CRAFT BREWERS CONFERENCE
& BrewExpo America

ASBC Lab-in-a-Fishbowl Session 2

Titratable Acidity (TA) and Potential Hydrogen (pH)

AMERICAN SOCIETY OF BREWING CHEMISTS
NEW BELGIUM
BREWERS ASSOCIATION

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Seminar Outline

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2. pH
3. The pH Scale
4. Changes to pH
5. Control of pH
6. Impact of pH – Mash Tun
7. Impact of pH – Boil Kettle
8. Impact of pH – Cold Side
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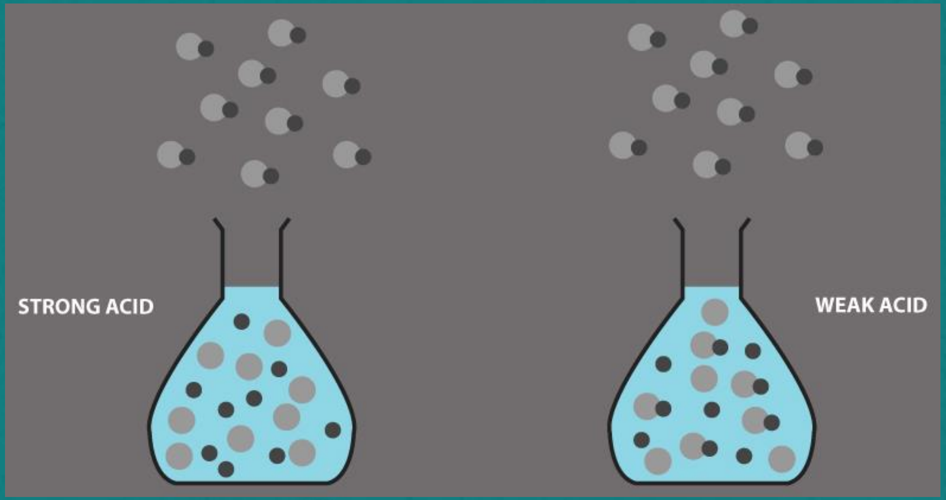
TA & pH



- General rule of thumb – the lower the pH, the higher the %TA.
- pH is a measurement of only dissociated H^+
- TA is a measurement of dissociated and associated H^+
- Sensorially, we taste both associated and dissociated H^+, so it's important to measure both from a quality standpoint
- Organic acids are weak acids and do not dissociate completely in solution.
- Organic acids are largely derived from the incomplete TCA cycle during anaerobic repressed growth of yeast.

pH

Method Supplies

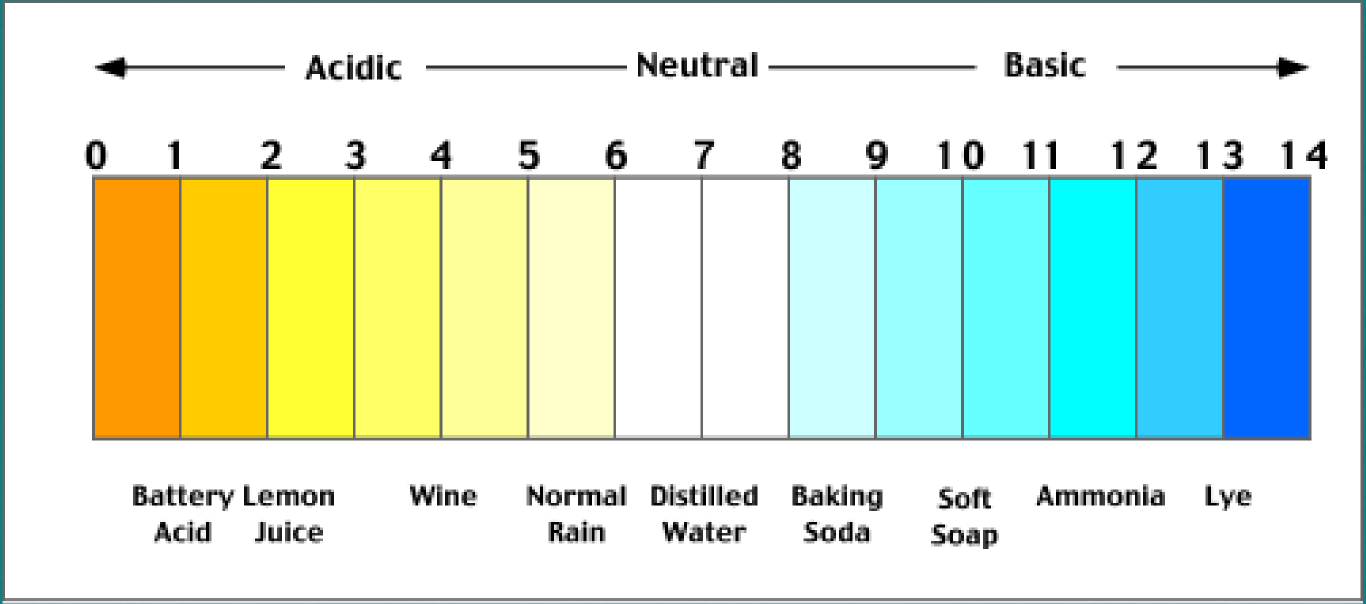
- Reagents
  - *Buffers*, pH 4.0, 7.0, and 10.0 are recommended
- Apparatus
  - *Commercial pH meter*, digital (±0.02 pH units)
  - *Electrodes*, glass and reference or combination
  - *Temperature compensating probe* or *Thermometer*
  - *Beakers* (100 mL)

- pH is a measurement of the acidity or alkalinity of a solution expressed logarithmically where 7 is the point of neutrality.

$$\mathbf{pH = -log[H^+]}$$

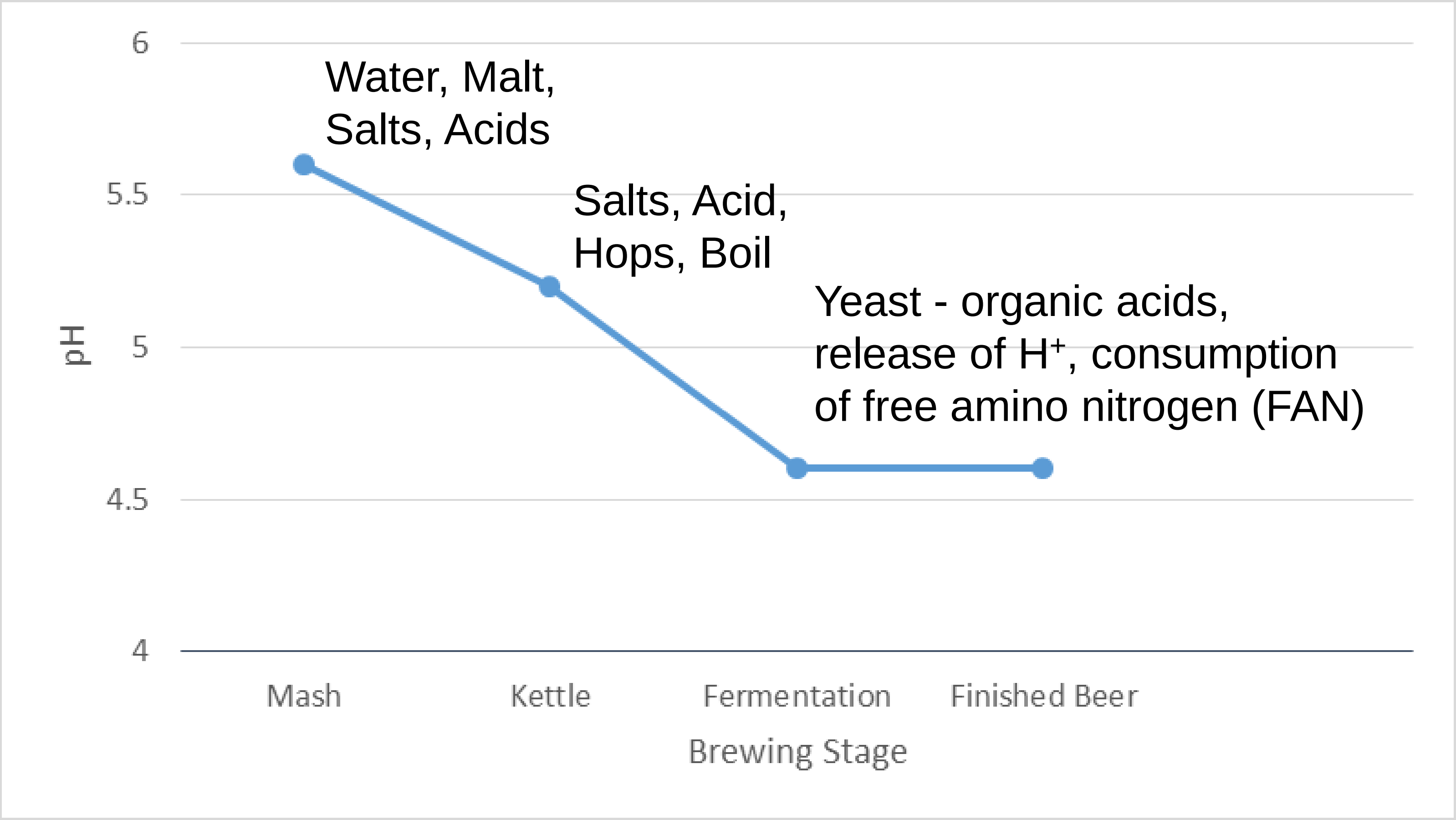
- Acidity is the tendency of a solution to supply hydrogen ions (H^+) to a reaction
- The tendency of a solution to supply H^+ is represented in calculations by a quantity called the “activity” of H^+ in the solution
- The “activity” is directly proportional to the concentration of H^+ in the solution and is also a function of any other substances in the solution whose molecules are close enough to H^+ to have any effect on them and is also a function of the solvent itself, which is usually water.
- pH will vary with temperature as H^+ dissociate at higher temperatures, but H^+ concentration will not

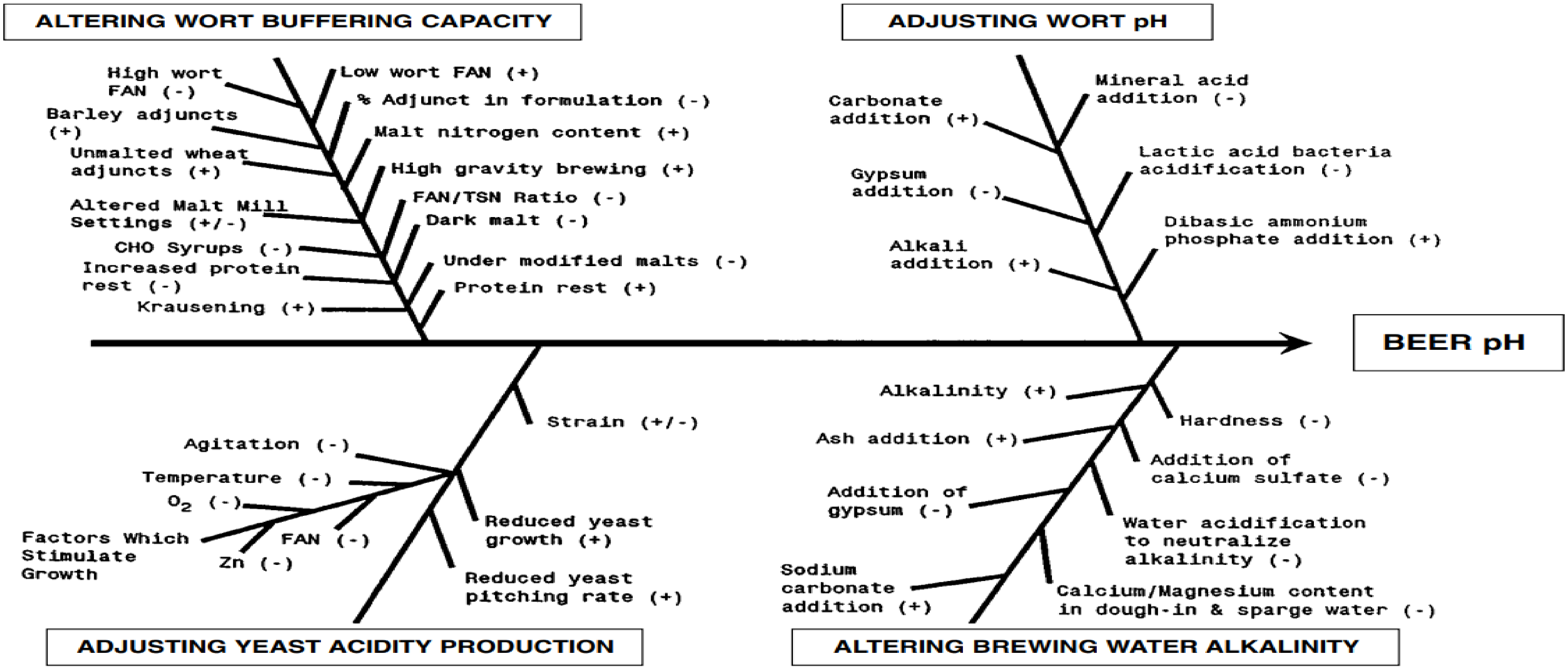
The pH Scale



	pH	H+ Activity		OH- activity
	0	1.E+00	1	0.00000000000001
	1	1.E-01	0.1	0.0000000000001
	2	1.E-02	0.01	0.000000000001
acid	3	1.E-03	0.001	0.00000000001
	4	1.E-04	0.0001	0.0000000001
	5	1.E-05	0.00001	0.000000001
	6	1.E-06	0.000001	0.00000001
neutral	**7**	**1.E-07**	**0.0000001**	**0.0000001**
	8	1.E-08	0.00000001	0.000001
	9	1.E-09	0.000000001	0.00001
	10	1.E-10	0.0000000001	0.0001
base	11	1.E-11	0.00000000001	0.001
	12	1.E-12	0.000000000001	0.01
	13	1.E-13	0.0000000000001	0.1
	14	1.E-14	0.00000000000001	1

Changes to pH





NB (+) = as the factor increases, so too does beer pH; (-) = as the factor increases beer pH decreases

Impact of pH

Mash Tun

Enzyme Activity

- α−amylase optimum pH = 5.5-5.8
- β−amylase optimum pH = 5.2-5.5
- Lipoxygenase optimum pH = 6.5
- Limit dextrinase optimum pH = 5.5

Ratio of $Cl^-/SO_4$2- is important

- For beers with more bitter character you can go up to a 1:2 or 1:3, but it could result in an unpleasant bitterness.

Mash

- Optimal pH of 5.3-5.8
- Can impact: attenuation, protein breakdown, viscosity, lautering performance, potential FAN, and potential TSN.
- High pH will lead to darker color and more astringency.
- Acidified sparge water can prevent a pH rise and can improve flavor stability.

Impact of pH

Boil Kettle

Boiling

- Optimal pH of 5.1-5.4.
- Clarification improves at lower pH,
- Hop utilization increases as pH increases.
- The pH of wort drops about 0.3 units during boiling.
- **Gypsum** (calcium sulfate) can lead to a dry bitter.
- **Calcium Chloride** can aid in body and fullness.

Gravity

- Lower gravity worts have a higher pH prior to boiling, but a larger drop in pH post-boil.

Fining

- Increasing the wort pH by as little as 0.1 - 0.3 pH units leads to a situation where less kettle finings (carrageenan) need to be used to promote clarification.
- Worts below a pH of 4.5 fail to fine

Dimethyl sulfide

- A shift in pitching wort pH from 5.75 to 5.46 led to a halving of dimethyl sulfide production during fermentation

Impact of pH

Cold Side

Primary Fermentation

- pH drop of 0.4 -1. The drop is a result of the consumption of free amino nitrogen and the release of organic acids.
- Optimizing (lowering) pH can also help with VDK reduction.
- The rate of diacetyl reduction will increase as pH drops.
- A rise in pH at the end of fermentation is usually indicative of yeast autolysis.

End of fermentation

- pH influences the flocculation behavior of yeast (strain-dependent)
  - The net level of surface negative charge dictating the opportunity for intercellular bridging via divalent cations

Finished Product

- A lower pH results in improved microbial stability, physical stability, and foam stability, though it can have a negative impact on flavor stability and the quality of perceived bitterness.

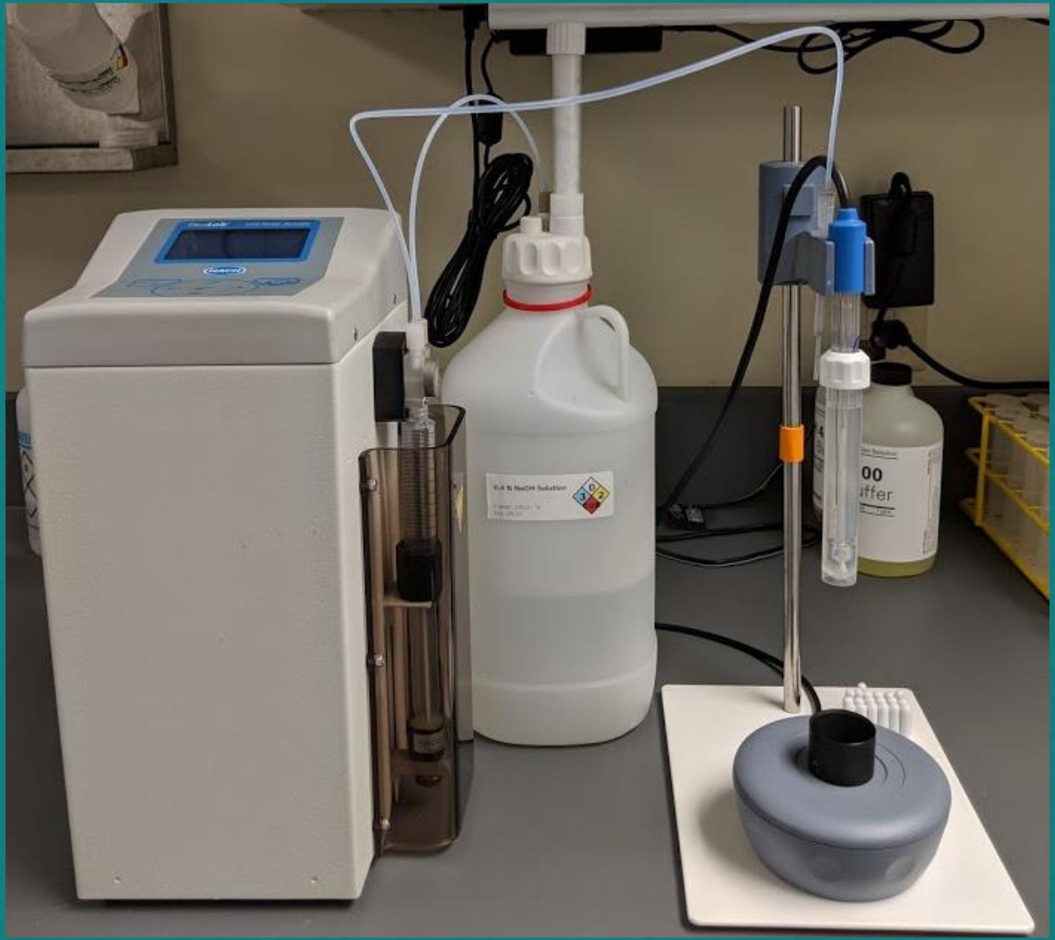
Titratable Acidity

Method Supplies

- Reagents
  - *Buffers*, pH 4.0, 7.0, and 10.0 are recommended
  - *NaOH*, 0.1*M*, CAS No. 1310-73-2
- Apparatus
  - *Commercial pH meter*, digital (±0.02 pH units)
  - *Beaker* (100 mL)
  - *Stir plate and magnetic stir bar*
  - *Buret*, 25 to 50 mL
  - *Pipette*, 50 mL (±0.1 mL)

- TA is defined as the number of acidic protons that the organic acids can potentially donate to the solution
- It is experimentally calculated by measuring the amount of sodium hydroxide (NaOH) required to raise the pH of a solution to 8.2
  - 8.2 is the pH level at which the neutralization of the acids occurs
- Titration does not dissociate all of the acids in solution, so referring to TA as “Total Acidity” is not entirely accurate
- However, TA is used as an approximation of total acidity, so using TA in place of total acidity is generally accepted.
- TA can be used as a critical control point (CCP) in sour production
  - Lactic to acetic ratio is important to monitor as a lower ratio indicates excessive oxygen ingress

Titration Setup



TA method considerations

- **Equation A**

$$\frac{mL\ 0.1M\ NaOH\ x\ 10}{mL\ beer\ x\ specific\ gravity}$$

- **Equation B**

$$C2 = \frac{V1C1}{V2}$$

  - Where:
    - V1 = mL of NaOH
    - C1 = molarity of NaOH
    - V2 = mL of beer
    - C2 = TA (H^+), mol/L

- **Equation C**

$$C2\ x\ [correction\ factor] = \frac{g}{L}$$

$$\%\ organic\ acid = (\frac{g}{L})/10$$

- pH measurement can be impacted by the temperature of your sample
- Calibrate your pH meter frequently
  - 1x/day with standards that have not expired
- Titratable acidity can be calculated for multiple acids

TABLE I
Correction Table for Organic Acids

Acid	Factor
Lactic	90
Acetic	60
Malic	67
Citric	64

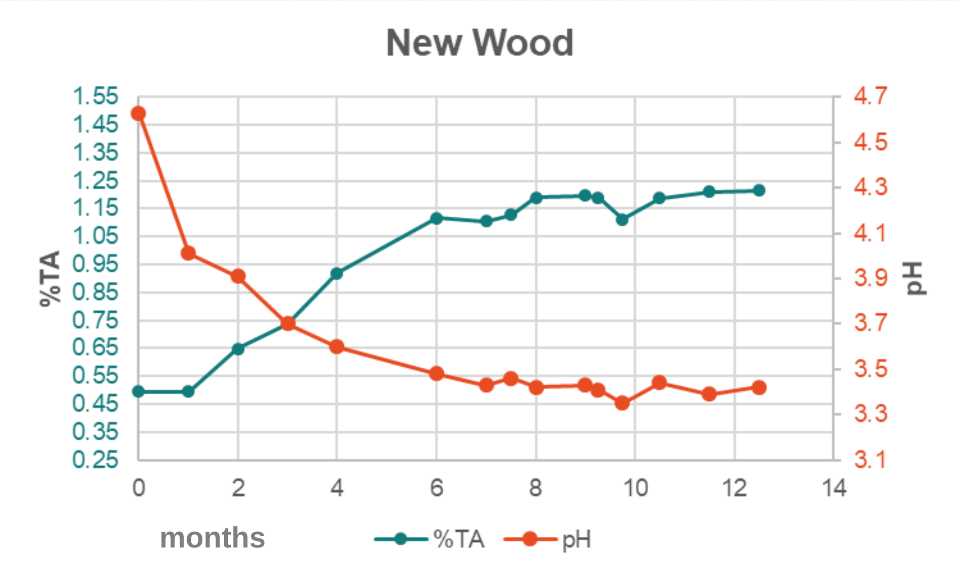
(ASBC method Beer-8)

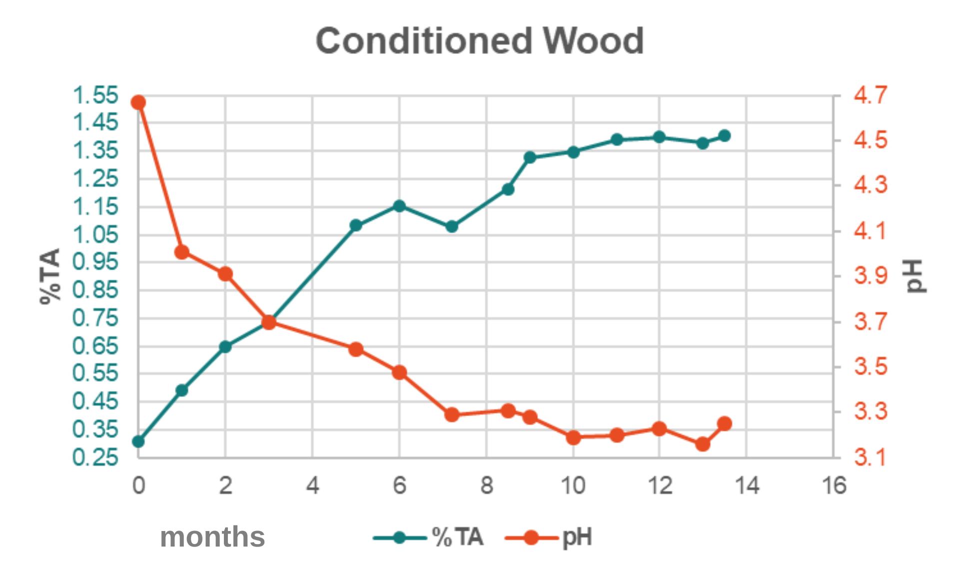
Note: When using the correction table to determine your acid content, it is vital that you use the correction factor for your acid of interest. (*i.e. our foeders' highest concentration acid is lactic acid, so we titrate and correct based on lactic acid's correction factor.*

Souring

Barrel-Aged

- Rapid drop in pH
- Steady incline in %TA
- New wood stabilizes both pH and %TA at an earlier point than conditioned wood does
- Conditioned wood has a higher potential %TA and lower potential pH
- Condition new wood with inoculation from healthy, conditioned wood
- Mixed culture of bacteria (LAB, *Pediococcus* spp.), and yeast (*Saccharomyces* spp., *Brettanomyces* spp., etc.)
- Producing many different acids within this matrix
  - Malic, lactic, acetic, citric, succinic, etc.





Souring

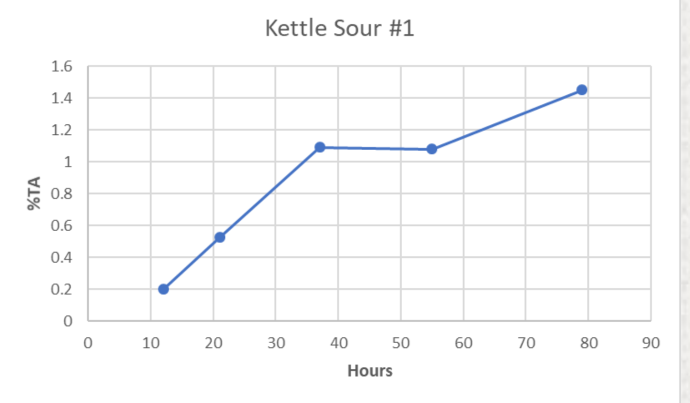
Stainless Sours

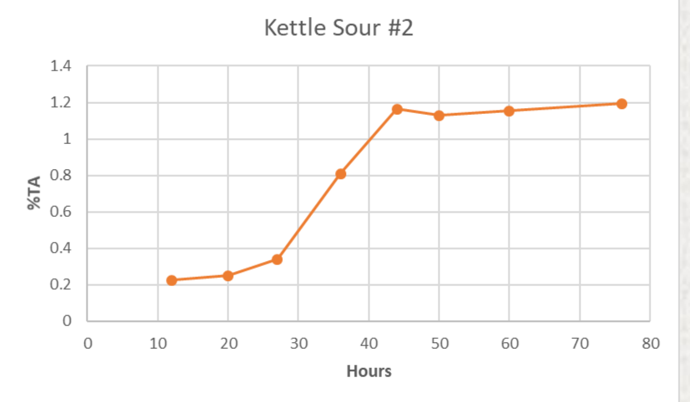
Common lactic acid bacteria (LAB)

- *Lactobacillus brevis*
- *L. lindneri*
- *L. delbrueckii*

Choosing the right LAB strain

- What is the optimal acidifying temperature?
- Is the strain homolactic fermentative?
  - Producing only lactic acid
- Is the strain heterolactic fermentative?
  - Producing lactic acid, ethanol, CO_2, acetic acid, and other metabolic products
- What are the risks for potential off-flavors?
- What is the average rate of acidification?





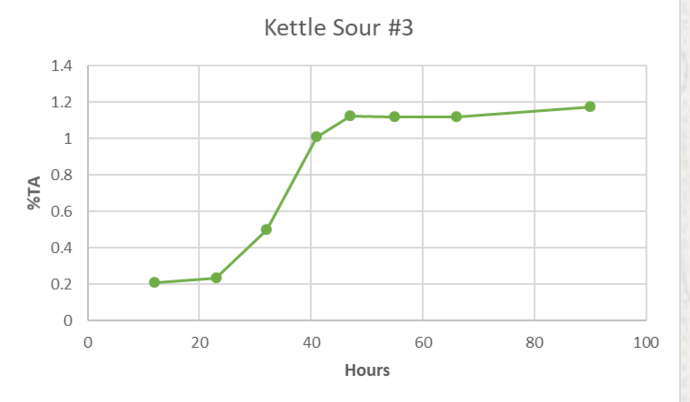


TABLE I
Correction Table for Organic Acids

Acid	Factor
Lactic	90
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TA vs pH Examples

Specialty

Sample A

- pH = 3.82
- Titratable Acidity = 0.44%
    - Lactic – 0.40%
    - Acetic – 0.27%
    - Malic – 0.30%
    - Citric – 0.28%

Food-grade lactic acid-treated on the hot side

Receives fruit additions during fermentation

Sample B

- pH = 3.35
- Titratable Acidity = 1.32%
    - Lactic – 1.19%
    - Acetic – 0.79%
    - Malic – 0.89%
    - Citric – 0.85%

Blend of lambic and mature foeder-aged beers

Sample C

- pH = 3.25
- Titratable Acidity = 1.36%
    - Lactic – 1.22%
    - Acetic – 0.81%
    - Malic – 0.91%
    - Citric – 0.87%

Acidification by LAB

See note on "TA Method Considerations" slide for clarification regarding the correction factors.

TABLE I
Correction Table for Organic Acids

Acid	Factor
Lactic	90
Acetic	60
Malic	67
Citric	64

TA vs pH Examples

Wood-Aged Sours

Sample D

- pH = 3.40
- Titratable Acidity = 1.31%
  - Lactic – 1.18%
  - Acetic – 0.79%
  - Malic – 0.88%
  - Citric – 0.84%

100% foeder-aged high EBC lager with lower FAN in the base beer

Sample E

- pH = 3.30
- Titratable Acidity = 1.46%
  - Lactic – 1.31%
  - Acetic – 0.87%
  - Malic – 0.98%
  - Citric – 0.93%

100% foeder-aged low EBC lager with higher FAN in the base beer

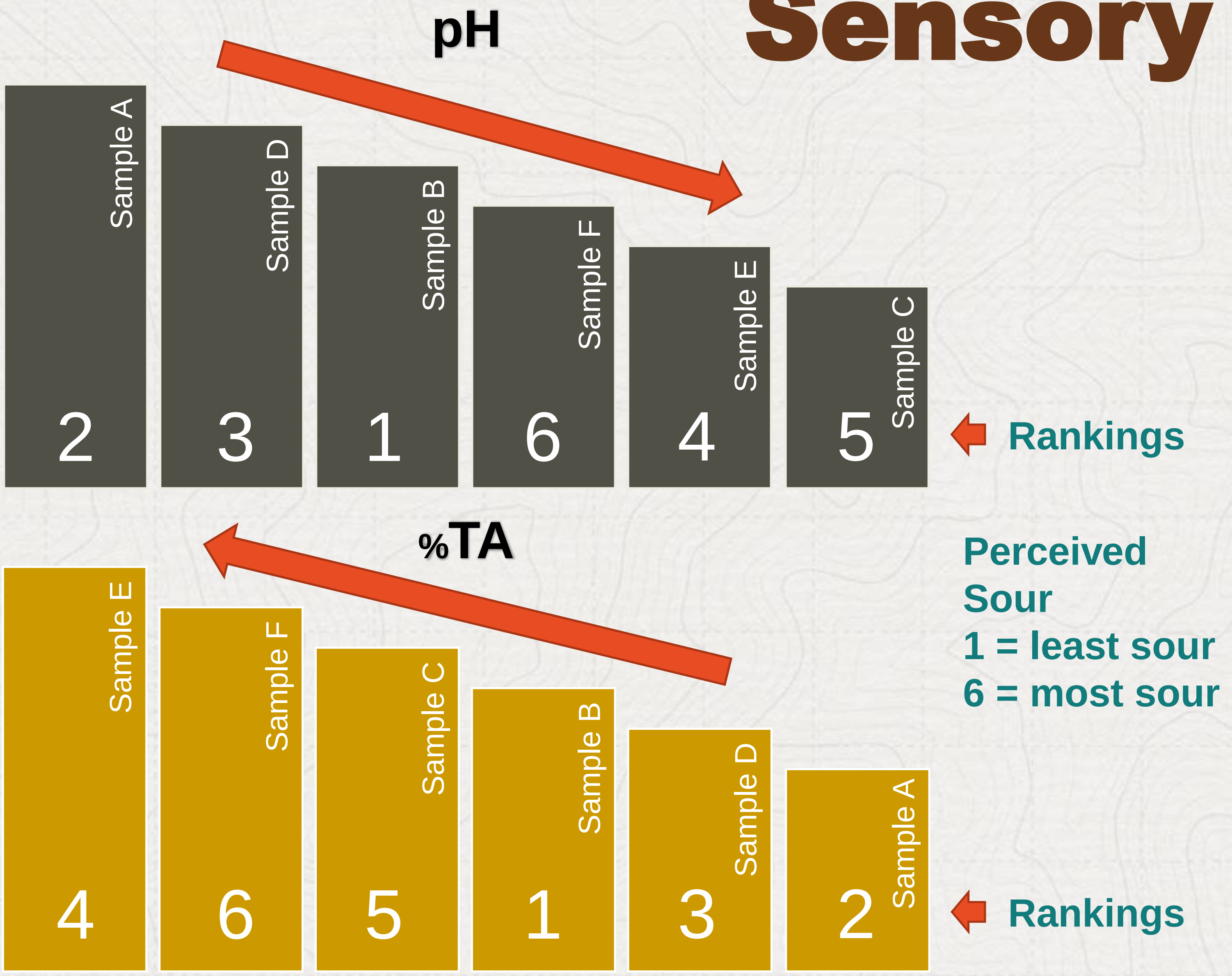
Sample F

- pH = 3.35
- Titratable Acidity = 1.44%
  - Lactic – 1.30%
  - Acetic – 0.87%
  - Malic – 0.97%
  - Citric – 0.92%

Blend of 100% foeder-aged beers

See note on "TA Method Considerations" slide for clarification regarding the correction factors.

Sensory



A panel of 10 tasters were given the following 6 samples and asked to rank each of the samples from least sour (1) to most sour (6).

Each beer's pH and %TA were kept from the panelists.

Takeaways:

- There is not a direct correlation of perceived sour to pH or %TA, though the general rule of thumb (the lower the pH/higher the %TA, the more sour the beer) holds true.
- Beer matrices differ significantly from brand to brand and style to style.
- It's important to taste your beers as they acidify and mature to ensure your brand goals are being met sensorially.

Going Further

pH → TA → UPLC

Ultra Performance Liquid Chromatography (UPLC)

- High-pressure separation and quantification of analytes using UV/VIS detection.

Organic Acids UPLC Chromatogram

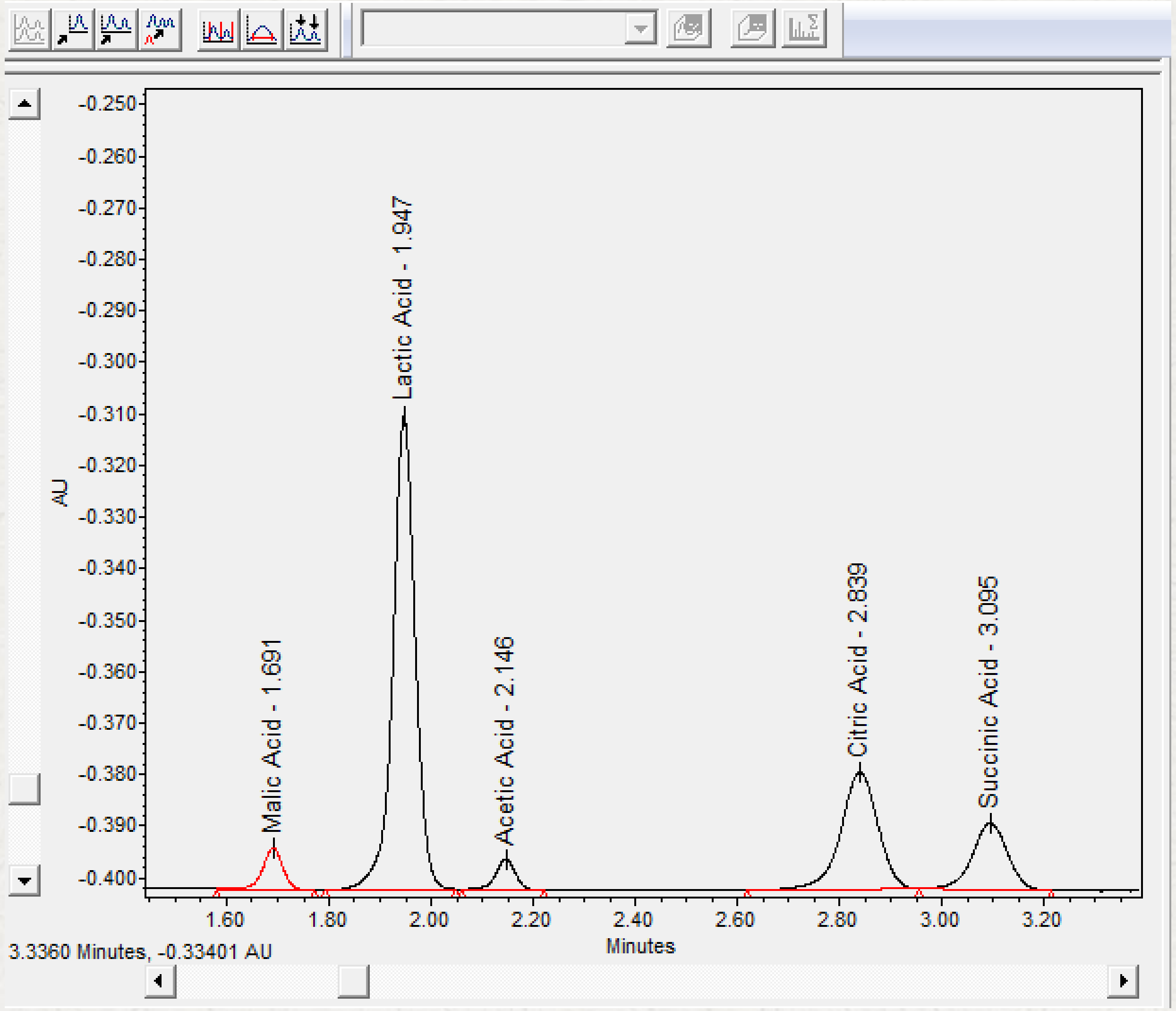


TABLE I Correction Table for Organic Acids	
Acid	Factor
Lactic	90
Acetic	60
Malic	67
Citric	64

TA vs pH vs UPLC

Specialty Sours

Sample A

- pH = 3.82
- Titratable Acidity = 0.44%
- Organic Acids by %TA:
  - Lactic – 0.40%
  - Acetic – 0.27%
  - Malic – 0.30%
  - Citric – 0.28%
- Organic Acids by UPLC:
  - Lactic – 550 ppm
  - Acetic – 50 ppm
  - Malic – 175 ppm
  - Citric – 1500 ppm
  - **Total – 2275 ppm (0.23%)**

Sample B

- pH = 3.35
- Titratable Acidity = 1.32%
- Organic Acids by %TA:
  - Lactic – 1.19%
  - Acetic – 0.79%
  - Malic – 0.89%
  - Citric – 0.85%
- Organic Acids by UPLC:
  - Lactic – 10100 ppm
  - Acetic – 400 ppm
  - Malic – 2000 ppm
  - Citric – 3900 ppm
  - **Total – 16400 ppm (1.64%)**

Sample C

- pH = 3.25
- Titratable Acidity = 1.36%
- Organic Acids by %TA:
  - Lactic – 1.22%
  - Acetic – 0.81%
  - Malic – 0.91%
  - Citric – 0.87%
- Organic Acids by UPLC:
  - Lactic – 12500 ppm
  - Acetic – 150 ppm
  - Malic – 70 ppm
  - Citric – 1350 ppm
  - **Total – 14070 ppm (1.47%)**

See note on "TA Method Considerations" slide for clarification regarding the correction factors.

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Correction Table for Organic Acids

Acid	Factor
Lactic	90
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Malic	67
Citric	64

TA vs pH vs UPLC

Wood-Aged Sours

Sample D

- **pH = 3.40**
- **Titratable Acidity = 1.31%**
- **Organic Acids by %TA:**
  - Lactic – 1.18%
  - Acetic – 0.79%
  - Malic – 0.88%
  - Citric – 0.84%
- **Organic Acids by UPLC:**
  - Lactic – 12500 ppm
  - Acetic – 550 ppm
  - Malic – 35 ppm
  - Citric – 6700 ppm
  - **Total – 19785 ppm (1.98%)**

Sample E

- **pH = 3.30**
- **Titratable Acidity = 1.46%**
- **Organic Acids by %TA:**
  - Lactic – 1.31%
  - Acetic – 0.87%
  - Malic – 0.98%
  - Citric – 0.93%
- **Organic Acids by UPLC:**
  - Lactic – 12600 ppm
  - Acetic – 450 ppm
  - Malic – 15 ppm
  - Citric – 6500 ppm
  - **Total – 19565 ppm (1.96%)**

Sample F

- **pH = 3.35**
- **Titratable Acidity = 1.44%**
- **Organic Acids by %TA:**
  - Lactic – 1.30%
  - Acetic – 0.87%
  - Malic – 0.97%
  - Citric – 0.92%
- **Organic Acids by UPLC:**
  - Lactic – 13000 ppm
  - Acetic – 600 ppm
  - Malic – 55 ppm
  - Citric – 5000 ppm
  - **Total – 18655 ppm (1.87%)**

See note on "TA Method Considerations" slide for clarification regarding the correction factors.

References

- ASBC. (Unknown). ‘pH and Titratable Acidity’ [PowerPoint Presentation]. Setting the Standard: A Deep Dive into Quality. Available by email. (Accessed: 7 December 2018)
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We would also like to thank the BA as well as the ASBC for the opportunity to present at this year's CBC.

Quality Brewing Starts with ASBC

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April 24–26, 2019 • Sonoma County, CA
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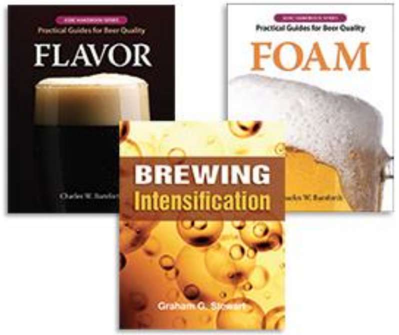

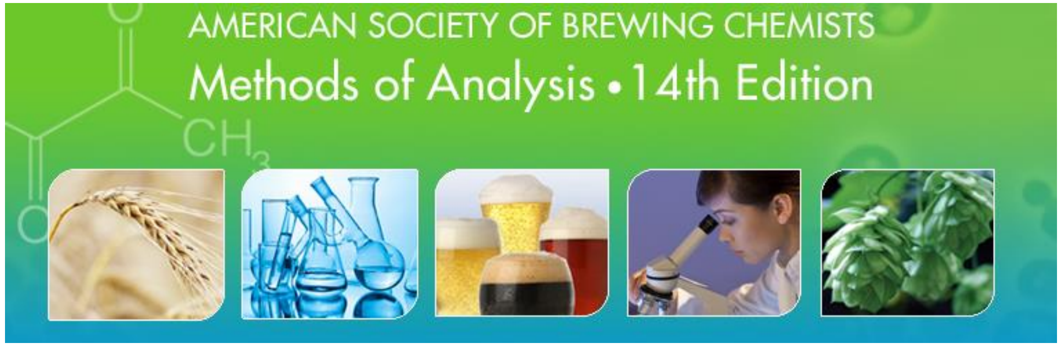

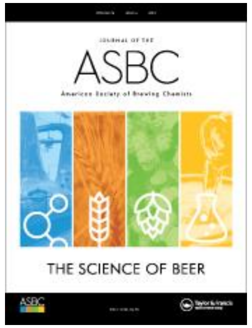

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- Fill out the form on your chair
- Stop by booth 9104

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- Use **code 3172** at asbcnet.org by May 1
- Bonus - join at booth 9104 and get a free Beer Geek t-shirt

ASBC
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Q & A

THE SCIENCE OF BEER

AMERICAN SOCIETY OF BREWING CHEMISTS

Stop by and say hi at booth 9104!

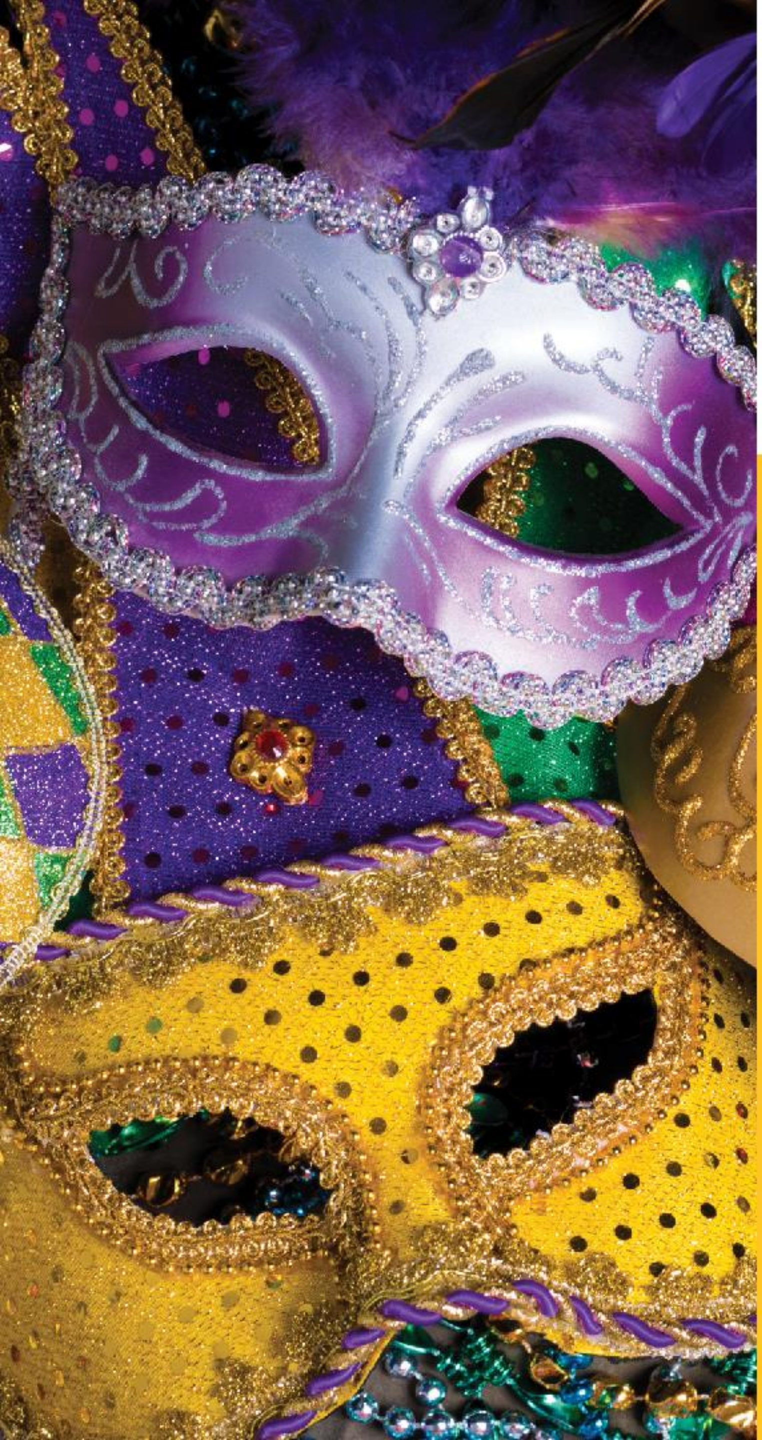
If you'll be attending the Craft Brewers Conference in Denver, CO April 8–11, come see us at booth 9104! In addition to the two Lab in a Fishbowl events we'll be holding in the Four Seasons Ballroom 4, we'll be hosting events in the booth ranging from yeast cell counting to testing titratable acidity and pH, and a meet-and-greet with ASBC President Dana Sedin.

Schedule of events:

(Subject to change)

Monday, April 8		
3:00 p.m.–4:00 p.m.	Lab in a Fishbowl: Yeast Cell Counting & Viability Measurement	Four Seasons Ballroom 4
4:30 p.m.–5:30 p.m.	Lab in a Fishbowl: Titratable Acidity and pH	Four Seasons Ballroom 4
Tuesday, April 9		
9:00 a.m.–5:00 p.m.	Stop by the ASBC booth in the BrewExpo America Trade Show	Booth 9104
11:00 a.m.–1:00 p.m.	Conversation with ASBC President Dana Sedin	Booth 9104
1:00 p.m.–2:00 p.m.	Titratable acidity and pH testing with Jeff Irby and Justin Alexander	Booth 9104
Wednesday, April 10		
9:00 a.m.–5:00 p.m.	Stop by the ASBC booth in the BrewExpo America Trade Show	Booth 9104
1:00 p.m.–2:00 p.m.	Titratable acidity and pH testing with Jeff Irby and Justin Alexander	Booth 9104
2:00 p.m.–3:00 p.m.	Try yeast cell counting with Rob Christiansen	Booth 9104
Thursday, April 11		
9:00 a.m.–3:00 p.m.	Stop by the ASBC booth in the BrewExpo America Trade Show	Booth 9104
11:30 a.m.–12:30 p.m.	Try yeast cell counting with Kelly Tretter	Booth 9104

Thank you for your time and attention!



ASBC

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2019 ASBC Meeting

June 24–26

Royal Sonesta Hotel

New Orleans, Louisiana