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Re-envisioning Carbon Dioxide Reference Materials in Seawater

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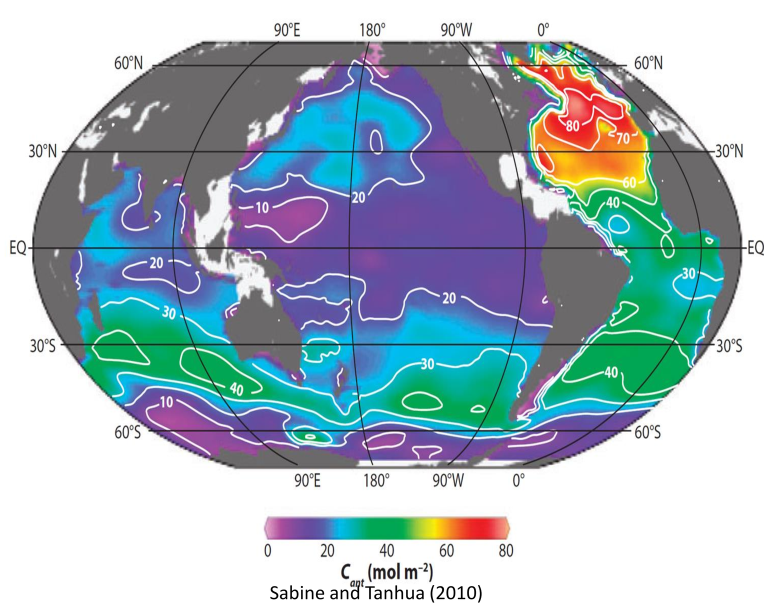
ABSTRACT: These ocean is a sink for approximately a fourth of the excess carbon dioxide released into the atmosphere by human activities, causing changes in ocean chemistry and thus pH (ocean acidification). Ensuring a sustained and adequate supply of reference materials for monitoring the carbon dioxide system in seawater is a critical global need. For the past 30 years, these reference materials have been value-assigned and provided by a sole supplier. With burgeoning demand for these materials and supply limitations stressed by the global COVID-19 pandemic, it is crucial to expand upon knowledge gained over the past few decades and work to create a robust network to supply and certify these materials. In this presentation, we will highlight some of the current challenges with the existing production model and will focus our discussion on plans to build the capacity to certify seawater reference materials for total dissolved inorganic carbon and total alkalinity at the National Institute of Standards and Technology (NIST). Additionally, we will explore ways in which NIST's measurement services and partnerships can address future seawater CO_2 measurement needs, expanding the reference material program to support additional measurands such as $\delta^{13}C$, ^{14}C, and pH. This new production model will leverage the measurement capabilities of NIST and other national metrology institutes in the areas of electroanalytical chemistry, stable isotope measurements, and gas metrology to provide metrological traceability to seawater CO_2 reference materials. Furthermore, we envision integrating the reference material program into the existing metrological infrastructure, such as participation in key comparisons associated with the International Committee of Weights and Measures (CIPM) and establishment of a quality assurance program for the user community and/or secondary reference material producers, to ensure long-term quality. These efforts will not only support the existing oceanographic research community but also enhance efforts to expand support for monitoring carbon dioxide in coastal regions and to quantify the effectiveness of ocean carbon dioxide removal technologies.

Ocean carbon is an indicator of climate change



Burning fossil fuels, increases the CO_2 of the atmosphere and about 27% of the cumulative emissions of CO_2 has dissolved into the ocean. The quantification of anthropogenic carbon in the ocean has been made possible due to sustained efforts at collecting interior ocean carbon measurements over several decades and indicate increase pCO_2 in the ocean causing decreases in ocean pH, a process called ocean acidification. Measurements of two of four variables are required to monitor ocean carbon: pH, total alkalinity, total dissolved inorganic carbon, and partial pressure of CO_2.

Seawater CO_2 Reference Materials

Andrew Dickson, at Scripps Institution of Oceanography, has provided reference materials for ocean carbon since 1990. At peak production capacity, the lab produces a little over 10,000 bottles of seawater per year which supply assigned values for:

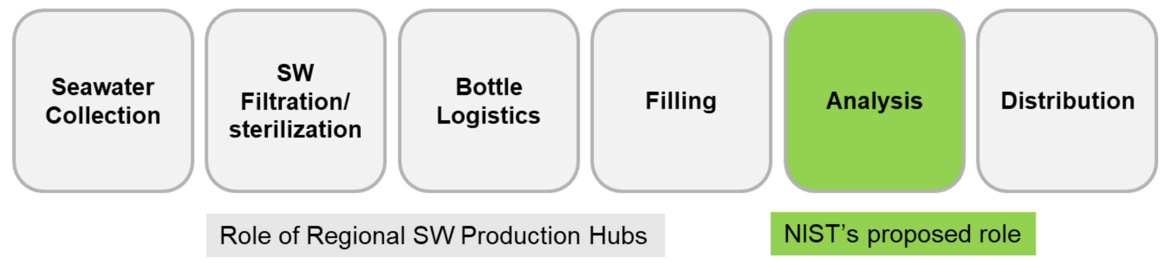
- Total alkalinity (A_T)
- Total dissolved inorganic carbon (DIC)

NIST National Institute of Standards and Technology

OAP NOAA OCEAN ACIDIFICATION PROGRAM

SCRIPPS INSTITUTION OF OCEANOGRAPHY UC San Diego

Proposed New Production Model



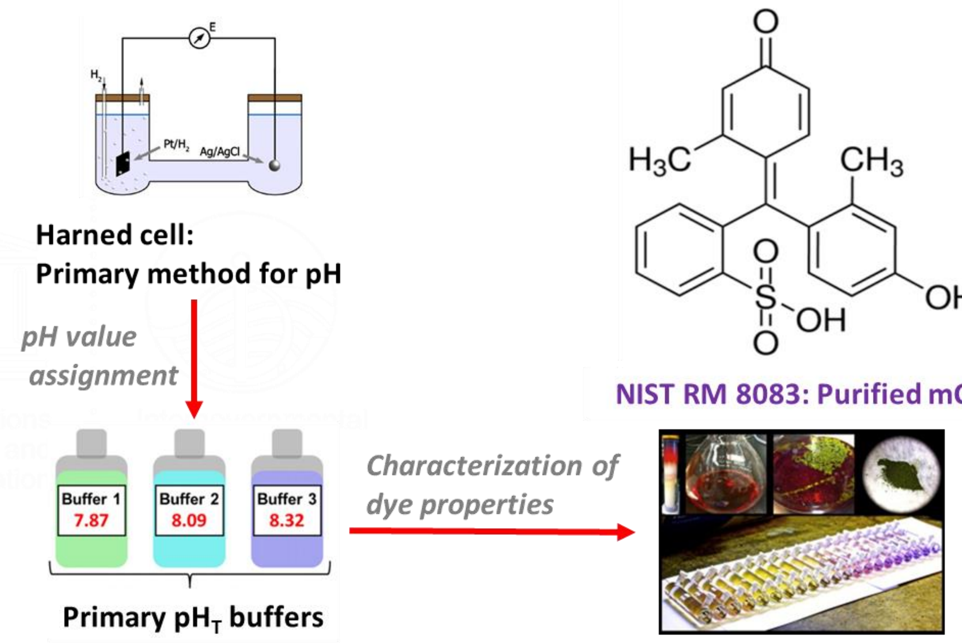
- A new model where multiple bottling and distribution centers for the seawater standards is being proposed by the oceanographic community.
- NIST is building measurement capabilities to provide services for the analysis of the seawater total alkalinity, dissolved inorganic carbon, and pH.

Total Alkalinity (A_T) Timeline ~ 3 years

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + \ldots - [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots$$

- Determined by potentiometric titration of a sample with strong acid.
- Titration data in the range pH = 3.5 to pH = 3.0, used to determine equivalence point.
- Coulometric determination of acid titrant amount content.

Spectrophotometric Seawater pH Timeline ~ 2 years



- NIST is developing a RM for spectrophotometric pH, m-cresol purple for seawater (RM 8083).
- Candidate RM 8083 is a purified mCP which will be characterized over a range of temperatures and salinities in buffers which have been assigned pH values using primary pH_T buffers in artificial seawater characterized with Harned cell measurements (primary pH measurements).

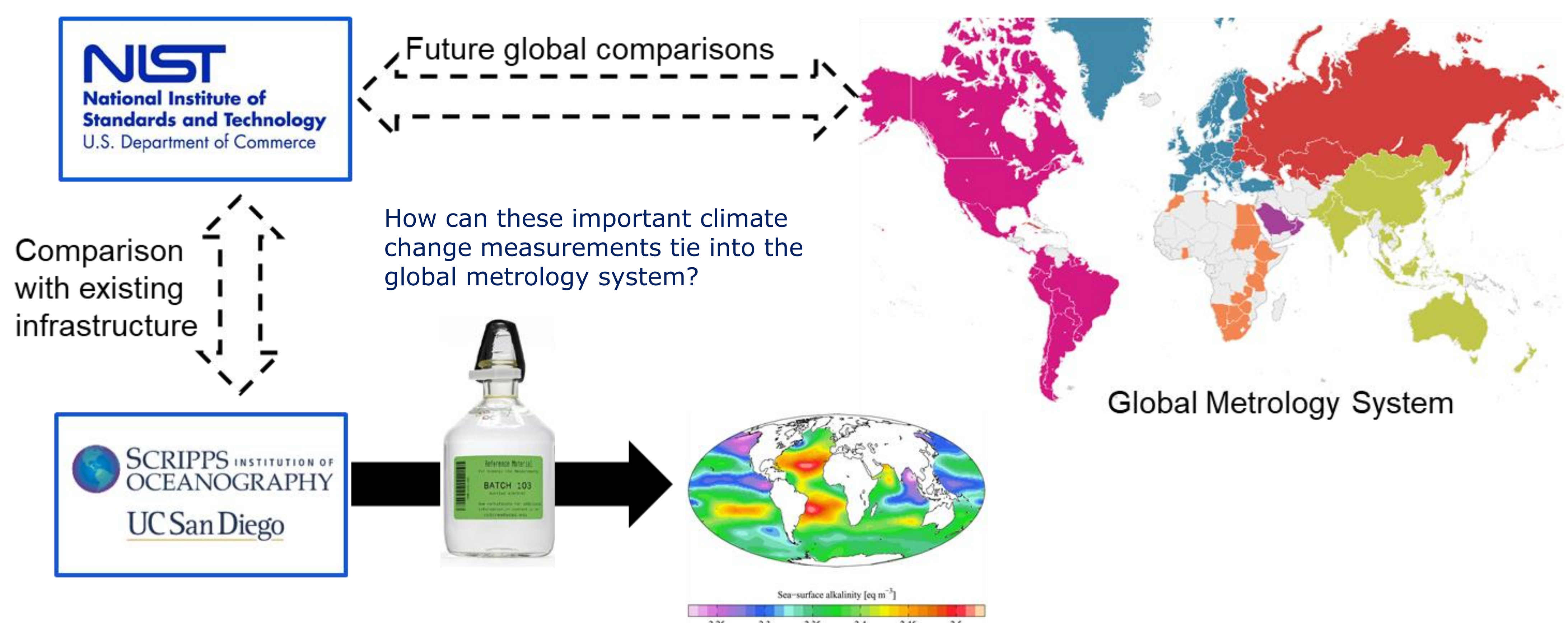
Total Dissolved Inorganic Carbon (C_T) Timeline ~ 3 - 5 years

$$C_T = [HCO_3^-] + [CO_3^{2-}] + [CO_2^*]$$

Quantifying total CO_2 from a water sample is quite different from gaseous samples requiring acidification and extraction before collection into flame-off tubes.

1. Construct a vacuum extraction line
2. Determine efficiency of gas extraction from seawater.
3. Develop methods using optical, GC and isotope ratio mass spectrometry analysis to determine total dissolved inorganic carbon and $\delta^{13}C$.

Global Metrology Connections



Recommendations:

- Use NMI's existing capabilities to certify values for seawater carbon RMs.
- Leverage the global metrological infrastructure in support of these measurements.
- Tie field measurements into the global metrology system to ensure long-term traceability.
- Create a structure to support the creation of regional production and distribution centers.