

Metrology for standardised seawater pH^T measurements in support of international and European climate strategies

Abstract

Seawater acidity is an increasing focus of international and European initiatives, such as the United Nations Educational, Scientific and Cultural Organisation (UNESCO) Sustainable Development Goal (SDG) 14.3 and the EU Marine Seawater Framework Directive (MSFD) (2008/56/EC), which monitor the status and progress of ocean acidification. As described in ISO 18191:2015 'Water quality — Determination of pH^T in sea water', the measurement of pH on a total scale, (expressed as pH^T) is one of the quantities used to determine ocean acidification. However, this ISO standard currently lacks fundamental metrological principles, as these have not yet been established for pH^T measurements. Therefore, new metrological methods, reference materials and technical specifications for the measurement of seawater pH^T are needed to improve ISO 18191:2015 and to support international and European climate strategies.

Keywords

Ocean acidification, seawater acidity, pH on a total scale, seawater pH^T, quality assurance, uncertainty evaluation, ocean

Background to the Metrological Challenges

Extensive CO₂ absorption by seawater causes acidification as evidenced by a reduction in pH^T. This ocean acidification can then lead to decreasing calcification, respiratory difficulties, and reproductive changes in marine species worldwide. At the European level, the MSFD (2008/56/EC) directly addresses the need to achieve a healthy marine environment through the establishment of robust measuring systems, and highlights the need for "methodological standards to ensure consistency and to allow for comparison between marine regions or subregions".

At international level, the UNESCO SGC 14.3 aims to "Minimise and address the impacts of ocean acidification, including through enhanced scientific cooperation at all levels" and includes a specific indicator highlighting the need for "Average marine acidity measured at agreed suite of representative sampling stations". Further to this, the Global Ocean Acidification Observing Network has defined ocean acidification water quality objectives for adoption by the international community, including a "weather goal" and "climate goal". A target level of uncertainty ($k = 2$) of ± 0.04 is associated with their "weather goal" and an uncertainty level ($k = 2$) of ± 0.006 is needed to support detection of long-term changes for "the climate goal". Standardised pH^T measurements are currently performed using ISO 18191:2015 "Determination of pH^T in seawater – Method using the indicator dye m-cresol purple". However, this standard lacks technical specifications for metrological traceability, uncertainty evaluation and method validation. Consequently, oceanographers use different strategies to estimate pH^T measurement uncertainty. This is also due to the fact there are no Certified Reference Materials for seawater pH^T. Only the University of California in San Diego, has so far produced and commercialised reference materials. These reference materials are mainly used for the validation of the pH^T spectrophotometric method. However, this validation is limited to 25 °C and relies on the comparison between the experimental pH^T value and the calculated pH^T value. Further to this, several marine expeditions have demonstrated inconsistencies between calculated and measured pH^T values.

An outcome of the EMRP project ENV05 "Metrology for Ocean salinity and acidification", was the implementation of a pH^T measurement procedure based on the Harned cell (primary cell) at several European NMIs. This pH^T measurement procedure is used to characterise standard buffer solutions that can be subsequently used to link spectrophotometric pH^T measurement to the higher order standards. However, the comparability of pH^T standard values as well as the degree of equivalence obtained at different NMIs level using this procedure has not been demonstrated.

Objectives

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the protocol.

The JRP shall focus on metrology research necessary to standardise seawater pH^{T} measurements in support of international and European climate strategies.

The specific objectives are

1. To develop methods for the SI-traceable pH^{T} measurements in seawater. This should include the pH^{T} range between 7.4 and 8.2, the temperature range between 10 and 30 °C and a practical salinity range between 5 and 40. In addition, to develop traceable standard reference solutions characterised with the (Harned cell) primary system with a target expanded uncertainty of 0.003 on the scale of pH^{T} .
2. To develop a comprehensive uncertainty model for spectrophotometric pH^{T} measurements of seawater, with a target expanded uncertainty of 0.006 on the scale of pH^{T} . In addition, to develop associated software tool(s) for uncertainty evaluation, based on the developed uncertainty model. These software tool(s) should be suitable for application by end users (e.g. oceanographers).
3. To develop improved methods for measuring pH^{T} in seawater by field laboratories and validated with an interlaboratory comparison. The comparison should include the methods and models from Objectives 1 & 2 and have a target expanded uncertainty of 0.006 on the scale of pH^{T} .
4. To contribute to the standards development work of ISO/TC 147 /SC2 “Physical, chemical and biochemical methods”, CEN/TC 230 “Water Analysis”, UNESCO SDG 14.3 and the EU MSFD (2008/56/EC) to ensure that the outputs of the project are aligned with their needs, communicated quickly to those developing the standards and to those who will use them (e.g. international oceanographic community), and in a form that can be incorporated into the standards at the earliest opportunity.

The proposed research shall be justified by clear reference to the measurement needs within strategic documents published by the relevant Regulatory body or Standards Developing Organisation or by a letter signed by the convenor of the respective TC/WG. EURAMET encourages proposals that include representatives from industry, regulators and standardisation bodies actively participating in the projects. The proposal must name a “Chief Stakeholder”, not a member of the consortium, but a representative of the user community that will benefit from the proposed work. The “Chief Stakeholder” should write a letter of support explaining how their organisation will make use of the outcomes from the research, be consulted regularly by the consortium during the project to ensure that the planned outcomes are still relevant, and be prepared to report to EURAMET on the benefits they have gained from the project.

Proposers should establish the current state of the art, and explain how their proposed research goes beyond this. In particular, proposers should outline the achievements of the EMRP project ENV05 Ocean, and how their proposal will build on those.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 0.8 M€, and has defined an upper limit of 1.0 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 30 % of the total EU Contribution across all selected projects in this TP.

Any industrial partners that will receive significant benefit from the results of the proposed project are expected to be unfunded partners.

Potential Impact

Proposals must demonstrate adequate and appropriate participation/links to the “end user” community, describing how the project partners will engage with relevant communities during the project to facilitate knowledge transfer and accelerate the uptake of project outputs. Evidence of support from the “end user” community (e.g. letters of support) is also encouraged.

You should detail how your JRP results are going to:

- Address the SRT objectives and deliver solutions to the documented needs,
- Feed into the development of urgent documentary standards through appropriate standards bodies,

- Transfer knowledge to the international oceanographic community and regulatory bodies.

You should detail other impacts of your proposed JRP as specified in the document “Guide 4: Writing Joint Research Projects (JRPs)”

You should also detail how your approach to realising the objectives will further the aim of EMPIR to develop a coherent approach at the European level in the field of metrology and include the best available contributions from across the metrology community. Specifically, the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of EURAMET Member States whose metrology programmes are at an early stage of development to be increased
- organisations other than NMIs and DIs to be involved in the work.

Time-scale

The project should be of up to 3 years duration.