Publishable Summary for 20NRM06 SapHTies
Metrology for standardised seawater pH_T measurements in support of international and European climate strategies

Overview

Seawater acidification is the lowering of pH due to the uptake of man-made atmospheric carbon dioxide by the oceans, with a range of detrimental ecosystem impacts, in particular on calcifying organisms such as shellfish and corals. As such, the status and progress of ocean acidification needs to be documented through reliable pH measurements. The measurement of pH on the total hydrogen ion concentration scale, noted pH_T, which is one of the variables used to quantify ocean acidification, is described in the International Organization for Standardization (ISO) document ISO18191:2015. However, the ISO standard does not conform with fundamental metrological principles such as metrological traceability to SI, fit-for-purpose uncertainty estimations and method validation. This project aims to establish for the first time robust metrological tools for the measurement of seawater pH_T necessary to improve the ISO18191:2015 and to prepare their transfer to the standardisation bodies ISO/TC147 and CEN/TC230.

Need

International and European organisations have expressed their concerns about the on-going trend towards a more acidic ocean; for example, the UNESCO Sustainable Development Goal (SDG) 14.3 and the Marine Seawater Framework Directive (MSFD) highlighted the need to better understand ocean acidification and its impacts on marine ecosystems and biogeochemistry. Nowadays, the quantity describing acidity (pH) is measured with potentiometric methods. Oceanographers, however, prefer to measure pH on the total scale, noted pH_T, with spectrophotometric methods, since it has better measurement reproducibility compared to potentiometric methods. The spectrophotometric pH_T method is described in ISO 18191:2015 ("Determination of pHt in seawater – Method using the indicator dye m-cresol purple"). Despite a widespread use of the spectrophotometric method, there is currently no agreed metrological link between the spectrophotometric pH_T measurement results on seawater and primary references considering all involved measured quantities and, in particular, their respective traceability. To this purpose, it is necessary to develop methods capable of providing SI-traceable pH_T measurement results in seawater, covering most marine environments represented by their pH_T (7.4 - 8.2), temperature (0 °C - 30 °C) and practical salinity (5 - 40). Validation of such methods requires the development of traceable standard reference solutions characterised with primary systems.

The experts of the Global Ocean Acidification Observing Network (GOA-ON) have defined two different quality objectives for the quantification of ocean acidification: a "weather goal" requiring a standard uncertainty of 0.02 to identify spatial patterns and short-term variation and a "climate goal" requesting a standard uncertainty of 0.003 to assess long-term (multi-decadal) trends. The marine chemistry community has rarely attempted to establish an uncertainty budget for the spectrophotometric pH_T method but instead provides uncertainty estimates based on measurement repeatability. To minimise the risk of misinterpreting the measurement results obtained there is a need to develop a comprehensive uncertainty model for spectrophotometric pH_T measurements of seawater.

Objectives

The overall aim of this project is to develop traceable measurement methods for pH_T in seawater to produce a draft of a revised standard for the standardisation work of CEN/TC 230/WG 1, ISO 18191:2015 standard "Determination of pH_T in seawater – Method using the indicator dye *m*-cresol purple" and ISO/TC 147/SC 2 "Physical, chemical and biochemical methods".

The specific objectives of this project are:

1. To develop methods for SI-traceable pH_T measurements in seawater, including the pH_T interval between 7.4 and 8.2, the temperature interval from 0 °C to 30 °C and a practical salinity interval 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 an associated software tool for uncertainty evaluation, based on the developed uncertainty model, suitable for application by end-users (e.g. oceanographers).
3. To develop an improved ISO 18191:2015 spectrophotometric method including the pH_T interval between 7.4 and 8.2, the temperature interval from 0 °C to 30 °C and a practical salinity interval between 5 and 40 for measuring pH_T in seawater by field laboratories using the indicator dye *m*-cresol purple and to validate these methods with an interlaboratory comparison. The comparison will include the methods and models from Objectives 1 and 2 and have a target expanded uncertainty of 0.006 on the scale of pH_T.
4. To contribute to the standards development work by extending the scope to low salinity range (down to practical salinity of 5) and including metrological concepts for ISO/TC 147/SC 2 "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.

Progress beyond the state of the art

Establishment of metrological traceability for pH_T measurements of seawater

The procedure described in ISO 18191:2015 relies on the use of an *m*-cresol purple (*m*CP) as indicator dye whose physico-chemical properties need to be accurately known. This pH_T-sensitive dye has a crucial role in linking the optical signals of spectrophotometric pH_T measurements of seawater to the primary standards characterised by metrology institutes.

During this project, the metrological traceability chain for spectrophotometric pH_T measurement results and the corresponding measurement model will be provided. A link to an agreed metrological reference will be established, preferably to the SI, through either an artificial seawater (ASW) or a standard seawater (SSW).

This project will produce two Reference Materials (RMs) consisting of buffer solutions prepared in an artificial seawater, with an expanded target uncertainty of 0.003. This type of buffers will be used for the physico-chemical characterization of *m*CP and thereby extend the scope of the ISO 18191:2015 to wider environmental conditions, from nearshore and estuarine to open ocean seawaters.

Establishment of a comprehensive uncertainty model for spectrophotometric pH_T measurements of seawater

This project will produce a complete uncertainty budget for spectrophotometric pH_T measurements. For the first time, all the relevant sources of uncertainty will be identified and quantified. Uncertainty evaluation will provide information to assess whether the method proposed in ISO 18191:2015 standard meets the "climate goal" requirements i.e. an expanded uncertainty of 0.006. A software for uncertainty calculation will become available.

Validation of improved methods for measuring pHT in seawater by field laboratories

An interlaboratory comparison (ILC) with invited users from ocean acidification observing community will be organized. The ILC aims to demonstrate the capacity of the method proposed in ISO 18191:2015 standard to satisfy the measurement needs to monitor pH_T for climate change purposes. Based on the results from the ILC, the project will propose tools to improve current oceanographic Quality Assurance/Quality Assessment (QA/QC) practices. An unambiguous vocabulary with respect to the traceability of pH_T will be proposed, tailored to oceanographic terminology and consistent with internationally accepted definitions.

Results

Establishment of metrological traceability for pHT measurements of seawater

The key points for a practical implementation of the traceability of spectrophotometric pH_T measurement results from national standards to in-situ measurements have been identified and discussed. Regarding the artificial seawater matrix, the composition of reference seawater defined in 2008 by IAPSO at a salinity of 35 with

simplifications compatible with the use of the Harned cell have been adopted. The preparation of solutions at salinities other than 35 will be carried out by keeping constant the ratios between all the constituents of the artificial seawater.

Regarding the definition of the measurand, the protocol currently implemented by the NMIs makes it possible to measure with the Harned cell pH_T values based on assumptions on the HCl activity coefficients and on the dissociation constant of the bisulphate ions. Therefore, the measured pH_T values are called “operational”. A linear extrapolation protocol of pH_T values, for solutions whose TRIS molality varies, will be applied and would make it possible to overcome the influence of the buffer on the artificial sea water and to assign at the same time to artificial seawater a thermodynamic pH value.

The partners have established a measurement model for the spectrophotometric seawater pH_T that reflects the entire measurement process starting from contribution of the higher order standard solutions down to routine optical measurements through the characterization of the indicator dye. The mathematical model that ties the measurand pH_T obtained spectrophotometrically to other input parameters has been documented starting from the Beer-Lambert law and considering chemical equilibria among the different forms of the indicator dye in the analyzed solution.

Project partners analysed the different routes of traceability linking the spectrophotometric pH_T measurement results to the internationally accepted pH_T standard solutions. These standards consist of solutions of equimolal Tris and its conjugate acid $Tris.H^+$ prepared in an artificial seawater (ASW). Traceability to SI relies on the existence of primary pH_T measurement method that requires themself a reliable and accurate speciation model. Because a complete speciation model as a function of the temperature is curently missing, the spectrophotometric pH_T measurement results produced during the project lifetime could only be linked to an operational pH_T value.

Three batches of standard solution consisting of TRIS (0.04 $mol.kg^{-1}$):TRIS·HCl (0.04 $mol.kg^{-1}$) prepared in the ASW at a practical salinity of 35, were produced. This Reference Materials have been characterised using Harned cell system, between 15 °C and 30 °C. The between-bottles homogeneity was assessed shortly after the production and a stability study has been performed up to 8 months in accordance with the guidelines provided by ISO Guide 35:2017 and a certificate according to ISO standard 17034:2016 has been produced. This materials have a standard uncertainty of 0.0025 for a shelf life of 6 months, which meets the data quality objective of GOA-ON for the monitoring of ocean acidification.

Additionally, the preparation of standard solutions of TRIS:TRIS·HCl in ASW at different ratios to cover the pH range between 7.8 and 8.2 in the practical salinity range between 5 and 40 has started. These solutions will be characterised by the Harned cell system at temperatures between 0 and 30°C and the assigned pH_T values will be used for the determination of the pK2e2 of the *m*-cresol purple.

The molar absorptivity ratios (e1 and e3/e2) have been characterised. An experimental set-up consisting on two microfluidic flow cells (1 cm and 10 cm path length) connected with optical fibers to a light source and a linear array photodiode spectrophotometer has been developed for this characterisation. This system, based on the use of a syringe pump controlled by a Python script would help saving big amounts of reagents i.e. the mCP dye and high-quality salts. The set-up validation was carried out by comparing its absorbance measurements with absorbance values obtained in a bench-top spectrophotometer. The validation studies showed promising results, with very good agreement between the absorbance measurements conducted with both systems. In spite of that, the system still presents some issues that make difficult the reliable automatization of the measurements (e.g. appearance of bubbles in the microfluidic cells) and require further improvement. Therefore, to avoid a further delay in the activities, it has been decided to conduct the measurements for mCP characterization using the bench-top spectrophotometer.

The results of both pK2e2 and molar absorptivity ratios characterisation will feed the update of the ISO 18191:2015 standard.

Establishment of a comprehensive uncertainty model for spectrophotometric pH_T measurements of seawater

There are basically two main approaches to estimate an uncertainty: (1) a probabilistic approach (GUM method) which requires a complete measurement model and relies on knowleges about all the possible parameters that could affect the final result of an analysis and (2) experimental approach based on information provided by the validation and quality control data (Nordtest method). The correct estimation of the uncertainty needs the understanding of the whole analytical procedure as uncertainty sources are found at any step of a measurement procedure.

The development of the GUM approach was begun. The construction of a measurement model was initiated and a list of sources of uncertainty was established based both on the experience of the partners with the spectrophotometric method and on the information available in the literature. A software tool was developed based on that model. While waiting for the results produced within the project, data from the literature were used to evaluate different approaches, making it possible to associate an uncertainty to the physico-chemical properties of the indicator dye (pK2e2 and molar absorption ratios).

As a first step, two existing pH models of the literature (Liu et al. and Muller et al.) were implemented in the software and tested with several absorbance, temperature and salinity measurements. Then, the propagation of the uncertainties of these measurements was also implemented in the software and tested with preliminary values using the GUM-S1 (Monte Carlo) method. The second step was to take the raw data from the two publications and recalculate the model coefficients with the uncertainty associated to each coefficient. The same was performed for the e3/e2 and pK2e2 models. The next step will be to apply the Bayesian approach, which directly propagates the uncertainty of the measurements, as well as to program the graphical interface of the software.

Validation of improved methods for measuring pHT in seawater by field laboratories

SapHTies project will address this issue by taking advantage from progress realized within the Objective 1 and Objective 2 through an interlaboratory comparison. The exercise will be open to both benchtop instrument and in-situ instruments whose operating principle is based on spectrophotometric (optical method) principle. At least one standard buffer solution and one natural seawater will be selected. This activity has not yet been addressed. However, 100 % of respondants to the survey organized within the project already expressed their interest to take part to the ILC.
The results of the ILC will contribute to the performance evaluation of the ISO 18191:2015 standard method.

Impact

The website of the project has been created. http://projects.lne.eu/jrp-saphties/. The project has produced 6 oral presentations at international conferences such as MetroSea and ICOS. Consortium partners had provided an internal training on Lab-on-chips spectrophotometer and two external trainings for an European project about metrological traceability, using the example of pHT. The project, its main objectives and current achievements have also been presented to national standardization bodies (AFNOR and IPQ).

Impact on industrial and other user communities

The progresses of the project have been served as base of discussion with several stakeholders and scientific communities. For example, at the BIPM/WMO workshop on Metrology for Climate Action 2022 (https://www.bipmwmo22.org/), the traceability an oral presentation within SCOR WG145 and JCS (Joint Committee on the Properties of Seawater) - pH subgroup.

A working group within the French network ODATIS (Ocean Data and Services Cluster) to discuss on how to make sustainable the production of reference materials for pH_T measurements.

The expected impact on the industrial community will be on the manufacturers of pH_T measuring devices. Developers of *in-situ* sensors will benefit from the project. As an example, recent developments have been reported on pH_T reagent-based sensors. The main advantage of such sensors lies in the possibility to perform continuous pH_T measurements while performing *in-situ* calibration automatically. QA/QC tools developed within the project can contribute to boost the development of *in-situ* sensors and consequently increase their use for environmental and climate-related monitoring activities. It is expected that some sensor manufacturers will participate to the interlaboratory comparison planned at the end of the project.

The feasibility of producing appropriate reference materials consisting of standard buffer solutions has been demonstrated. For the first time, 3 batched characterised according to ISO 17034:2016 have been produced. These materials, which have a standard uncertainty of 0.0025 for a shelf life of 6 months, meet the data quality objective of GOA-ON for the monitoring of ocean acidification and have been purchased by the oceanographic community within the French network SOMLIT (Coastal ocean observation service – Service Observation en Milieu LITtoral).

Impact on the metrology and scientific communities

Most of the project partners are active members in working groups and technical committees of the Electroanalysis Working Group (EAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) of the BIPM and EURAMET. Both organisations encourage the progress beyond the state of the art in chemical measurement science. Activities carried out within the project will provide supporting evidence on National Metrology Institutes' (NMIs') ability to perform high precision pHT measurements and will lead to international equivalence of pH_T at primary NMIs level.

A task group has been initiated within the BIPM-CCQM Working Group on Electrochemical Analysis (CCQM-EAWG). The aim of this TG is to evaluate how to establish the metrological traceability of pHT, possibly to SI or eventually to the primary pH measurement standard (Harned cell). This TG will mainly use the output of the SapHties JRP and will include among its members the JRP partners and external collaborators (mainly the members of the SCOR WG145).

Based on the knowledge under development in the JRP SapHties, a pilot study has been organised under the BIPM-CCQM-EAWG. This comparison has been co-cordinated by LNE and NIST and other partners of the JRP have participated. The results are under exploitation and will contribute to the understanding of the possible route to establish metrological traceability for pH_T.

The outputs of the JRP also feed the EMN for Climate and Ocean Observation, in particular the ocean observation section.

Strong collaborations have been created with the MINKE community (Metrology for Integrated Marine Management and Knowledge-Transfer Network) which is a European H2020 project formed by 16 key European partners from the European oceanographic community. MINKE's aim is to form a starting community to create an EU metrology infrastructure for marine monitoring. Four SapHies partners, LNE, PTB, Syke and Ifremer, are partners of MINKE.

3 JRP partners have contributed to a training organised by the H2020 MINKE project ("Introduction to metrology for young and early career marine scientists"). The progress of the work done in SapHties on the traceability and the uncertainty issues of pHT have been presented to and discussed with the training attendees.

Impact on relevant standards

The project will produce a draft document of a revised ISO 18191:2015 to initiate standardisation actions within CEN/TC 230/WG1 and for review at the ISO/TC 147 level.

For the first time, a documentary standard tailored to the oceanographic community's needs will be produced, bridging the gap between the standardisation and oceanographic communities. The technical achievements from the project as well as the involvement of stakeholders in dissemination activities will provide the basis for a sustainable collaboration between different communities involved in assessement and quantification of ocean acidification.
Once available, the improved ISO 18191:2015 documentary standard could serve as reference document for Minke starting community. Thus, Minke partners will have the possibility to carry out more appropriate calibration services and thereby encourage them to implement NMI-supported accreditation schemes for measurements of seawater pH_T.

Longer-term economic, social and environmental impacts

The improvement of ISO 18191:2015, expected after the end of this project, will foster the harmonisation of pH_T measurements. Long-term comparability of pH_T measurement results will be guaranteed by the provision of a sound route of traceability and validated uncertainties. This will improve the reliability of pH_T data included in European and international databases and increase confidence in the established trend models used for climate change tracking. Such models are used to show the variation in the oceanic pH_T and possible decline under climate change and CO_2 emissions. Obtaining high-quality pH_T measurement results will contribute to the effort of public authorities to illustrate and communicate on complex phenomena related to climate change. Thereby, the project supports implementation of international and European environmental related strategies, and provides the scientific basis for the design of more effective remediation measures.

Project start date and duration:	1st of May 2021 (36 Months)	
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