

# Metrology to support ocean science

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pH buffers for the calibration of marine pH instrumentation

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**MESURES ET RÉFÉRENCES**

VECTEUR DE COMPÉTITIVITÉ  
ET DE SÉCURITÉ



**LNE**

Le progrès, une passion à partager

# Laboratoire National de Métrologie et d'Essais (LNE)

The **National Metrology Institutes (NMIs)** maintain **national measurement standards** and carry out services that **link** field measurements to the International System of Units (**SI**).



*Paris headquarters*

Key figures:

- ✓ 750 employees
- ✓ 55 000 m<sup>2</sup> of laboratories
- ✓ 9 sites
- ✓ A turnover of 80 M€, including 50 M€ sales
- ✓ 25 M€ investments over 5 years
- ✓ 21% of budget dedicated to R&D

[www.lne.fr](http://www.lne.fr)

LNE attached to French Ministry of Industry

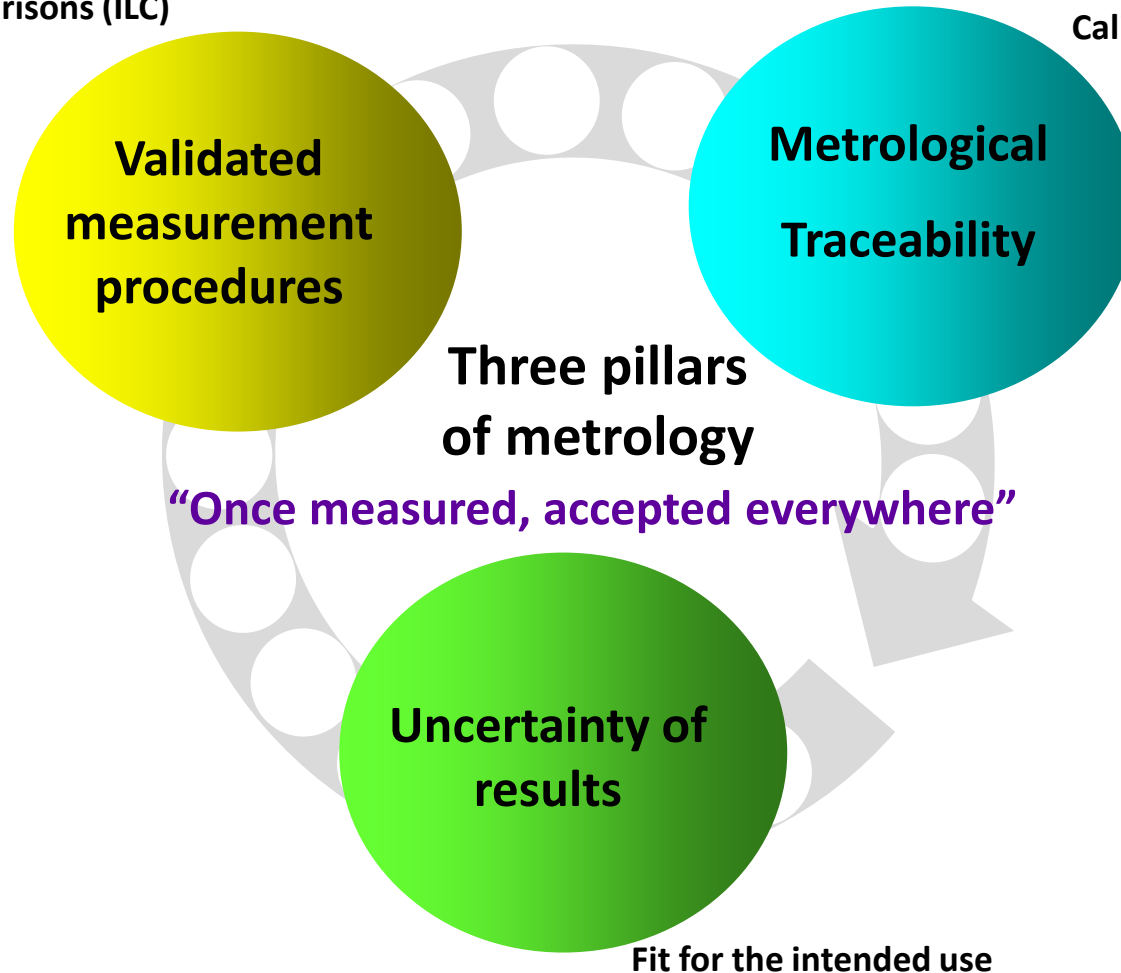


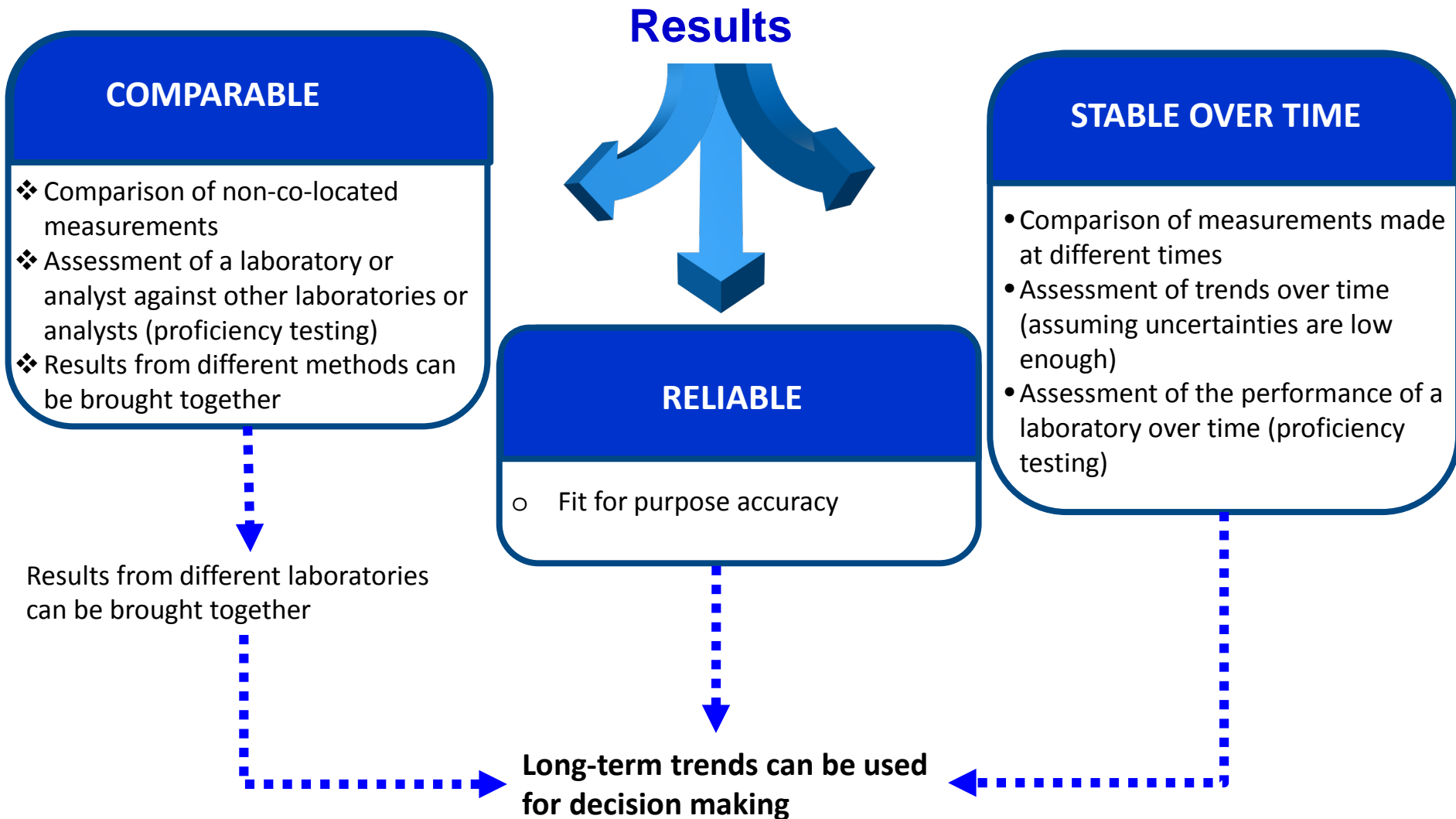
# Ensure the quality of measurement results

Metrology is the “science and practice of measurement”.

Certified Reference Materials (CRM)  
Interlaboratory comparisons (ILC)

Definition of measurand  
Primary methods  
Measurement standards  
Calibrated instruments





**Metrological traceability** : property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty (\*)

$$\text{pH} = -\lg \left[ a_{\text{H}^+} \right]$$

Internationally harmonized and agreed definition based on the free protons activity

**Measurand: quantity** intended to be measured (\*)

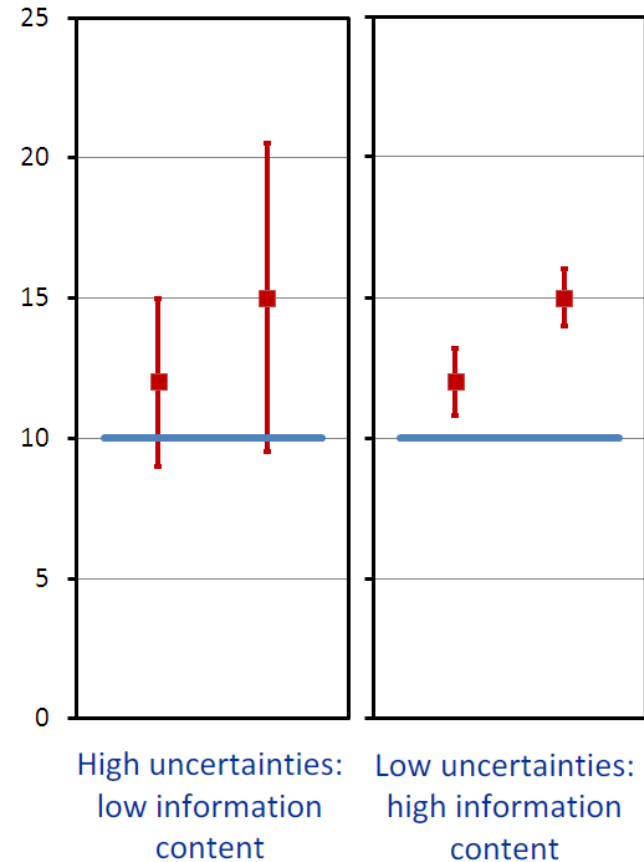
NOTE 1: The specification of a measurand requires knowledge of the **kind of quantity**, description of the state of the phenomenon, body, or substance carrying the quantity, including any relevant component, and the chemical entities involved.

NOTE 3 The **measurement**, including the **measuring system** and the conditions under which the measurement is carried out, might change the phenomenon, body, or substance such that the quantity being measured may differ from the **measurand** as defined. In this case, adequate **correction** is necessary.

$$\text{pH} \neq \text{pH}_T$$



- **Uncertainty** (VIM definition): “Non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used”
- Measurement uncertainties which are too high mean that meaningful comparisons of quantities across time and location is not possible
- Low uncertainties are desirable if the properties of stability, comparability and coherence of SI traceable measurements are to be best utilised
- High measurement uncertainties will often expose defined measurement procedures or standard approaches which are not fit for purpose



Andrew Dickson: “*It is essential to ascertain (and report) the uncertainty of measurements made as part of the GOA-ON, and to characterize the GOA-ON measurement quality goals in terms of such uncertainties.* »

# Different types of standards

“In science and technology, the English word “standard” is used with two different meanings: as a widely adopted **written standard**, specification, technical recommendation or similar document and as a **measurement standard**.”

## METROLOGICAL REFERENCES

Typically the role of NMIs

**Calibrators  
(Measurement  
standards)**

→ e.g. buffer solutions

**(Certified) Reference  
Materials**

→ e.g. natural seawater with a certified pH value used for Quality Control (QC)

**Reference Values**

→ e.g. Inter-Laboratory Comparison (ILC) for QC purposes

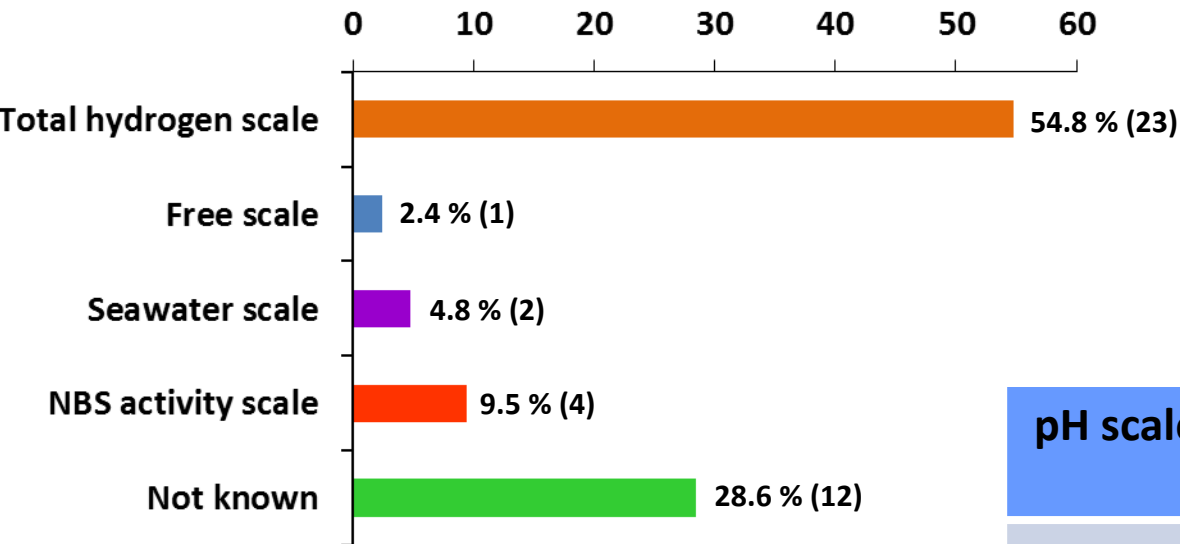
## WRITTEN STANDARDS (Standardized specification)



- Documents describing the operations and processes that must be performed for a particular end to be achieved.
- Produced by standard bodies: e.g. International Organization for Standardization (ISO) accepted at international level

# Diffent seawater acidity scales (1/2)

Survey realised within Alliance for Costal Technologies (2012) (<http://www.act-us.info/evaluations.php#ph>)



pH scale	Ionic strength (mol/kg)	Acidity value
pH	< 0.1	8.332
Total	0.4 – 0.9	8.087
Free	0.4 – 0.9	8.195
Seawater	0.4 – 0.9	8.078

Multiple pH scales yielding a pH range largely greater than 0.005\* pH target uncertainty for climate change studies.

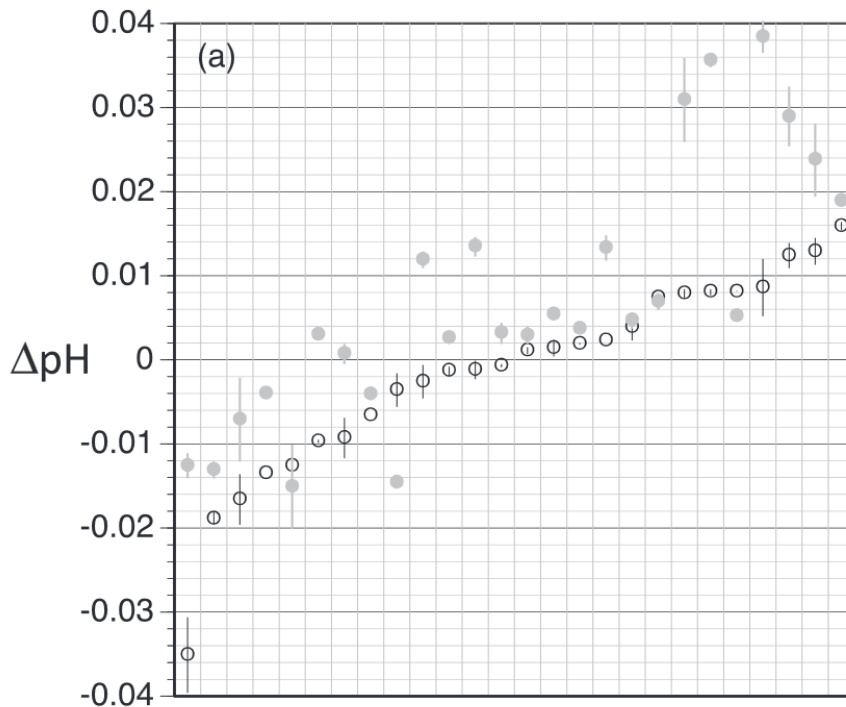
\* <https://www.ncdc.noaa.gov/gosic/gcos-essential-climate-variable-ecv-data-access-matrix/gcos-ocean-biogeochemistry-ecv-inorganic-carbon>



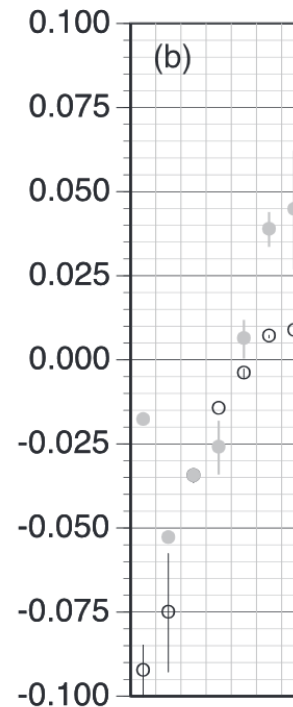
# Diffent seawater acidity scales (2/2)

Two seawater test samples of different CO<sub>2</sub> content were prepared according to the usual method for the creation of seawater reference materials in the A. Dickson Laboratory at Scripps Institution of Oceanography.

**Spectrophotometric method  
(80 % of participants)**



**Electrometric method  
(20 % of participants)**



**Differences between the pH values (25 °C) reported by the participating laboratories and the assigned values for the test samples.**

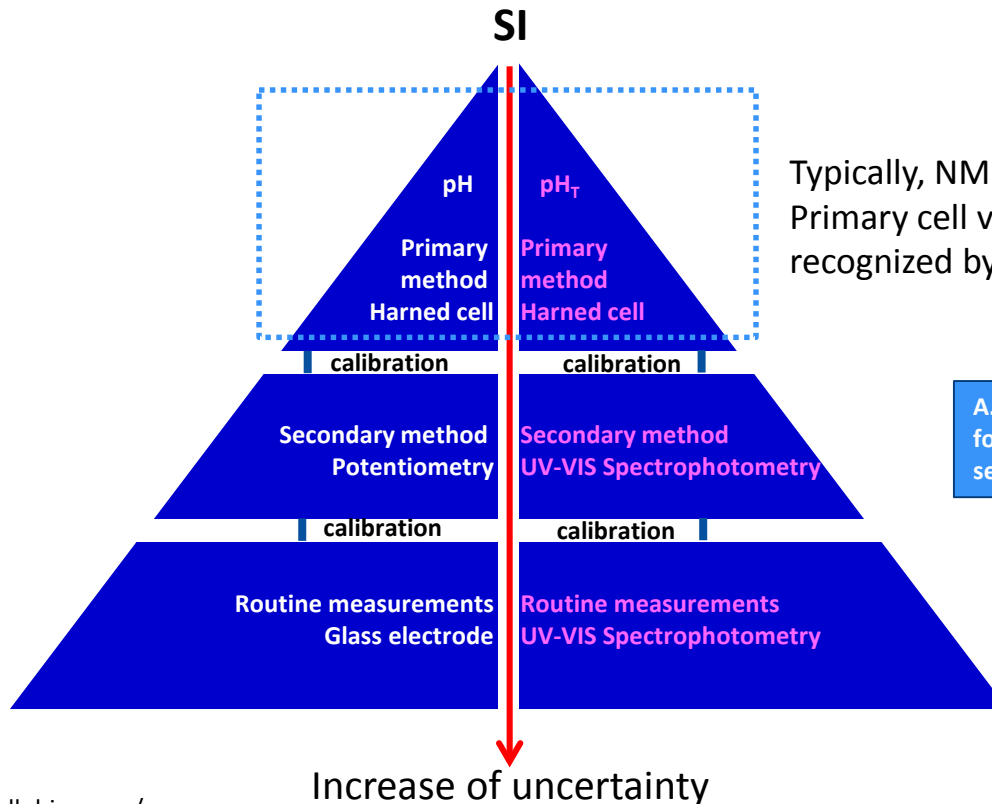
From E.E. Bockmon, A.G. Dickson, *Marine Chemistry*, (2015)

A. Dickson: *“Thus measurement uncertainty is not a synonym for measurement repeatability or even reproducibility.”*

# European NMIs Objectives

## Main interests:

- 1) Measurement standards for  $\text{pH}_T$
- 2) Measurement standards for pH suitable for seawater matrix
- 3) Establish robust link between pH and  $\text{pH}_T$  in order to ensure comparability between these two scales, and continuity from fresh waters to seawater



Typically, NMIs activities  
Primary cell validated by NMIs,  
recognized by BIPM \*

A. G. Dickson, ..., P Fiscaro, D Stoica, ..., "Metrological challenges for measurements of key climatological observables. Part 3: seawater pH", Metrologia 53 (2016) R26–R39

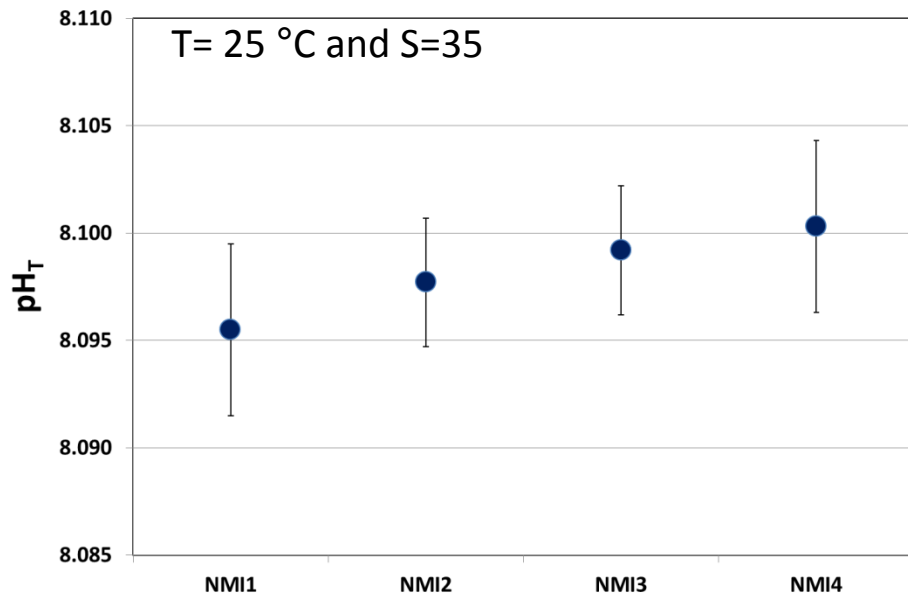
"The BIPM is an intergovernmental organization established by the Metre Convention, through which Member States act together on matters related to measurement science and measurement standards".

\* <https://kcdb.bipm.org/>

# Comparability of $pH_T$ values

Comparison on primary level organized within European Joint Research Project « Metrology for Ocean salinity and acidification » (2011-2014)

NMI participants from 3 geographical area: USA(NIST-USA), Asia (NMIJ-Japan) and Europe (LNE-FR and PTB-DE)



Uncertainty budget established for primary measurements: less than  $0.005\text{ }pH_T$  ( $k=2$ )



Availability of reference materials for  $pH_T$  (QA/QC for spectrophotometric method)



Oceanographic community lacks procedures to estimate the measurement uncertainty in the field

**THIS IS WHAT METROLOGY CAN CONTRIBUTE TO**

# Comparability of pH values

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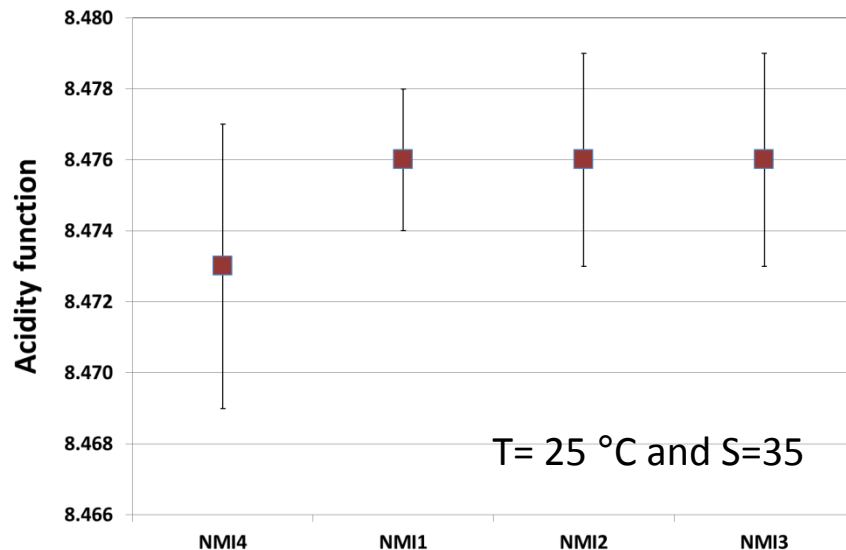
$$pH = -\lg(a_H) = -\lg(a_H \gamma_{Cl}) + \lg(\gamma_{Cl})$$

Assessed experimentally  
with Harned cell

Established by convention



Currently, restricted convention  
conditions ( $I < 0.1$  mol/kg)



**Collaboration with SCOR WG 145**

# Perspective from NMIs point of view

EURAMET is starting to promote the creation of European Metrology Networks (EMNs). The overall objective is to create **sustainable structures** in areas of **strategic importance** for the future of **European metrology** by:

- (1) Creating and disseminating knowledge
- (2) Gaining international leadership and recognition
- (3) Building coordinated infrastructure

## European Marine Reference Network: Specific Objectives

- Research devoted to the **definition of new or improved standards** for marine quantities
- Definition of suitable **procedures** for the determination of **measurement uncertainties**
- Development of **calibration facilities** for **marine sensors**
- **Development** and/or **metrological characterization** of **new instruments** for marine measurements

Potential NMIs partners: **LNE (FR)**, PTB (DE), INRIM (IT), CEM (SP), ...

**Open to non-NMIs partners**

Euramet: European Association of National Metrology Instituts ...

# Thank you!

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