Wine Spoilage and Defects

Wine 3
Introduction to Enology

4/22/2014

Tonight’s Lecture

- Review Exam #2
- What the most common wine defects are
- How to identify wine defects
- How to treat defective wines

Exam 2 Review

- Mean = 75.8
- Range 104 to 32
- Grading:
  - A = 90 to 105
  - B = 80 to 89
  - C = 70 to 79
  - D = 60 to 69
  - F = Below 60

Wine defects

- With the proper techniques you can greatly improve a spoiled wine, but it is rarely as good as it might have been if it had not gone bad to begin with.

Prevention is the best cure

- The best way to prevent spoilage is to keep a close eye on your wine and taste often.
- Especially true if the wine is not stored under ideal conditions.
- Also if you are doing a risky procedure (like no SO₂ or not filtering) it is best if your product is already in good shape to begin with.
Types of wine defects

- Defects that take place during wine storage & processing.
- Defects from the growth of wine spoilage microorganisms.
- Defects that take place after the wine is bottled.

Sulfides

- Off odors caused by H$_2$S (Hydrogen Sulfide), mono, and di-mercaptans. Not to be confused with the sulfite in SO$_2$.
- Aromas can be strong or subtle:
  - H$_2$S Rotten eggs, roasted coffee, fecal
  - Mono-Mercaptans Garlic/onion, skunk
  - Di-Mercaptans Vegetables, (artichoke, asparagus), petroleum products

Hydrogen Sulfide

Threshold for H$_2$S is 1 PPB, at low levels the smell is non-distinct.
- Most often caused by late or excess sulfur on grapes; yeast convert sulfur to H$_2$S during fermentation.

Hydrogen Sulfide

Other Causes:

- Low nutrients during fermentation (yeast breaking down amino acids).
- Use of a high H$_2$S strain (Montrachet).
- Extended contact with dirty (primary) lees.
- Variety, Syrah is more likely to get stinky.

Mercaptans

Products of the addition of H$_2$S and carbon compounds. Skunk spray and the odorant added to natural gas are both examples of mercaptans.
Sub-threshold amounts of H$_2$S can become full-blown mercaptans in the bottle.

Reported Sensory Thresholds for Sulfur Compounds

<table>
<thead>
<tr>
<th>compound</th>
<th>structure</th>
<th>sensory description</th>
<th>range (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen sulfide</td>
<td>H$_2$S</td>
<td>rotten egg, sewage-like</td>
<td>0.9-1.5</td>
</tr>
<tr>
<td>ethyl mercaptan</td>
<td>CH$_3$CH$_2$SH</td>
<td>burnt match, sulfidy, earthy</td>
<td>1.1-1.8</td>
</tr>
<tr>
<td>methyl mercaptan</td>
<td>CH$_3$SH</td>
<td>rotten cabbage, burnt rubber</td>
<td>1.5</td>
</tr>
<tr>
<td>diethyl sulfide</td>
<td>CH$_3$CH$_2$SCH$_2$CH$_3$</td>
<td>rubbery</td>
<td>0.9-1.3</td>
</tr>
<tr>
<td>dimethyl sulfide</td>
<td>CH$_3$SCH$_3$</td>
<td>canned corn, cooked cabbage, asparagus</td>
<td>17-25</td>
</tr>
<tr>
<td>diethyl disulfide</td>
<td>CH$_3$CH$_2$SSCH$_2$CH$_3$</td>
<td>garlic, burnt rubber</td>
<td>3.6-4.3</td>
</tr>
<tr>
<td>dimethyl disulfide</td>
<td>CH$_3$SSCH$_3$</td>
<td>vegetal, cabbage, onion-like at high levels</td>
<td>9.8-10.2</td>
</tr>
</tbody>
</table>

From ETS Labs
Sulfide Treatment During Fermentation

- Often H₂S that forms during fermentation will disappear with time and racking, so some say do not treat until the wine has been racked off fermentation lees.
- It is best to catch this early so sniff wine every day while you are taking Brix readings.

Sulfide Treatment During Fermentation

- Sometimes a nutrient addition will stop the formation of H₂S.
- When yeast grow in low nutrient situations they can break down protein as a nitrogen source liberating sulfur in the process.

Sulfide Treatment

- Treatment for sulfides depends on the type that is present, aeration removes H₂S but forms di-mercaptans from mono-mercaptans.
- There is a simple diagnostic test that can be performed to see what types of sulfides are present in a wine.

Diagnostic test

- There is a simple diagnostic test for sulfide, the test kit is inexpensive.
- Step one, fill 3 glasses with 50 ml wine.
- Glass 1, Control, no addition
- Glass 2, 1 ml of 0.05% CuSO₄ (removes mono mercaptan & H₂S)
- Glass 3, 2 ml 1% ascorbic acid; wait several minutes then add 1 ml 0.05% CuSO₄ (removes mono, di, & H₂S)
### Cellar Treatment of H₂S
- Aeration (racking and splashing) works for slight H₂S but not mercaptans.
- In more severe cases, copper sulfate (CuSO₄) can be added to remove H₂S and mono-mercaptans. Historically, wine was racked through a copper screen.
- The most common form of copper sulfate is CuSO₄·5H₂O which is 25% copper by weight.

### Removal of Copper
- Blue fining uses potassium ferrocyanide to remove copper, not legal in the USA.
- Up until 1991, you could use a fining agent called Cufex that would remove excess copper and iron, but it is no longer made because it contained some cyanide and the manufacturer was afraid of the liability of lees disposal.

### Treatment of Mercaptans
- Mono-mercaptans are treated with copper sulfate like H₂S, but di-mercaptans must be converted to mono before treatment.
- Ascorbic acid (Vitamin C) is added to shift di to mono, the trial rates are 17ppm, 33ppm, 75ppm (75ppm is the recommended Max).
Treatment of Mercaptans
- Addition of ascorbic acid should be 1 to 5 days prior to copper sulfate addition to give it time for the reaction to take place.
- In stubborn cases, a little deodorizing carbon can be added to remove off aromas.
- As always, do trials first!

Deacidification
- Wines that are too high in acidity can have their acid level lowered by use of calcium carbonate (CaCO$_3$) or potassium carbonate (KCO$_3$).
- Usually not necessary in California.
- Best used if a wine is too tart and you do not want to do MLF.
- CaCO$_3$ is sold under the trade name Acidex

Deacidification
- 2.52 grams of calcium carbonate per gallon of wine lowers the TA of a wine by 1g/ L.
- 3.49 grams of potassium carbonate per gallon of wine lowers the TA of a wine by 1g/ L.
- Do trials first for taste and to see pH and TA shift.
- Treat 15% of total blend.
- Cold stabilize the wine before bottling

Oxidation
- Acetaldehyde threshold is 0.1 to 0.125g/ L normal is < .075 g/ L
- Exposure to air also reduces fruitiness, browns phenols and promotes the growth of aerobic wine spoilage microorganisms.
- Cause: Ageing the wine for too long or neglect!

Oxidation
- Treatment:
  - Sulfur dioxide binds acetaldehyde so adjust with acid and get SO$_2$ to 0.8 molecular.
  - Finning to remove oxidized aromas in whites, trials with bentonite, gelatin, casein, PVPP, and carbon. Reds can be more stubborn.
Preventing Oxidation

- Very best way to treat is prevention
- Keep tanks topped or headspace gassed
- Keep SO₂ levels adequate
- Prevent O₂ pick up during processing (Sparging etc)

Preventing Oxidation

- This is probably the most common problem with homemade wines so keep things topped!
- Using "inert" gasses to purge out oxygen in headspace of tanks and barrels.
- Several gases are available to winemakers to gas the headspace of un-topped tanks to protect them from oxygen.

Inert gasses

- CO₂ ~ Carbon Dioxide heavier than air so blankets the top and will purge out the oxygen.
- CO₂ is soluble so it tends to absorb into the wine leaving the surface of the wine unprotected. In young red wines excess CO₂ can delay aging when the wine is placed in BBDs.

Inert gasses

- N₂ ~ Nitrogen, does not absorb into wine however it has the same density as air so it does not blanket a tank as well.
- Ar ~ Argon, the best of both worlds, heavier than air but does not absorb into wine. Expensive, five times the cost but ten times as effective.

Safety With Gas Cylinders

- Contents of gas cylinders are under extreme pressure.
- Close stem valve when not in use.
- Do not stand in front of regulator/ gage when opening stem valve.
- Be careful during transport
- Chain to wall when not in use.

Wine Spoilage Organisms

- Wine spoilage microorganisms are bacteria and yeast that produce off-flavors or aromas.
- It also includes beneficial yeast and bacteria that are growing where you do not want them to. Such as ML or yeast fermentation in a wine that is bottled.
Aerobic vs. Anaerobic

- **Aerobic** microbes (yeast and bacteria) need oxygen so they grow on the surface of the wine.
- **Anaerobic** microbes do not need oxygen so they grow throughout the wine.
- What are wine yeast?

Volatile Acidity or "VA"

- **Symptoms:** Vinegar aroma, finger nail polish remover aroma (ethyl acetate), cherry lifesavers.
- **Cause:** Growth of *Acetobacter*, a bacteria that grows on the surface (mandatory aerobe). Converts ethanol to acetic acid and ethyl acetate. Grows best in high pH wines.

Volatile Acidity or "VA"

- Wines are usually infected during cellaring but moldy grapes or grapes that have bird damage can come in with VA. Ethyl acetate accounts for much of the "VA" character.
  - Acetic Acid: \( \text{CH}_3\text{COOH} \)
  - Ethyl acetate: \( \text{CH}_3\text{COOC}_2\text{H}_5 \)

Volatile Acidity or "VA"

- The legal limits for VA (acetic acid) are different for US and California:
  - Red Wine: 1.4 g/L (1.2 g/L in CA)
  - White Wine: 1.2 g/L (1.1 g/L in CA)
  - Dessert Wine: 1.2 g/L (1.1 g/L in CA)
  - Wines for export: 0.9 g/L

Removal of Volatile Acidity

- Filter and then try blending the number down with better wines.
- Volatile Acidity can be removed using reverse osmosis combined with ion exchange.
- The process works but it is expensive and it has other sensory effects. Again, prevention is the best cure.
Removal of Volatile Acidity

- All wine has some degree of acetic acid. If it is completely removed it adversely affects flavor and body.

Vinegar Production

- Start with a good wine, dilute it with non-chlorinated water to get alcohol to 10%, inoculate with mother of vinegar put in a half full carboy with cheesecloth over the top.
- If you cannot get hold of a starter mother, use 3/5 Wine 1/5 water & 1/5 unpasteurized commercial vinegar.
- Keep it in the dark at about 60 to 68ºF.

Vinegar Production

- Takes about three to six months; taste often for acidity levels. Then bottle the vinegar and seal with a T-top cork to stop the fermentation, herbs can be placed in the bottle for more flavor.

Surface Film Yeasts

- Hansenula, Kloeckera and Metschnikowia, These wine spoilage yeasts can only grow in the presence of oxygen.

Surface Film Yeasts

- They can form a thick wrinkly film on top of the surface of wine stored with headspace, the yeast form acetaldehyde giving an oxidized aroma.
- Prevented by using SO₂ and keeping oxygen out of the headspace. Common but easy to control.
Brettanomyces/Dekkera (sporulating / non-sporulating)

- Two organisms—one fault
- Often found in Belgian style beer.

Symptoms:
- May be spritzy, lack of fruitiness, horse sweat-BBQ sauce aroma, bitter metallic finish in reds, tuna fish smell in whites.

Brettanomyces/Dekkera (sporulating / non-sporulating)

- Grows primarily in dry, high pH, reds; throughout the wine (not just at the surface). Slow growing infection usually from dirty wooden cooperage, easily spread during topping.
- Can become a problem many years after bottling.
- Only bug that will grow in a dry, MLF complete wine, without oxygen.

Treatment:
- Resistant to sorbate and SO₂ < 0.5 molecular cannot be killed easily by SO₂ but goes dormant until level falls to below 0.5 molecular.
- Only way to protect wine is sterile bottling (0.65 microns). If you are plating directly after a sulfur addition it will show no growth.

Brett in premium reds?

- Aroma primarily from a unique fermentation product of Brett, 4-ethyl phenol.

- Some winemakers say a small amount Brett growth makes a wine more complex, more "French" in character, is it better or worse? Lets just say it is say it's a different style.
- Some high-end wineries feel that rough treatment to eliminate Brett is worse than a little Brett growth.
- One researcher says French Brett produces less 4-ethyl phenol.
Lactic Acid (Malolactic) Bacteria

- Any MLF where you do not want it is spoilage but there are some bacteria that do a worse job than others.

Pediococcus
Undesirable malolactic bacteria that can give a vegetal or dirty sock aroma.

Lactobacillus

- This is a very vigorous malolactic bacteria, some strains of can produce an earthy aroma when the wine goes through ML.

Lactobacillus

- Lactobacillus can out compete Saccharomyces at the end of the primary fermentation and make it stick. Then large amounts of acetic acid are produced 2 g/L or higher (illegal levels).
- Ethel acetate is not produced so nail-polish smell is not as prevalent as spoilage from Acetobacter.

Lactobacillus

- Used to be rare, now it's more common due to high sugar/ high pH musts with slow fermentations.
- Can be discouraged by 30 PPM SO₂ at the first pumpover. Almost all Lactobacillus spoilage occurs in red wines greater than 3.5 pH.

Lactobacillus

- If the infection has already started you can use 150 to 400 PPM Lysozyme.
- This type of MLF in the presence of sorbate gives a strong geranium smell.

Zygosaccharomyces bailii

- A spoilage yeast can tolerate much higher sugar levels than Saccharomyces. Mainly a problem in grape juice concentrate and in dessert wines. Sensitive to SO₂.
Identifying Spoilage Microbes
- Traditionally done by microscope or plating:
  - **Microscope**, difficult & inaccurate.

Plating, growth on Petri dishes using selective media. Expensive, difficult, slow results, possible to get false negatives.

Identifying Spoilage Microbes
- Now the fastest and most accurate method uses genetic identifiers and is inexpensive, fast, accurate, and has quantifiable results!
- Seems expensive, but not when compared to the cost of plating for growth on Petri dishes.

Scorpion® Test
- ETS Labs in St. Helena has an assay for microbes using specific genetic markers for common spoilage microbes.
- The Scorpion Test analyses for:
  - *Brettanomyces*
  - *Zygosaccharomyces*
  - *Pichia*
  - *Hansenula*
  - *Pediococcus*
  - *Lactobacillus*
  - *Acetobacter and Gluconobacter*

Bottle Defects
- Problems that take place after the wine has been bottled that do not involve microbes
Fermentation In The Bottle

Yeast or malolactic fermentation, comes from sweet or partial M-L wines that are not sterile bottled.

- This is most common with winemakers that think that their wine is done with ML but do not bother to check.

Fermentation In The Bottle

- **Symptoms:**
  - **Yeast:** Spritzy to explosive, pushed corks, cloudy, bready smell.
  - **M-L:** Spritzy, buttery smell, pearlescence,
  - Both can form H₂S or off aromas, rule is if your wines are not microbially stable then you better sterile bottle!

Cork Taint or Corkeyness

- By far the most common spoilage problem in commercial wines today, and corks are getting more expensive.
- In 2012 3.7% of the cork-sealed wines submitted to the WineSpectator were suspected to be corked.
- That’s down from 9.5% in 2007!

Cork Taint or Corkeyness

- Corkeyness is an aroma that ranges from loss of fruitiness to basement/mildew smell. This is what you smell for when you taste the wine before serving in a restaurant.
- The problem is that the average consumer getting a corked bottle of your wine will not know it is corked, they will just think that it tastes bad.

Cork Taint

- The major component is TCA (2,4,6-Trichloroanisole) which is a mold bi-product. The threshold is 4 PPT. Some have said that this comes from the chlorine bleaching of corks but peroxide treated corks get it too.

Cork Taint

- Mold growth can occur in improperly stored dry barrels and damp wine cellars and you can get the same effect.
- PVPP can be used to treat wines with TCA.
TCA in corks usually comes from mold growth in the forest.

Cork Quality Control

- You can test a batch of corks by placing a representative sample in baby food jars with a neutral wine, soaking overnight, and sniffing.
- Statistics are then used to see if the lot passes, if the lot does not it can be rejected. You analyze for TCA with a GC/Mass spectrometer.

Cork taint Continued

- This is the primary reason for wineries moving to screw caps and synthetic corks. However, you are also dealing with product image so there is resistance to change.
- With more wineries paying more attention to cork taint the cork suppliers are too and things seem to be getting a little better.

Light Struck

- Ultraviolet light from the sun or fluorescent lights react with sulfur and other compounds in wine to affect aroma.
- "Light struck" refers to the catalysis by ultraviolet light of reactions forming methyl mercaptan and alpha-amino butyric acid.
- Being "light struck" lowers fruitiness gives wine a plastic or smoky aroma.

Light Struck

- Champagne green, brown and amber glass have UV protection, flint (clear) does not. SB and Wt Zin are problems. So some wineries do not use flint glass.
- Beer is even more sensitive than wine, example: "skunky" smell of Heineken in bottles.
**Pinking**
- Related to skin contact (more phenols) best treatment is PVPP in juice or wine.
- Prevention
  - Minimize skin contact
  - Avoid aeration
  - PVPP troublesome varieties

**Remember!**
- Neglect, **not** trying is usually the first step in failure.
- Many of the problems that we have discussed can be avoided if you are attentive to you wines.

**Next Lecture**
- Sparkling Wine