

OPTIMIZING OXIDATION TECHNIQUES:

MEASURING NUTRIENT CONCENTRATIONS IN SURFACE SEAWATER

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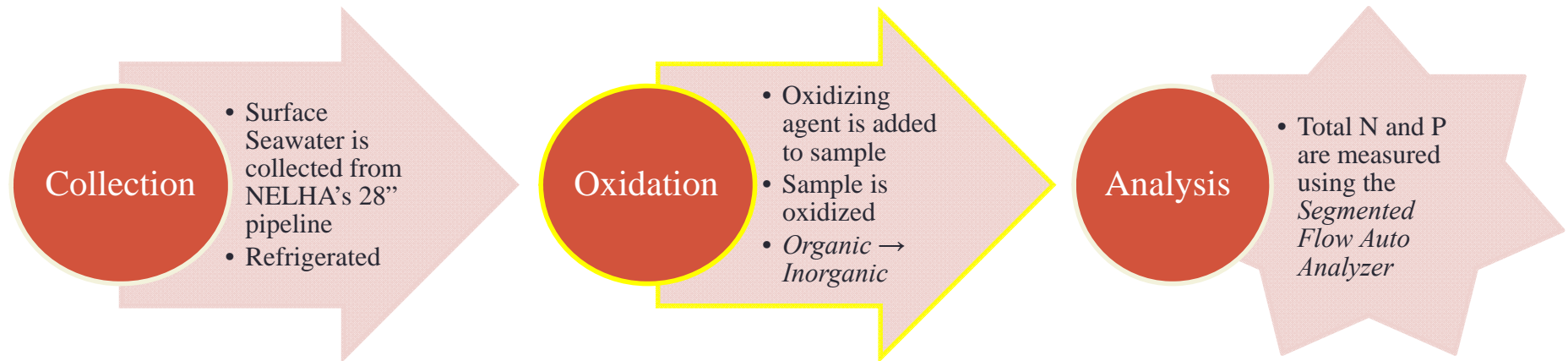
PURPOSE

- Are NELHA businesses affecting water quality?
 - 23 Commercial Aquaculture, Mariculture, pharmaceutical, and Renewable Energy Companies
 - Increasing nutrient levels?
 - EPA and DOH Standards
- To develop a standard operating procedure for oxidation using potassium persulfate to convert *organic* materials into measurable *inorganic* materials in water samples
 - **Nitrogen and Phosphorus**
- Parameters
 - Time-efficiency, cost-efficiency, **accuracy**



NUTRIENT ANALYSIS IN THE LAB

- How do we measure nitrogen and phosphorus concentrations?



WHAT IS OXIDATION?

- Converts *organic* nitrogen and phosphorus → *inorganic* nitrogen and phosphorus
- Excess oxygen in Oxidizing Agent + Catalyst
 - hydrogen peroxide (H_2O_2) and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$)

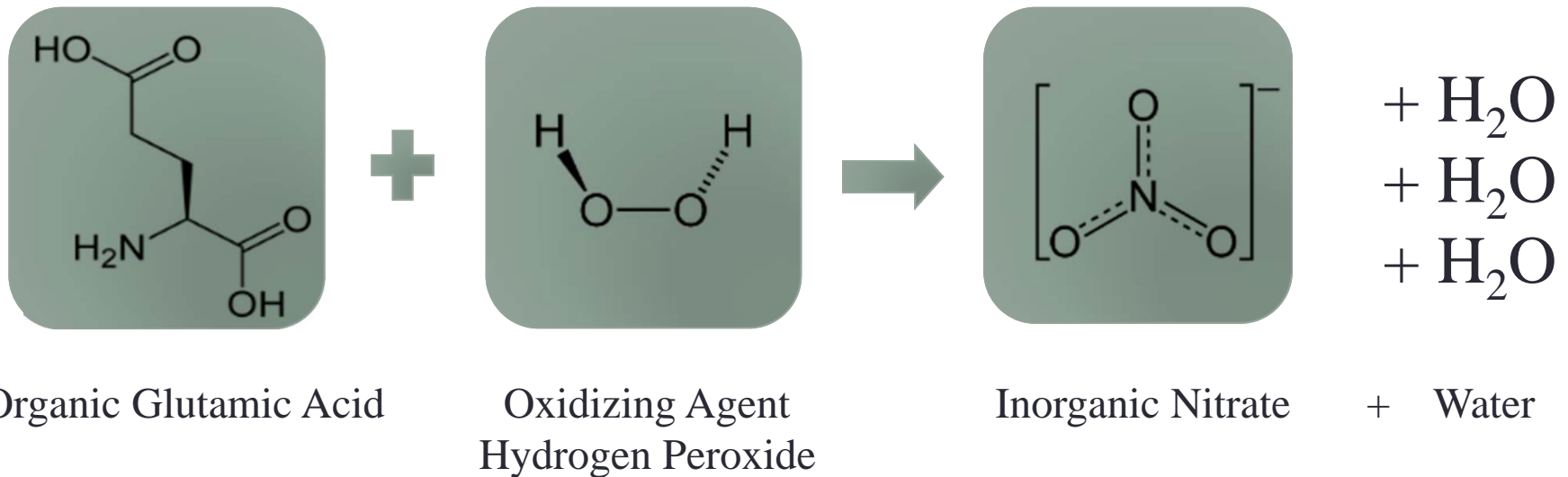
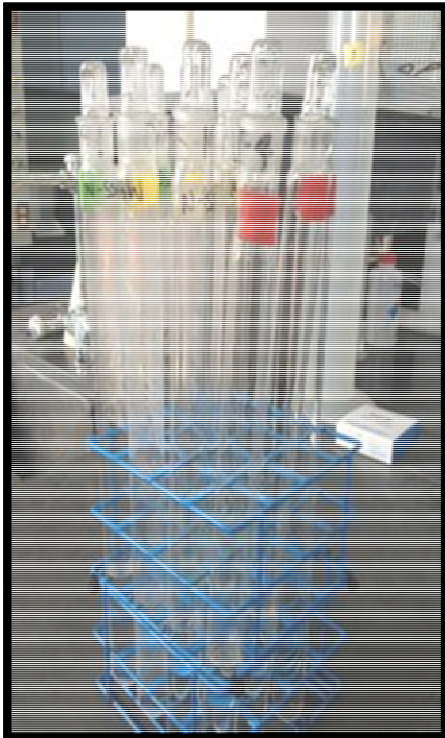


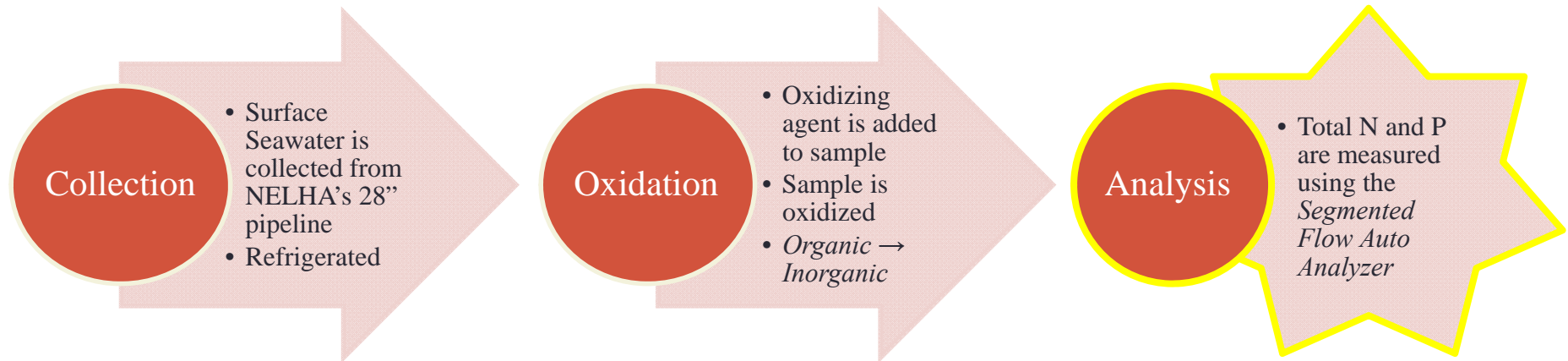
PHOTO OXIDIZER



- UV radiation initializes reaction

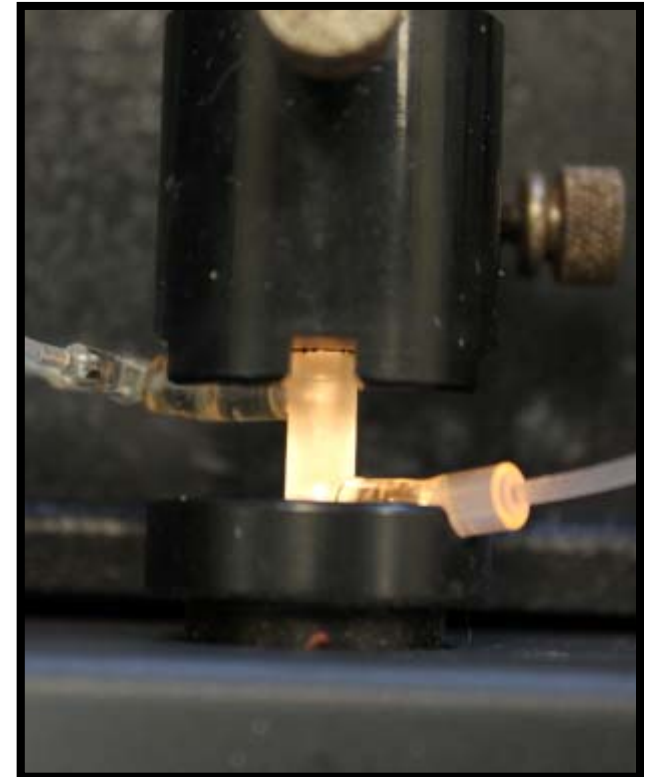
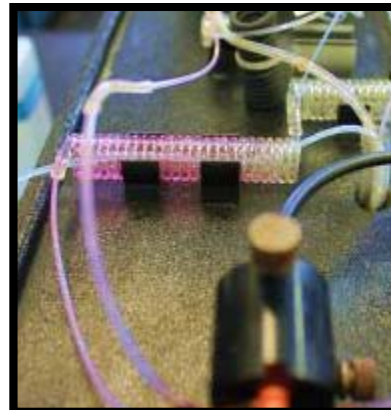
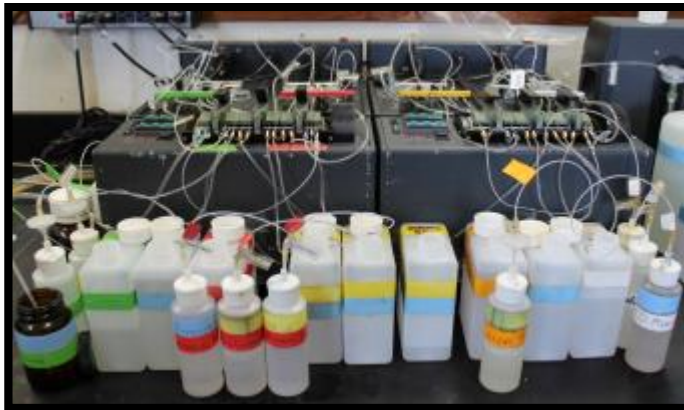
NUTRIENT ANALYSIS IN THE LAB

- How do we measure nitrogen and phosphorus concentrations?



SEGMENTED FLOW AUTO-ANALYZER

- Evaluates nutrient concentrations by measuring the absorbance of solutions in sample cell



- Limitations:
 - Human Error (bubbles in sample chamber)
 - Measuring extremely small concentrations (ppb)

OPTIMIZATION

- Oxidation Reagent:
 - Traditional NELHA Hydrogen Peroxide
 - *NELHA Method, 1982*
 - Potassium Persulfate Forms
 - *Lachat Method, 2002*
 - *Elsevier Marine Chemistry, Bronk, et al, 1999*
 - *U.S.G.S. National Water Quality Lab, 2003*
 - *Standard Methods 18th edition, 1992*
- Oxidation Time:
 - Length of time samples are in oxidation chamber
 - Traditional 2.5 Hours
 - 1-4 Hours

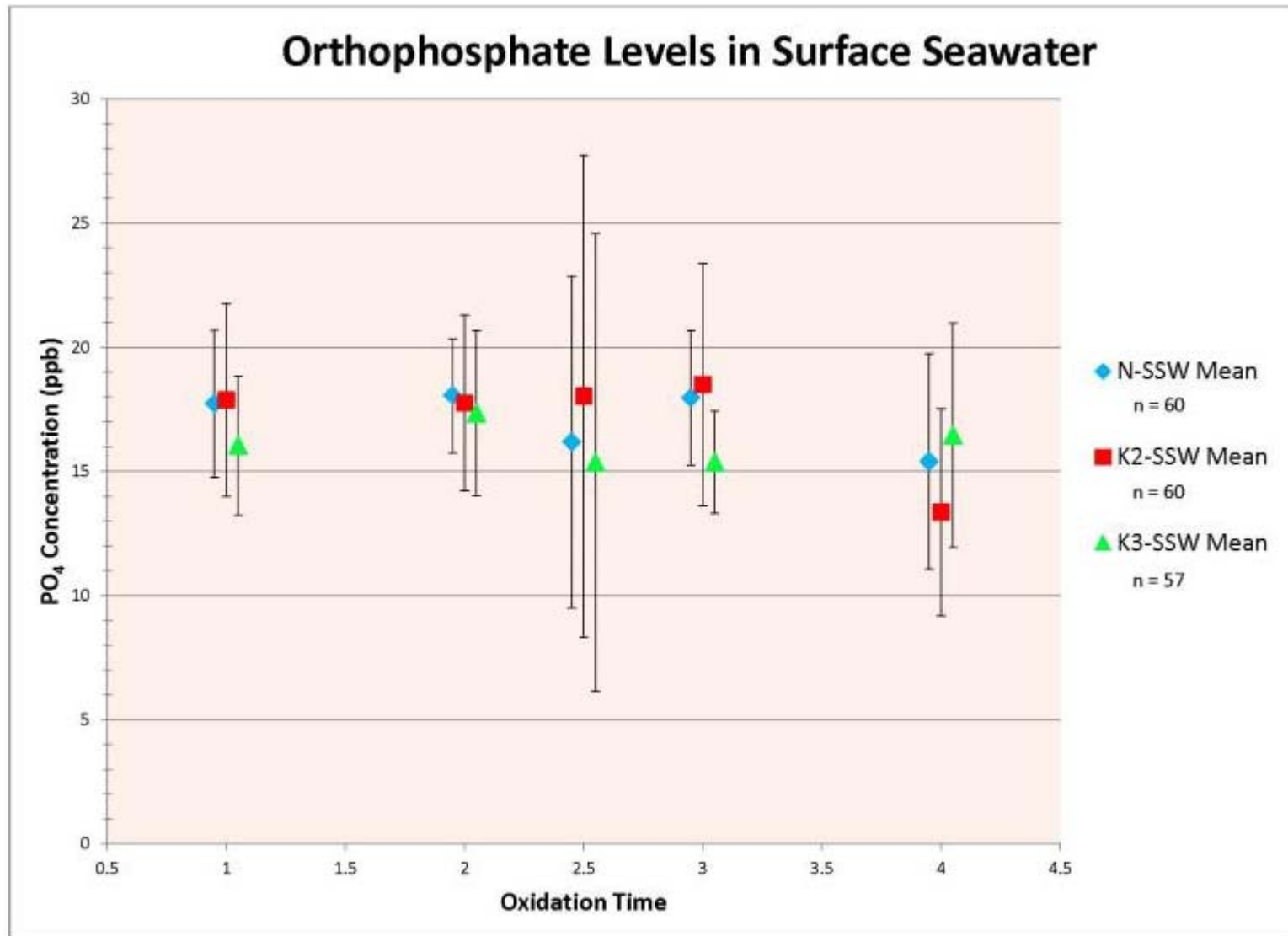


SCOPING STUDIES 2.5 HOUR OXIDATION TIME

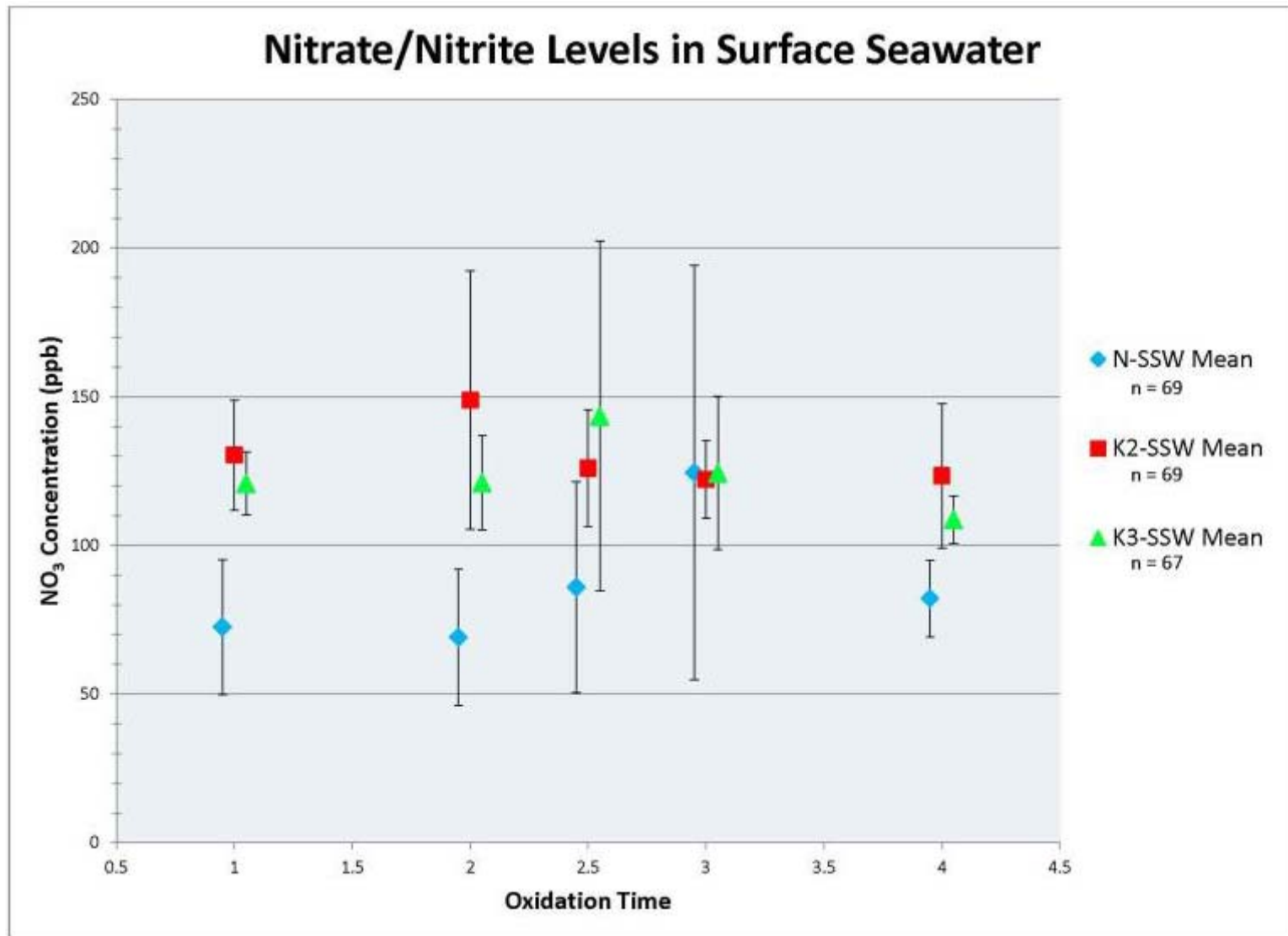
Oxidizing Agent	PO ₄ Mean	NO ₃ Mean	Std Dev PO ₄	Std Dev NO ₃	# of Samples
NELHA Method	16.2	86	6.7	35.4	12
Lachat Method	15.4	143.5	9.2	15.8	12
Elsevier Marine Chem.	18.0	126.0	9.7	19.6	12
U.S.G.S.	19.7	175.3	1.3	34.8	6
Standard Methods	39.4	5.9	2.2	0	6

HISTORIC NELHA DATA: n = 863
 Mean NO₃ 73.3 ppb ± 19.3
 Mean PO₄ 11.1 ppb ± 3.2

RESULTS



RESULTS



GLYCINE SPIKE

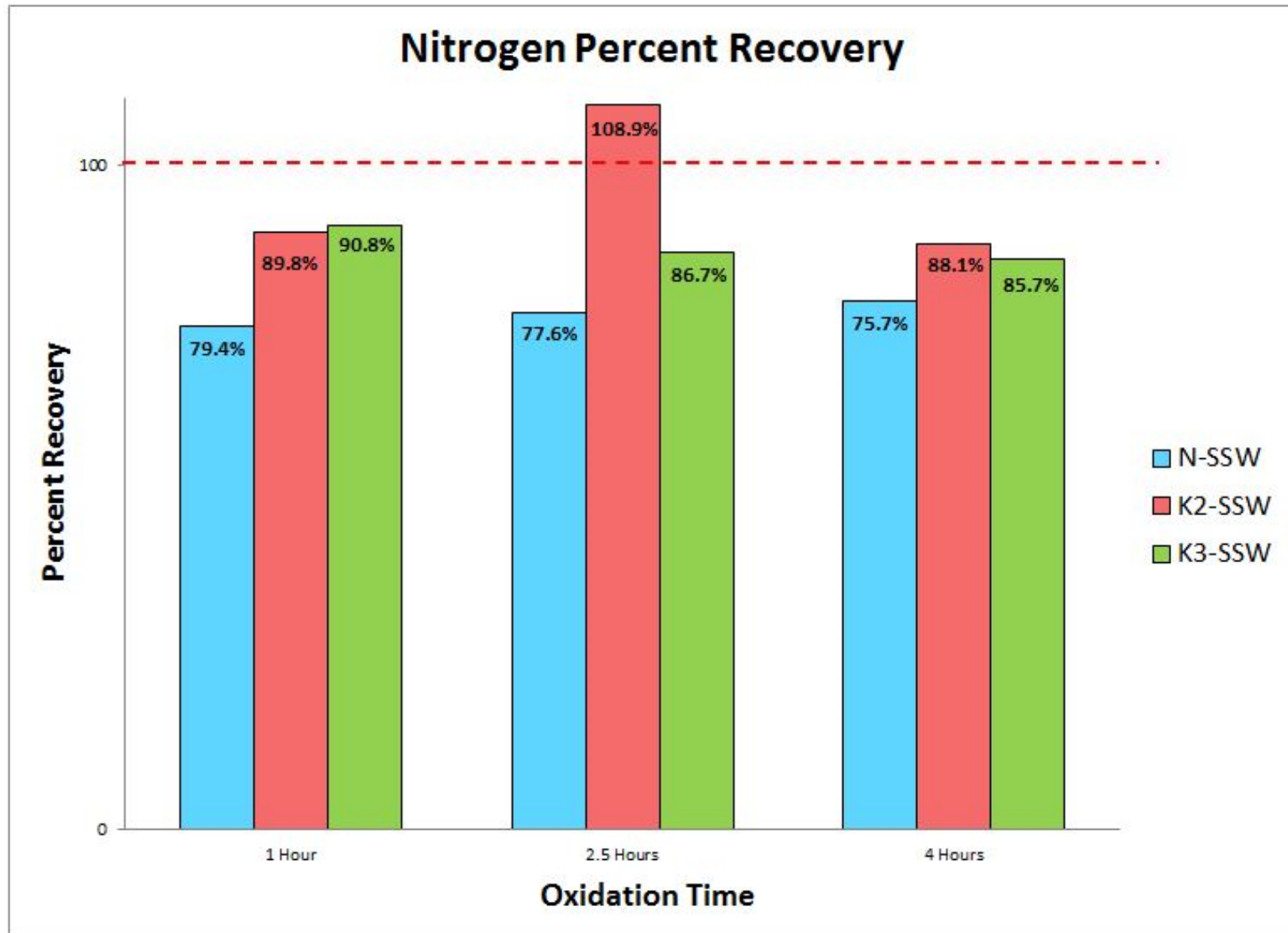
- Use glycine to increase the *organic* nitrogen concentration by 100 ppb
 - Measure a **percent recovery**

$$= \frac{\text{Measured Value for Spiked Sample}}{\text{Measured Value for Unspiked Sample} + \text{Amount of spike}}$$

$$= \frac{\text{What you found in spiked sample}}{\text{What you would expect to find}}$$



GLYCINE SPIKE



CONCLUSION

- **Lachat method** potassium persulfate method yielded
 - Reagent preparation time of less than 20 minutes
 - Up to 100 samples processed per reagent preparation
 - Similar results for phosphorus to hydrogen peroxide method
 - 17.7 ppb hydrogen peroxide, 16.1 ppb potassium persulfate
 - Reduced oxidation time with similar results
 - 1 hour vs. traditional 2.5 hours with hydrogen peroxide
 - Increased accuracy when spiked with a known quantity of glycine
 - Percent recovery 90.8% at 1 hour

FUTURE WORK

- Implementing the recommended change to potassium persulfate
 - Increase accuracy
 - Increase time-efficiency
- Further research
 - Optimizing glycine as nitrogen internal standard
 - Developing a phosphorus internal standard



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