during this stage of winemaking. Cork taint, smoke taint, bacteria, spoilage can all contribute compounds that ruin the flavor and aroma of a wine. Prior to bottling, different wines may be blended to impart specific characteristics as well. This is also the stage where a significant amount of analysis occurs including pH, titratable acidity, dissolved carbon dioxide and oxygen, free and total sulfur dioxide, alcohol content, and volatile acidity.

The course concluded with each professor sharing a specific research project. The two most relevant to my interests were the study of chemicals is used oak barrels compared to new oak, analyzes by GCMS. This study demonstrates that old oak barrels could be used to make battens and still impart some oak characteristics on the wine. The other study was the odorless thiols (a class of sulfur compounds) in grapes that contribute to pleasant aromas in Sauvignon Blanc grapes. The research groups determined a way to analyze the compounds in the liquid form using HPLC. The paper is published *Analytical Chemistry*, 2015, 87.

Overall, this was a good overview. I took copious notes about specific chemicals in wine and the flavor and/or aromas they impart on the wine. I look forward to seeing and participating in many of the processes described in the course while working in the wine lab. While I wasn't really interested in making formal tasting notes, I do find myself trying to describe the aroma and flavor of wine, and then looking on the label to see if the winemaker included a description.

Wine Blending at Foundry in Napa, August 31, 2020

Our task was to blend three barrels of Cabernet Sauvignon for customer holiday gifts. Barrels were available from Melrose vineyard in Rutherford, J Squared, and Galloway vineyards near Yonteville. The first decision the group had to make was which barrels to blend. Melrose was the only option for a single vineyard. The winemaker prepared the blends, each labelled A to D, all Cabs but from different vineyards. Sample A was an even blend of all three vineyards, sample B contained 2/3 Melrose and 1/3 J Squared, sample C was all Melrose, and sample D was 2/3 Melrose and 1/3 Galloway. I found A to be acidic but have a lovely aroma. B was pretty bland at the front and astringent in the finish, C was more even and acidic in the finish, and D had a late acidic finish that was also astringent. B was the least favorite of the group, with A and D the favorites.

Once the group determined which barrel blend we liked the best, D, that blend was further blended with other Bordeaux grapes. D1 contained 3% Petit Verdot and 1% Malbec and was less acidic in the finish. D2 contained 3% Petit Verdot and 1% Merlot. Changing the Malbec to Merlot sharpened the acidic finish and brought something different to the front. D3 was D2 with 0.5% Cabernet Franc added. This small addition reduced the acid at the end. The last blend, D4, was D3 with 0.25% of additional Petit Verdot added, and that's what the group selected. The goal is to alter the acidity (makes you salivate) or the astringency (takes away the saliva), the sweetness, the finish, etc. The winemaker described the palate of wine like a football so if something was missing from the beginning or end, a small amount of a different varietal could be added. It was amazing how even 0.5% of a different varietal could alter the mouthfeel and taste of the

wine. One of the considerations was how long the wine would be stored before consumption. Petit Verdot increases the shelf-life of the wine as well as the astringency. The final blend then was a Cabernet Sauvignon, 2/3 from Melrose Vineyard, 1/3 from Galloway Vineyard, blended with 3.25% Petit Verdot from Stagecoach vineyard, 1% Merlot from Broken Rock vineyard, and 0.5% Cabernet Franc from Stagecoach vineyard. Most customers will likely drink their gift shortly after receiving it, so shelf-life isn't as big an issue as it was for the personal barrel that was also blended.

Once the customer blend was complete, we moved on to the personal barrel to be split amongst several business associates. The barrel was a 2018 Cabernet Sauvignon from Broken Rock Vineyard, aged in oak for 22 months. Sample A was only Cab. It tasted sweet at the front with a little acid at the finish but really no finish. Sample A1 contained 2% Petit Verdot and 1% Merlot and these small additions elongated the finish and reduced the sweetness at the start. Sample A2 replaced the Merlot with Cabernet Franc (still 2% Petit Verdot) and this brought back the sweetness at the start and shorten the finish (so a lot like A (Cab only)). A3 contained 2% Petit Verdot, 1% Cabernet Franc and 0.5% Malbec. This blend had a longer finish and peaked in the middle. Sample A4 contained 2% Petit Verdot, 0.5% Cabernet Franc and 0.5% Merlot and had a shorter finish, was less sweet and more astringent. The final sample A5, contained 2.5% Petit Verdot, 0.5% Cabernet Franc and 0.5% Merlot. This wine was less sweet, had a longer finish and will age well (3 to 5 years) because of the Petit Verdot.

It was amazing to me how a small percentage change (0.25 to 0.5%) could have such an impact. It's hard to describe wine but necessary in this process so the winemaker knows what we like and don't like about the blend and then can modify the next blend. It

was reassuring when someone else described the sample the same way I did but often what I thought was sweet, others (often my spouse) thought was the opposite. The great thing about wine blending, there is no wrong answer. It will be interesting to taste these wines again in December. We tasted a lot of wine, and except for the final blend of the A5, I spit all the wine out (my teeth looked horrendous at the end, thank goodness masks are required). A5 contained 96.5% grapes from Broken Rock Vineyard and thus can be labelled Broken Rock (95% is the minimum).

Once the blended was done, we toured the facility. The lab was small but contained a $200k machine called a WineScan™ that would analyze brix, glucose, pH, total acidity, volatile acidity and free sulfur. Very efficient and saved the Foundry from having to send out samples to the local labs.

Napa, and much of northern California experienced lightening caused fires in August. The smoke was visible in the air. We asked several wineries about their concern of smoke taint in the grapes. Many said they would be sending grapes to the lab for analysis of the chemical associated with smoke taint. Some wineries were concerned, others were not. It was an interesting reply given they all are facing similar situations. I'll be reading more about smoke taint and how the specific chemical is identified in the lab. Notice the date at the top of the first page, August 31, 2020. I had no idea at this time the smoke events the Willamette Valley would experience for fall harvest just a week away.

I was fortunate to be able to return to the Foundry to blend wine again in May of 2021. The process was remarkably the same, with two small differences. We elected to blend the personal wine first (the one that was more likely to age) and we didn't have to

select different barrels for the blending, we started with only one barrel. The football

analogy of mouthfeel has become common practice in our household, both when we were

blending the wine and simply tasting wine.

Textbook Summary

Concepts in Wine Chemistry by Yair Margalit included chapters about the identity

and quantity of compounds found in wine. The compounds include weak acids, alcohols,

esters, amino acids, proteins, phenols, salts, sugars, etc. (so basically an organic

chemistry textbook). The text included background concepts on pH, acid structure, lab

analysis of pH and TA, and equilibrium. Fermentation phases (7 total) were discussed in

chapter 2, as well as the kinetics of fermentation and the thermodynamics, including

calculations using the ideal gas law (all relevant to general chemistry topics). Chapter 3

discussed phenolics, including tannins and anthocyanins, the compounds responsible for

wine's color, astringency, bitterness and taste. Phenolics also play a role is aging wine.

The chemistry of phenolics includes topics from second term general chemistry of

resonance. Chapter 4 explained aroma and flavor compounds in wine and the impacts of

pH and other factors on the compounds responsible for aroma and flavor. Barrel aging

was discussed as well. Chapter 7 focused on sulfur dioxide and its role as a food

preservative in wine. This chapter included more equilibrium reactions and impacts of

pH on the equilibrium (and more general chemistry themes). The text contained other

chapters but I stopped by review at chapter 7.

I took thorough notes on the chapters. This text summarized many published

research articles identifying compounds in wine, determining their concentration range in

wine, as well as studies on the impacts of these compounds on different aspects of wine

such as color, taste, aroma, etc. Basic concepts of chemistry were also outlined however, I found some of the descriptions to be much more complicated than necessary, especially with equilibrium reactions and pH calculations (so complicated in fact, I reworked the examples). The text also included many chemical structures of different compounds in wine. These compounds involve conjugated aromatic rings (think many hexagons connected together). An aromatic ring consists of six carbon atoms arranged in a hexagon shape with alternating double bonds between the carbons. If two or more aromatics are connected, the ring will have one less double bond, as carbon can only form four bonds. There were several examples of structures in the text showing carbon with more than four bonds.

After visiting Abacela Winery in Southern Oregon and interviewing the winemaker Andrew Wenzl, I read *PostModern Winemaking* by Clark Smith (at Andrew's suggestion). Andrew uses many of these concepts as head winemaker and during our conversation continually referred to the chapter in the text called Vicinal Diphenol Cascade. According to the author, modern wines "are clean and consistent but missing something". Good wine structure supplies aromatic integration and a process called elevage includes micro-oxygenation, lees work and a sophisticated understanding of oak. The process develops wines better suited to aging but perhaps not so well suited to the drink now mindset of many wineries. It takes patience and skills and guts. Given all the aspects of my sabbatical, I appreciated Smith's thought about the "proper place for science in postmodern winemaking is in service to the winemaker's purpose to bottle something when opened months or years later, satisfies human appreciation". Chapter 1 discussed the solution problem, and the impact oxygen can have on the solubility of

compounds in red wines. Smith suggested "wine is a solution" is the basis of scientific enology and is false. Instead, selective extraction is key and composition (what's in the wine and at what concentrations) is less important than structure. In a structured wine, tannins, anthocyanins and other insoluble aromatics aggregate into colloids of various sizes and compositions. This colloidal structure allows for interaction between aqueous compounds (those that dissolve and are soluble in water) and the insoluble phenolics. Chapter 2 discussed conditions for graceful aging and chapter 3 focused on building structure. This text, also unfortunately, included molecular structures of compounds showing carbon with too many bonds. Chapter 4 focused on the functions of oak and chapter 5 was about vineyard enology (making sure the grapes contain the right ingredients to make the intended wine).

Chapter 6, Vicinal Diphenol Cascade, and the chapter referenced frequently by Andrew, explained this chemical process builds structure in red wines and its structure, not composition, that determines flavor. The shape and size of the wine's suspended particles determine its sensory characteristics. "To make wine is to choose a path". Phenols, a class of compounds consisting of an aromatic ring with at least one -OH attached to the ring repel water and ring stack. The compounds can either evaporate or aggregate into colloids and with enough colloids, the volatile phenols (the ones that want to evaporate) will also ring stack and diminish their aroma impact. Aromatic integration works better with smaller colloids because there is more surface area to interface with the aqueous (water based) surroundings. The goal of the vicinal diphenol cascade is to react the ortho diphenol with oxygen so it can attach to another phenol and then make another o-diphenol in a polymerization process. According to Smith, this reaction is "magic".

The compounds giving red wine their color, anthocyanins can participate, as can tannins (they give wine their astringency). The more anthocyanins, the shorter the polymers and the finer the tannins. This results in a softer/finer feel and better aromatic integration, and ultimately, a wine with better aging potential. Chapter 7 focused on the redox redux, a clever title for discussing a measure of wine's oxygen uptake capacity. Chapter 8 discussed minerality in wine, and the last chapter I reviewed talked about making wine at high pH (this is unusual because wine is naturally acidic and at low pH). The last two chapters focused on Brettanomyces (Brett) years and harmony and astringency.

Ultimately, this text used some chemistry to support a process, different than used in many wineries, to produce wines with the potential to age, rather than to be consumed early. In addition to the molecular structures showing carbon with too many bonds, there were some gaffs in the chemistry description, specifically in the vicinal diphenol cascade chapter. The goal is to balance color and tannins and the reaction is temperature dependent, as most chemical reactions are. The author described the cascade involving two reactions, one with each -OH group on the phenol) and stated it was second order. This is classic kinetics lingo. The problem was with the explanation that followed. Second order means the speed or rate of the reaction, defined as change of concentration over change in time, is dependent on the product of concentrations of two reactants (either two different reactants or the same reactant squared). Instead, the author wrote "this is a fancy was of saying it's temperature dependence is squared". I forwarded this passage to my colleagues, and we had a good discussion about the error. In general, a 10°C increase in reaction will double the rate of a reaction, regardless of reaction order. Reaction order is defined as the change in rate of the reaction based on the change in

concentration of a reactant. Another experience from my sabbatical I can share with students during the second term of general chemistry.

Lab Challenges: the automatic titrator

For more than a month, work in the lab began with testing the Brix, pH and TA of the samples collected the previous day. Beginning the week of September 29th, we noticed the TA tests were all reading high. More sodium hydroxide was being used to reach the pH endpoint of 8.2. We could see air bubbles in the tubing, and this would account for the increased outputs. Additionally, many trials showed decreases in pH with the addition of strong base. This observation makes no sense as the addition of a strong base raises the pH of the solution. The spikes in pH often occurred near the equivalence point (the point where the moles of acid equal the moles of base or the spike in the titration curve, but the initial part of the curve was smooth. We flushed and rinsed the tubing with sodium hydroxide, standardized the NaOH and remade the tartaric acid standard. The prepared 6 g/L standard read 6.791 and 6.858 g/L on two runs: too high. I remade 500. mL of standard using 3 grams of acid and measured a TA of 6.918 g/L. Something was not working. It would be possible to calculate a correction factor, however, given the horrible air conditions outside and the stress the grapes were under, being able to measure correct values is key. In the few weeks I had been working in the lab, it didn't take long to realize how all the employees involved in monitoring the grapes and making the harvest decisions, including the head winemaker, the assistant winemaker, the vineyard manager, and the cellar manager, knew what values of Brix, pH and TA the grapes should be at to be harvested. Giving them precise and accurate measurements was key, and the machine was not working. Clearing out the air bubbles

didn't fix the problem. We recalibrated the pH meter and tested the pH of the sodium

hydroxide. If the NaOH was in fact at a concentration of 0.10 M, the pH of the solution

should be 13.00. After calibrating the probes, the pH read at 12.411, corresponding to a

calculated concentration of 0.0258 M, significantly less than expected. If the NaOH was

less concentrated that would increase the volume of NaOH required to reach the endpoint

and would result in a higher concentration of tartaric acid. I also calculated the expected

volume of sodium hydroxide needed to reach the equivalence point. This calculation is a

practical application of stoichiometry and a major theme of the general chemistry

curriculum. Chemists work mostly in molarity for units of concentration:

$$6.0 \frac{g}{L} \; tartaric \; acid * \frac{1 \; mol \; acid}{150.09 \; g \; acid} = 0.040 \frac{mol \; acid}{L \; acid}$$

The volume of each juice or wine sample titrated was 10.00 mL:

$$10.00 \; mL \; tartaric \; acid * 0.040 \frac{mol \; acid}{L \; acid} * \frac{2 \; mol \; acid}{1 \; mol \; NaOH} * \frac{1 \; L \; NaOH}{0.10 \; mol \; NaOH}$$
$$= 8.0 \; mL \; NaOH$$

The titrator is automatically set to record the endpoint at a pH of 8.2. The above

calculation indicates the endpoint should around 8 mL of NaOH but it trials, the pH was

in the mid 7's range after 10 mL of NaOH was added. Continuing to try to figure out

what was going on the titrator, I ran trials using 0.10 M hydrochloric acid. These trials

indicated an error in how the machine was programed to calculate acid levels. Reviewing

the Thermoscientific Orion T900 manual was a painful experience. Stoichiometry is

challenging but repetitive. The calculation involves the same set of steps, the volume of

titrant (sodium hydroxide or whatever else is being used to titrate the sample) is

multiplied by the molarity of the solution to give moles of titrant. The moles of titrant are

converted to moles of sample using the mole ratio from the balanced equation. If the

volume is in milliliters, then millimoles are calculated (mmol).

$$mL\ titrant * \frac{mol\ titrant}{L\ titrant} * \frac{mol\ sample}{mol\ titrant} = mmol\ sample$$

The molarity of the sample is then calculated by dividing the moles of the sample by the

volume of the sample:

$$molarity\ sample = \frac{mmol\ sample}{mL\ sample}$$

After completing several trials with 0.10 M hydrochloric acid, I determined the machine

was actually calculating the concentration of the sample incorrectly because it was

switching the volumes of titrant (NaOH) and sample (HCl). In one trial completed on

September 29th, 2020, the automatic titrator indicated an endpoint volume of 11.947 mL

of NaOH.

$$10.00\ mL\ HCl * \frac{0.10\ mol\ HCl}{1\ L\ HCl} * \frac{1\ mol\ NaOH}{1\ mol\ HCl} * \frac{1}{11.947\ mL\ NaOH}$$

$$= 0.08370\ M\ NaOH$$

This calculated volume is below the expected 0.10 M NaOH. A lower

concentration of NaOH would require a larger volume to reach the end point of 8.2 pH

and would result in higher acid concentrations. The machine is programed to run

standardized NaOH trials, so the lab operator doesn't have to complete the calculations

by hand, the machine does it for them (shh, don't tell the general chemistry students

about this). The machine indicated a NaOH molarity of 0.1195 M, greater than the

expected 0.10 M and even greater than the calculated molarity of 0.08370 M.

$$11.947\ mL\ NaOH * \frac{0.10\ mol\ HCl}{1\ L\ HCl} * \frac{1\ mol\ NaOH}{1\ mol\ HCl} * \frac{1}{10.00\ mL\ HCl}$$

$$= 0.1195 \; M \; NaOH$$

The volumes of NaOH and HCl were used incorrectly to calculate the molarity of the acid, as shown above. Following through with the units gives an answer that doesn't makes sense. Multiplying the volume by the molarity of the same solution gives moles of the solute in that solution (mL HCL * molarity HCl = moles HCl). Multiplying a volume of on solution by a molarity of another solution gives nothing useful. Clearly the programmers of the machine did not pay close enough attention in general chemistry class. This is why units are so important, they help ensure the calculation is correct.

Running another trial to standardize the NaOH, the machine indicated a NaOH molarity of 0.1081M (calculated with the volume of HCl and NaOH switched). The bottle label indicated the molarity of 0.10 M, and completing the calculation correctly, the molarity of NaOH was 0.09251 M. How do each of these different molarities alter the calculated tartaric acid concentration?

Molarity NaOH	0.1081 M	0.10 M	0.09251 M
Calculated tartaric acid concentration (g/L)	6.638	6.231	5.760

If the actual molarity of the NaOH is lower than expected (0.09251) but the machine is using a higher concentration (0.1081) the calculated acid concertation will be even larger. Not good, especially when decisions about when to pick the grapes is based partly off these values. That being said, this error in the calculation bothered me more than the assistant winemaker and lab director. He said "as long as it's close enough". I admit, this was a bit hard to hear as a teacher, close enough is not good enough in my mind, especially when the calculation is done incorrectly. We also had values from earlier in

the month to compare to and ultimately, it was this comparison that was most useful. How did the TA values change from one analysis of the same block to the next? Did the values drop or remain relatively the same? Brix and pH also contributed to harvest decisions.

Interviews with winemakers

Below is a list of questions I intended to ask each winemaker I interviewed. Ultimately the interviews were more of a conversation than a formal interview so not all questions were asked.

1) What chemistry classes did you take in college?

2) What path did you take to becoming a winemaker?

3) What previous experience did you have?

4) What chemistry skills and knowledge do you use in your job that you didn't learn in school?

5) What skills and knowledge are you looking for in future employees?

6) What continuing education do you complete?

7) What equipment or analytical tests do you have (or would you like to have) in your wine lab?

8) What was the impact of the smoke in 2020 on your winery and/or wine?

9) What are the impacts of warmer temperatures?

Chantal Forthun head winemaker at Flowers Winery and Rebekah Wineburg, head winemaker at Quintessa

I spoke with both of these winemakers over Zoom. Flowers and Quintessa are owned by the same company that owns Benton-Lane. Because the interviews were over Zoom with two people, I wasn't able to get through all the questions.

Rebekah has degrees in biology and chemistry from a liberal arts school in Minnesota. She became interested in making wine at age 16 on a trip to Napa. After graduating, she attended UC Davis and earned a M.S. degree. Her thesis was on the effects of winemaking techniques on phenolics in Cabernet Sauvignon. She has been at Quintessa for 6 years and in Napa since 2003. She also worked in Italy, New Zealand, Australia and Oregon. Chantal has a biology degree with a minor in botany from Chico State. Her college boyfriend suggested wine making as a career. Her original career focus was habitat restoration. She wanted to be outside and not dress up. She looked into UC Davis but did not apply. Her first job was at the winery where her mother was CFO where she worked in the lab. She was later told she was given the job because she was "the cutest applicant". During the lab work, she was given a small Chardonnay project and loved it. Chantal eventually moved out of the lab (where it's common for women to work and stay) and moved into the cellar, a step necessary to be someone's boss someday. This is her 9th harvest at Flowers, and she was assistant winemaker prior to that at a different winery. Both winemakers do not currently work in the lab but both have experience doing so and both wineries have extensive equipment. They send out for analysis they can't run on-site. Rebekah talked about the thermocyler they use to test for Brett (a bacteria). LCC has a thermocycler for forensics. Quintessa picked all their wine and has two years before the wine will be bottled to make decisions about the smoke impact. Flowers makes Pinot and did not pick all their harvest. One property was picked

at 90%, the other at only 15%. Chantal said she had just recently tasted a 2008 Pinot which was the last time the smoke occurred at harvest. The wine apparently tasted like an ashtray. At Flowers winery, the harvest used to be in November, now with warming temperatures, it's at the end of August.

Andrew Bandy-Smith, head winemaker and general manager, Antiquum Farm, Junction City, OR

Andrew earned a philosophy and history degree in college. He spent many years working in the restaurant business in Seattle where he moved with the intention of going to law school. During that time, Andrew was a consumer of wine and as part of his job he would purchase wine from local wineries for the restaurant. He is from a family of famers and found the agriculture divorced from the vineyards in Seattle. While working at an event in the Willamette Valley, Andrew appreciated the closeness of the farm and winery (and it's suiting now that he works on a very unique farm). In 2011, Andrew left the restaurant business and worked his first harvest at Shae wine cellars in Carleton with Drew Voit as the head winemaker. In 2012, he worked in Australia and then returned to Oregon to work at Archery Summit as an early intern (meaning he worked longer than the seasonal harvest interns). Andrew worked again for Drew Voit from 2013 to 2015 at Harper-Voit in the cellar but also in sales and marketing. He formally became an assistant winemaker when he promoted himself on the Harper-Voit website. Andrew left that winery to work at Soder in sales and travelled extensively. His current employer was a customer of Harper-Voit (custom crush). Andrew took AP chemistry in high school and waited until his 5th year of undergrad to take the required Chem 101 class. He

completed enough of the class to pass but in his own words "hated science" and needed a relevant focus. Andrew learned how to make wine working as a harvest intern. He now enjoys learning about the contribution of science as it relates to wine. For professional development, Andrew is a member of the Oregon Wine Board education committee. He finds the research aspect of wine not as useful to winemakers and thinks more focus on sales would be better. Andrew indicated that certain jobs in the wine industry require a degree. He said he's never been asked about his degree but having one helped him get an interview. "A formal education doesn't make good wine or sell it." The liberal arts degree is useful for running a wine company. Future plans include an MBA. All analysis at Antiquum is sent out to commercial labs. Andrew finds it more efficient to send the samples, rather than spend the time in the lab correcting the errors. He does run Brix and pH on grape samples himself, as well as tasting samples from the relatively small farm (22.5 acres). The winery picks at night and does not hire interns. All the grapes were harvested but there will be no 2020 vintage of red wines from Antiquum. Some wine will be bottled for later analysis but it won't be sold.

Andrew Wenzl, head winemaker at Abacela winery in Winston, OR

Andrew has a B.S. degree in both biology and chemistry from Eastern Oregon University. He started at King Estate with the job title of yeast inoculator, a job requiring a science background. He then worked as Sylvan Ridge as the assistant enologist (this was the lab work), and lastly moved to Abacela where he has been since 2003. Abacela hires mostly international interns during the harvest to complete, among other tasks, the lab work. The applicant pool is strong, and all interns have a background or are studying science or an enology program. This year local interns were hired because of COVID

travel restrictions. For professional development, Andrew attends symposiums in California and Oregon. These symposia, however, focus on varietals not grown at Abecela. He also attends webinars sponsored by ETS labs or LaForte. One of the more challenging aspects of the job for Andrew was training employees and delegating tasks as the head winemaker. All he knows about winemaking he learned on the job and through professional development. In terms of lab needs, Abacela is remote and some tests need to be sent out to the lab. For example, the winery has no way of testing alcohol for the sweet wines they make because the sugars interfere. Despite using different tests than Benton-Lane, Andrew didn't indicate any analytical equipment missing from the lab. Regarding the smoke, Abacela did not get more than a day or two of smoke in 2020 so there was no impact on their grapes. They did send berry samples and microferments to ETS but were still waiting on the results when I visited in November. Andrew stated no smoke characteristics could be tasted in the wine. The eldest son of the owners of Abacela is a major contributor to research on climate and viticulture. Abacela is unique in its space as it can grow a variety of grapes, some liking hot weather and others cooler weather. The vineyard has 77 acres, some at higher elevation and facing north for the cooler varietals. The winery also has unique and ranging soil types and has set aside land for conservation. Additionally, the winery grows hay for Wildlife Safari and receives elephant dung for composite (called Zoo Doo). The winery also composts.

It was interesting to me to see the difference in the lab equipment. At Benton-Lane, pH and TA are measured with an automatic titrator. At Abacela, TA is determined by titration (by hand) to a pH of 8.2. To measure residual sugars (glu-fru), Abacela uses diabetic reducing sugar tablets, not an enzymatic test. Abacela cannot test for nitrogen

nutrients prior to fermentation (PANS and ammonia), nor can they test for malic acid. Because they can't test of nitrogen, the nutrients are added slowly once fermentation has started. Lastly, they use a spectrophotometer to test color of the rose, something not done at Benton-Lane. The overall message Andrew wants interns to take with them is bench trials. Run the tests in small scale before doing something on a large scale to the wine.

Andrew recommended the text Post Modern Winemaking by Clark Smith. I was able to download a pdf of the book from ebsco via the LCC library. The chapter from the book he suggested is called "The Vicinal DiPhenol Cascade". I copied a sentence from chapter and sent it to my chemistry colleagues because it described kinetics in a way a chemist never would. Andrew also mentioned the bifutrification point; something I need to look up, and as we were talking about smoke impact, he mentioned the concern some wineries have on the impact of volatiles from the growing of marijuana on property adjacent to vineyards and their impact on wine flavors.

During August of 2021, I was finally able to arrange a tour of the lab at King Estate with the lab director Leah Lyon. Leah had worked previously at King Estate and then took a ten-year break during which time she earned a B.S. in landscape architecture from the University of Oregon. Leah did complete the two-year winemaking program at Chemeketa Community College, and she worked previously at a different winery in Beaverton as well. The lab at King Estate is highly automated and able to complete most tests and can run multiple samples at one time. They did send 2020 samples to a lab in Canada for analysis of the smoke compounds and will use the commercial labs for a small selection of tests (sulfide panel). Leah is assisted in the lab by Kelsey, a graduate of OSU's fermentation science program. King Estate's lab is much bigger than Benton-

Lane, as would be expected because the winery is much bigger. Brix is tested the same at each site but at King Estate, TA and pH, as well as the enzyme tests are completed on a Thermo Fisher gallery machine. The lab also has the set-up to run up to four free sulfur tests at a time. Percent alcohol is determined using an alcolyzer machine instead of an ebulliometer. King Estate can also complete other tests Benton-Lane would need to send out for, such as volatile acids, PCR for Brettanomyces bacteria. I focused my questions to Leah on the lab work and did not ask all the interview questions listed. At the end of the tour, I met one of the assistant winemakers, who happened to be a former LCC student. He took one term of general chemistry for me, completed the sequence at LCC with a different instructor, took all the organic chemistry at Lane, as well as the biology sequence and then transferred to OSU and graduated with a degree in Fermentation Science. He had nothing but good things to say about the science courses he took at Lane. It was a lovely way to wrap up my "formal" sabbatical activities.

Wine related course outcomes for General Chemistry

Listed below are course specific objectives and outcomes from the general chemistry sequence taught at LCC. Below each objective is a short note on the relevance to the chemistry of wine. Overall, stoichiometry, pH, weak acids are the main topics of general chemistry relevant to wine. Wine, however, contains so many compounds to be used as examples throughout the course.

CH 221

Understand the distinction between accuracy and precision and determine if a set of data is accurate or precise

> TA and Brix levels were used to determine when to harvest each block

Understand the distinctions between elements, compounds, pure forms of matter and mixtures (hetero/homogeneous).

> Wine is an example of a mixture. Depending on the stage of production, it may be homogeneous or heterogenous

Understand and use the factor label method; includes unit conversions within a measurement system and between measurement systems

> Unit conversions were used regularly to determine how much yeast, nutrients, and water should be used to start fermentation, as well as any other additions during wine production

Understand and calculate density

> Part of the fermentation calculations

These concepts are all part of the titratable acidity calculations to determine the g/L of tartaric acid in a sample, as well as calculating the ppm of SO_2 in wine.

> Calculate molar mass
> Write and balance chemical equations
> Do mass → mol, mol → mol, and mol → mass calculations: stoichiometry (multi-step)

Identify types of reactions including acid-base (neutralization, proton transfer), oxidation-reduction (electron transfer), and precipitation reactions

> Acidity is a key component of wine and wine provides many examples of acid-base reactions

Describe the preparation and dilution of molar solutions

In order to analyze wine samples, standard solutions must be prepared, and many samples are diluted prior to analysis using TA and when determining free sulfur dioxide levels

Use molarity in the context of chemical equations (aka solution stoichiometry, titrations)

All samples are aqueous solutions, so solution stoichiometry is required for TA and free SO_2 calculations.

Calculate $\Delta Hrxn$ from $\Delta H°_f$ and quantify the relationship between reaction stoichiometry and heat of reaction

The energy released from fermentation can be calculated and must be considered in the design of fermentation tanks to control temperature of the tank

Use the ideal gas law and use stoichiometry for reactions involving gases

The volume of carbon dioxide produced from fermentation can be calculated

CH 222

Draw Lewis Structures, draw resonance structures, determine formal charge for each atom in a Lewis structure, Understand the significance of resonance structures and formal charge

Wine contains many compounds to be used as examples, including some structures with errors printed in wine chemistry texts

Interconvert between condensed structural formulas, Lewis structures and line drawings

Line structures are used in many wine chemistry textbooks to provide examples

Explain the influence of resonance on acidity and stability of molecules and ions

Wine contains a significant number of weak acids with different acid strength

Identify sigma and pi bonds and extended pi bonding, write descriptions of bonds as overlapped atomic orbitals (localized electron model)

Wine contains many compounds to be used as examples

Understand the nature, origin, relative strengths, and impact of intermolecular forces on physical properties including melting point, boiling point, and vapor pressure

Boiling point is used to determine the percent of alcohol by volume for wine

Relate polarity and solubility in water

Wine contains hundreds of compounds, many are soluble in water, but many others are not.

Define and explain nature of solutions, explain and apply the nature and energy implications of the solution process (e.g. the reasons for the "like dissolves like" rule), describe the nature and effect of colligative properties (boiling point elevation, freezing point depression and osmosis)

Wine provides a real-life example of colligative properties of solutions, specifically with freezing point depression (this is why wine doesn't freeze in the freezer)

Explain the ways in which structure, including steric hindrance and stability of intermediates relates to observed rate laws/mechanisms, explain collision theory, describe the importance and the nature of catalysts

Wine provides a real-life example of kinetics however because wine contains so many compounds, specific mechanisms and calculations are not possible

Understand the nature of chemical equilibrium, the value of the equilibrium constant, and the factors affecting the value of K, write equilibrium constant expressions from balanced chemical equations

The large number of weak acids in wine provide many examples

Explain why the "x is small approximation" works, set up an ICE or RICE table, calculate final concentrations of all species given initial concentrations and K_{eq}, explain and apply simplifications when solving for change in equilibrium concentrations, use/apply the "x is small" approximation

The large number of weak acids in wine provide many examples

CH 223

Use the Arrhenius and Brønsted-Lowry definitions to identify acids and bases, write autoionization reactions and identify amphoteric species, calculate molarity of a solution given volume or mass of solute or dilution, calculate pH and/or pOH from $[H_3O^+]$ or $[OH^-]$ (in any combination), determine if a solution is acidic, basic, or neutral given pH, pOH, $[H_3O^+]$ or $[OH^-]$, relate the $[H_3O^+]$ or $[OH^-]$ to pH, pOH, K_a or K_b, use molecular structure to rank acids by strength, use the "x is small" approximation to calculate the pH of a weak acid or base solution

Wine contains many weak acids to use as examples, specifically for calculating pH using a RICE table, Ka value and x is small approximation. The pH of grapes juice or wine is also measured frequently.

Calculate acid or base molarity, predict pH of equivalence point relative to pH 7, describe common titration curves, including indicator selection.

> Titratable acidity (TA) is a major analytical technique in the wine lab and the automatic titrator shows a titration curve for each analysis

Apply terms exothermic and endothermic, and temperature changes, to heat and enthalpy of reaction values and signs, calculate enthalpy of reaction using either enthalpies of formation, entropy of reaction or Gibb's free energy, predict whether a process is spontaneous or nonspontaneous, calculate a thermodynamic value given the other two, relate values of thermodynamic properties to equilibrium constants.

> The fermentation reaction can be used, as well as other reactions known to occur during the wine making process. Reactions used in lab analysis can also be used as examples.

Identify a redox reaction, oxidation, reduction, the oxidizing agent and the reducing agent, balance redox reactions.

> Redox reactions are less common in wine, however, many of the enzyme tests completed in the lab use redox reactions.

Identify different functional groups by name from line drawings, structural and condensed structural formulas

> Wine contains hundreds of compounds, many with multiple functional groups.

pH of wine example from pages 13 and 14 of Concepts in Wine Chemistry Text

pH of pure tartaric acid, $Ka1 = 9.10*10^{-4}$ and $Ka2 = 4.25*10^{-5}$

A typical wine concentration is 7.5 g/L so for tartaric acid: 7.5 g/L * 1mol/150.1 g = 0.050 M as an initial concentration

	H_2A	$\leftrightarrow$	H^+	$+ HA^-$
I	0.050		0	0
C	-x		+x	+x
E	0.050-x		x	x

$Ka1 = [H^+][HA^-] / [H_2A]$ so $9.10*10^{-4} = (x)(x) / (0.050 -x)$ and technically the x is small approximation doesn't work because $100 (9.10*10^{-4}) = 0.091>$ [initial of 0.050M]

Using quadratic $x^2 + 9.10*10^{-4}x + 4.55*10^{-5} = 0$, x = 0.0063 (pH = 2.20)
Using x is small, x = 0.0067 (this is the value given in the text) so pH = -log 0.0063 = 2.17.

In wine, other acids with a higher pKa and sodium and potassium salts increase the pH of the wine. Assume an average pKa of all wine acids of 3.6 so $Ka = 10^{-3.6} = 2.51*10^{-4}$. In white wine [salt] = 0.025 and for red wine [salt] = 0.035 so taking an average, [salt] = 0.030 so the $[HA^-] = 0.0063 + 0.030 = 0.0363$ (the total from the acid alone plus the added salt).

	H_2A	$\leftrightarrow$	H^+	$+ HA^-$
I	0.050		0	0.0363
C	-x		+x	+x
E	0.050-x		x	0.0363+x

$2.51*10^{-4} = (x)(0.0363+x) / (0.050 -x)$ and using x is small the expression simplifies to:
$2.51*10^{-4} = (x)(0.0363) / (0.050)$ and $x = 3.46*10^{-4}$ and pH = 3.46

Print and online resources

from Adelaide online course

https://www.youtube.com/watch?v=t3d2hC2dAJw&feature=youtu.be

https://www.youtube.com/watch?v=a0sb3dS5120&feature=youtu.be

http://www.aromadictionary.com/winemakinglist.pdf

https://winemakermag.com/article/97-blending-to-improve-wines

https://winefolly.com/tips/wine-faults/

https://winetitles.com.au/wvj/

https://www.abc.net.au/news/rural/2013-07-30/vineyard-of-the-future/4851180
(preparing wines for climate change)

Others

https://winesvinesanalytics.com/features/article/195118/Smoke-Taint-in-Wine, read
09/14/2020

https://www.etslabs.com/library/49, read, notes taken 09/12/2020

https://onlinelibrary.wiley.com/doi/pdf/10.1111/j.1755-0238.2011.00128.x, read, notes
taken 09/13/2020

https://catalog.extension.oregonstate.edu/em9253/html

https://onlinelibrary.wiley.com/doi/10.1111/j.1755-0238.2009.00056.x, read 09/13/2020

https://cen.acs.org/analytical-chemistry/Wine-sleuths-seek-answers-mystery/96/i19, read,
notes taken 09/14/2020

https://www.enartis.com/en-us/video-and-webinar/smoke-taint-analysis-and-remediation-strategies/, watched 09/14/2020

https://pubs.acs.org/doi/abs/10.1021/jf800927e?source=cen

TLC of phenols pdf saved

Smoke-derived Taint in Wine: Postharvest exposure to smoke
https://pubs.acs.org/doi/pdf/10.1021/jf072509k, read and notes taken, 09/24/2020

https://industry.oregonwine.org/resources/webinars/oregon-wine-industry-round-table-on-wildfire-smoke-2/

https://www.registerguard.com/story/news/2020/09/24/west-coast-vineyard-grapes-tainted-taste-wildfire-smoke/3515415001/

KLCC report from local winery, everything will be fine.

Oregon wine board webinar Navigating Smoke-Related Challenges
https://zoom.us/rec/play/LQoBr5nQ_H61DqaD5CPkZerKVj0t9xoHBNaoN_J_2i29EZBsq-3mIVCVGby7xmrLZt6_9YHotC0UTXpE.P9MSstCJIeiLQk8_ watched and notes taken 09/25/220

Conversation with AWRI
https://drive.google.com/file/d/11sreMHaMfItH5__TAuZ3ePzHcau1wr72/view

Comparisons of methods for measuring guaiacol
https://onlinelibrary.wiley.com/doi/full/10.1111/j.1755-0238.2011.00147.x

https://www.awri.com.au/industry_support/winemaking_resources/frequently_asked_questions/acidity_and_ph/ relationship between TA and pH, read 11/10/2020

Determining the % alcohol using ebulliometer

https://sakeassociation.org/wp-content/uploads/2019/07/2.-Alcohol-Content-by-Ebulliometry.pdf

http://www.chemguide.co.uk/physical/phaseeqia/idealpd.html

Measuring Phenols in the Winery, James Harbertson, Sara Spayd, American Journal of Enology and Viticulture, https://www.ajevonline.org/content/57/3/280#sec-7, reviewed 11/17/2020

FTIR Spectroscopy in Grape and Wine Analysis, reviewed 11/24/20202
https://pubs.acs.org/doi/pdf/10.1021/ac086051c

Anthocyanins in wine, https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6268338/, read, notes taken, completed 11/30/2020

Other citations

Structure of lignin: Figure 1- available via license: Creative Commons Attribution 4.0 International

Mahmood, Zahed & Yameen, Muhammad & Jahangeer, Muhammad & Riaz, Muhammad & Ghaffar, Abdul & Javid, Irum. (2018). Lignin as Natural Antioxidant Capacity. 10.5772/intechopen.73284.

https://www.foodandwine.com/news/smoke-taint-wine-solution (read 07/12/2021)

https://wineindustryadvisor.com/2021/03/01/musing-on-smoke-taint-from-harvest-2020 (webinar viewed July 12 and 13, 2021)

https://www.acs.org/content/acs/en/molecule-of-the-week/archive.html?archive=All for facts about smoke compounds

The Chemistry Of Wine infographic
https://www.compoundchem.com/2014/05/28/redwinechemicals/

Applications of CH 223 topics

From Vine to Bottle, the Chemistry of Wine
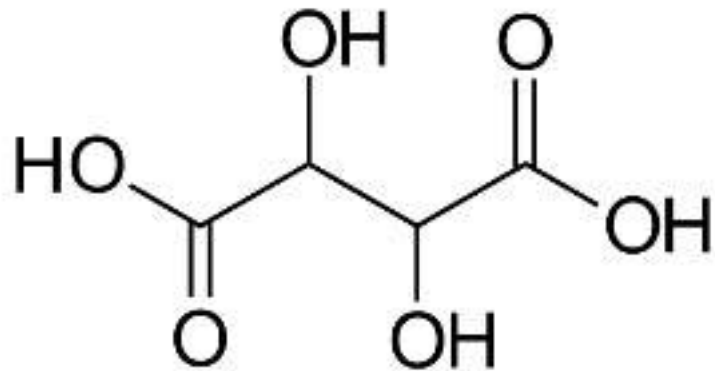
Harvest 2020,

Benton-Lane Winery
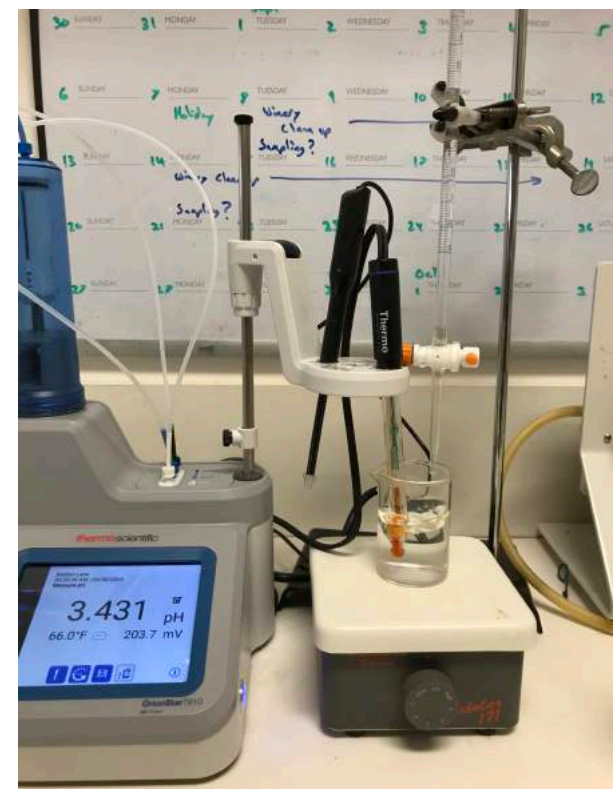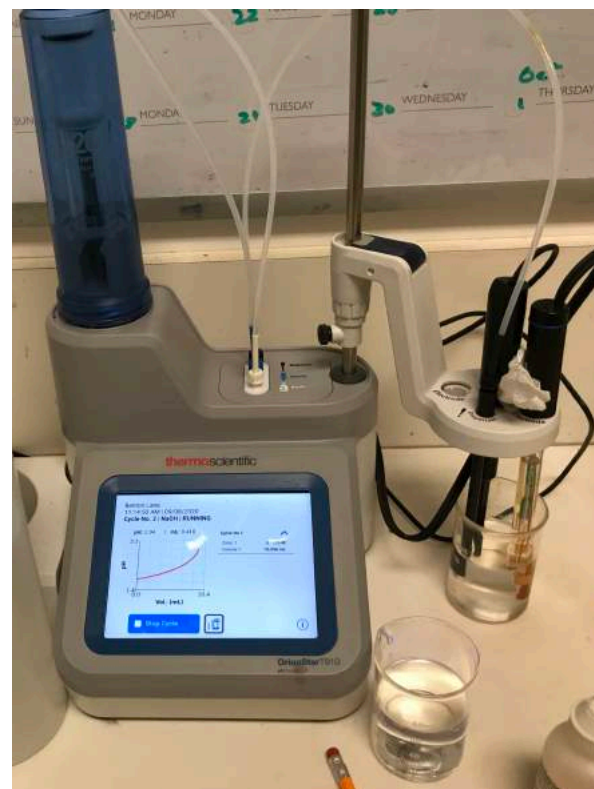
Brix

Sugar content: g solute/ 100 g solution

TA

Titratable acidity: $[H^+]$ by titration with strong base

pH

$= - \log [H^+]$

Wines are acidic

Tartaric acid: most prevalent weak acid in grapes

- H_2O_2 with 3 drops of indicator (purple), then NaOH added dropwise until green

- Pipet 20.00 mL of wine into bulb, add 10 mL H_3PO_4

- Volatize SO_2, and green returns to purple: $SO_2 + H_2O_2 \rightarrow H_2SO_4$

- Titrate with 0.01 M NaOH diluted from 0.1 M

- Multiple mL NaOH by 16 to determine ppm free SO_2 (ppm = mg /L)
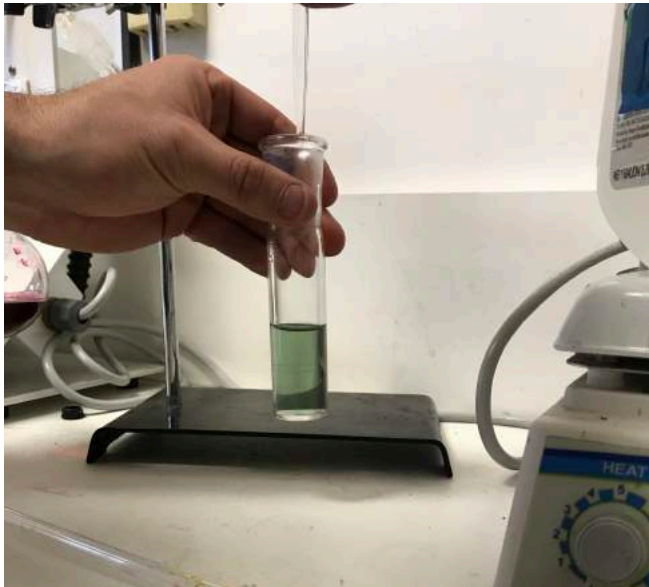
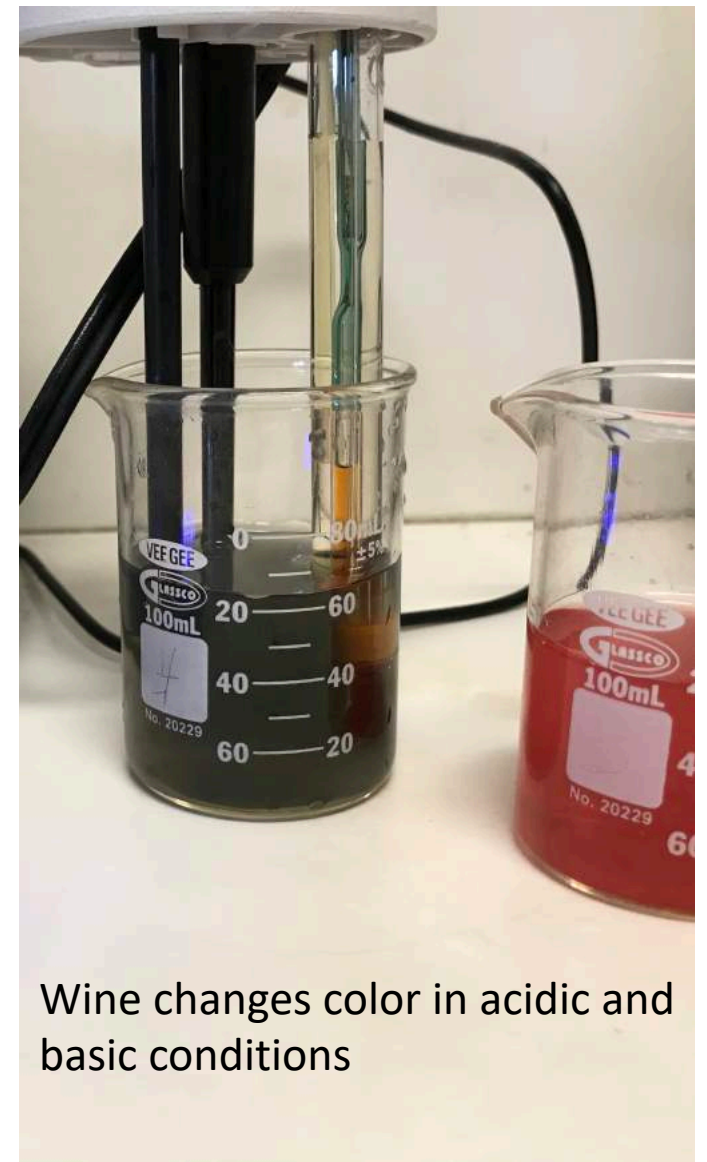Determining free sulfur dioxide levels in wine

Enzyme tests measures ammonia, absorbance read at 540 nm, oxidation-reduction reaction

Similar tests for amino acids and Glucose-fructose levels when fermentation is complete
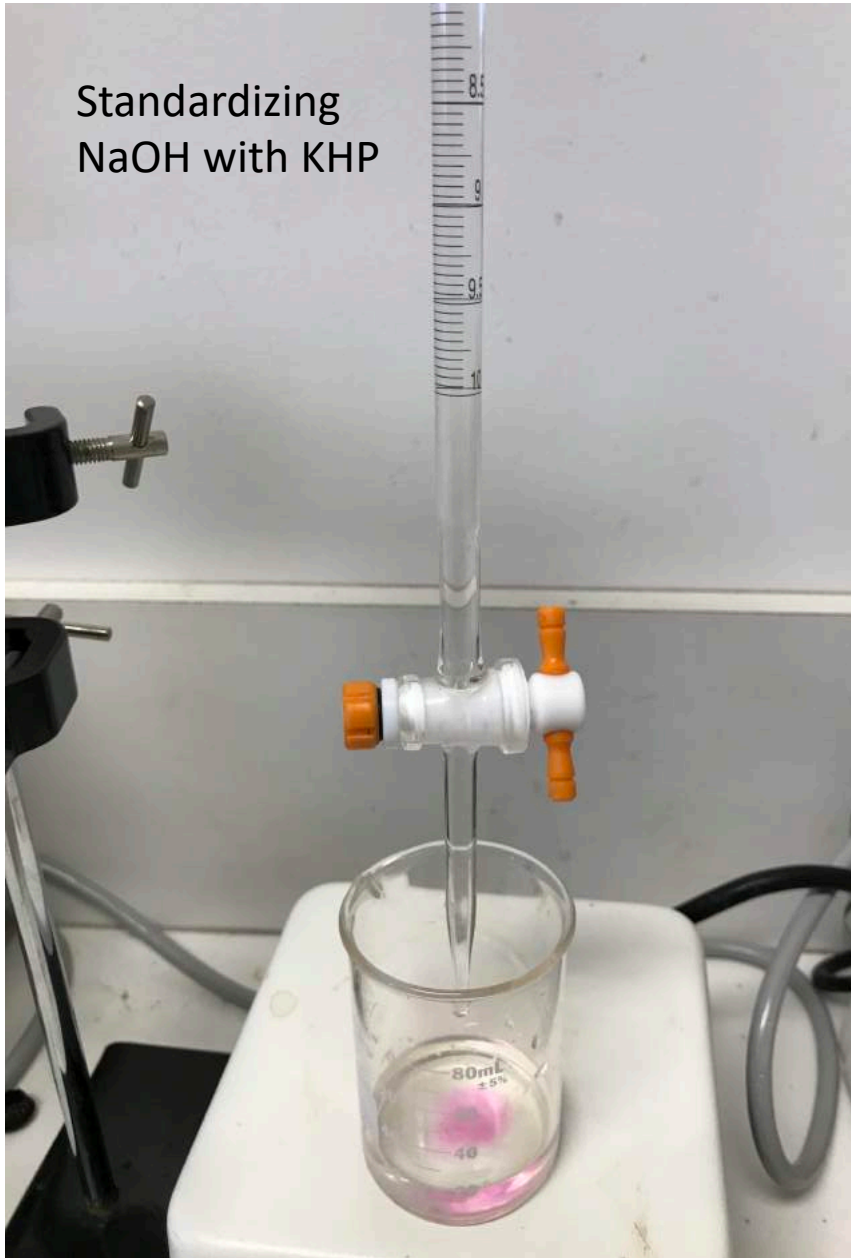

Lots of pipetting, and sometimes, Earwigs

Wine changes color in acidic and basic conditions

Standardizing NaOH with KHP

Preparing yeast to start fermentation or any nutrient additions require unit conversions

Tons grapes → gal → g yeast → lb yeast