METROLOGICAL CHALLENGES FOR OCEAN ACIDIFICATION OBSERVATIONS: THE EXAMPLE OF pH

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The ocean and the climate

The ocean is a heat reservoir
Storage of about 90% of the excess of energy resulting from the human induced Green House Gases content in the atmosphere

The ocean is a carbon pump
Absorption of about 25-30 % of CO$_2$ human emissions
Ocean acidification

Impact on the calcification process of marine organisms with an exoskeleton (plankton, shellfish, corals, etc.)

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^-$$

$$\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^-$$
Ocean acidification: state of the art

- GCOS ECV* to evaluate the carbon cycle: Inorganic carbon, defined by 4 sub-variables: pH, Total Alkalinity, pCO2, Dissolved Inorganic Carbon  
  **GCOS required measurement uncertainty: 0.005 pH**

- The Global Ocean Acidification Observing Network (GOA-ON) was established in 2012 under the umbrella of the Intergovernmental Oceanographic Commission of UNESCO (IOC)  
  **GOA-ON “Climate goal” standard uncertainty requirement: 0.003 pH**  
  ➔ Uncertainty requirements very close to the level of primary standards

- The average pH of ocean surface waters has fallen by about 0.1 units, from 8.2 to 8.1, since the beginning of the industrial revolution

*Global Climate Observation System Essential Climate Variables*
DEFINITION OF THE MEASURAND
Definition of the measurand

\[ \text{pH} = -\log(a_{H^+}) \]

\[ a_{H^+} = m_{H^+} \cdot \gamma_{H^+} \]

- Only free protons
- Solvent is water

**Potentiometry**

\[ U (k=2) > 0.01 \]

\[ \text{pH} = 8.332 \]

\[ \text{@ Sp = 35 & T = 25°C} \]

**Example**

*G.M. Marion and All, Marine Chemistry, 2011*
METROLOGICAL TRACEABILITY
SI Traceability of pH measurement results

\[ \text{pH} = -\log(a_H) = \left( -\log(a_H \gamma_{Cl})^0 \right) + \log(\gamma_{Cl}) \]

- Experimentally determined
- Acidity function
- Convention
- Activity coefficient

Activity coefficient: key parameter to ensure SI traceability for pH results

International consensus
Bates–Guggenheim convention validity: ionic strength < 0.1 mol/kg

Seawater ionic strength ~ 0.7 mol/kg at salinity (S) 35

Harned cell
**pHₜ** measurements by optical method

An **indicator dye** (usually m-cresol purple) is added to the solution

The pHₜ obtained from the resulting absorbance spectrum

\[
pH_T = pK^*_2 + \log \frac{[I^{2-}]}{[HI^-]}
\]

\[\text{pK}^*_2 = 2^{\text{nd}} \text{dissociation constant of the dye under the total scale}\]

*Liu, X. and All, *Environmental science & Technology*, 2011*
Traceability of $pH_T$ measurement results

Traceability to the A. Dickson SOP 6b *Determination of the pH of sea water using the indicator dye m-cresol purple* (become ISO 18191:2015 standard)

Estimated from measurements with standard buffer solutions whose $pH_T$ is known over the desired range of $S$ and $T$

Quantified from absorbance spectrum

\[
pH_T = pK^*_2 + \log \frac{[I^2^-]}{[HI^-]} \]

Dye calibration

Measurement of real samples

$[I^2^-]$ and $[HI^-]$ absorbance spectra with different pH levels.
Traceability of $pH_T$ measurement results

“Primary” buffer solutions

Indicator dye
Secondary standard?

$[I^{2-}] + [H^+]_T = [HI^-]$

Unknown sample

$pH_T = pK^*_2 + \log \frac{[I^{2-}]}{[HI^-]}$
How to establish traceability of pH₇ measurement results

I. Define an artificial matrix with a known and reproducible composition

*Composition for nominal salinity = 35

<table>
<thead>
<tr>
<th>Component</th>
<th>Molality (mol·kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.427531</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.029264</td>
</tr>
<tr>
<td>KCl</td>
<td>0.010580</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.054742</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.010751</td>
</tr>
</tbody>
</table>

*Adapted from Millero et al., Deep Sea Research Part I, 2008

II. Select a suitable buffer solution as reference material: TRIS/TRIS.H⁺

III. Implement the Harned cell measurements

\[
pH_T = \frac{(E - E^0*) \cdot F}{R \cdot T \cdot \ln(10)} + \lg\left(\frac{m_{Cl}}{m^o}\right)
\]

\[
E^0* = \lim_{m_{HCl} \to 0} [E' + k \cdot \lg(m_H) + k \cdot \lg(m_{Cl})]
\]

IV. Characterise reference materials
On-going activities

Collaboration between LNE, NIST, NMIJ, PTB
EURAMET Joint Research project *OCEAN*
(EMRP ENV05, 2011-2014)

**On going CCQM P221**
Measurement of the activity function and pH$_T$ of a TRIS-TRIS.HCl buffer prepared in an artificial seawater background at ionic strength ~ 0.7 mol/kg

**Proposal for a CCQM EAWG task group**
Aim: how to establish traceability to SI: understanding of pH$_T$ from the thermodynamic point of view (similarly to what done for pH in the past)
UNCERTAINTY ESTIMATION
Where we are with the uncertainty

- GOA-ON and GCOS uncertainty requirements: 0.003 to 0.005 pH
- Harned cell pH\(_T\) measurements: about 0.005 (k=2)
- Reproducibility of spectrophotometric method: about 0.003 but a complete uncertainty budget has not yet been established
- A preliminary interlaboratory comparison has shown an standard uncertainty not better than 0.005
EURAMET EMPIR Joint Research Project "Metrology for standardised seawater pH$_T$ measurements in support of international and European climate strategies”
(Coordinated by LNE. 2021 – 2024)

**General objective:** to establish robust metrological tools to improve the ISO 18191:2015 standard

- Develop uncertainty estimation of pH$_T$ measurements following the GUM and the Nordtest approaches
- Compare (and hopefully reconcile!) bottom-up and top-down approaches

http://projects.lne.eu/jrp-saphties/
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Thank you for your attention!