METROLOGY FOR CLIMATE ACTION
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# Metrological needs for traceable oceanic pH measurements

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**CLIMATE CHANGE** refers to a **systematic change in the statistical properties** of climate variables (e.g., mean and variance) occurring over a prolonged time scales (e.g., decades to centuries).

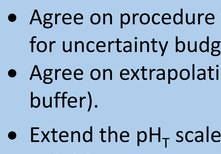
## BACKGROUND AND CONTEXT: CLIMATE CHANGE

United Nations Educational, Scientific and Cultural Organization · Intergovernmental Oceanographic Commission

**SDG 14.3**: Minimize and address the impacts of ocean acidification, including through enhanced scientific cooperation at all levels.

**Indicator Description 14.3.1** – Average marine acidity (pH) measured at agreed suite of representative sampling stations.

**Ocean acidification is a key *climate change* indicator**




**GCOS Essential Climate Variables (Inorganic carbon)**
Defined by at least 2 of the following:
**pH**, **Total Alkalinity, $pCO_2$, Dissolved Inorganic Carbon**
Target pH uncertainty specification: ± 0.005*

* https://gcos.wmo.int/en/essential-climate-variables/inorganic-carbon/ecv-requirements

## DISCRETE MEASUREMENT OF SEAWATER pH

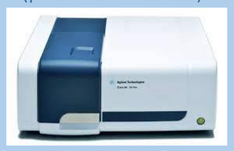
**Electrometric probes**

**ISFET (Ion Sensitive Field Effect Transistor) devices sensitive to $H^+$**

Relatively small, fast response time

Need regular calibration, as can drift over time

**Spectrophotometer** (preferred method)



**Inferred from the absorbance spectrum after the addition of a pH indicator dye**

Provides very precise data

Accuracy requires high-purity reagent: meta-cresol purple (*m*CP)

## PRACTICAL REQUIREMENTS OF OCEANOGRAPHERS

1. **Consistency** – calibration/measurement/validation procedures needed to enable consistent measurements to be made over long (> 10 y) time scales and/or by different groups
2. **Well characterized reagents**
   - Standard buffer solutions
     - Characterized over a wide range of salinity (*S*) and temperature (*T*)
   - Pure indicator dye
3. **Uncertainties**
   - Clear understanding of what uncertainty means
   - Estimation using metrological concepts
   - Encourage reporting uncertainties for field measurements
4. **Sample handling**
   - Needs standard operating protocol
5. **Interlaboratory comparisons** for quality control (QC) purposes

# SEAWATER 'TOTAL' pH SCALE, $pH_T$

## DEFINITION

Total pH is a measure of the total amount content of hydrogen ion, $[H^+_T]$, in seawater. It is defined to include hydrogen sulfate ion ($HSO_4^-$) formed by reaction of $H^+$ with the sulfate ion ($SO_4^{2-}$) in seawater.

$$H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$$

$$[H^+_T] \approx [H^+] + [HSO_4^-]$$

$$pH_T \approx -\log_{10}([H^+] + [HSO_4^-])$$

$$[H^+_T] \equiv [H^+] \cdot \left(1 + [SO_4^{2-}{}_T]/K^*_{HSO_4}\right)$$

$$K^*_{HSO_4} = [HSO_4^-]/([H^+] \cdot [SO_4^{2-}])$$

where $K^*_{HSO_4}$ is a function of *T*, *S* and *p*.

The use of $pH_T$ as a quantity enables **equilibrium studies**, including speciation of the dissolved carbon dioxide system, to be carried out in seawater without any need to correct for the effect of the $HSO_4^-$ equilibrium.

The use of $pH_T$, opposed to the 'free' pH, $-\log_{10}([H^+])$, enables **lower uncertainties** to be achieved, however, equilibrium constants must be defined to be consistent with the 'total' pH scale.

## CALIBRATION

The calibration of the total pH scale involves two sets of electromotive force (*E*) measurements, both carried out in Harned cells over the range of *S* and *T* of interest.

**1. Artificial seawater + HCl**
HCl (various molalities) substituted for NaCl.

**2. Artificial seawater + TrisHCl/Tris**
**TrisHCl (various molalities) substituted for NaCl, and Tris.**

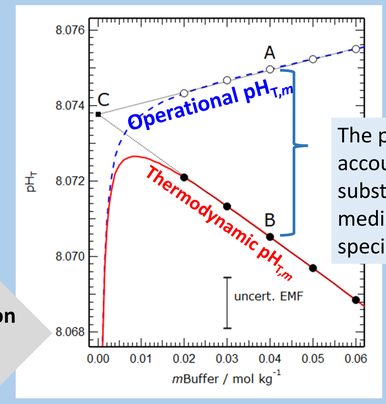
$E^*$ $E$

$$pH_{T,m} = (E - E^*)F/(RT\cdot\ln(10)) + \log_{10} m\,(Cl^-) + [\gamma_{HCl} \text{ and } K^*_{HSO_4} \text{ terms}]$$

Speciation models

Our recent work suggests that the unknown terms (grey) can be quantified by chemical speciation models of activities and equilibria in these solutions. **Speciation models allow the quantification, for the first time, of assumptions inherent to the *total* pH scale, and aid in linking the scale to the SI.**

## SPECIATION MODEL




**Blue** – operational $pH_{T,m}$ in $S = 35$ Tris buffer solution, for different buffer molalities, obtained from Harned Cell measurements.

The $pH_{T,m}$ difference between **A** and **B** accounts for the influence of the buffer substance on the artificial seawater medium. This is only accessible using a speciation model.

**Red** – conventional thermodynamic $pH_{T,m}$ ($-\log_{10}\{m(H^+) + m(HSO_4^-)\}$) in the same solutions.

Point **C**, the hypothetical $pH_{T,m}$ for which the buffer influence on the artificial seawater is zero, is obtained in practice by linear extrapolation from measurements. Its meaning, and equivalence to the extrapolated value of thermodynamic $pH_{T,m}$ is confirmed by models.

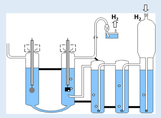
# METROLOGICAL SUPPORT FOR QUALITY REQUIREMENTS

### Calibration and measurement of Tris buffers

- Can a single seawater pH scale be recommended?
- Agree on suitable composition of buffered artificial seawaters.
- Agree on procedure for Harned cell measurements including the model for uncertainty budget.
- Agree on extrapolation to chosen artificial seawater composition (zero buffer).
- Extend the $pH_T$ scale, and spectrophotometric dye response, to lower salinities.
  - Current **EURAMET SapHTies** project

### Disseminate Calibration Standards and Reference Materials

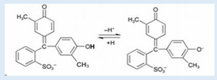
- Guidance on making spectrophotometric $pH_T$ measurements metrologically traceable.
- Availability of TRISHCl/TRIS buffer reference materials.
- Availability of pure dye.



**1. Harned Cell**

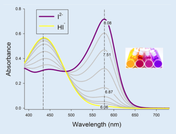
**2. Calibrated buffers**

$[TrisH^+] = [H^+_T] + [Tris]$

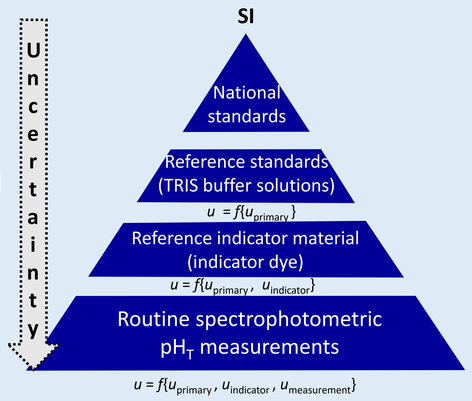


**3. *m*-cresol purple**

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




**4. Dye spectra**




### Quantifying how $pH_T$ differs from thermodynamic total pH

Requires the development and use of **chemical speciation models (activity coefficients)**, especially for low salinity buffers.
**Collaborative effort of many different measurement communities**

**Develop of a draft model and clarify technical aspects**
SCOR WG 145 activities: collaboration with NMIs (USA, Germany, France, Japan)

In progress **Extend speciation model, with quantified uncertainties**

In progress **Complete model including practical needs of oceanographers**

### Promote metrological traceability of field measurements

- Calibration of different sensors
- Encourage measurements of natural seawater samples.
  - QC procedure(s) to assist in supplying appropriate estimate of uncertainties for various situations reporting of uncertainties with $pH_T$
  - Account for performance characteristics of spectrophotometers & Consider sample handling, a key issue for reliable $pH_T$ measurements
- Can see pH as a case study for other oceanographic measurands