

Final Publishable JRP Summary for ENV05 OCEAN Metrology for ocean salinity and acidity

Overview

The project has contributed to improving the metrology infrastructure required for reliable monitoring and modelling of ocean processes. It covers the oceanic observables salinity, density, speed of sound, pH, dissolved oxygen content (DO), and seawater composition. The project has provided validated methods, tools and measurement standards with well characterised uncertainties necessary for calibration of *in-situ* observing sensor networks and satellite systems traceable to SI units. This will allow scientists to more accurately detect small changes in long-term oceanographic data series. The availability of reliable data strengthens European integrated ocean observation and allows the building of more reliable climate models, providing the basis for any political and social decisions on the response of European society to climate change.

Need for the project

The dynamics of the ocean and its interaction with the atmosphere are strongly linked to the properties of seawater. Moreover, climate change affects ocean acidification and is threatening food security and biodiversity of the ocean. The characterisation of the status of the oceans requires a wide variety of physical and chemical observables. These observables are monitored world-wide and commonly over the long-term; their changes are typically small but have a large impact on oceanic and climate behaviour. Measurement results in this context are stored in databases of global observation systems and are used for oceanographic and climate change research. The Marine Strategy Framework Directive [MSFD 2008] directly addresses the necessity of having reliable data to monitor the ocean status. The problem is that often data are not comparable over a long timescale and lack the low uncertainties required for accurate measurements. In addition, measured parameters do not cover the full range of pressure and salinity, necessary to describe deep-water behaviour. The development of SI traceable measurement methods, covering the whole traceability chain from primary references to field devices, including uncertainty estimations at any measurement level, allows reliable data to be obtained. This enables the comparison of data on a multi-decadal to centennial scale even when measured at different places with different devices. Traceability to the SI is also required for the observables salinity, density and speed of sound, with such low uncertainty that the measurement results are useful input quantities to the International Thermodynamic Equation of Seawater 2010 (TEOS-10) – a key tool in oceanography that enables consistent and comparable assessments of the properties of seawater.

Scientific and technical objectives

In reaction to these issues, the project aimed to provide validated reference measurement methods with ensured traceability of the measurement results for the parameters salinity, density, pH, composition of major and minor seawater components and micronutrient elements, and dissolved oxygen content of seawater. In addition, speed of sound was measured to feed into the TEOS-10 database. One of the main challenges of the project was to set-up the metrology infrastructure able to cover the wide range of parameters to be addressed. The project has enabled European National Metrology Institutes (NMIs) to build up primary calibration facilities for seawater observables and accumulate knowledge on ocean monitoring, allowing metrological concepts to be established in oceanography. The experience has been disseminated among the NMIs and has been made available to user communities via publications, training activities, workshops and by direct communication.

The project aimed to achieve the following objectives:

1. Provision of a quantitative link between the conductivity ratio K_{15} and the density of standard seawater, in order to establish SI traceability of practical salinity measurement results.

2. Provision of a reference measurement method that enables SI traceability of Practical Salinity results, measured at pressures and temperatures typical for oceanography, i.e. pressures of up to 70 MPa and temperatures between 0 °C and 40 °C.
3. Provision of measurement data, which quantify the influence of composition anomalies, in particular of the Baltic Sea, on practical salinity measurement results traceable to density standards.
4. Provision of improved speed of sound measurement data with a relative uncertainty of 0.1 % for both high accuracy laboratory and *in-situ* measurements of seawater, measured over a pressure range of up to 70 MPa and a temperature range between 0 °C and 40 °C. This also includes improved temperature measurements with an uncertainty of 5 mK.
5. Provision of thermodynamic data of seawater calculated from the obtained measurement results.
6. Provision of a primary reference procedure for pH measurements in seawater.
7. Provision of harmonised and validated pH measurement procedures with respect to potentiometric pH measurements in seawater.
8. Provision of uncertainty budgets according to GUM, with respect to potentiometric and spectrophotometric pH measurement methods in seawater.
9. Provision of new, robust, and validated methods for the determination of important seawater components such as strontium, nitrate, phosphate, silicate and iron traces.
10. Provision of an improved gravimetric titration procedure for dissolved oxygen concentration, with an uncertainty of 0.03 mg/l - 0.05 mg/l (at saturation).
11. Provision of an improved coulometric measurement procedure for dissolved oxygen concentration, with an uncertainty of 0.04 mg/l - 0.06 mg/l (at saturation).

Results

1. Provision of a quantitative link between the conductivity ratio K_{15} and the density of standard seawater, in order to establish SI traceability of practical salinity measurement results

Currently, ocean salinity is measured in terms of a polynomial of a conductivity ratio between the conductance of a seawater sample and that of a defined potassium chloride solution (K_{15}). To this end salinity measurement devices are calibrated with so-called IAPSO¹-Standard Seawater (SSW). SSW is a primary reference solution, prepared from natural seawater from the North Atlantic. It has a conductivity ratio assigned according to procedures defined in the Practical Salinity Scale documentation that has been endorsed by UNESCO in 1978 (PSS-78). However, the current calibration and production procedures of IAPSO Standard Seawater cannot sufficiently guarantee the required stability, since a stable reference to verify the replicability of SSW over a long timescale is missing.

A significant achievement of the project is the establishment of a link between the conductivity based “Practical Salinity” and the SI through an empirical conductivity ratio–density relationship.

The empirical relationship thus obtained covers the salinity range 5 to 35, the temperature range 5 °C to 35 °C, and pressures up to 650 bar (65 MPa).

2. Provision of a reference measurement method that enables SI traceability of Practical Salinity results, measured at pressures and temperatures typical for oceanography, i.e. pressures of up to 70 MPa and temperatures between 0 °C and 40 °C

A method for measuring the density of seawater with a relative uncertainty of 2 ppm was established, which means a reduction by a factor of 10 compared to common density measuring methods was established. A novel primary conductivity sensor which can be used at pressures up to 200 bar (20 MPa) and temperatures between 5 °C and 40 °C was developed, tested and linked to density measurements at the same pressure. The reduction in the pressure range was discussed with stakeholders and collaborators due to leaking of the cell at higher pressures. It was confirmed that the range up to 200 bar (2000 m depth) covers the most relevant measurement range for ocean climate research. Using the conductivity ratio–density relationship it is now possible to monitor the production of standard seawater for changes in the incorporated Practical Salinity with respect to stable SI standards over long timescales and consistent with the PSS-78. More than fifteen laboratories took part in comparison measurements of conductivity ratios and density at selected salinities and

¹ International Association for the Physical Sciences of the Oceans

temperatures to estimate the inter laboratory reproducibility. The intercomparison revealed some additional challenges (previously unknown) that reduce the reproducibility of conductivity ratios. This has triggered activities in the oceanographic and metrological communities to further investigate the reproducibility of SSW and secondary conductivity reference solution calibration.

3. Provision of measurement data, which quantify the influence of composition anomalies, in particular of the Baltic Sea, on practical salinity measurement results traceable to density standards

The composition of marginal seas like the Baltic show deviations from the composition present in the oceans. The effect of such anomalies on conductivity is different than the effect on density. Therefore the effect of composition anomalies on the conductivity ratio–density relationship was investigated using natural water from the Baltic Sea. The results prove that composition anomalies have an effect on the conductivity ratio–density relationship. They roughly increase its uncertainty by a factor of seven. It must be concluded that a change of (Atlantic) seawater composition also affects the K_{15} value of IAPSO Standard Seawater, which makes obvious the necessity of a stable metrological reference for Practical Salinity measurement results.

4. Provision of improved speed of sound measurement data with a relative uncertainty better than 0.1 % for both high accuracy laboratory and *in-situ* measurements of seawater, measured over a pressure range of up to 70 MPa and a temperature range between 0 °C and 40 °C, including improved temperature measurements with an uncertainty of 5 mK;

5. Provision of thermodynamic data of seawater calculated from the obtained measurement results

Accurate speed of sound results are required for validating and improving the Equation of State of seawater. They are very useful for establishing a relationship between thermal and mechanical quantities of seawater and for obtaining, together with density and specific heat capacity, all the remaining thermodynamic quantities.

A significant achievement of the project is to be able to quantify the effect of the anomalous relative salt composition of a seawater sample on the speed of sound, which can be seen as an estimate for the speed of sound standard uncertainty, using modern time-of-flight sensors in seawater. For a Baltic seawater sample with a salinity of 7.766, the effect was quantified as $(0.067 \pm 0.014) \text{ m} \cdot \text{s}^{-1}$. This has been determined for the first time by direct measurements and will contribute to the recent development of equations of state.

Commercial time-of-flight sensors were calibrated in pure water on a regular basis throughout the duration of the project to track the long-term stability of the sensors. Temperature dependent sound speed according to the equation of state for pure water was fitted to the measured time-of-flight. The investigations revealed that the given manufacturer calibration and associated uncertainty, respectively, are of limited reliability. As a result of the pure water measurements an overall reproducibility of $0.015 \text{ m} \cdot \text{s}^{-1}$ to $0.030 \text{ m} \cdot \text{s}^{-1}$ (equating to 11 ppm to 20 ppm, respectively) for modern time-of-flight sensors was demonstrated. On the basis of these results the potential use of the sensors as acoustic thermometers was evaluated. In pure water a reproducibility of 3 mK to 12 mK in the investigated temperature range can be reached for the temperature determination by sound speed measurements. The variability is due to the varying sensitivity of sound speed with temperature.

A new set-up, based on the pulse-echo technique, including a pressure vessel, has been designed and realised with the aim of measuring seawater speed of sound at pressures of up to 70 MPa. A study focused on the lowest uncertainty limit theoretically reachable using a pulse-echo technique was undertaken. It has been proved that uncertainties below 30 ppm cannot be considered reliable today; while, more typically, the limit is in the order of 100 ppm (0.01 %) under laboratory conditions.

Speed of sound has been measured in the temperature range 0 to 40 °C, at pressures up to 70 MPa and salinities of 38, 35 and 10. The overall uncertainty is in the order of 500 ppm (0.05 %).

6. Provision of a primary reference procedure for pH measurements in seawater

Research in marine science requires an extremely small standard uncertainty in pH measurements (of about 0.004), over a fairly narrow range of pH, and this is far smaller than the differences between many of the operationally defined 'pH' quantities, which may be up to 0.2 'pH'.

A metrological traceability hierarchy between the conceptual pH value defined in terms of hydrogen ion activity and pH measured in the field by glass electrodes is currently only established for a few selected calibration procedures in media of low concentration of ionic charges below 0.1 mol/kg. In contrast, seawater has a high concentration of ionic charges (around 0.7 mol/kg for a practical salinity of 35) which causes accuracy

problems when using conventional (commercially available) pH calibration standards. Two different methods can be used to measure seawater acidity: the potentiometric method that is based on a voltage measurement of an electrode system providing a pH value, and the spectrophotometric method that is based on an optical measurement of the protons concentration providing a so-denoted pH_T value. The potentiometric method is particularly established in metrology to define the pH scale, realised with some defined buffer solutions, while in oceanography mainly the optical method is used.

One of the main achievements of the project is the development of primary and reference methods for acidity measurements. As a representative matrix for seawater acidity measurements, artificial seawater with IAPSO approved reference composition (salinity 35) in Tris-Tris-HCl buffer was selected and characterised by a primary pH system (Harned cell), with the aim of determining pH and the pH_T value.

7. Provision of harmonised and validated pH measurement procedures with respect to potentiometric pH measurements in seawater

The pH measurement procedure including buffer preparation in an artificial seawater matrix (starting from stock solutions, gravimetric preparation, well characterized salts in terms of amount content) and Harned cell measurements was validated through a comparison measurement between five NMIs. The expanded uncertainties ($k=2$) of experimentally determined acidity functions were 0.004 for most of the participants, similar to those obtained in standardized buffer solutions (concentration of ionic charges below 0.1 mol/kg).

The good agreement between the participants demonstrates the robustness of the developed procedure and paves the way for the metrological characterisation of other buffers appropriate as standards for seawater acidity measurements at salinities other than 35, as requested by end users.

8. Provision of uncertainty budgets according to GUM, with respect to potentiometric and spectrophotometric pH measurement methods in seawater

For the first time a complete uncertainty budget was assessed for pH_T values of seawater buffer with respect to Harned cell measurements. Expanded uncertainties ($k=2$) of about 0.004 between 15 °C and 35 °C were obtained. These solutions were used to assess the accuracy of the spectrophotometric method proposed by ISO standard ISO/CD 18191 "Water quality -- Determination of pH in sea water -- Method using the indicator dye m-cresol purple". This represents the first step in the establishment of the uncertainty budget of the field method.

A traceability chain for the optical method that is consistent with potentiometric method has not been established yet. An equation used to link the pH_T value to the conceptual pH value was tested but further research and experimentation are necessary before to state on its applicability for mentioned purposes.

9. Provision of new, robust, and validated methods for the determination of important seawater components such as strontium, nitrate, phosphate, silicate and iron traces

The complexity of the marine environment introduces an additional difficulty due to matrix effects, making it difficult to determine the mass fraction of major seawater components (Na^+ , Mg^{2+} , Sr^{2+} , Cl^- , SO_4^{2-}) and trace elements. Reliable determinations of such micronutrient elements in marine waters are essential to enhance our understanding of their impact on ocean productivity and processes (e.g. ocean acidification). Iron in particular, as a key micronutrient for the plankton communities (primary production), is considered to limit growth in half of the world's ocean and, therefore, influence the oceanic sequestration of atmospheric CO_2 . This is because iron concentrations, in most cases, are extremely low (sub-nanomolar levels). Elucidating the cycle of this element in the ocean thus has great scientific significance, but measuring reliably such low iron concentrations in seawater is extremely difficult. Data from exercises of inter-laboratory comparisons for the same water mass are distinctly inconsistent. Overlooking uncertainty estimation is a recurring problem, with negative consequences for data interpretation.

For the determination of major components, methodologies based on ionic chromatography have been developed in the project. Reference methods for quantification of anions with expanded uncertainties of a few percent are now available for silicates, phosphates, sulfates, nitrites and nitrates.

Quantifications of nutrients in seawater have posed a number of difficulties, particularly in terms of matrix interference and calibration. Shipboard measurement procedures are the most commonly applied approaches. Flow analysis techniques offer the potential for on-line sample manipulation and preconcentration. Flow

injection with chemiluminescence detection allows high temporal and spatial resolution measurements at sea without the need for sample storage and transport. This procedure was revisited with a double objective: attempts were made at estimating typical combined uncertainties, and at identifying the main factors influencing these results and uncertainties. A set of equations was proposed to handle uncertainty propagation according to the rules of the Guide to the Expression of Uncertainty in Measurement. A measurement procedure for measuring the dissolved Fe concentration in $<0.2 \mu\text{m}$ filtered and acidified seawater samples by isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS) was developed.

10. Provision of an improved gravimetric titration procedure for dissolved oxygen concentration, with an uncertainty of 0.03 mg/l - 0.05 mg/l (at saturation)

A significant achievement of the project has been the development of the most accurate method to date for determination of dissolved oxygen (DO) content. DO content in natural waters is an indispensable quantity in oceanographic and hydrobiological investigations. The majority of DO measurements use amperometric and optical sensors. The performance of these sensors has dramatically improved over the years but the measurement is influenced by numerous uncertainty sources. Therefore, the often observed disagreements between the sensor-based DO data from different laboratories have caused a negative perception of the data in the oceanography community. In this project, a high-accuracy modification of the gravimetric Winkler titration method has been developed. Depending on measurement conditions and on the dissolved oxygen content the expanded uncertainty ($k = 2$) of the method is in the range of 0.023 – 0.035 mg/l (0.27 – 0.38 %, relative). This development enables more accurate calibration of electrochemical and optical DO sensors for routine analysis than has been possible before. Titration is one of the few chemical measurement techniques that can be used as the basis of realizing *primary measurement procedures* – measurement procedures that, if carefully implemented, can provide traceability without calibration with the analyte (substance to be determined). The developed titration method is implemented with great care and is thus very suitable for providing traceability for DO measurements.

Two interlaboratory comparisons were performed. In ESTDO-2012, an in situ interlaboratory comparison carried out at the University of Tartu, 52% of the results were out of range. Based on analysis of the results, a set of tools and recommendations were given to the participants and compiled as a Good Practice Guide for Improving Accuracy of Dissolved Oxygen Measurements. The field (*in situ*) intercomparison FIELDOXY 2014 was performed on board the research vessel Aranda and jointly organised by Proftest SYKE, Envical SYKE and the University of Tartu (UT). In total, 88 % of the results were satisfactory when total deviation of 8 % from the assigned values were accepted.

11. Provision of an improved coulometric measurement procedure for dissolved oxygen concentration, with an uncertainty of 0.04 mg/l - 0.06 mg/l (at saturation)

Coulometry is another of the few chemical measurement techniques that can be used as the basis of realizing primary measurement procedures. Coulometric procedures of primary nature are used e.g. in analysis of high-purity materials and determination of low water levels in different samples (coulometric Karl Fischer titration). An improved coulometric cell was fabricated in order to minimise oxygen diffusion through the cell cover. It was found that hydrogen peroxide is generated at the cathode as an intermediate and is not reduced completely within the time-frame of the experiment. This means that the reaction does not proceed in a uniform way (which is a strict requirement for coulometry). This finding is also supported by calculations from published kinetic data. This behaviour leads to systematic errors in oxygen determination in the order of several percent, an order of magnitude higher than the target uncertainty. Since the development of the gravimetric titration procedure for dissolved oxygen (item 10) was a success, the failure to develop the high-accuracy coulometric measurement procedure did not cause problems with achieving the overall goals of the project.

Actual and potential impact

Dissemination

The project outcomes have improved the metrological infrastructure required for reliable monitoring and modelling of ocean processes and have been disseminated widely to the intended user communities.

The project has resulted in ten high impact publications in key journals and two PhD theses. In total about 20 papers have been submitted, or are in preparation, and more than 60 presentations were given at general and specialised conferences. A review paper: Metrological challenges for measurements of key climatological observables: oceanic salinity and pH, and atmospheric humidity has been submitted to *Metrologia*. Options for future improvements are being discussed with the international community responsible for the recent seawater standard TEOS-10 for salinity and pH.

A training school covering the metrology of dissolved metals concentration in seawater samples has been conducted for early career researchers, with a seminar organised for experienced researchers by UoP in conjunction with international GEOTRACES study as part of COST action EOS0801. Four stakeholder workshops were held, of which two – one on salinity and one on pH – were organised in conjunction with the 16th ICPWS (Greenwich, 2013) and the JCS.

As a result of the project the Joint Committee on the Properties of Seawater (JCS), responsible for developing and maintaining standards for ocean science, has approved four of the project consortium members as JCS members.

Early impacts

During the project European NMIs have built up knowledge on the requirements of monitoring key oceanographic observables and collaboration links have been established with the oceanographic research community. This will strengthen the position of the European NMIs in environmental metrology. Primary calibration facilities will be available for other NMIs as well as for other users, not only from oceanographic laboratories but from environmental laboratories in general. Seawater reference labs and calibration centres in France and Germany are already in contact with the consortium.

Providers of seawater pH standards have cooperated with consortium members and the JCS in the development of harmonised pH standards for quality control of oceanic carbon dioxide.

Cooperation between the producer of IAPSO Standard Seawater (SSW), the National Metrological Institutes and the JCS is providing more confidence in international seawater standards. The SSW producer is going to integrate the conductivity ratio–density relationship into the procedure of SSW fabrication to deliver SI traceable salinity values.

Improved speed of sound data with a relative uncertainty better of 0.1 % over a pressure range of up to 70 MPa and a temperature range between 0 °C and 40 °C has delivered reliable input data for extended equations of state in the International Thermodynamic Equation of Seawater (TEOS-10). Reliable thermodynamic data are a categorical prerequisite for deep sea research and the exploration of ocean resources. The data obtained will be considered in future standardisation work of IAPWS (International Association for the Properties of Water and Steam). Extensive further activities beyond the project have been started and are in progress, e.g. laboratory measurements including pressure as thermodynamic property.

Consortium members are continuing to work with the International Union of Pure and Applied Chemistry (IUPAC) on their project 2013-013-1-500 addressing “pH measurement of seawater”.

The project results represent important steps towards a European integrated ocean observation based on a robust metrology infrastructure, indispensable to more accurately measure small changes in long-term oceanographic data series. A reliable database at high pressure advances the deep sea research important not only for climate forecasting but also for sustainable economic use of the ocean.

The project met the objectives of the European Marine Strategy Framework Directive (MSFD 20089) to have measurement techniques in place to monitor the Ocean’s status. The project outcomes deliver the required metrological basis for simplified sensor calibration on sea and will help to establish links to European and worldwide monitoring projects.

List of publications

See list in the Final Publishable JRP Report.



JRP start date and duration:	01 September 2011 for 36 months	
JRP-Coordinator: Petra Spitzer, PTB	Tel: +49 531 592 3130	E-mail: petra.spitzer@ptb.de
JRP website address:	http://www.ptb.de/emrp/705.html	
JRP-Partners: JRP-Partner 1 PTB, Germany JRP-Partner 2 INRIM, Italy JRP-Partner 3 IPQ, Portugal JRP-Partner 4 JRC, European Commission JRP-Partner 5 LNE, France	JRP-Partner 6 MKEH, Hungary JRP-Partner 7 NPL, United Kingdom JRP-Partner 8 SMU, Slovakia JRP-Partner 9 SYKE, Finland JRP-Partner 10 UT, Estonia	
REG-Researcher 1: (associated Home Organisation)	Robert Clough UoP, United Kingdom	
REG-Researcher 2: (associated Home Organisation)	Maria Filomena Camões FFCUL, Portugal	

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union