METROLOGICAL CHALLENGES FOR OCEAN ACIDIFICATION OBSERVATIONS: THE EXAMPLE OF pH

> Paola Fisicaro Daniela Stoica Gaëlle Capitaine

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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 CO₂ human emissions





Ocean acidification





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

рΗ







 pH_{τ} (pH in total scale)

METROLOGICAL TRACEABILITY



SI Traceability of pH measurement results



$$lg(\gamma_i) = \frac{-Az_i^2 \sqrt{I}}{I + a_0 B \sqrt{I}}$$

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

pH_T measurements by optical method

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

0.8

HI

The pH_T obtained from the resulting absorbance spectrum



 $pK_2^* = 2^{nd}$ dissociation constant of the dye under the total scale*

lye under the total scale*



8.08

Wavelength (nm)



*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)





Traceability of pH_T measurement results





How to establish traceability of pH_T measurement results

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

*Composition for nominal salinity = 35	
Component	Molality (mol [.] kg ⁻¹)
NaCl	0.427531
Na ₂ SO ₄	0.029264
KCI	0.010580
MgCl ₂	0.054742
CaCl ₂	0.010751

*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

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

$$\mathbf{E}^{0*} = \lim_{m \in \mathcal{U} \to 0} [E' + k \cdot lg(m_H) + k \cdot lg(m_{Cl})]$$

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



Perspectives



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 reconciliate!) bottom-up and top-down approaches

http://projects.lne.eu/jrp-saphties/



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Thank you for your attention!

