

## Metrology for coherent measurement of the variables of the seawater CO<sub>2</sub> system in ocean observation

### Abstract

The seawater CO<sub>2</sub> system, and its measurable variables  $C_T$ ,  $A_T$ ,  $pCO_2$  and  $pH_T$ , play a key role in the interaction of the oceans with atmospheric CO<sub>2</sub>, the main driver of climate change. Key stakeholders have been articulating a strong demand for relevant certified seawater reference materials to serve their operational needs. Moreover, observed inconsistencies between these variables, measured during oceanographic cruises, require a thorough investigation of the metrological coherence of the corresponding, complex traceability chains. Submitted proposal should address both issues in collaboration with stakeholders such as IOCCP and GOA-ON, aiming to help meeting stated target uncertainties, and to anchor NMI services in Ocean Observation.

### Keywords

Seawater CO<sub>2</sub> system, total dissolved inorganic carbon, total alkalinity,  $pCO_2$ ,  $pH_T$ , seawater reference material, SI traceability, ocean observation, ocean acidification

### Background to the Metrological Challenges

The seawater CO<sub>2</sub> system is the key mechanism underpinning the interaction of the world's oceans with atmospheric CO<sub>2</sub>, the most important greenhouse gas driving climate change. Variables determining the seawater CO<sub>2</sub> system are frequently monitored in ocean research and observation programmes and activities. The coherent measurement of these variables is crucial to estimate the air-sea flux of CO<sub>2</sub> and the ocean acidification rate due to absorption of anthropogenic CO<sub>2</sub>. Typically, the seawater CO<sub>2</sub> system is characterised by measuring at least two of four variables, which are indicators of ocean acidification: total dissolved inorganic carbon ( $C_T$ ), total alkalinity ( $A_T$ ), the partial pressure of CO<sub>2</sub> ( $pCO_2$ ) and seawater pH on the total hydrogen ion scale ( $pH_T$ ). Inorganic carbon, including the products  $A_T$ ,  $C_T$  and  $pCO_2$ , belong to the groups of essential climate and ocean variables (ECVs and EOVs, respectively). The importance of observing these variables of the seawater CO<sub>2</sub> system in a global and reliable way cannot be overestimated.

If two out of the four variables are measured, the other two variables can be calculated. However, reviews of observed data have revealed inconsistencies and synthesised likely sources of uncertainty for the measured variables. Furthermore, the procedures employed to measure these variables are very complex with respect to their traceability. In practice, measuring instruments are often calibrated with seawater reference materials, which are considered the standard reference materials for measurements of the variables of the seawater CO<sub>2</sub> system, even though they have no certification within the habitual metrology framework, i.e. with respect to SI traceability. Moreover, the metrological coherence of the measured variables with respect to their traceability to a common metrological reference, the SI in particular, has not been addressed yet. However, it is a challenging task to follow the route of traceability for each variable and assess their coherence, since the respective investigations cover technical areas that are typically addressed by different metrological fields, namely gas analytics, inorganic chemistry and electrochemistry. A thorough review of the traceability of spectrophotometric  $pH_T$  measurements has been conducted and traceability has been established within the EMPIR project 20NRM06 "SapHTies". A similar investigation of the other above-mentioned variables is needed to put their measurements on solid metrological grounds.

It must also be emphasised that seawater reference materials are currently provided by the Scripps Institute of Oceanography at the University of California (USA) and the provision of such reference materials is

uncertain in future. Therefore, efforts have been undertaken by the International Ocean Carbon Coordination Project (IOCCP) and the Global Ocean Acidification – Observation Network (GOA-ON) to put the provision of primary reference materials with certified values (CRMs) for the measurements on a broader international basis. On various occasions, the oceanographic community has expressed its need to involve metrology institutes in the characterisation and provision of CRMs covering the values expected in all oceanic areas for the measurement of variables of the seawater CO<sub>2</sub> system. This need has for instance been explicitly expressed in the Stakeholder Needs Report of the European Metrology Network for Climate and Ocean Observation (EMN-COO) and has also been included in the Strategic Research Agenda [1] of the EMN-COO as one of the most important issues to be addressed by the members of the EMN ocean section.

## 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 proposal shall focus on traceable measurement the currently four measurable variables of the seawater CO<sub>2</sub> system: total dissolved inorganic carbon ( $C_T$ ), total alkalinity ( $A_T$ ), partial pressure of CO<sub>2</sub> ( $pCO_2$ ) and seawater pH on a total hydrogen ion scale ( $pH_T$ ).

The specific objectives are:

1. To develop SI traceable primary calibration procedures and reference materials for measuring  $C_T$ ,  $A_T$ , and  $pCO_2$  with the expanded uncertainties required by GCOS ECV specifications in the framework of world-wide observation programs (2  $\mu\text{mol kg}^{-1}$  for  $A_T$  and  $C_T$ , and 0.5 % (2  $\mu\text{atm}$ ) for  $pCO_2$ ).
2. To identify and minimise systematic measurement errors contributing to observed inconsistencies between the above-mentioned variables of the seawater CO<sub>2</sub> system by performing measurements of each variable in artificial seawater solutions at the primary level and with common, calibrated instruments, and by analysing the metrological coherence of the corresponding complex traceability chains.
3. To establish facilities for the provision of reference materials and calibration procedures at the NMI level to ensure metrologically consistent measurement results of these four variables of the seawater CO<sub>2</sub> system, and to establish metrological services for the certification of the developed reference materials at the primary level.
4. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (e.g. instrument manufacturers and accredited calibration laboratories) standards developing organisations (e.g. International Association for the Physical Sciences of the Oceans, and end users (e.g. research institutes, marine monitoring organisations).

These objectives will require large-scale approaches that are beyond the capabilities of single National Metrology Institutes and Designated Institutes. Proposers shall give priority to work that meets documented needs, in particular those supporting the European Green Deal. To enhance the impact of the research, the involvement of the appropriate user community such as industry, standardisation and regulatory bodies is strongly recommended, both prior to and during methodology development.

Proposers should establish the current state of the art and explain how their proposed project goes beyond this. In particular, proposers should outline the achievements of the EMPIR project 20NRM06 “SapHTies” and how their proposal will build on those.

Proposers should note that the programme funds the activity of researchers to develop the capability, not the required infrastructure and capital equipment, which must be provided from other sources.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 2.8 M€ and has defined an upper limit of 3.5 M€ for this proposal.

EURAMET also expects the EU Contribution to the external funded beneficiaries to not exceed 35 % of the total EU Contribution across all selected projects in this TP.

Any industrial beneficiaries that will receive significant benefit from the results of the proposed project are expected to be beneficiaries without receiving funding or associated 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 proposal's 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,
- Facilitate improved industrial capability, or improved quality of life for European citizens in terms of personal health, protection of the environment and the climate, or energy security,
- Transfer knowledge to the oceanographic sector.

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 the Metrology Partnership 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.

## Timescale

The project should be of up to 3 years duration.

## Additional information

The links provided in this section are only correct at the time of publication up until the end of the Call year.

The references below were provided by PRT submitters; proposers should therefore establish the relevance of any references.

- [1] EMN Climate and Ocean Observation Strategic Research Agenda  
<https://www.euramet.org/research-innovation/metrology-partnership/strategic-research-and-innovation-agendas>