XCELIS® Ethanol Solutions

USING A PORTABLE PROBE TO QUICKLY MEASURE SODIUM IN PROCESS SAMPLES

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FELC, October 5th, 2021

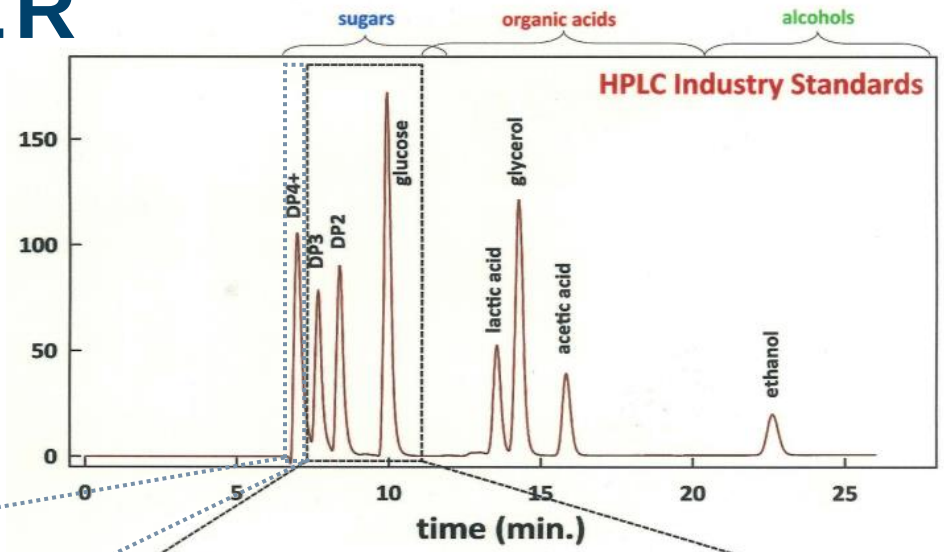
GRAIN PROCESSING
APPLIED INNOVATION CENTER

- **Technical team dedicated to our Fuel Ethanol and Carbohydrate Processing customers**
- **Product development**
  - DISTILLASE® XP
  - DISTILLASE® CX
  - DISTILLASE® DXT
  - SPEZYME® HN
- **Lab-based support**
  - Pre-trial testing
  - Trial evaluation
  - Optimization
  - Troubleshooting
- **Located in Cedar Rapids, IA**

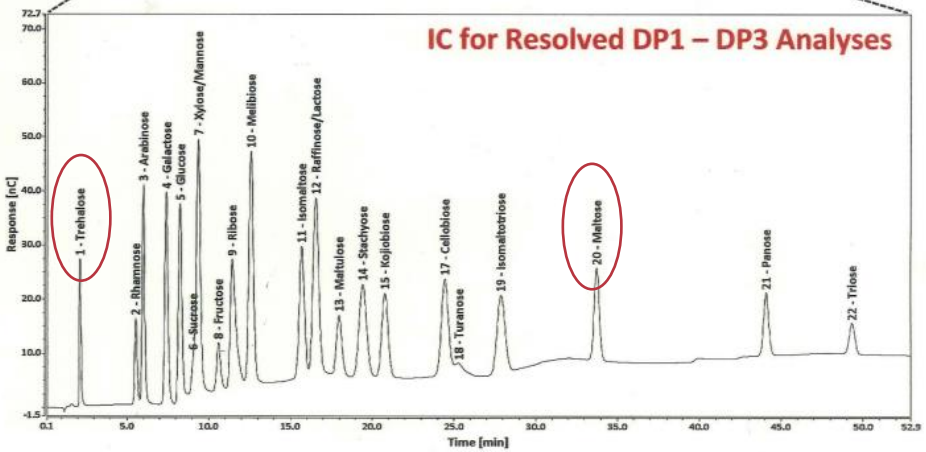
GRAIN PROCESSING APPLIED INNOVATION CENTER

- **Fermentation Services**
  - Prop and ferm studies
  - DP4+ composition
  - Detailed sugar analysis
  - HPLC checks
  - Residual starch
  - Nitrogen measurements
  - Inhibitors (fusels, sodium, sulfite, organic acids, etc)

- **Liquefaction Services**
  - Cook studies
  - Solubility
  - Cations (Sodium, etc)



Component	%w/v
Available Starch	0.04
Phytic Acid and Breakdown Products	0.14
Non-Starch Polysaccharides	0.06
Sulfate	0.03
Chloride	0.02



- Sodium sources and its importance in the dry grind process
- Sodium probe background and protocol development
- Case Studies

- **Sodium sources and its importance in the dry grind process**
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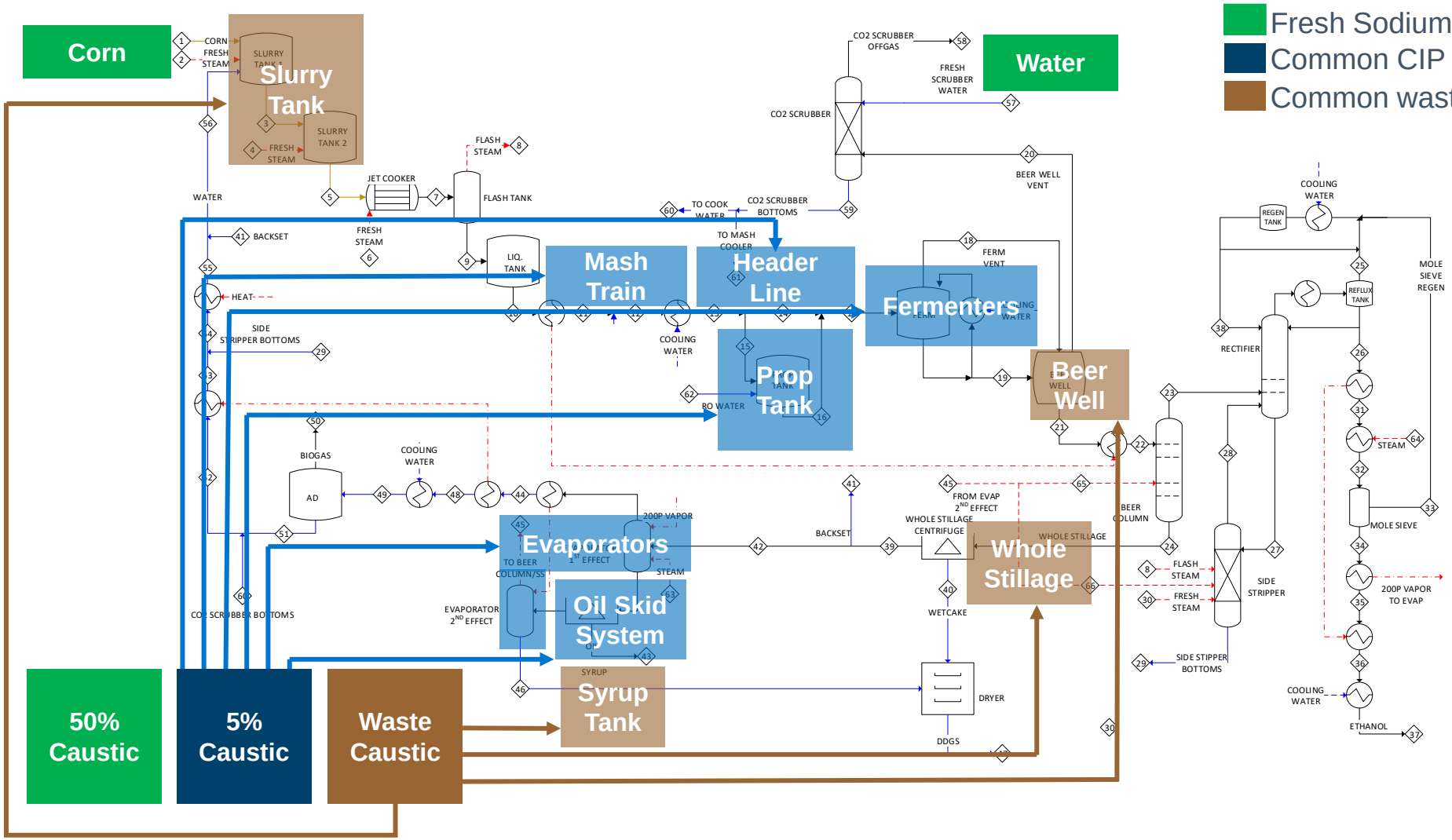
SODIUM SOURCES IN THE DRY GRIND PROCESS



- **Waste caustic is the primary source of sodium in most plants**
- **In ICM-style plants, methanator effluent is no longer a significant source in the front end**

FACTORS THAT CAN AFFECT SODIUM LEVELS

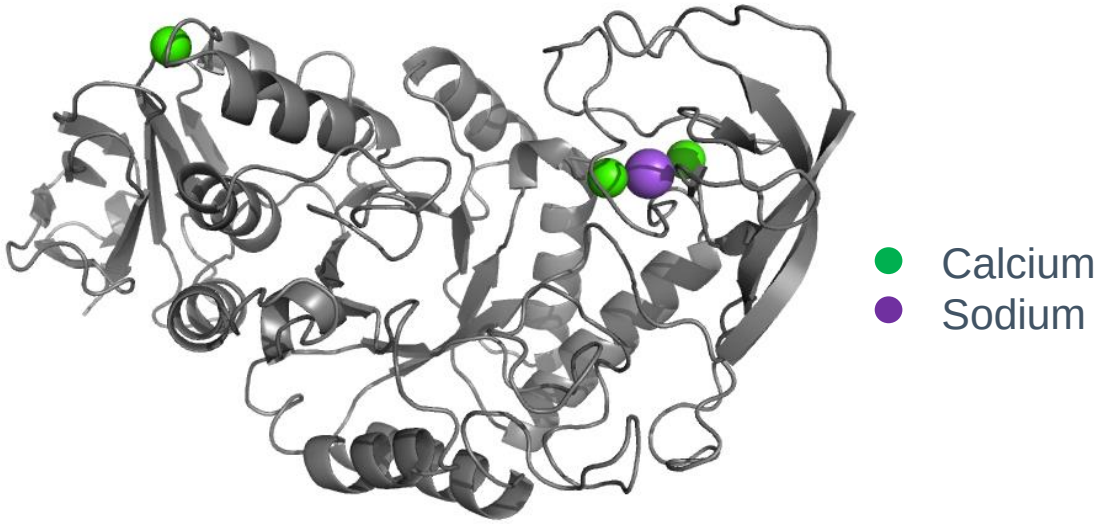
- **Changes in CIP procedure**
- **Leaks in CIP valves (e.g. spray ball in ferm)**
- **Change in waste caustic destination**
- **Change in CIP agent (e.g. acid CIP)**
- **Change in well source**

Potential Impacts

- Sodium levels that are too low can negatively affect liquefying alpha-amylase performance
- Sodium levels that are too high can negatively affect yeast performance

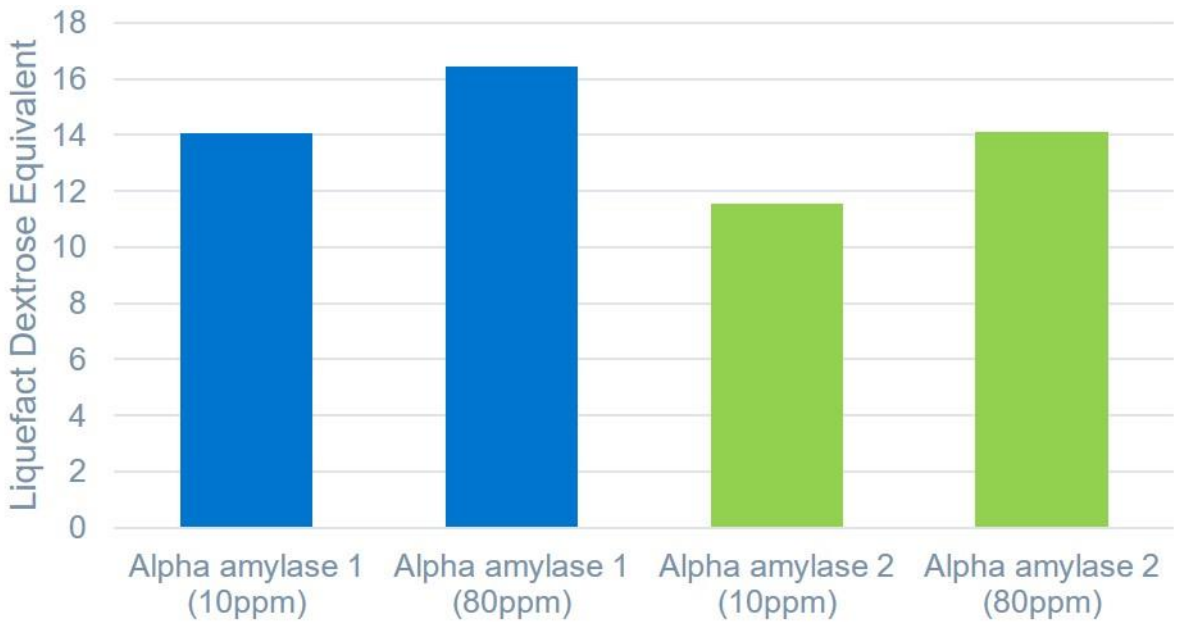
SODIUM EFFECTS ON ALPHA-AMYLASES

- The rate at which alpha amylase breaks down starch can be affected by multiple factors such as - temperature, pH, substrate concentration, enzyme concentration, inhibitors, and sodium concentration
- Ca2+–Na+–Ca2+ triad helps preserve the ordered folding of secondary structures, thereby stabilizing the tertiary structure of the enzyme.



Sihui Pan, Food Chemistry 283 (2019) 170–176

SODIUM EFFECTS ON ALPHA-AMYLASES



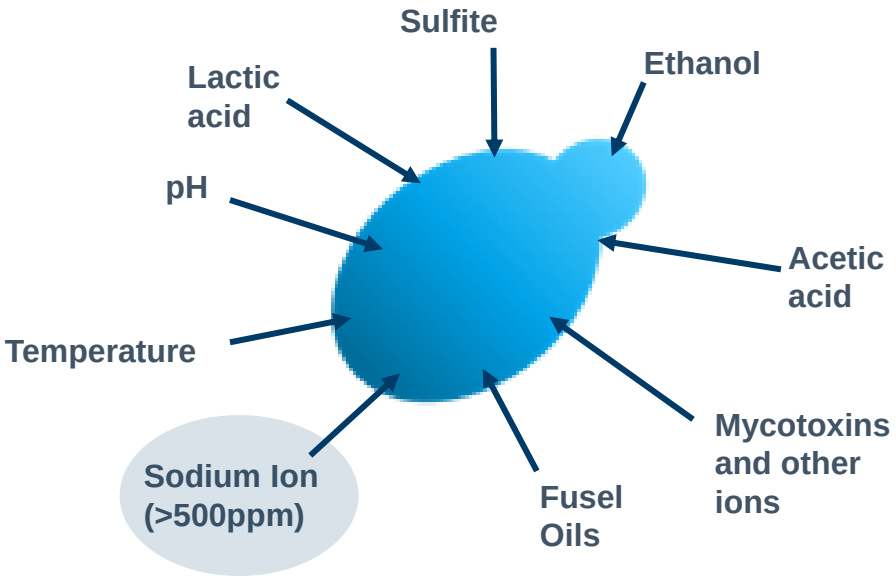
Typical sodium values in slurry:

- ICM-style plant using caustic CIP: ~100ppm
- ICM-style plant not using caustic CIP: ~10-30ppm

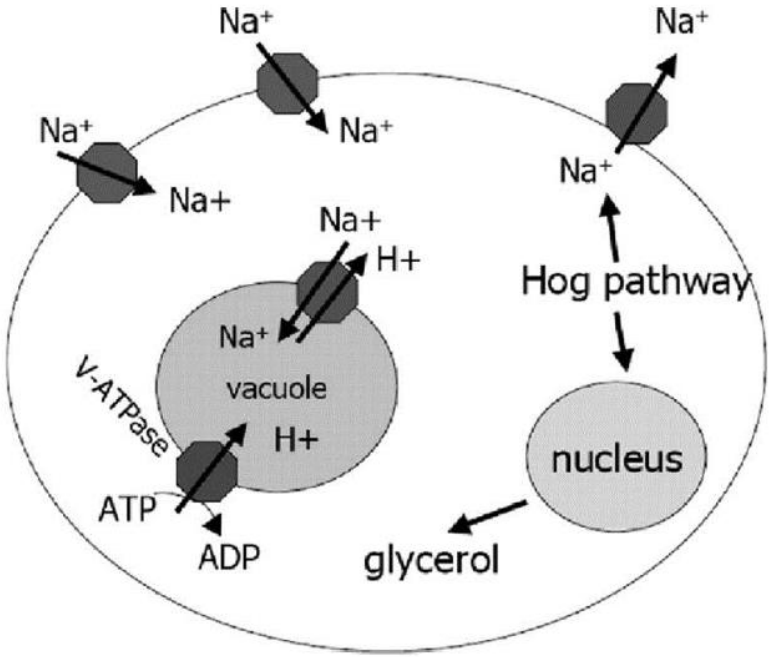
- Delta T-style plant using caustic CIP: ~40ppm
- Delta T-style plant not using caustic CIP: ~10-30ppm

- Depending on the level, sodium can affect liquefying alpha-amylases in the dry grind process
- Some alpha-amylases have been engineered to perform in a variety of conditions

SODIUM EFFECTS ON YEAST



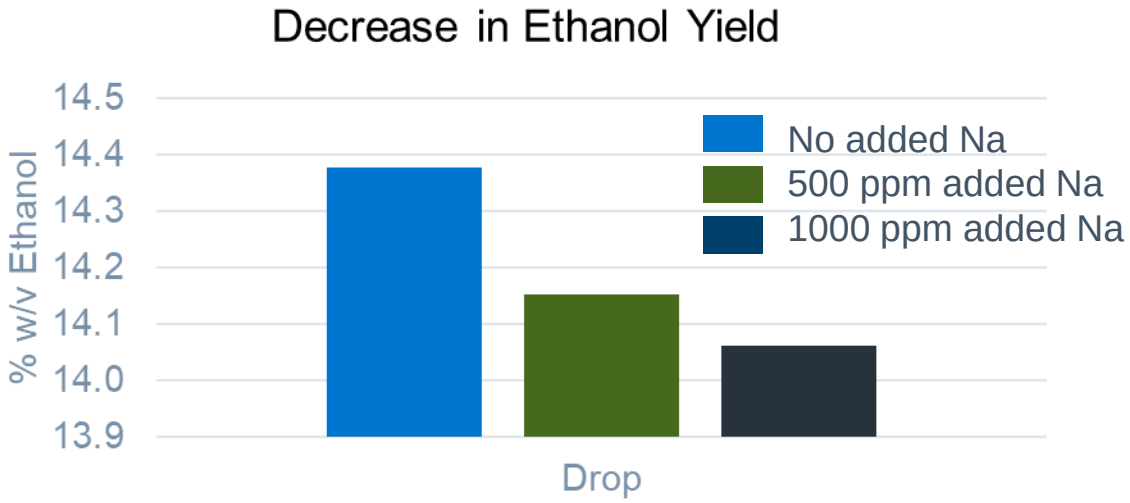
Yeast Stress Factors

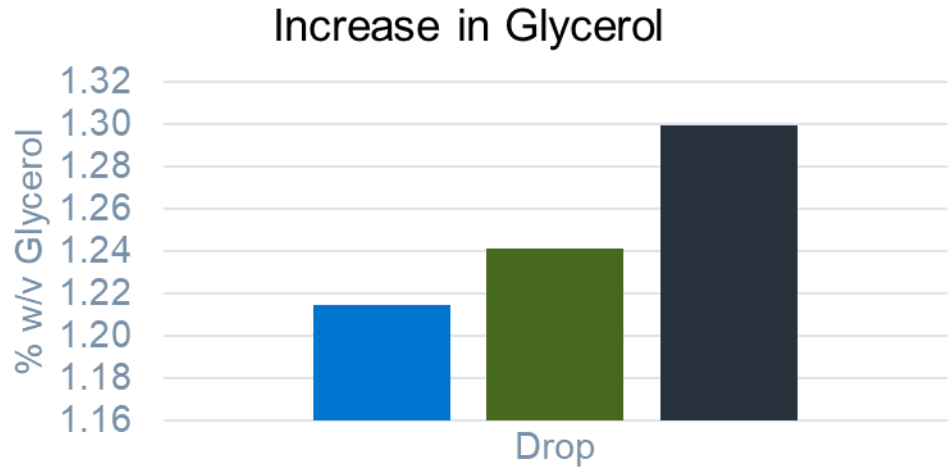


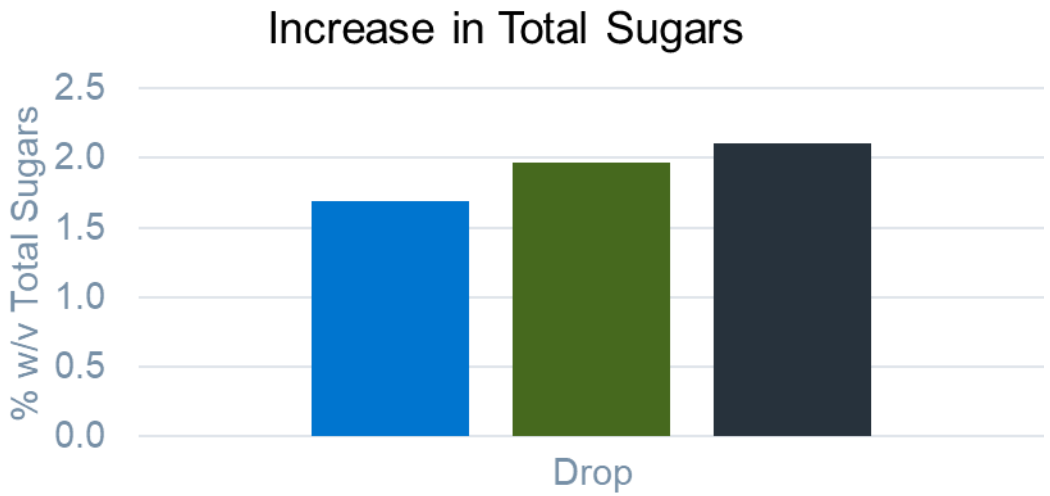
Potential Impacts
- Decrease in ethanol yield
- Decrease in yeast growth rate
- Increase in glycerol

figure adapted from The Alcohol Textbook, 6th Edition
figure from Li SC *et al*. Eukaryot Cell. 2012 Mar;11(3):282-91. doi: 10.1128/EC.05198-11

SODIUM IMPACT ON YEAST – LAB DATA

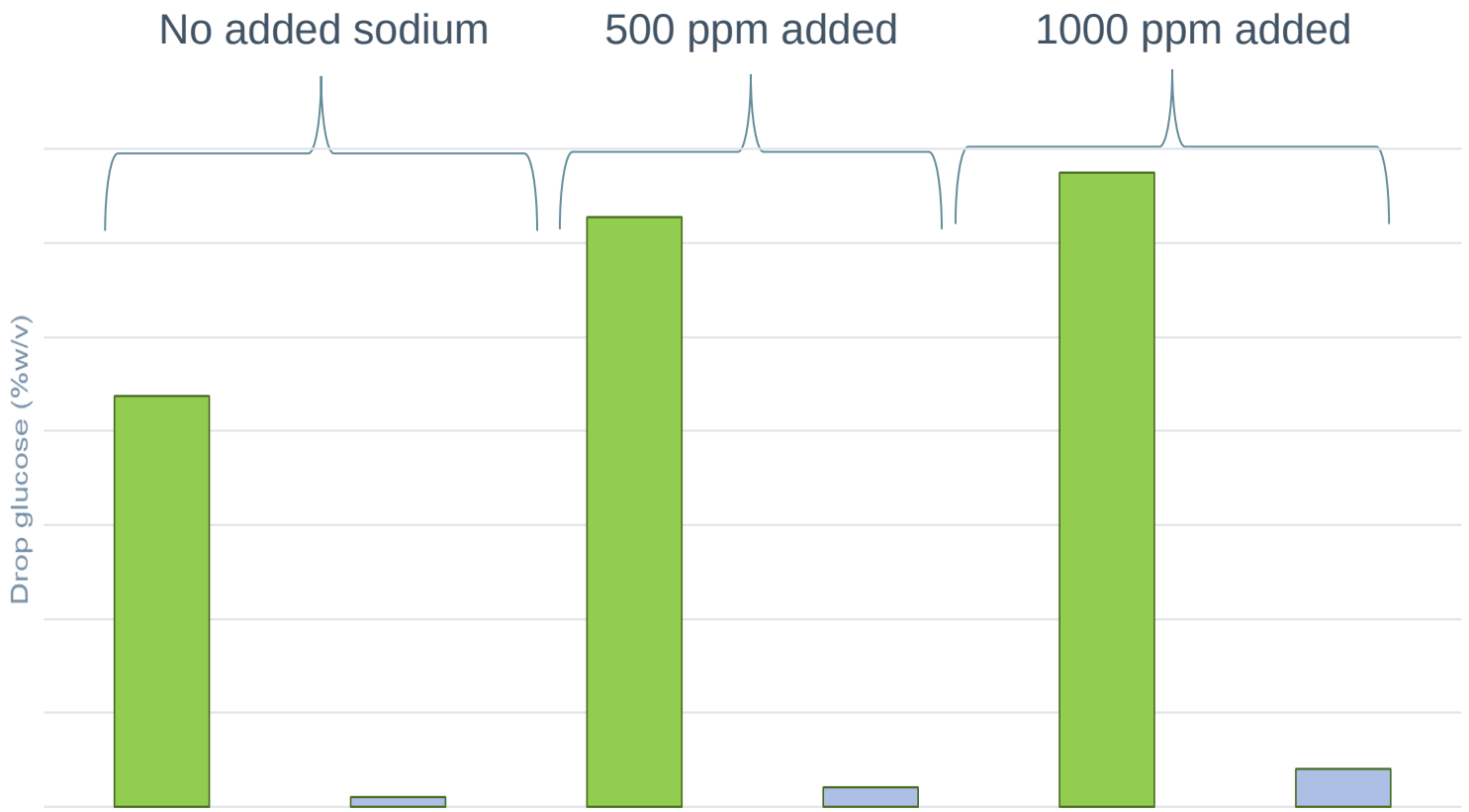






- Depending on the level, sodium can affect yeast performance in the dry grind process
- Some yeasts have been engineered to perform at elevated sodium levels

SODIUM IMPACT ON A VARIETY OF YEASTS



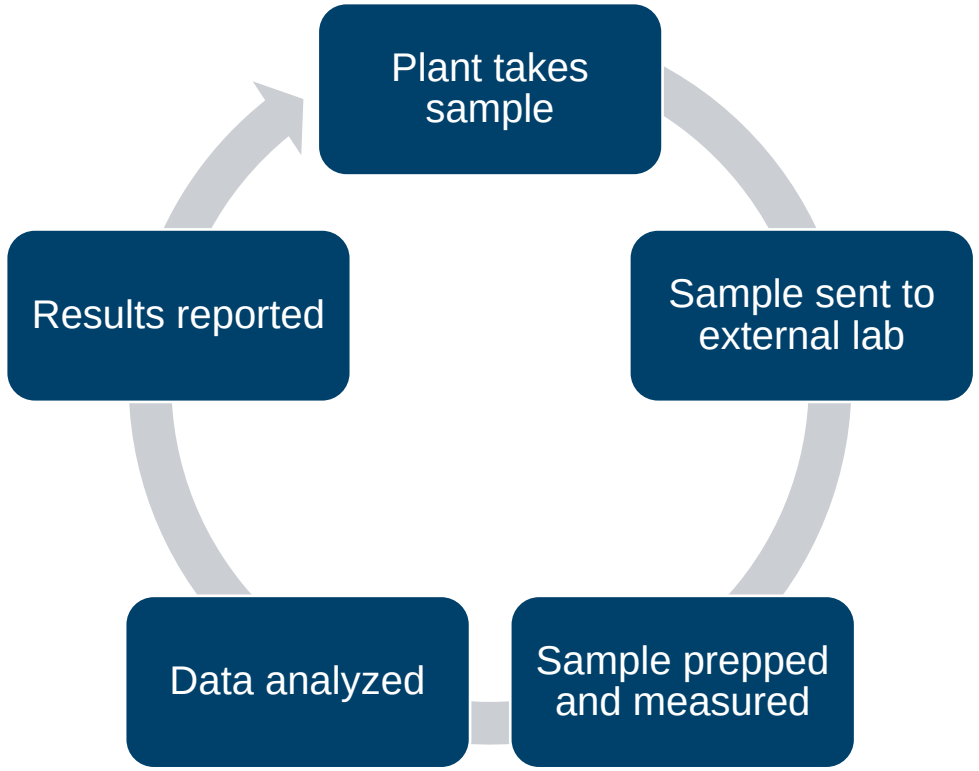
Yeast 1 - Conventional yeast
Yeast 2 – Engineered to be robust

- Some yeasts have been engineered to perform at elevated sodium levels

- Sodium sources and its importance in the dry grind process
- **Sodium probe background and protocol development**
- Case Studies

CHALLENGE AND OPPORTUNITY

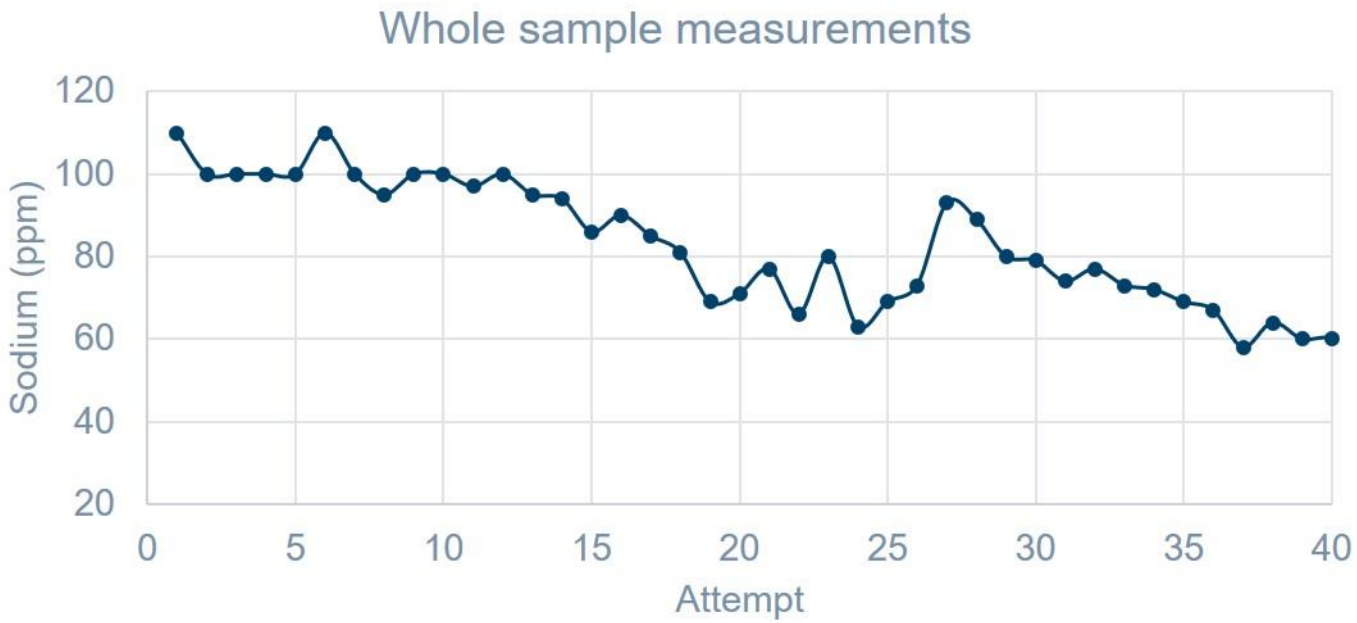
Typical sodium measurement workflow can take days to weeks to obtain results



https://www.horiba.com/en_en/laqua/detail/action/show/Product/laquatwin-na-11-796/
IFF is not affiliated with probe manufacturer

SHORT PROBE LIFESPAN

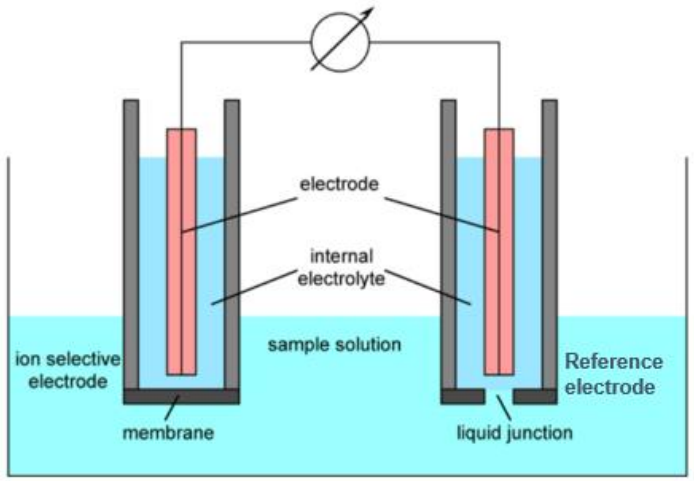
Issue #1



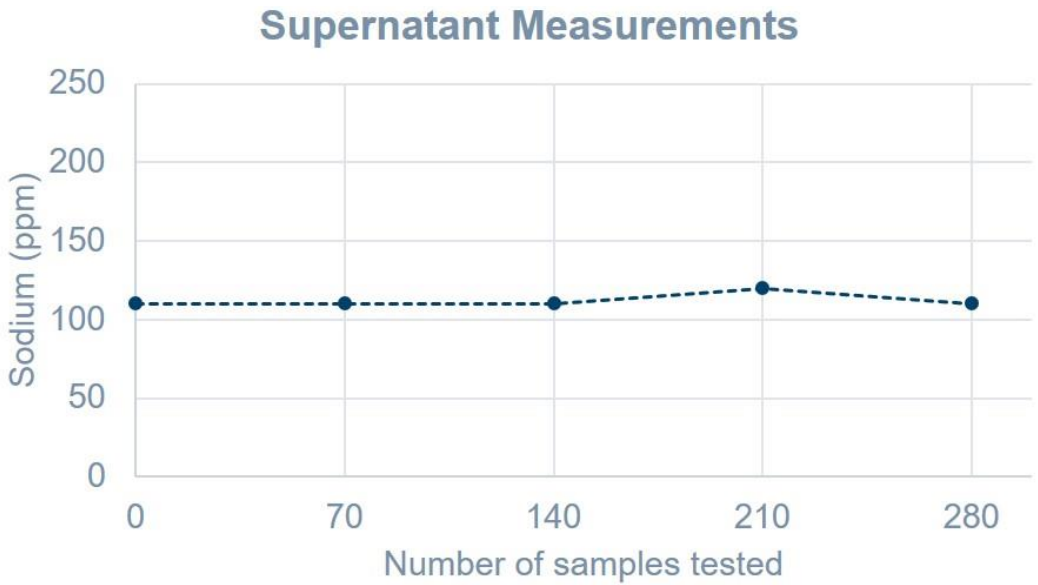
"Error Display" message on probe screen

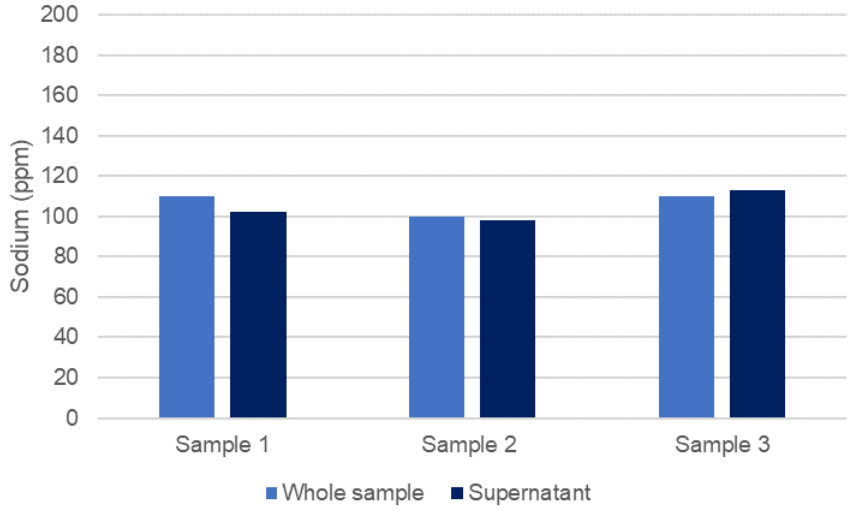
- **Multiple measurements results in drifting values and error over time**
- **Tried extra rinses, fresh standards, etc**

SHORT PROBE LIFESPAN – POSSIBLE CAUSE AND SOLUTION
Issue #1



- **Figured out that probe was fouling from solids in samples**
  - Recommendation: use clarified samples – centrifuge and/or filter

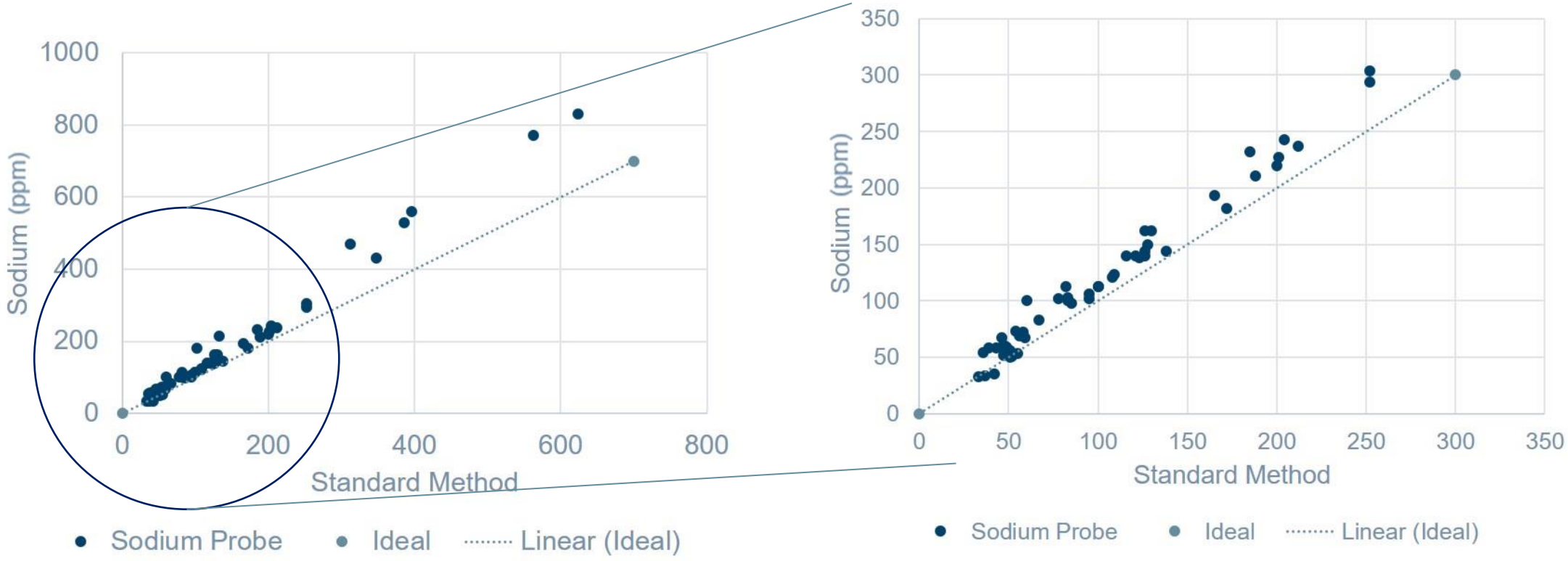




adapted from
/chem.libretexts.org/Bookshelves/Analytical_Chemistry/Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/01%3A_Elemental_Analysis/1.07%3A_Ion_Selective_Electrode_Analysis

ACCURACY

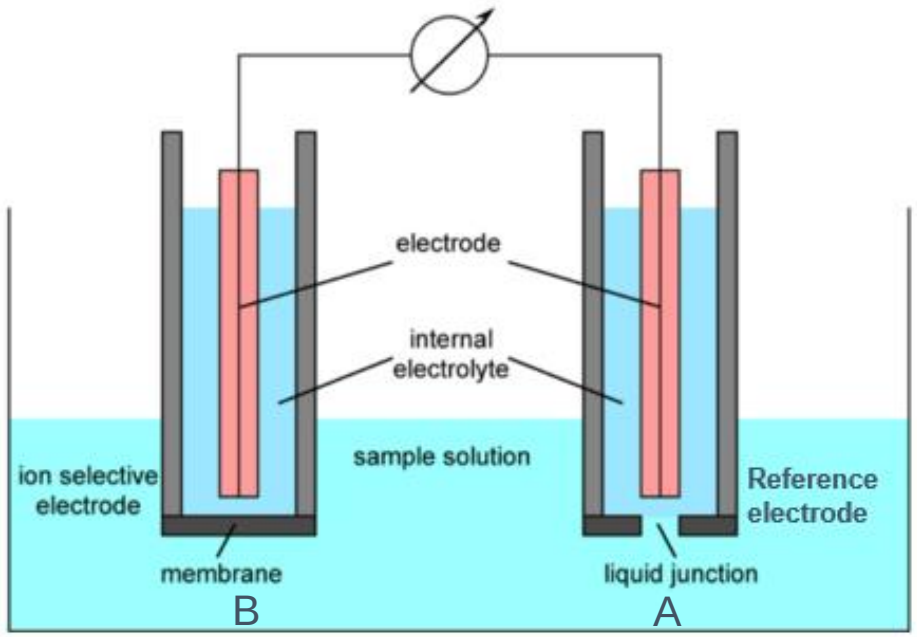
Issue #2

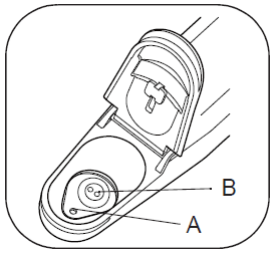


- Sodium probe values are nearly always higher than standard methods (IC, ICP-OES)
- In some cases, the probe values could lead to false positives for fermentation stressors

ACCURACY – POTENTIAL CAUSE

Issue #2





Flat Sensor: This sensor consists of a liquid junction (A) and response membrane (B). Both A and B must be covered with the sample.

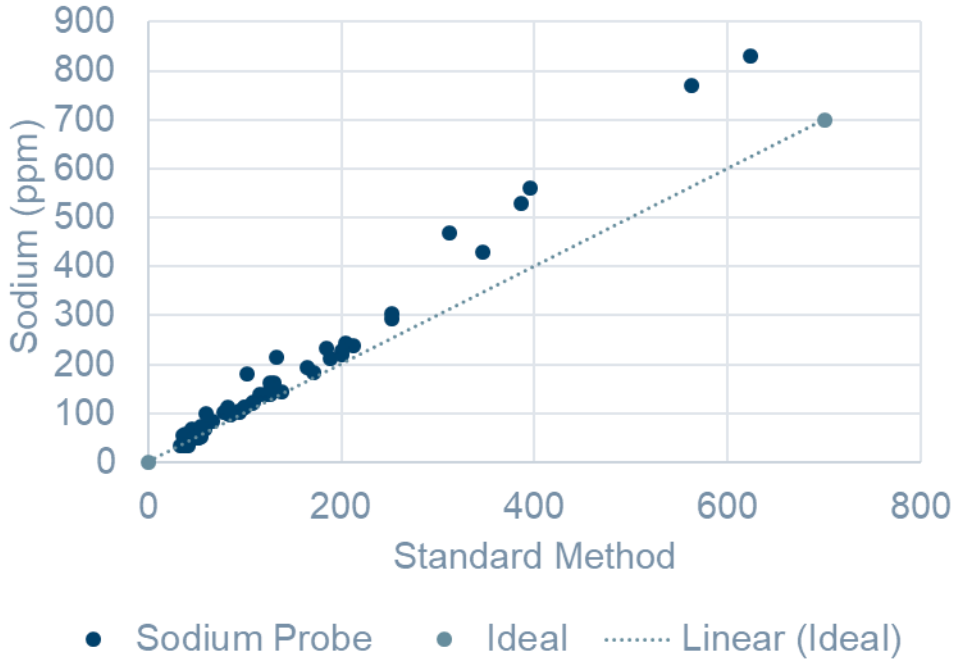
- **Ion selective electrodes can be sensitive to other ions, eg potassium**
- **There are many cations beyond sodium in many dry grind samples.**
  - Eg, slurry typically contains ~2000 ppm potassium, 10-20 ppm Ca, and 400-600 ppm magnesium ions
  - **Selectivity Coefficient (k) describes how the interfering ion affects the sodium measurement**

HORIBA LAQUAtwin Na+ B-722, Manual code – GZ0000297060

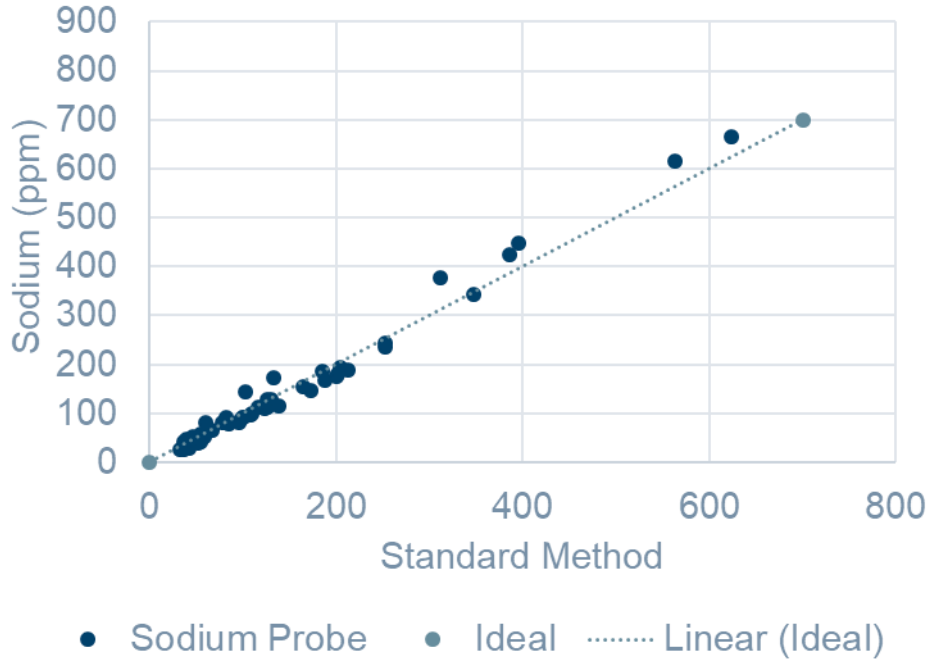
figure adapted from https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/01%3A_Elemental_Analysis/1.07%3A_Ion_Selective_Electrode_Analysis

ACCURACY – SOLUTION

Issue #2



Correction

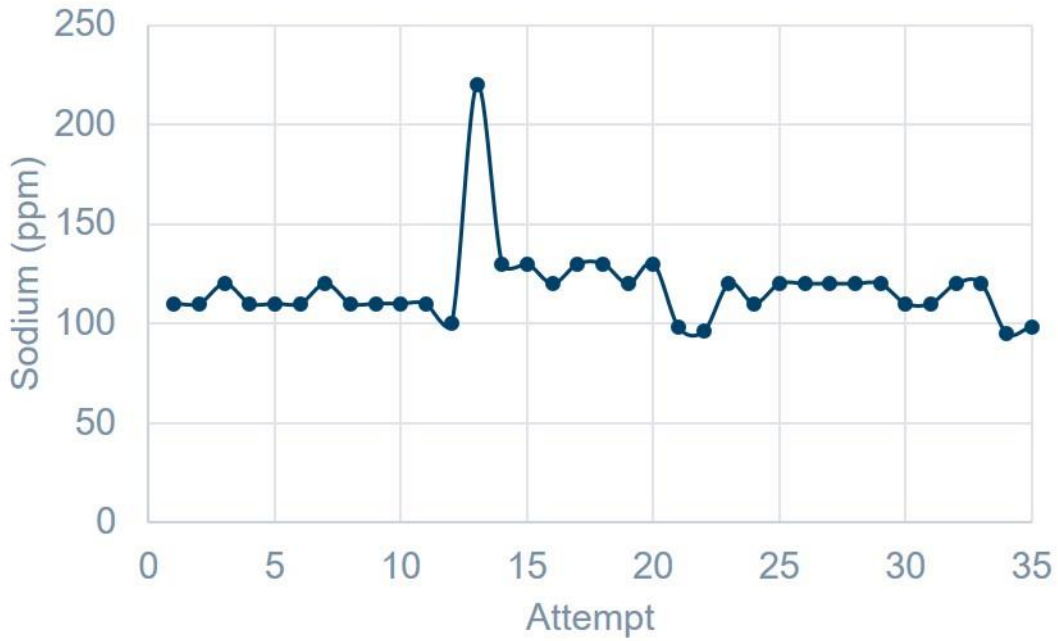


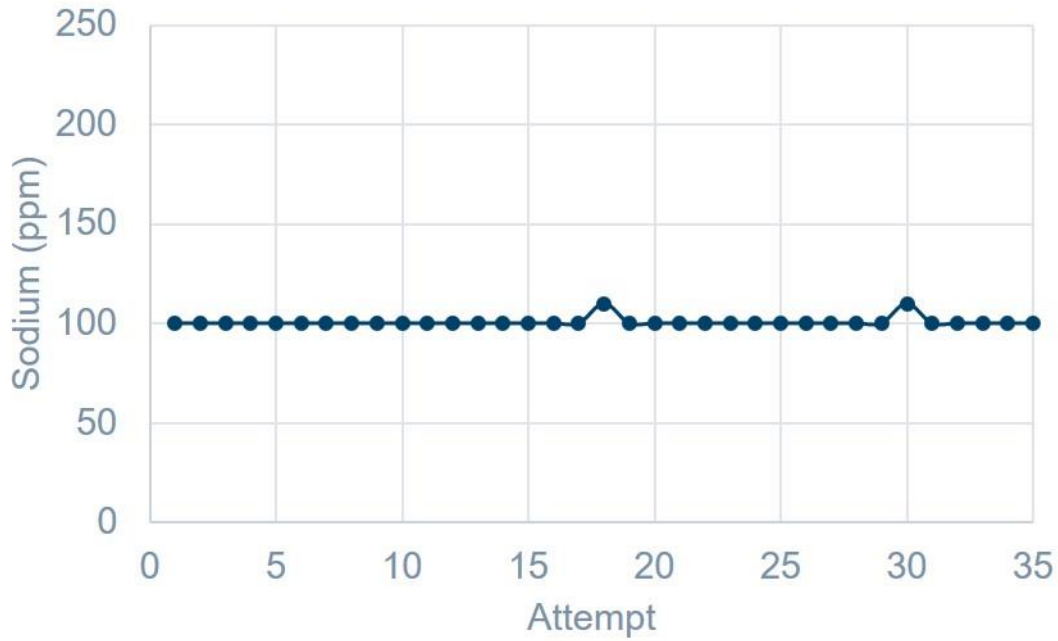
- **To address accuracy, we measured sodium values in many samples using the probe and standard methods (IC, ICP-OES)**
- **Tried different ways of correcting and came up with a correction strategy**
- **Correction strategy is simple and works well in most cases for relevant sample types across plants**

DRIFTING

Issue #3

- **After measuring multiple samples the probe values starts to drift**
- **This may not be obvious if measuring a variety of samples in the plant**
- **Solution: periodic recalibration**

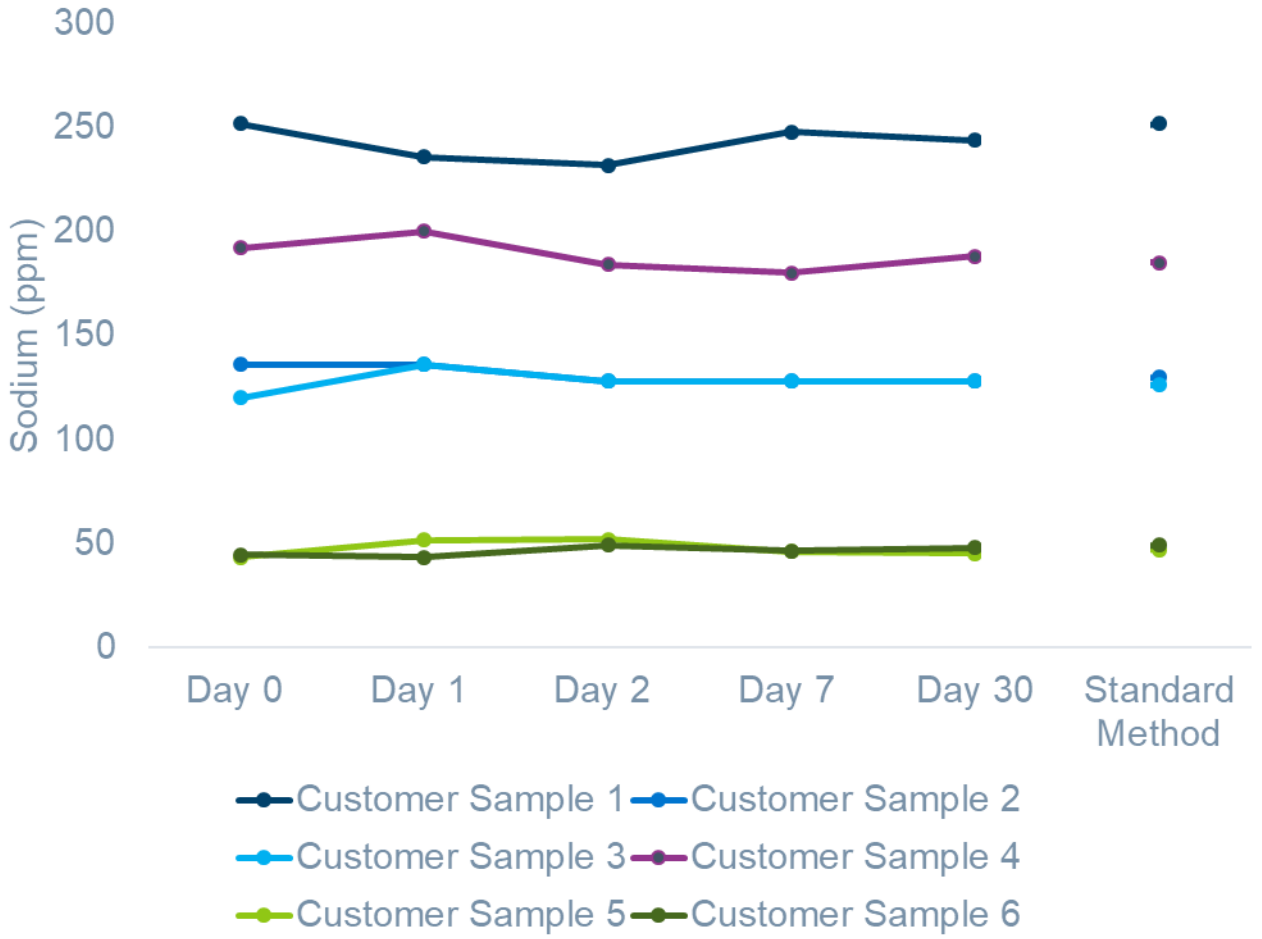




PUTTING IT ALL TOGETHER

Fouling, accuracy and drifting issues resolved

- **With our protocol, the probe is accurate, stable, and lasts a long time**
- **We have validated it on a variety of samples from a variety of ethanol plants**



- Sodium sources and its importance in the dry grind process
- Sodium probe background and protocol development
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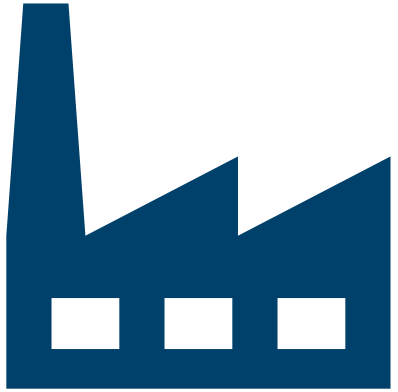
SODIUM MAPPING DURING ACID CIP TRIAL

Case Study #1

- **Background:**
- An ethanol plant wanted to start an acid CIP trial.
- The plant was concerned about not having the optimum sodium concentration for alpha-amylase performance as sodium levels would be reduced in the plant.

- **Plan:**
- The IFF Tech Service Account Manager set up a sampling plan to measure sodium concentrations so that if levels got too low, the plant would not be surprised with impacts to alpha-amylase performance
- Liquefact, backset, and other relevant process streams were measured onsite with the sodium probe before, during, and after the trial

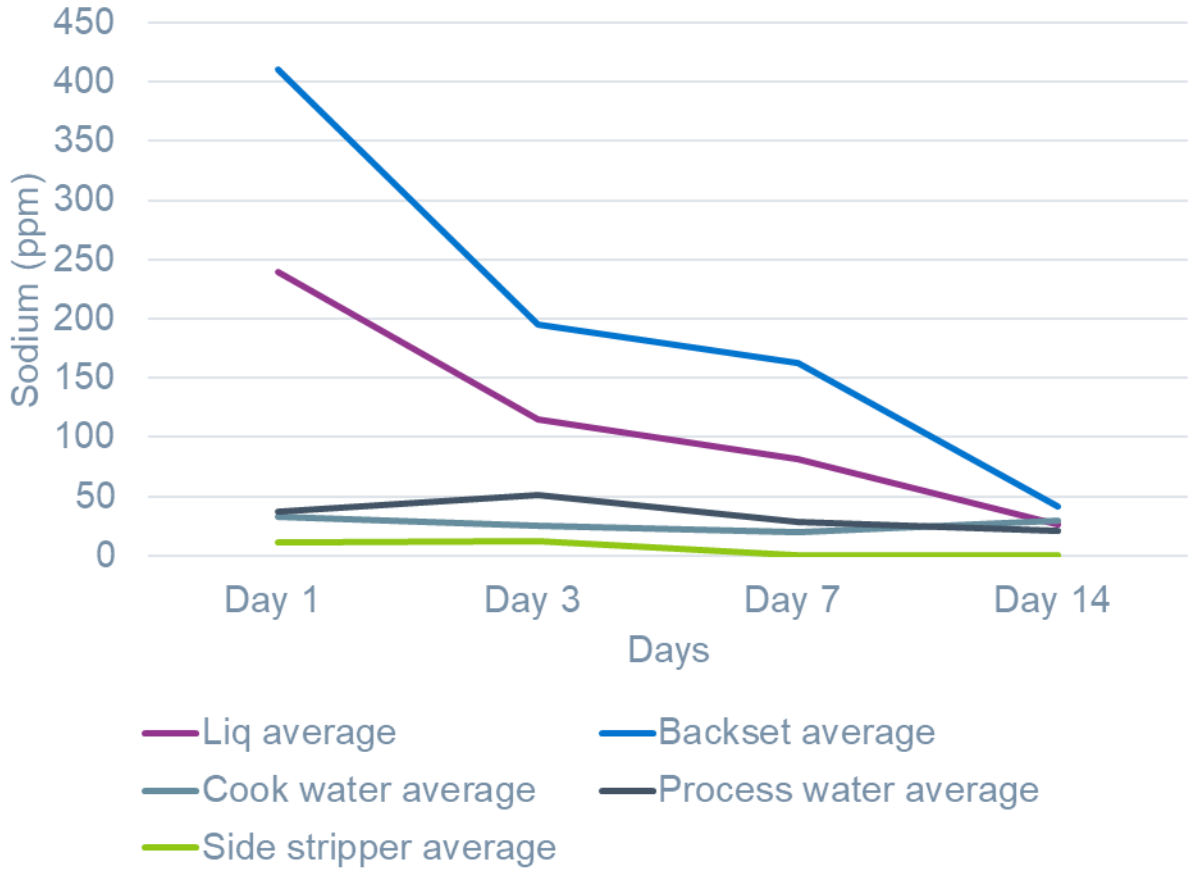


Caustic CIP

Acid CIP

SODIUM MAPPING DURING ACID CIP TRIAL

Case Study #1



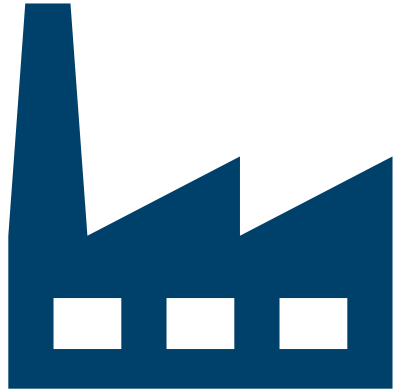
- **Sodium cycled down quickly**
- **However, the final sodium levels in the liquefact were sufficient for the alpha-amylase and no issues were observed**
- **Plant uses bleach in their fresh water and we could measure the sodium that this provided**
- **Understanding the water treatment and what water feeds the cook area are all critical to finding the right sample set to collect/test**
- **Handheld sodium probe was very helpful in keeping track of sodium concentration in real time to potentially identify issues early**

DIAGNOSING A CAUSTIC LEAK

Case Study #2

- **Background:**
- Ethanol plant noticed their caustic tank level dropping over time
- Suspected a leak but did not know the location

- **Plan:**
- The IFF Tech Service Account Manager brought his sodium probe to the plant and conducted a detailed sodium mapping across the plant on two different days to find the source of the leak



Caustic Tank Level Dropping

Leak?

DIAGNOSING A CAUSTIC LEAK

Case Study #2

SUMMARY

- **We think this sodium probe is a simple, effective, and inexpensive way to measure sodium in your plant**
- **We developed a Standard Operating Procedure that incorporates the findings presented here and are happy to share it with plants. Talk to your Technical Service Account Manager or Sales Account Manager for details.**
- **Please stop by the IFF booth for goodies and a chance to win a sodium probe**
  - Booth #27

HORIBA LAQUAtwin Na-11

https://www.horiba.com/en_en/laqua/detail/action/show/Product/laquatwin-na-11-796/
IFF is not affiliated with probe manufacturer

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