A Rigorous Metrological Basis for Seawater pH

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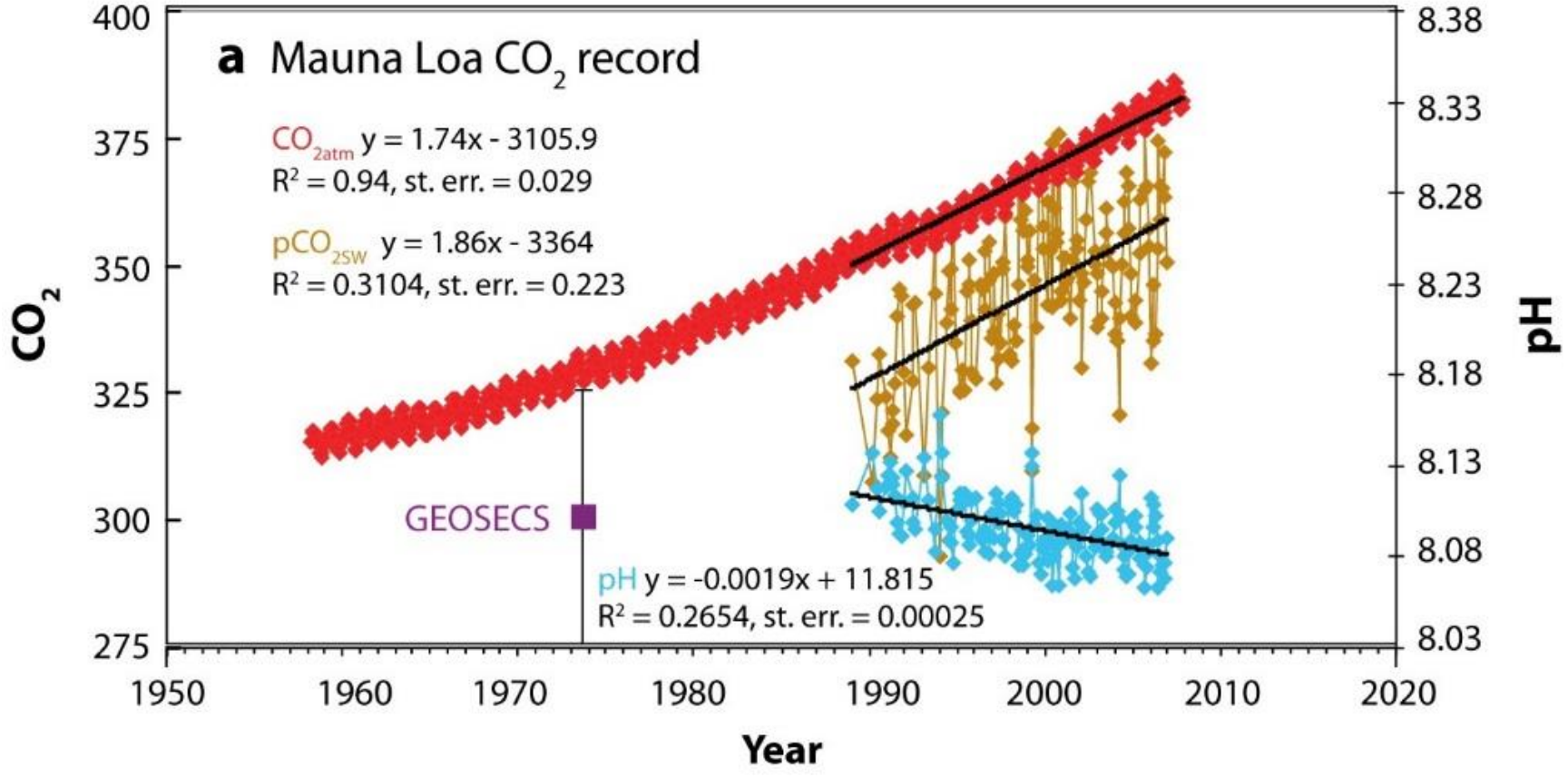
"The Other CO_2 Problem"



Doney SC, et al. 2009.
Annu. Rev. Mar. Sci. 1:169–92

Image: Doney et al., *Annual Review of Marine Science*, 2009

Current state of SW pH:

1. Multiple definitions of “pH” are applied to seawater

2. Only one SW pH CRM is available – no multi-point calibrations

3. Secondary measurement is precise, but requires purification of reagents and suffers from poor traceability to the primary method

Current state of SW pH:
Multiple SW pH definitions

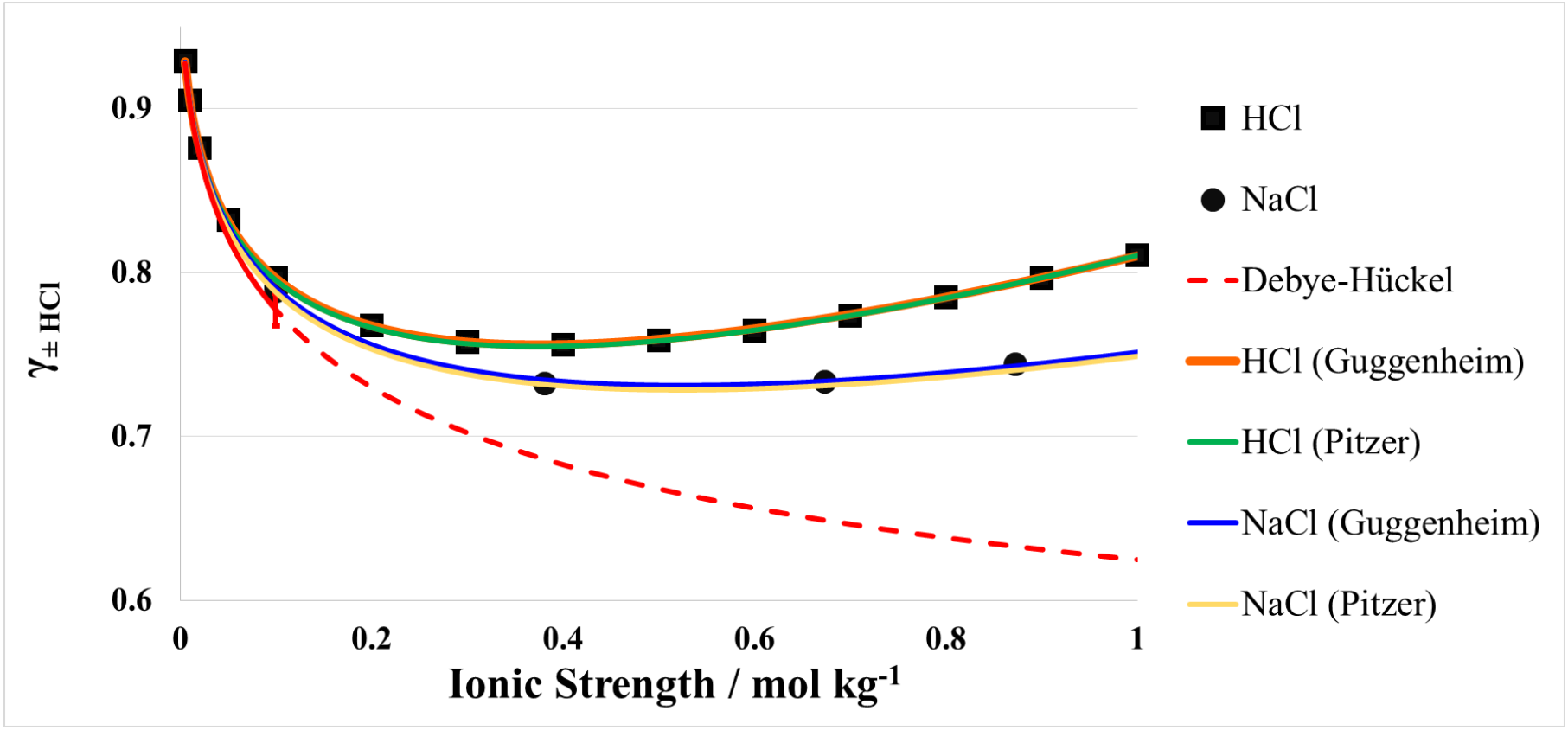
Multiple SW pH definitions yield a pH range >50X greater than 0.002 pH unit target uncertainty for climate change studies.

pH scale	Definition of "pH"	Ionic Strength / mol kg^{-1}	"pH" value
NIST SRMs	$-\log_{10} a(H^+)$	< 0.1	8.332
Free	$-\log_{10} c(H^+)$	0.4 – 0.9	8.195
Total	$-\log_{10} \Sigma[c(H^+) + c(HSO_4^-)]$	0.4 – 0.9	8.087
Seawater	$-\log_{10} \Sigma[c(H^+) + c(HSO_4^-) + c(HF)]$	0.4 – 0.9	8.078

NIST research:

Activity coefficients at higher ionic strength

$$pH_{SRM} = -\log a_H \gamma_{Cl}^{\circ} + \log \gamma_{Cl}^{\circ}$$



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Current state of SW pH:

Single point calibration

Certificate of Analysis

pH reference material (tris buffer in synthetic seawater)

Batch 10 (Bottled on August 3, 2011)

Analysis Results

The pH

$$pH = -\log_{10}\left(\frac{[H^+]}{\text{mol kg-soln}^{-1}}\right)$$

was determined on the total hydrogen ion scale using a hydrogen / silver – silver chloride cell (DelValls & Dickson, 1998). Two separate samples were measured in triplicate, on two different dates

The pH estimated was 8.0924 ± 0.0004 (6; 2)

The cited uncertainty represents the standard deviation. Figures in parentheses are the number of analyses made (total number of analyses; number of separate bottles analyzed).

Estimated Overall Uncertainty

Although the measurements are capable of high precision, the overall uncertainty will be significantly greater. We are working to understand this value better, but presently expect it to be of the order of 0.004 in pH.

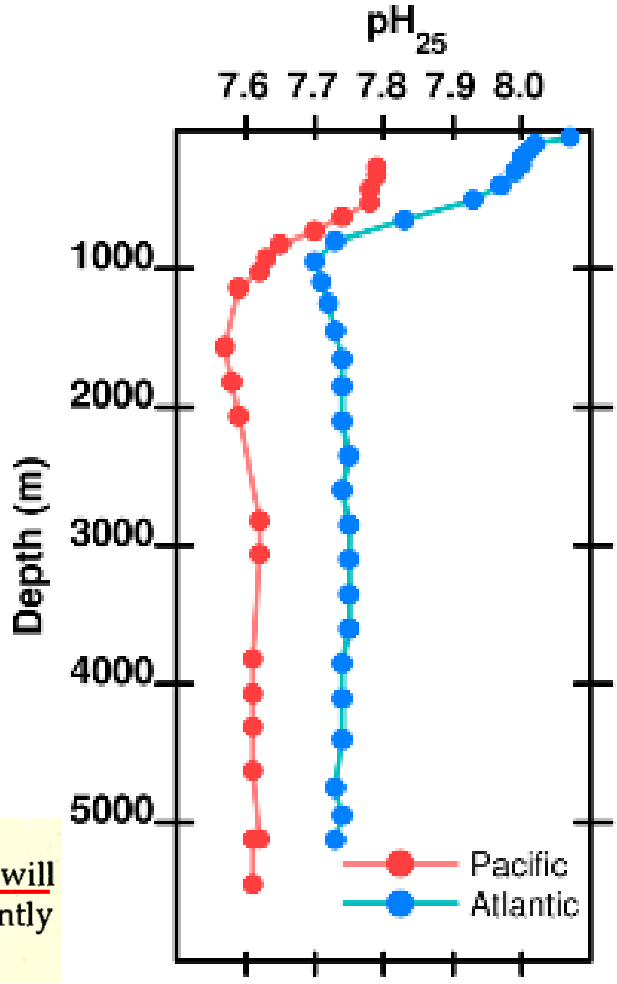


Image: noaa.gov

NIST research:

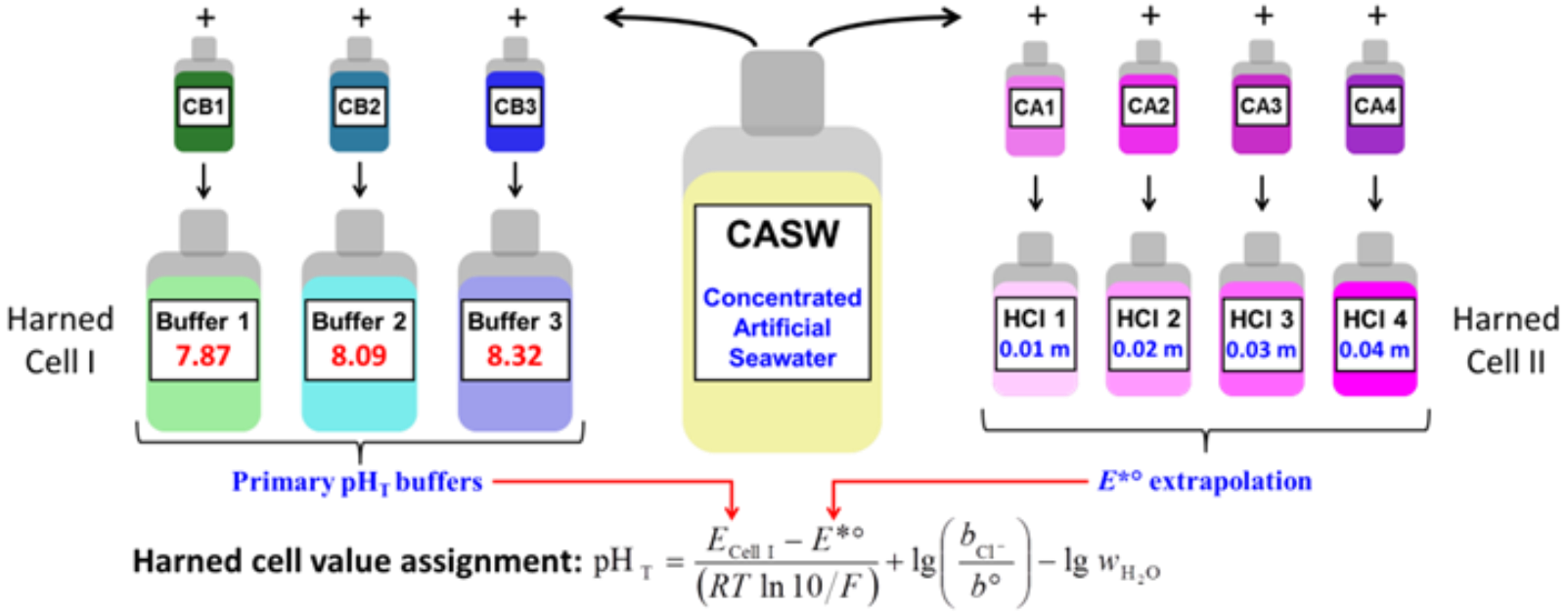
Development of buffers for multi-point calibrations

1. Multi-point pH calibration
2. GUM compliant *U*

Marine Chemistry
Volume 162, 20 May 2014, Pages 89–95

Measurement of pH_T values of Tris buffers in artificial seawater at varying mole ratios of Tris:Tris·HCl

Kenneth W. Pratt



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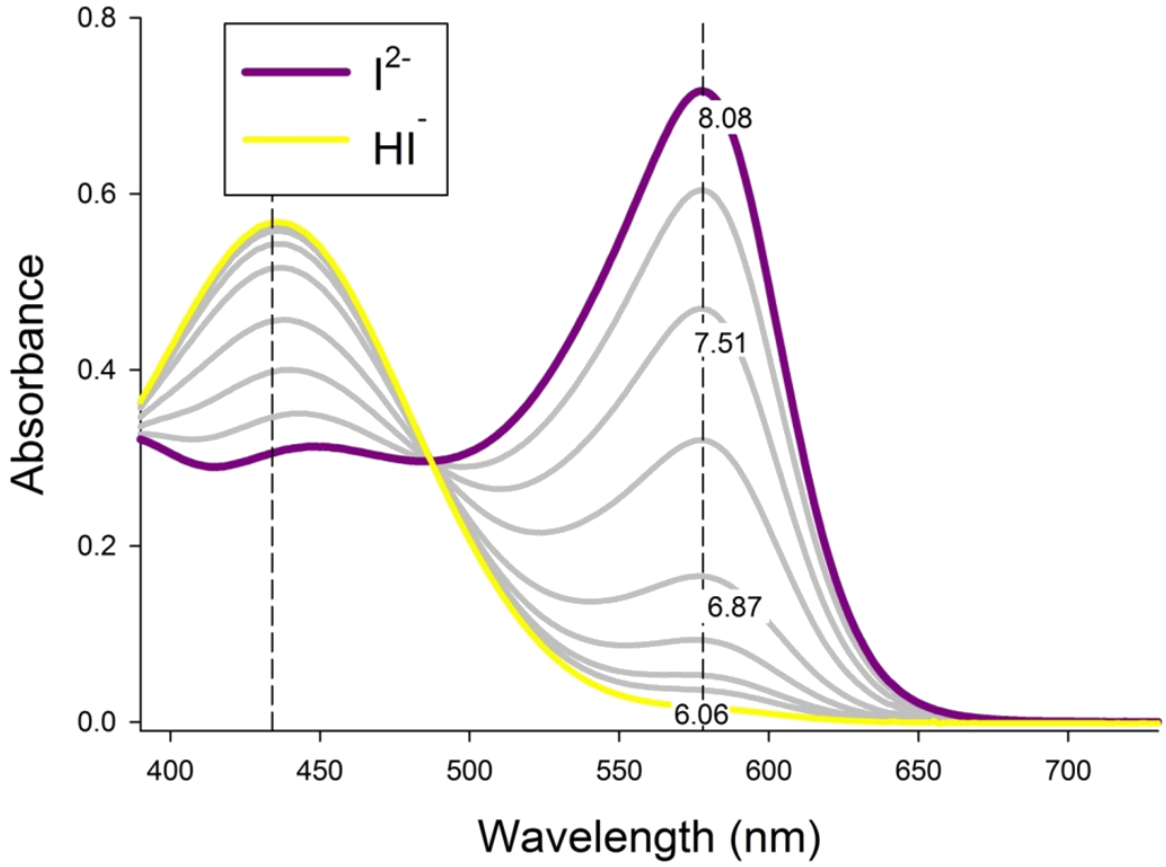
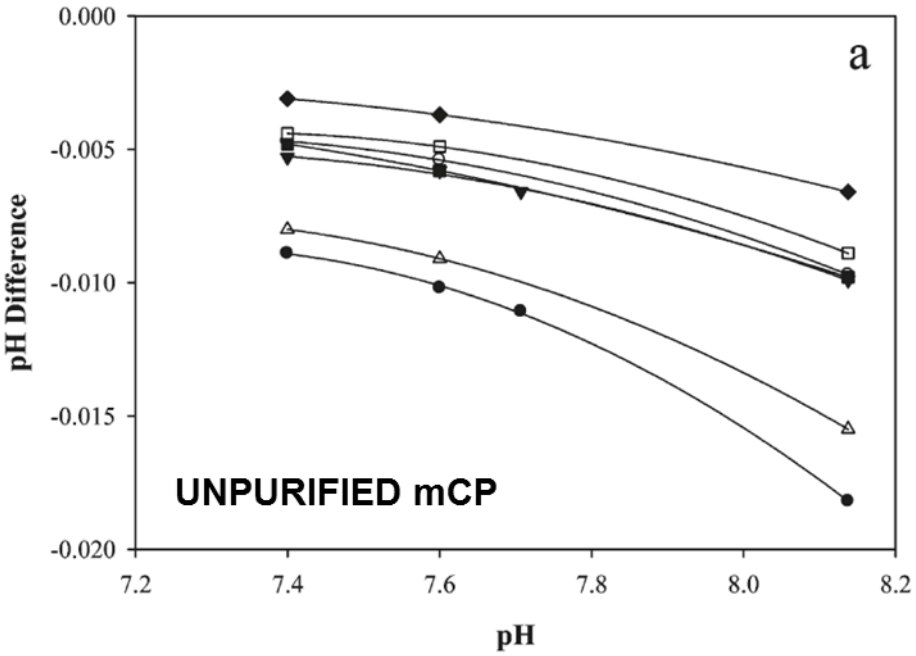
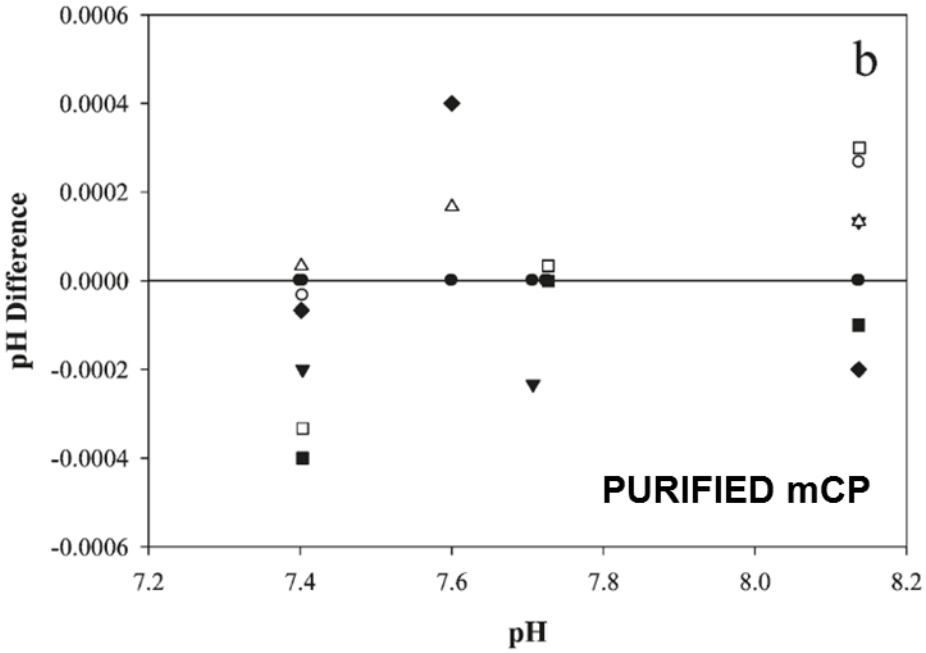
Measurement of SW pH(S):

Spectrometric detection via *meta*-cresol purple



*m*CP impurities and SW pH(S)



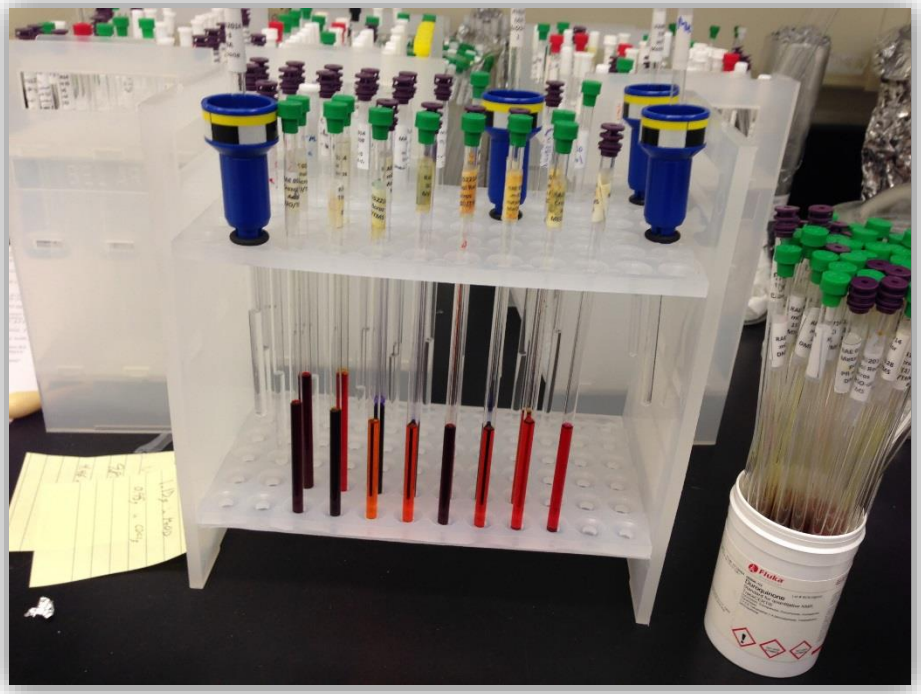


- Identify impurities to improve dye synthesis and purification process
- Molecular characterization of high purity dye: qNMR

Images: Liu, Patsavas, and Byrne. Environ. Sci. and Technol. 2011, 45 (11) pp 4862-4868.

NIST research:

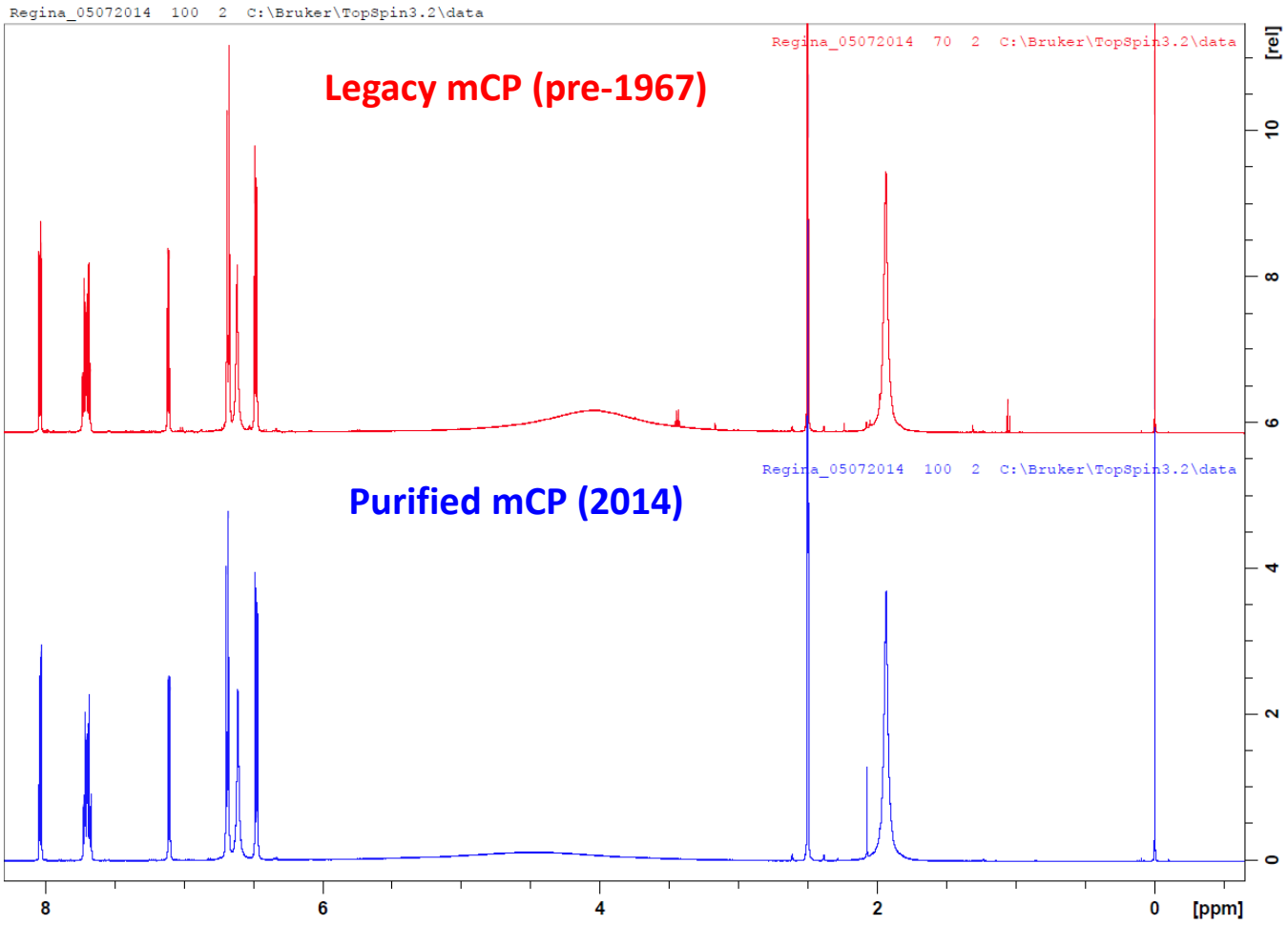
qNMR – Bruker Avance II Spectrometer



DISCLAIMER: Certain commercial equipment, instruments, or materials are identified in this presentation to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

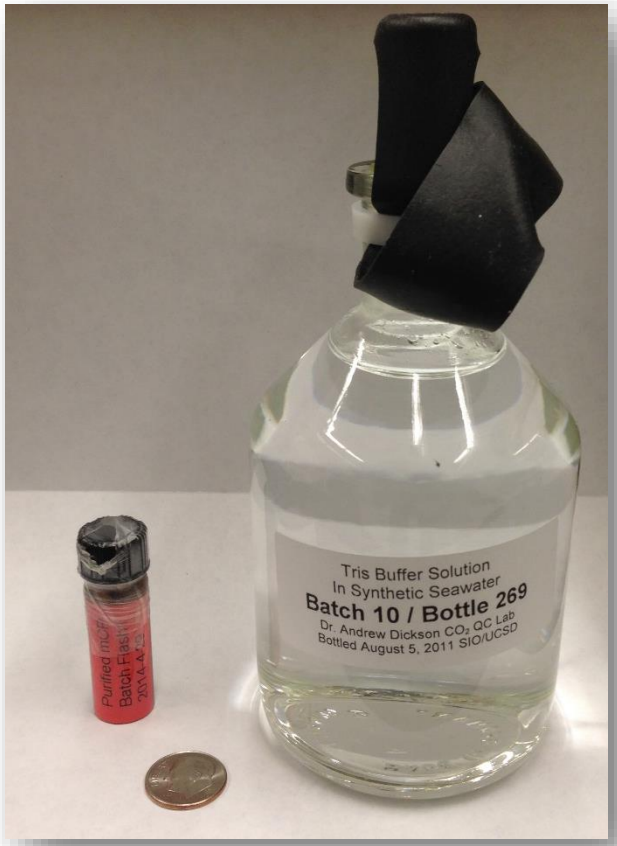
NIST research:

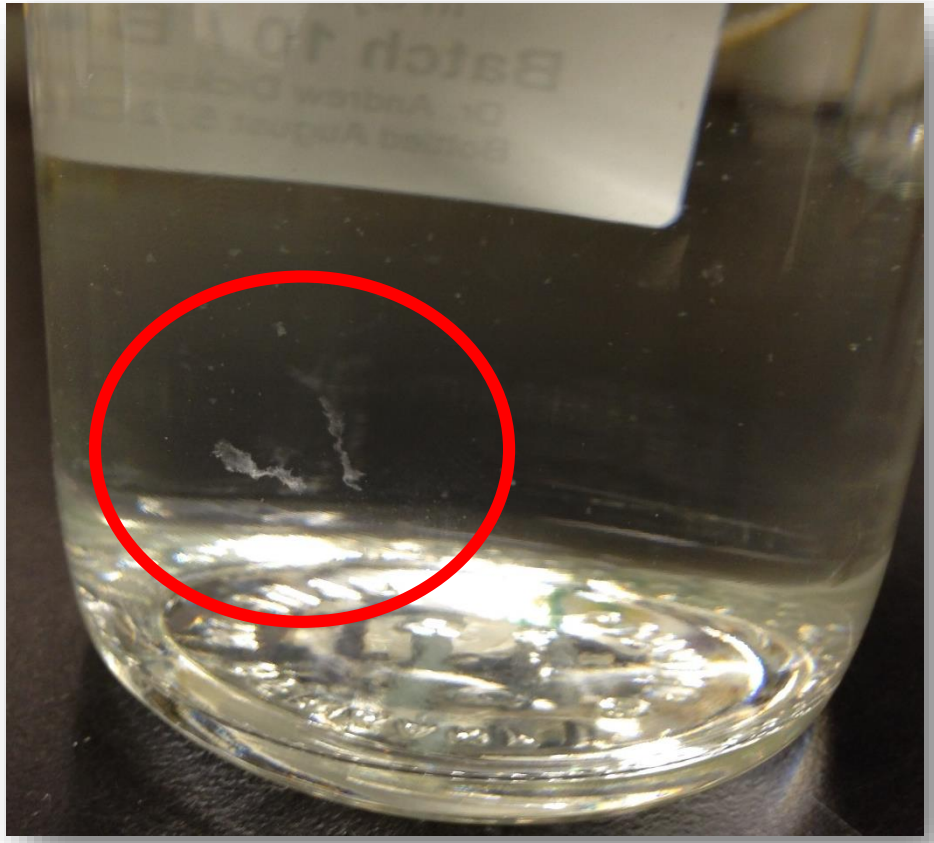
qNMR preliminary results for *m*CP



Where do we go from here?

Problems with candidate RMs:





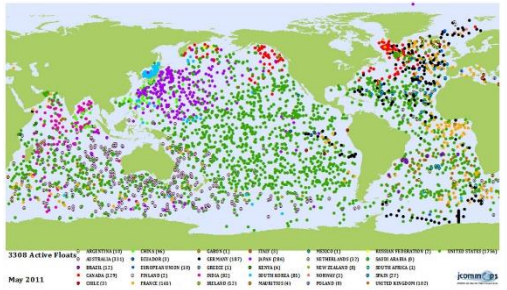
Traceability of SW pH(S) :

From the SI via NIST to field measurements

Harned Cell

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

RM



Images: noaa.gov

Traceability of SW pH(S) :

Ocean acidification and public policy

OCEAN ACIDIFICATION

Community Forum: Monday, April 15, 2013

Join us to learn about ocean acidification and the strategies and actions to protect marine resources recommended by the state's Blue Ribbon Panel on Ocean Acidification

Local/State

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1ST SESSION

H. R. 14

To provide for ocean acidification research and monitoring, and for other purposes.

Federal

UN-DESA
Division for Sustainable Development

Copenhagen
Policy Brief No. 1

International

Ocean Acidification: A Hidden Risk for Sustainable Development