Wine Chemistry

Wine 3
Introduction to Enology

Tonight: Exam # 1
- Use Scantron and #2 Pencil
- Leave one empty seat between you and your neighbor.
- All backpacks, bags, and notebooks on floor.
- You will have 20 minutes to complete the test.
- When your finished hand in your test face down by section and wait quietly at your desk or outside the classroom.
- Write name on both Scantron & Test

Tonight's Lecture
- Wine chemistry
  - Juice composition
  - Acid and sugar adjustments
  - Wine composition

Chemistry of Juice & Wine
- We will begin with the composition of must/grape juice and then cover the composition of wine.
- Constituents are covered in highest to lowest concentrations.

Old English Money vs. US
- 2 farthings = 1 halfpenny
- 2 halfpence = 1 penny (1d)
- 3 pence = 1 thruppence (3d)
- 6 pence = 1 sixpence (a ‘tanner’)
- 12 pence = 1 shilling (a bob)
- 2 shillings = 1 florin (a ‘two bob bit’)
- 2 shillings and 6 pence = 1 half crown
- 5 shillings = 1 Crown
- 20 shillings = 1 Pound

OR
- 100 pennies = 1 Dollar

Metric System
- The preferred method of measurement worldwide (except for the US, Burma & Liberia)
- Look over handout and get comfortable with converting US to Metric & vice versa.
- Units change by factors of 10
- Use the handout on conversions of a website to help you out.
Metric Units

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Metric Unit</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight/mass</td>
<td>Grain</td>
<td>1000 grains (14g) = 2.2 Pounds</td>
</tr>
<tr>
<td>Volume</td>
<td>Hectoliter</td>
<td>1 Hectoliter = 0.264 Gallons</td>
</tr>
<tr>
<td>Length</td>
<td>Meter</td>
<td>1 Meter = 39.37 inches</td>
</tr>
<tr>
<td>Temperature</td>
<td>°Celsius</td>
<td>°Fahrenheit = (°C x 1.8) + 32</td>
</tr>
</tbody>
</table>

Composition of Must

- Water, 70 to 80%, the sweeter the grapes, the lower the % of water. Most important role is as a solution in which all other reactions take place.
- Sugars, 15 to 35%, they are about 90% of the soluble solids or extract in the juice.

Water, 70 to 80%, the sweeter the grapes, the lower the % of water. Most important role is as a solution in which all other reactions take place.

Sugars, 15 to 35%, they are about 90% of the soluble solids or extract in the juice.

Some definitions:

- **Soluble**: A substance that can be dissolved, sugar being dissolved in water is an example. Insoluble substances do not dissolve, an example would be mixing sand into water.
- **Precipitate**: A substance that comes out of solution in a liquid and reverts to its solid form.
- **Suspended Solids**: Solids suspended in the solution that have not settled.

Metric System

- Winey laboratories use the metric system.
- European made wine equipment use metric units.
- Most problems occur when converting between US system and metric system.
- NASA lost $125,000,000 Mars spacecraft to due incorrect conversion.

Sugars (carbohydrates)

- The primary sugars are **glucose and fructose** in about equal amounts. These sugars are both hexoses (6 carbons) have the same formula $C_6H_{12}O_6$ but different structures.
Molecules Containing Carbon

- Remember from our chemistry review that the corners of the hexagon represent carbon atoms.

![Carbon atoms are at the corners of the hexagon](image)

Unfermentable sugars

- Yeast do not have the ability to consume ferment every type of sugar.
- Very small amounts of residual sugar remain in all dry wines due to unfermentable sugars that are present (mostly pentoses).

![An oxygen atom makes up one corner of the hexagon](image)

Sugars

- Sucrose (table sugar) is a molecule that combines one molecule of glucose and one molecule of fructose. It is present in native American grape varieties like Concord up to about 25%. Not a lot in V. vinifera.
- Yeast can ferment sucrose.

Measuring Sugars

- Sugars can be measured directly in the lab through analysis. This is how low levels of sugar in finished wines are measured.
- Sugars make up a very large percentage of the juice before fermentation so it is much easier to measure the sugar by density.

![Sucrose](image)

Measuring Sugars

- Degrees Brix (sometimes called balling) is how sugar is represented as a density measurement.
- 1 degree Brix (°B) = (% by weight) = 1 gram of sugar per 100 grams solution (water & sugar combined).

![Sucrose](image)
Example ~ Brix Standard

- To make a 20 ºBrix solution for calibrating a refractometer mix:
  - 20 Grams of sugar
  - 80 Grams of water (80 ml)
  - 100 Grams total solution weight

Other Units for Measuring Sugars

- Units of sugar measurement are different outside of the United States.
- **Baumé**, this method is popular in Europe
  \[ \text{Brix} = \text{Baumé} \times 0.55 \]
  - Baumé is an convenient method because the degrees Baumé approximates what the alcohol will be if the juice is fermented dry.
  - 13.5º Baumé ferments to about 13.5% Alcohol

Specific Gravity

- Specific gravity is useful when buying or selling bulk wine.
- Wine is usually sold by the gallon, however the amount of gallons will increase or decrease based on a wines temperature.
- So when selling wine it is best to determine the amount of gallons by weight which is constant.

Other Units for Measuring Sugars

- In brewing **specific gravity** is the preferred method of measuring sugar.
  - Using specific gravity sugar expressed as density in grams/ ml, water by definition has a SG of 1.000
  - 1º Brix = SG of 1.004
  - 20º Brix = SG of 1.083

Methods of Sugar Measurement

- **Refractometers**: Easy to use and usually more accurate than hydrometers. The changing density of a liquid changes the refraction (bending of light passing through it) measures dissolved solids.
Methods of Sugar Measurement

- Refractometers Cont.
  - Problems: Expensive, delicate instruments, alcohol affects refraction, so they cannot be used during fermentation. Temperature also affects refraction so it must be temperature compensated.

Optical Refractometer

- Most hydrometers are calibrated to 60 °F or 20 °C (68° F), so they need to be temperature compensated.
- The more accurate, the more expensive and delicate.
- Several hydrometers with different ranges give better accuracy.

Digital Refractometers

- Recently portable digital refractometers have become more affordable and more popular.
- Water resistant, not waterproof!

Methods of Sugar Measurement

- Hydrometers: Not quite as easy to use but relatively cheap, measures the weight of a solution by displacement. Can be used during fermentation but the lower density of alcohol affects the Brix reading.
- Will read negative at the end of fermentation because alcohol has lower density than water.

Hydrometers can also give false readings by the presence of suspended solids or gas bubbles. Some hydrometers have internal thermometers for compensation.
- Using clarified juice reduces error from suspended solids. Spinning the hydrometer dislodges bubbles.
Hydrometers

Methods of Sugar Measurement

- **Digital Density Meters** More accurate and easy to use, they are definitely worth the investment for commercial wineries.

Adjusting Sugar

- The sugar left in the wine after fermentation is called the Residual Sugar or RS.
- When adding sucrose the Brix or RS can be added by gm/L to the desired level.

To adjust 10,000 Gallons of dry wine 0.1% RS to 0.4% RS how much juice at 10% RS do you add?

Let \( X \) = Gallons of sweet wine to add

\[
(10,000 + X) \times 0.4\% = (10,000 \times 0.1\%) + X \times 10\%
\]

\[
4000 + 0.4X = 1000 + 10X
\]

\[
3000 = 9.6X
\]

\[
312.5 = X
\]
Acids Present in Juice
- Juice and wine are dilute acid solutions. The acidic nature of wine has a profound affect on the sensory qualities of wine, microbial stability, color, protein (heat) stability, and tartrate (cold) stability.

Principal Acids in Juice
- Malic acid
- Tartaric acid
- Citric acid

\[
\begin{align*}
\text{Malic acid} & : 
\text{Citric acid} \\
\text{Tartaric acid} & : 
\text{CH}_2 \\
\text{COO}^- + \text{H}^+ & : 
\text{COO}^- + \text{H}^+ \\
\text{HCH} & : 
\text{HC-OH} \\
\text{HO-CH} & : 
\text{HC-OH} \\
\text{COO}^- + \text{H}^+ & : 
\text{COO}^- + \text{H}^+ \\
\text{Disassociated Carboxylic acid groups} & : 
\text{Disassociated Carboxylic acid groups}
\end{align*}
\]

Titratable Acidity TA
- TA is determined by titration with a base to an endpoint of pH 8.2 (phenolphthalein) it is then expressed as grams/100ml or grams/ liter (g/ L) of tartaric acid.
- Example: 8.9 g/L = 0.89 g/100 ml
- In France TA is expressed as grams of sulfuric acid/ Liter
- g/L tartaric acid X 0.65 = g/L sulfuric acid.

Titration
- When performing a the endpoint of 8.2 pH is just as the solution turns pink. The endpoint can be difficult to see in red wines.

Principal Acids in Juice
- Tartaric and malic make up over 90% of grape juice acid. Tartaric acid is rarely found in other fruits. Other acids are: lactic, present in small amounts in juice, ascorbic (vitamin C), fumaric, pyruvic and many more.
- Titratable Acidity (TA) Measures the sum of hydrogen ions free or attached; it does not measure the total acidity (all acid anions).

Acids
- You can add tartaric, malic, citric, or lactic. For most adjustments tartaric acid is used because it disassociates best (lowers the pH more/ gram) and is microbially stable.
- Other acids taste different than tartaric and have different affects on perceived acidity.
- Since TA (Titratable Acidity) is measured as gm/ L Tartaric acid, 1g/ L citric will not raise TA 1 g/ L.
**Acids in Wine**

### Table 2: Acidity Conversion Factors

<table>
<thead>
<tr>
<th>Acid</th>
<th>Tartaric</th>
<th>Malic</th>
<th>Citric</th>
<th>Lactic</th>
<th>Succinic</th>
<th>Acetic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wine</td>
<td>1.000</td>
<td>0.850</td>
<td>0.953</td>
<td>1.200</td>
<td>0.653</td>
<td>0.860</td>
</tr>
<tr>
<td>Malt</td>
<td>1.199</td>
<td>1.090</td>
<td>0.995</td>
<td>1.343</td>
<td>0.731</td>
<td>0.996</td>
</tr>
<tr>
<td>Citric</td>
<td>1.712</td>
<td>1.647</td>
<td>1.000</td>
<td>1.406</td>
<td>0.796</td>
<td>0.938</td>
</tr>
<tr>
<td>Lactic</td>
<td>0.403</td>
<td>0.744</td>
<td>0.711</td>
<td>1.000</td>
<td>0.544</td>
<td>0.687</td>
</tr>
<tr>
<td>Succinic</td>
<td>1.557</td>
<td>1.387</td>
<td>1.308</td>
<td>1.837</td>
<td>1.000</td>
<td>1.225</td>
</tr>
<tr>
<td>Acetic</td>
<td>1.230</td>
<td>1.117</td>
<td>1.087</td>
<td>1.546</td>
<td>0.817</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Example: Have TA of 4 grams/L. Want as tartaric. 4 g x 0.860 = 3.44 g tartaric L.

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**Adding Acid**

- **Very easy using the metric system,**
  
  1 gm/L addition tartaric acid raises TA 1 gm/L

- **To raise the TA 1 gm/L of 100 Gal. wine**
  
  
  \( (1 \text{ gm/L}) (3.785 \text{ L/Gal.}) (100 \text{ Gal.}) = 378.5 \text{ gm} \)

- **In English (American) units:**
  
  Approximately 8.3 #/1000 Gal. = 1 gm/L

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**High pH + High TA Wines**

- A common problem in red wines made from high Brix grapes is high pH and high TA. This is because of the high potassium content in the juice.

- The pH is too high but the wine tastes sour.

- Best to adjust the wine to the proper pH before ageing and then de-acidify if needed (usually it’s not) before bottling.

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**Adjusting Acid before Aging**

- **Ballpark numbers,**

  - Try to keep reds pH < 3.70
  - Try to keep whites pH < 3.40

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**Adding Acid**

- Acid can be mixed with juice wine or water.
  
  Hot water works well but gives off more fumes.

- Never mix acid and SO\(_2\) in the same bucket, the low pH will release lots of SO\(_2\).

- When adding acid it is never a bad idea to perform bench trial first for taste and analysis for pH shift.
Potassium Bitartrate

- KHTa, potassium bitartrate, also called cream of tartar.
- Potassium bitartrate is not completely soluble in juice or wine. Solubility is influenced by concentration and temperature.

Potassium Bitartrate

- It is made by a ionic bond between an tartaric acid anion (negative) and a potassium cation (positive).

Potassium Bitartrate

- It is very common for KHTa to become insoluble and precipitate (come out of solution) in juice or wine lowering the TA and changing the pH slightly.
- Do not confuse:
  - TA (Titratable Acidity) with
  - Ta⁺ (Tartrate ion).

Potassium Bitartrate

- Potassium bitartrate is important in wine stability and we will learn more about it in the wine processing lecture.
- Potassium bitartrate will often form on corks of older wines.

Polyphenols

- Grapes and wine contain a number of polyphenols. A phenol is a molecule that contains a hydroxyl (OH) group on a benzene ring.
- Phenol itself is not found in wine.

Polyphenols

- Polyphenols are chains of these molecules, that are present in the skins and seeds of grapes. They can also come from the wood during barrel aging.
- Approximate amounts
  - whites 100 to 300 PPM GAE (Gallic Acid Equivalents)
  - reds 1500 to 4000 PPM GAE
Polyphenols
- Responsible for color and sensory characteristics (astringency and bitterness) that distinguishes reds from whites. Also a source of browning compounds.
- Very complex compounds that are responsible for much of the body & color of a wine.
- They can have positive affects on health.

Anthocyanins
- Polyphenolic red and blue pigments widely distributed in plants. Found in the skins of red grapes; white grapes do not have anthocyanins.
- Different anthocyanins have the same basic structure with variations.
- Anthocyanin reactions with acids and sulfur dioxide affect color.

Tannins
- Tannins are a class of polyphenolic molecules found in grapes that are similar to anthocyanins.
- They contribute to a wine's astringency and bitterness but are colorless.
- They get their name from leather tanning where plant tannins are used to cure animal skins.
- Link to tannin article on class website.
**Tannins**

- Tannins are characterized by their ability to combine with proteins and polysaccharides.
- These tannins can also polymerize with themselves, anthocyanins and other tannins and then settle out over time making older wines softer (less astringent).
- They come from the skins, seeds, and stems of grapes. Oak tannins will also come from wood during barrel aging.

**Tannins**

- There are three major types of tannins in wine:
  - **Condensed**, These tannins can polymerize (form chains). Catechins are an example they are found in grape skins, seeds, and stems.
  - **Hydrolysable**, ellagitannins are an example, their primary source is wood (barrels).
  - **Complex**, these are large chains of tannin molecules that have formed polymers.

**Tannins**

- Tannins provide bitterness (flavor), astringency (sensation) to wine (as well as coffee & tea).
- They help to protect the wine from oxygen and greatly influence how a wine will age.
- As tannins polymerize and grow larger they will eventually precipitate out of the wine making the wine softer and less tannic.

**Nitrogenous substances**

- Important because **amino acids** (AAs) are made from nitrogen; AAs are the building blocks of proteins which all life is made up from.
- **Ammonia** 25 to 300 PPM in juice; rapidly assimilated by yeasts leave about 0 to 50 PPM in wine.
- **Amino acids and proteins** Contain about 90% of the nitrogen in grape juice.
Nitrogenous substances

- Amino acids & proteins are important because:
  - Nutritional requirement by microbes
  - Associated with formation of higher alcohols that affect sensory properties.
  - Protein instability
  - If nitrogen levels are too low, fermentation can stick or produce H₂S.

Other must constituents

- **Enzymes**, are proteins that are catalysts, polyphenol oxidase is the most important.
- **Vitamins**, important as growth factors.
- **Inorganics**, potassium, calcium, copper, iron, magnesium.
- **Pectins**, colloidal substances such as polysaccharides.
- **Volatile constituents**, such as esters and pyrazines, very important but least understood.

Composition of Wine vs. Juice

- Differences in composition are a result of microbial action (fermentation) on must or juice.
- We will now deal with the composition of wine.
- There are literally hundreds of compounds that exist in wine that contribute to its taste. Each wine has its unique combination that gives its signature taste.

Alcohols

- **Ethanol CH₃CH₂OH** Ethanol has many important sensory effects aroma, body, viscosity, and taste. Main effect is due to alcohol acting as a solvent.
- Also can have both positive & negative heath effects, as well as psychogenic effects.
Alcohols
- Glycerol \( \text{CH}_2\text{OH-CHOH-CH}_2\text{OH} \) third most prevalent compound in most wines, averages 0.6 to 0.8%. Has a big effect on body or viscosity of a wine.
- Isoamyl alcohol \( \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH} \) A fusel oil that has a hot or heady smell mostly important in brandies.

Acetals - \( \text{CH}_3\text{CHO} \)
- Product of fermentation also a byproduct of aerobic spoilage organisms, results from and indicates exposure to oxygen. Has a nutty-sherry-like smell, 25 to 50 PPM.

Alcohols
- Methanol, \( \text{CH}_3\text{OH} \) extremely small amounts present, it is a poison! 6 to 10 ml can cause blindness. Yeast do not produce nearly enough to be a danger.
- There have been cases of methanol poisoning in wine but they were the result of adulteration by adding methanol to the wine.

Acids from Fermentation
- Lactic acid Small amounts formed by yeast, much more converted from malic acid by ML bacteria 3 - 5 g/ L.
- Acetic acid \( \text{CH}_3\text{COOH} \) Vinegar, small amounts formed by yeast much more formed by spoilage bacteria, \( \text{Acetobacter} \) & \( \text{Lactobacillus} \). About 0.3 to 0.6 g/ L.
- Succinic acid byproduct of alcoholic ferm 0.5 - 2.0 g/ L.

Diacetyl
- Produced by ML bacteria \( \text{ML} \) and has an intense buttery aroma.

Gasses
- \( \text{CO}_2 \) Leftover from fermentation it contributes to taste,. Young wines will have from 500 to 1500 PPM (parts per million). Contributes to the fresh flavor of young wines.
- \( \text{O}_2 \) Contributes to aging and spoilage. Try to keep it under 1 PPM for whites and less than 2 PPM for reds. Too much is a sign of NEGLECT!
Urethane (ethyl carbamate)

- Carcinogen (also found in yogurt, bread) present in the ppt range, product of fermentation increased dramatically when urea is added for nitrogen source.

\[
\begin{align*}
\text{UREA} & \quad \text{URETHANE} \\
\text{H}_2\text{N} & \quad \text{C} & \quad \text{NH}_2 & \quad \text{O} & \quad \text{C} & \quad \text{O} & \quad \text{C}_2\text{H}_5
\end{align*}
\]

Other Flavor Constituents

- There are many more volatile compounds that are created or modified by microorganisms that are present in wine at very low levels.

\[
\text{GC-MS} \quad 1\text{H-NMR}
\]

Some of the aroma compounds found in wine

- **Norisoprenoids** Carotenoid derived aromatic compounds including zingerone (spice notes), raspberry ketone, damascenone (rose oil) and vanillin.

- **Thiols**, sulfur containing compounds that contribute to much of the varietal aromas of Cabernet Sauvignon, Sauvignon Blanc, Merlot, & Gewürztraminer. They include mercaptans (garlic and onion).

Some of the aroma compounds found in wine

- **Esters**, formed during fermentation and aging, aromas have wide range from fresh and fruity to nail polish.

- These compounds are some of the most important and least monitored flavor components in wine.

Some of the aroma compounds found in wine

- **Methoxypyrazine**, grassy, herbaceous aroma compound associated with Cabernet Sauvignon and Sauvignon Blanc.

- **Monoterpenes**, responsible for the floral aromatics of Gewürztraminer, Muscat and Riesling. Includes geraniol, linalool and nerol.

Some of the aroma compounds found in wine

- Tonight we have gone over the natural compounds commonly found in wine.

- Next week we will go over compounds that can be added to wine to affect its stability and flavor.

- **Sulfur Dioxide** and **Wine Additions lecture next week** after we review the test.