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JRP-Coordinator		
Name, title, organisation	Petra Spitzer, PTB	
Tel:	+49(0)531592 3130	
Email:	petra.spitzer@ptb.de	
JRP website address	<a href="http://www.ptb.de/emrp/env05.html">http://www.ptb.de/emrp/env05.html</a>	
Other JRP-Partners		
Short name, country	INRIM, Italy IPQ, Portugal JRC, European Commission LNE, France MKEH, Hungary NPL, United Kingdom SMU, Slovakia SYKE, Finland UT, Estonia	
REG1-Researcher	Robert Clough	Start date: 01 Sep 2012
(associated Home Organisation)	UoP, United Kingdom	Duration: 24
REG2-Researcher	Maria Filomena Camões	Start date: 01 Sep 2011
(associated Home Organisation)	FFCUL, Portugal	Duration: 36

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## 1 Executive Summary

### 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 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 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 enough uncertainties required for these 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.

### Scientific and technical objectives

This 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 (DO) content of seawater. In addition, speed of sound was measured to feed into the International Thermodynamic Equation of Seawater 2010 (TEOS-10) database.

### 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 IAPSO<sup>1</sup>-Standard Seawater (SSW). However, the current calibration and production procedures of IAPSO SSW 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 5 °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 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

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<sup>1</sup> International Association for the Physical Sciences of the Oceans

measurement range for ocean climate research. Using the conductivity ratio–density relationship it is now possible to monitor the production of SSW 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 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 of the project proved 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 SSW, 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

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’.

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 were selected and characterised by a primary pH system (Harned cell), with the aim of determining pH and the  $\text{pH}_T$  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 characterised 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 standardised 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 the Guide for Uncertainty in Measurements (GUM), with respect to potentiometric and spectrophotometric pH measurement methods in seawater

For the first time a complete uncertainty budget was assessed for  $\text{pH}_T$  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  $\text{pH}_T$  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

For the determination of major components, methodologies based on ionic chromatography were developed in the project. Reference methods for quantification of anions with expanded uncertainties of a few percent are now available for silicates, phosphates, sulphates, 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 (DO) 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 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 DO 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 realising *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, 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 project partners SYKE and 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 DO concentration, with an uncertainty of 0.04 mg/l - 0.06 mg/l (at saturation)

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) and the finding is 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 DO 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

The project's 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 more than 60 presentations were given at general and specialised conferences and a training school covering the metrology of dissolved metals concentration in seawater samples has been conducted for early career researchers. Four stakeholder workshops were also held, of which two were organised in conjunction with the 16<sup>th</sup> ICPWS (Greenwich, 2013) and the Joint Committee on the Properties of Seawater (JCS).

As a result of the project the JCS, responsible for developing and maintaining standards for ocean science, has approved four of the project members as JCS members. Providers of seawater pH standards have also cooperated with consortium members and the JCS in the development of harmonised pH standards for quality control of oceanic carbon dioxide.

In addition, cooperation between the producer of IAPSO 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 TEOS-10. The data obtained will also be considered in future standardisation work of the IAPWS.

The project's 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. The project also met the objectives of the MSFD 20089 i.e. to have measurement techniques in place to monitor the Ocean's status, and the project's outcomes will deliver the required metrological basis for simplified sensor calibration at sea and will help to establish links to European and worldwide monitoring projects.

## 2 Project context, rationale and objectives

### 2.1 Context

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.

## 2.2 Objectives

This 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 (DO) 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 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 SSW, 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 5 °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 measurement procedure for DO concentration, with an uncertainty of 0.03 mg/l - 0.05 mg/l (at saturation).
11. Provision of an improved coulometric measurement procedure for DO concentration, with an uncertainty of 0.04 mg/l - 0.06 mg/l (at saturation).

### 3 Research results

#### 3.1 Reference Methods and Data for Ocean Salinity

##### Introduction

The aims of this work were

- Provision of a quantitative link between the conductivity ratio  $K_{15}$  and the density of SSW, in order to establish SI traceability of practical salinity measurement results (objective 1).
- Provision of a reference measurement method that enables SI traceability of Practical Salinity results (PSS-78), measured at pressures and temperatures typical for oceanography, i.e. pressures of up to 70 MPa and temperatures between 5 °C and 40 °C (objective 2).
- 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 (objective 3).

##### Results

Some of the main achievements of this project were in the development of a sound metrological framework for Salinity measurements that results are traceable to the SI and consistent with the Practical Salinity Scale of 1978 (PSS-78), i.e. the current metrological reference for Practical Salinity. To achieve this the project completed the following:

- 3.1.1. Preparation of IAPSO SSW with salinity levels between 2 and 42.
- 3.1.2. Measurements of conductivity ratio and density measurement setups, in particular with respect to measurement stability and repeatability.
- 3.1.3. Comparison measurements of density and conductivity ratios at selected salinities and temperatures in order to estimate the interlaboratory reproducibility.
- 3.1.4. High precision density and conductivity ratio measurements of samples at temperatures between 5 °C and 35 °C and pressures up to 200 bar.
- 3.1.5. An empirical measurement function linking density and conductivity ratios in the aforementioned salinity, temperature and pressure ranges and a comparison with TEOS10.
- 3.1.6. Investigation of the influence of composition anomalies on the measurement in Baltic Sea samples.

##### 3.1.1 Sample preparation

Samples were prepared at salinity levels of 2, 5, 10, 15, 20, 25, 30, 35, 40 and 42 from IAPSO SSW. The salinity of each set of samples was calibrated using weight diluted SSW. In this way, except for the reference with a salinity of 35, the salinity values were scaled independently from the Practical Salinity Scale 1978 (PSS-78). Homogeneity of the samples was tested with a Salinometer and the relative spread around the mean was  $10^{-5}$ .

##### 3.1.2 Measurement Setups for Conductivity Ratios

Conductivity ratios at atmospheric pressures were measured using a two electrode Jones type cell. Two round and flat electrodes (diameter 2 cm), made of blank platinum (Pt), were fixed opposite each other in a cylindrical body (inner diameter 2.2 cm), made of borosilicate glass. The cell was placed in a temperature controlled oil bath that was placed inside a temperature controlled air bath. The cell was cleaned, dried with argon, rinsed and filled with the solution under investigation, using a specialised tubing and pumping system in order to avoid sample evaporation. The conductance of the seawater between the electrodes was determined with electrochemical impedance spectroscopy and the real parts of the measured impedances were plotted against inverse frequency. The solution resistance was deduced by linear extrapolation versus infinite frequency and conductance calculated from the inverse of the solution resistance. A Pt100 sensor was also placed in the solution to measure temperature synchronously.

The high pressure conductivity ratio measurement setup included a commercial High Performance Liquid Chromatography (HPLC) pumping system for pressure generation. The cylindrical conductance cell was built of three cylindrical ceramic bodies, each with a 5 mm diameter hole. The ceramic bodies were arranged along the cylinder axis and separated by two washers made of 1 mm thick tantalum, also with a 5 mm hole in the



centre. The cylinders and washer were pressed together by a massive steel housing in order to withstand the pressure. The washers, separated by one of the ceramic cylinders served as electrodes, with the solution flowing through the centre of the cylindrical arrangement. The cell was then connected to the HPLC pump and placed in an oil bath and the conductance was determined analogously to the measurements at atmospheric pressure. Temperature was measured in the oil bath, using Pt100 sensors.

Absolute conductivity, i.e. traceable to the SI, can typically be measured with a relative standard uncertainty of  $2 \times 10^{-4}$  at best, however, this is insufficient for oceanographic purposes where tiny differences in salinity need to be considered. It is assumed that systematic uncertainties can be cancelled out by conductivity ratios, such that measurement uncertainty is only determined by measurement stability and repeatability. Thus measurement stability and repeatability in the measurement ranges of interest were the most relevant criteria for characterising the conductivity ratio measurement setup. Several measurement series were made to quantify them and in generally, the relative measurement stability over 24h and the relative repeatability values were a few  $10^{-5}$ , depending on temperature and salinity. At high pressures the relative stability was 0.02 % and relative repeatability 0.7 %.

### 3.1.2 Measurement Setups for Density

For the determination of the conductivity ratio–density relationship, the density of IAPSO SSW must be measured with very low uncertainty. This because, in contrast to the conductivity of seawater which spans a range of 0.3 S/m to 5 S/m across a salinity range of 2 to 35, the density of IAPSO SSW only changes by 2.5 %. Therefore, density measurements must be performed with a much lower level of uncertainty to yield reliable results for the calculation of the conductance ratio-density relationship. A relative target uncertainty of  $2 \cdot 10^{-6}$  (coverage factor  $k = 2$ ) for the density measurements at atmospheric pressure was aimed for in the project.

Measurements were performed using an oscillation-type density meter, which typically give a relative uncertainty of  $2 \cdot 10^{-5}$  for measurements at atmospheric pressure. The project showed that it was possible to further reduce this uncertainty by modifying this method. To do this a special substitution method was developed which reduced the uncertainty by a factor 10. Substitution was made by sequentially measuring the density of the IAPSO SSW sample and a reference liquid with precisely known density (i.e. ultrapure water as published in the IAPWS formulation 1995 and with an uncertainty smaller than 1 ppm) and by repeating this procedure several times. A sequence of 10 measurements of SSW and of ultrapure water allowed the elimination of most of the effects contributing to the uncertainty of density measurement, such as drifts in the parameters in the device's mechanical and electrical system and even temperature misalignment.

At the ppm-level an oscillation-type density meter showed dependence on the history of the device. Thus, a reliable substitution at this level can only be guaranteed when the filling procedure of the liquids into the measurement device is consistent. To test this, of the project conducted many studies on how to guarantee the consistency of filling processes, as well as the equality of temperature, the volume of the samples and the cleaning procedure used in between two adjacent measurements. The influence of the cleaning procedure is essential as it can affect the initial temperature of the density meter at the beginning of the stabilisation procedure, and for a reliable substitution this must be consistent.

The project showed that using this substitution measurement method the target uncertainty of 2 ppm could be achieved. This uncertainty at atmospheric pressure is even smaller than that uncertainty achieved using a hydrostatic weighing apparatus as predominantly used for high precision measurements of liquid densities.

To establish the relationship between conductance ratios and the density for deep seawater the measuring method for density for atmospheric pressure was adapted for high pressure measurements up to 650 bar corresponding to a water depth of 6500 m and produced an expanded uncertainty of 30 mbar. The density meter used had a smaller resolution and higher uncertainty compared to the device at atmospheric pressure as the walls of the measuring cell have to withstand the high pressure and, therefore, have a larger mass and a smaller ratio sample mass to cell mass. The uncertainty in standard mode was  $2 \cdot 10^{-4}$  under pressures up to 100 bar and could be further reduced by using the substitution mode to  $2 \cdot 10^{-5}$ .

### 3.1.3 Comparison Measurements of Density and Conductivity Ratios

The long term comparability of measurements is not only affected by the stability of a reference standards but also how they are prepared at different institutions. The reproducibility contribution to the uncertainty of the quantity value assigned to the reference standard is determined by interlaboratory reproducibility rather than

the capability of an individual institution to reproduce the value. Therefore comparison measurements of conductance ratio and density were performed in this project to quantify this contribution with respect to Practical Salinity results traceable to the SI.

Project partners PTB, MKEH, INRIM, LNE and SMU participated in two conductance ratio comparisons. Conductance ratios of seawater samples at nominal salinities of 7, 19 and 35 were measured at 5 °C, 15 °C, 25 °C and 35 °C in the first comparison. In a second comparison conductance ratios of natural seawater from the Baltic Sea were measured at 15 °C. Collaborators and other NMIs (outside of the project consortium) were invited to participate in the comparisons. The relative uncertainties of the reference values were used as an estimate for the interlaboratory reproducibility and were in the order a few  $10^{-4}$ , depending on temperature and salinity. The expected uncertainty was in the order of  $10^{-5}$ . However, the equivalence was unexpectedly rather poor, even amongst those experienced institutes who had proven good performance in former comparisons.

A density comparison measurement at atmospheric pressure was performed by project partners PTB and NPL. Two samples of nominal salinities of 7 and 35 were measured at 5 °C, 15 °C and 35 °C. The difference of the results from the corresponding mean value was within the expected uncertainty level of  $10^{-5}$  (relative 7 ppm at maximum), which supported the low measurement uncertainty for density measurements. A similar comparison at high pressure was also carried out and results showed systematic deviations which were significantly larger than the uncertainties achieved.

#### High Precision Conductance Ratio and Density Measurements

Conductance ratios and the density of the samples described previously were measured at between 5 °C and 35 °C with 5 °C steps at atmospheric pressure. At higher pressures the density of 4 samples with salinities between 5 and 35 were measured at 4 temperatures between 5 °C and 35 °C and at pressures up to 650 bar. Conductance ratio of 5 samples with salinities between 2 and 42 were measured at 4 temperatures between 5 °C and 35 °C and at pressures up to 200 bar.

The measured conductance ratios were then used to calculate Practical salinity according to the PSS-78. The results were compared with values that had been previously gravimetrically determined. Figure 3.1.1 illustrates the relative deviation at atmospheric pressure and 15 °C (reference point) and it can be seen that the deviation is in the range of several  $10^{-4}$  and increases with increasing difference from the reference point at 15 °C (with a conductance ratio of one). The purpose of the comparison was to validate the measurement procedure and as verification of the reproducibility of PSS-78. However, although Figure 3.1.1 indicates a deviation with increasing difference from the reference point, it cannot be stated whether this is due to a change in SSW or due to the instrument dependence on conductance ratios. The limits of reproducibility also make it difficult to assess the significance of the deviation. Nevertheless, it must be emphasised that the deviation does not result from problems with stability, repeatability or homogeneity.

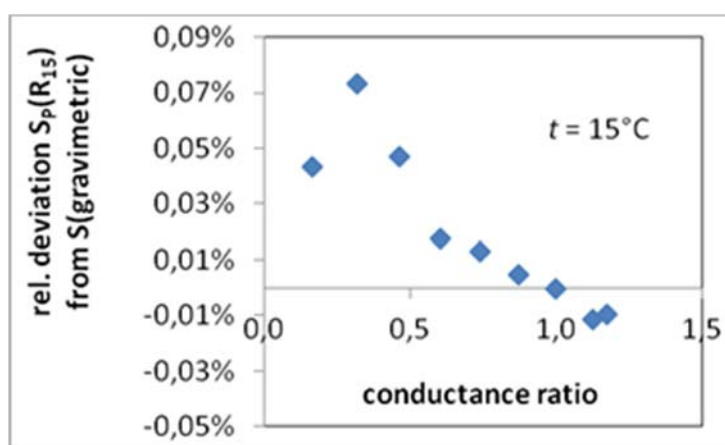


Figure 3.1.1 Deviation of Practical Salinity calculated from the measured conductance ratios from the value determined by gravimetric dilution of the SSW samples.

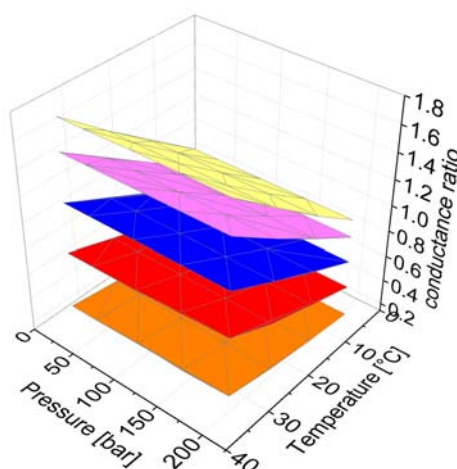


Figure 3.1.2. Illustration of conductance ratio measurement results of samples having salinities 5, 15, 25, 35, 42 (from bottom to top).

Figure 3.1.2 illustrates the conductance ratio measurement results at various pressures and temperatures. The deviation from PSS78 is comparable to that measured at atmospheric pressures and, the standard uncertainty of the conductance ratio is about 0.7 %. The predominant contribution is from measurement repeatability and the combined uncertainty of all other contributions is about 0.03%.

Densities were measured up to a salinity of 42. The measured density values at salinities 40 and 42 showed inconsistencies during fitting and significant steps in residuals were found. A comparison against TEOS- 10 data also showed much larger deviations at these salinities compared to lower salinity levels. This indicates a possible mismatching of the seawater at salinities of 40 and 42 compared to seawater with lower salinities. In contrast to salinities of less than 35, salinities of 40 and 42 are produced by a boiling down process, which may results in a disturbed composition. Thus, salinities of 40 and 42 were excluded from measurements at high pressure and also data fitting in order to determine the conductance-density relationship more accurately.

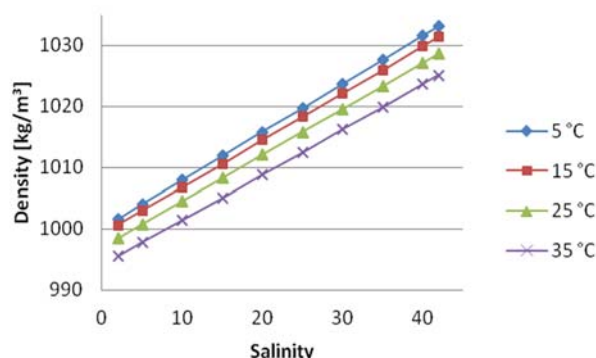


Figure 3.1.3 Illustration of density measurement results of samples at various temperatures.

Figure 3.1.3 shows density results at atmospheric pressure at various temperatures. The standard uncertainty of the measurement values is about 2 ppm and the expansion coefficient increases significantly with temperature.

#### Empirical Measurement Function Linking Density and Conductivity Ratios

The conductance ratio data was weighted based on a modified Weibull distribution function, which was found to accurately fit the relationship of the conductance ratio and density at constant temperature and atmospheric pressure. Therefore, rational exponents of the relationship were determined iteratively using least squares fitting of the linear coefficients and minimising the residual sum of squares (RSS) by varying the exponents. The number of coefficients in the final set was reduced by trial and error using the RSS. The resulting data give a maximum residual smaller than the measurement uncertainty. Densities at higher pressures were also fitted as a residual term relative to density at atmospheric pressure and produced a single equation that

covered the entire measurement range. The residual term was a polynomial and was determined using least squares fitting. But because of the relatively large uncertainties of the measured conductance ratios the gravimetrically determined salinities of the samples were used to calculate the corresponding conductance ratios by inverting PSS-78 in order to be consistent with the actual salinity scale. The conductance ratio-density relationship found was:

$$\rho = \sum_{i=0}^4 \sum_{j=0}^4 a_{i,j} \cdot \frac{R_*^{n_i}}{T^{m_j}} + (p - p_0) \cdot \sum_{i=0}^2 \sum_{j=0}^3 \sum_{k=0}^1 a_{i,j,k} \cdot \frac{R_*^i \cdot p^k}{T^j}$$

with  $R_* = -\ln\left(1 - \frac{R}{R_0}\right)$ ,  $R_0 = 4$ , and  $p_0 = 101325$  Pa

The relationship covers the salinity range 2 to 35, temperature range 5 °C to 35 °C, and pressures up to 65 MPa. The uncertainty increases depending on pressure; i.e. at atmospheric pressure the uncertainty is 1 ppm, up to 100 bar the uncertainty is 10 ppm, and up to 650 bar the uncertainty is 20 ppm.

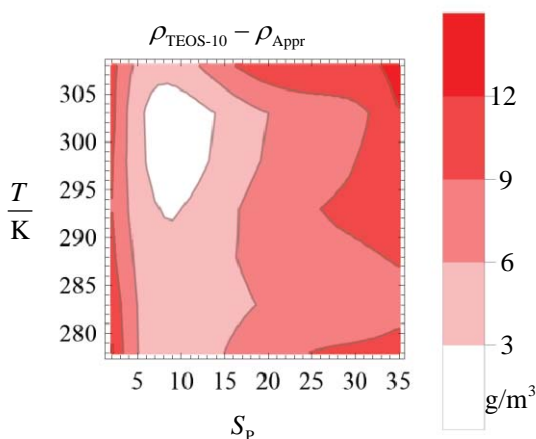


Figure 3.1.4 Deviation of conductance-density relation at atmospheric pressure from TEOS-10.

Figure 3.1.4 shows the deviation of conductance-density relation at atmospheric pressure from TEOS-10. The expanded uncertainty of the deviation at a 95 % level is 0.009 kg/m³. At salinities of 2, 30, and 35 as well as at higher temperatures the uncertainty of the deviation increases significantly. Thus, with the data gained in this project a significant improvement of the current standard equation of state of seawater is possible.

#### Influence of Composition anomalies on the Measurement in Baltic Sea Samples

PSS-78 is based on the assumption that the relative mass fraction of a dissolved constituent with respect to the total mass of all dissolved constituents is constant, i.e. only the amount of water varies with time and location. As a consequence of this assumption a single parameter like conductivity can be used as a measurand for salinity. However, this assumption for PSS-78 is not necessarily true, as the composition of marginal seas like the Baltic show deviations compared to the composition of large oceans. The effect of such anomalies on conductivity is different compared to the effect on density and therefore the effect of composition anomalies on the conductance ratio-density relationship was investigated using natural water from the Baltic Sea. Firstly, samples from various locations within the Baltic Sea were chemically analysed using ion chromatography to quantify the anomalies in terms of relative mass fractions. Then the conductance ratios and density of a natural seawater sample from the Atlantic Ocean was measured and compared to those of a two representative samples from the Baltic Sea (from Kiel bay and the Arkona Basin).

The results of the ion chromatography are shown in Table 3.1.1. The table shows the mass fraction of the reference composition, given in g per kg solution; the % values which indicate the relative deviation of the mass fraction from the reference composition with respect to the mass fraction of chloride (assumed not to show composition anomalies); and the deviation of a SSW sample. If the constituent from a sample of natural seawater showed a deviation larger than that of SSW, and more than the expanded (coverage factor  $k=2$ ) measurement uncertainty (1%), it was assumed an anomaly. Calcium, sulphate and bromide showed the most significant (relative) anomalies.

	Ref. Comp.	SSW P151	Atlantic Ocean (33°N 22°W) 5000m	Kiel Bay (Baltic Sea)	Arkona Basin (Baltic Sea)
Constituent	$w_{ref} (i)$	relative deviation from reference composition			
	g/kg-sol				
Cl <sup>-</sup>	19.35	0.0%	0.0%	0.0%	0.0%
Br <sup>-</sup>	0.06728	-1.2%	4.8%	-1.2%	-1.8%
SO <sub>4</sub> <sup>2-</sup>	2.712	-0.2%	0.2%	0.9%	1.5%
Na <sup>+</sup>	10.78	-0.4%	0.6%	0.1%	-0.6%
K <sup>+</sup>	0.3991	-2.1%	-0.2%	-0.9%	0.3%
Ca <sup>2+</sup>	0.4121	-0.9%	-1.5%	24.9%	21.3%
Mg <sup>2+</sup>	1.284	0.6%	2.0%	2.6%	2.0%

Table 3.1.1 Results of an ion chromatographic analysis.

Table 3.1.2 shows the effect of composition anomalies on the conductance ratio-density relationship. The deviation of the conductance ratio calculated from the conductance ratio density relation is significantly larger than the uncertainty of the calculated value only for the Baltic Sea II sample. It must be noted that the Atlantic Ocean sample also shows a deviation somewhat larger than the uncertainty, even though it was expected to have a reference composition. However, the ion chromatographic results of the Atlantic Ocean sample show deviations that are also larger than that of SSW, which may explain the unexpected difference between the measured conductance ratio and that calculated from the density.

In summary the results prove that composition anomalies have an effect on the conductance ratio density relationship and increase its uncertainty up to a factor seven. However, it must also be concluded that a change in (Atlantic) seawater composition affects the  $K_{15}$  value of SSW, which means that a stable metrological reference is needed for Practical Salinity measurement results.

Sample	Density measured kg/m <sup>3</sup>	Conductance ratio measured	Conductance ratio calculated	Uncertainty	Deviation
Atlantic Ocean (33°N 22°W)	1025.893	0.99744	0.99765	0.00011	0.00021
Baltic Sea I sample (Kiel bay)	1012.462	0.53174	0.53185	0.00012	0.00011
Baltic Sea II sample (Arkona basin)	1005.105	0.25319	0.25411	0.00013	0.00092

Table 3.1.2 Effect of composition anomalies on the conductance ratio-density relation

## Conclusions

### 1. Provision of a quantitative link between the conductivity ratio $K_{15}$ and the density of SSW, 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 IAPSO SSW. SSW is a primary reference solution, prepared from natural seawater from the North Atlantic and has a conductivity ratio assigned according to procedures defined in PSS-78. However, the current calibration and production procedures of IAPSO SSW 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 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 SSW 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 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 SSW, which makes obvious the necessity of a stable metrological reference for Practical Salinity measurement results.

### 3.2 Improved Speed of Sound Data and Thermodynamic Data of Seawater

#### Introduction

The aims of this work were:

- 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 (objective 4).
- Provision of thermodynamic data of seawater calculated from the obtained measurement results (objective 5).

#### Results

A significant achievement of this project has been the ability to quantify the effect of the anomalous relative salt composition to the speed of sound. This was been done for the first time by direct measurements (with reliable uncertainties) of the speed of sound in the temperature range between 0 and 40 °C, at pressures up to 70 MPa and with salinities of 38, 35 and 10.

Based on a series of successful tests (at project partner PTB), during the initial phase of the project using a commercial time-of-flight sensor (ToF-sensor), it was decided to focus on the use of TOF-sensors as they are specifically designed for use in seawater. This approach also had a practical application in oceanography as well as complementing the double-pulse-echo technique, which was refined for seawater by project partner INRIM.

An experimental setup was developed with a bath thermostat and using bulk volumes for the water samples. A large/bulk sample (~55 L) was advantageous with respect to the stabilisation of the thermodynamic properties determining the speed of sound (i.e. temperature and salinity) and was less sensitive to effects influencing the sample purity (e.g. contamination, evaporation). With this setup measurement temperatures could be spatially and temporally stabilised at a level of 1 mK. Together with the use of calibrated normal thermometers and modern oceanographic conductivity probes (at PTB), the setup also provided the necessary conditions in conjunction with a highly accurate measurement technique for the project's speed of sound investigations.

Several TOF-sensors from two different manufacturers and with different technical configurations were acquired and used. The TOF-sensors were calibrated in pure water using the experimental setup (at PTB) and then measured. The speed of sound investigations revealed that the manufacturer's stated calibration and associated uncertainty, were of limited reliability for the TOF-sensors and therefore recalibration is essential for minimising their uncertainty. As result of the recalibration of the TOF-sensors with pure water an overall reproducibility of 0.015 m·s<sup>-1</sup> to 0.030 m·s<sup>-1</sup> (according to 20 ppm to 11 ppm, respectively) was achieved by the project. On the basis of the recalibration results the potential use of the TOF-sensors as acoustic thermometers was evaluated. In pure water a reproducibility of 3 mK to 12 mK was achieved for temperature determination using speed of sound measurements. The variability was found to be due to the sensitivity of the speed of sound with temperature.

Another aspect of this part of the project was relative measurements of the speed of sound in aqueous solutions of three different salts Sodium Chloride (NaCl), Magnesium Chloride (MgCl<sub>2</sub>) and Sodium Sulphate (Na<sub>2</sub>SO<sub>4</sub>) in pure water diluted and 'original' samples of North Atlantic seawater, and in 'original' samples of Baltic seawater. The reproducibility of the speed of sound in these different salt samples was virtually the same as in pure water, however, the experimental uncertainties of the state variables (i.e. temperature, salinity, pressure) caused additional, but not dominant, contributions. Methodical measurements in the 3 different salt solutions and seawater samples with varying temperatures and salinities revealed systematic differences for different TOF-sensors, reaching a maximum of 270 ppm, which could be due to a deficiency of the manufacturer's stated TOF determination. However, this did not affect the high stability of the TOF method.

For the seawater samples agreement was found with existing values available within the current literature of 0.3 m·s<sup>-1</sup> (200 ppm), which gives an estimate for the uncertainty of speed of sound measurements when using modern TOF-sensors in seawater. This level of uncertainty is also comparable to established pulse-echo or double-pulse-echo techniques for measuring the speed of sound in liquids.

PTB used the high resolution and stability of the TOF-sensors to study the effect of the anomalous relative salt composition on the speed of sound. For a Baltic seawater sample with a salinity of 7.766, PTB quantified the effect to (0.067±0.014) m·s<sup>-1</sup>.

With the aim of measuring the speed of sound in seawater up to 70 MPa, in the temperature range of 0 to 40 °C, a new ultrasonic sensor (based on the pulse-echo technique) and a novel pressure vessel was designed and produced by project partner INRIM. Both the sensor and the pressure vessel were manufactured using AISI- 316L stainless steel in order to exploit its chemical resistivity to seawater. The pressure vessel was equipped with a new 5-way, (2 electric and 3 hydraulic), feed-through was also produced, using materials suitable for preventing the pollution of the measured samples. Another innovation in INRIM's new pressure vessel was the presence of a stirring device capable of mixing the sample under pressure. Although samples of artificial seawater didn't show settling effects, this new pressure vessel is suitable for studying the properties of suspensions that do show settling such as coastal waters.

As part of the new pressure vessel, the measuring sensors available at INRIM were not suitable for working with conductive fluids (i.e. seawater) and therefore a new insulated mounting system was designed and made of Macor. The piezoelectric (PZT) source was positioned inside a dielectric casing and, in this way, flat surfaces of PZT, immersed into the sample, were insulated from each other. Moreover the distances between the source and two reflectors were accurately calculated taking into account the effective diameter of the emitting surface and the working frequency of the PZT disc. Following its production the PZT measurement cell was calibrated and then measurements were carried using INRIM's new pressure vessel on seawater samples obtained from IAPSO SSW. Measurements were carried out by INRIM for SSW (S35), for Low salinity SSW (S10) and for High salinity SSW (S38) up to 70 MPa. Furthermore, two North Atlantic seawater samples, supplied by project partner PTB, were measured at atmospheric pressure in order to compare the speed of sound results obtained by PTB (using TOF-sensors) and INRIM.

The results showed that the producers of commercial speed of sound sensors tend to over-estimate the uncertainty budget for their products, which is typically stated in the order of 0.02 m/s (or approximately 13 ppm). This value is more than two times better than the best laboratory results obtained in pure water using a coherent phase detection technique (Fujii, Masui, 1993). Therefore, the project focused on the lowest uncertainty limit theoretically achievable using a pulse echo-technique (i.e. as used by commercial sound velocity sensors) and it showed that uncertainties below 30 ppm cannot be considered reliable. Further to this, the limit of uncertainty is typically, in the order of 100 ppm under laboratory conditions for commercial speed of sound sensors.

The speed of sound was measured by INRIM using their new pressure vessel in the temperature range between 0 to 40 °C, at pressure up to 70 MPa and with salinities of 38, 35 and 10. The results showed that the overall uncertainty for speed of sound measurements was in the order of 500 ppm up to high pressures.

## Conclusions

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 TOF-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 TOF. 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 TOF 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 %).

### 3.3 Primary Reference Methods for pH in Seawater

#### Introduction

The aims of this work were

- Provision of a primary reference procedure for pH measurements in seawater (objective 6).
- Provision of harmonised and validated pH measurement procedures with respect to potentiometric pH measurements in seawater (objective 7).
- Provision of uncertainty budgets according to GUM, with respect to potentiometric and spectrophotometric pH measurement methods in seawater (objective 8).

#### Results

The pH is a critical parameter for characterising many important processes in the ocean, and is in turn affected by these processes. In particular, the ocean CO<sub>2</sub> system is central to a wide variety of biological processes, with CO<sub>2</sub> being taken up by photosynthetic organisms, and remineralised by respiration processes. The changes in the concentration of different carbon-related species in the ocean are more complex than that in the atmosphere due to the chemical equilibria in the carbonate system. Thus trends in oceanic pH may be small but are highly relevant. Therefore, for the detection of pH in long-term observations, an unambiguous definition and comparable measurement and calibration procedures are essential.

The concept of pH is expressed in terms of a logarithmic function of the hydrogen-ion activity in aqueous solutions, as:

$$\text{pH} = -\lg a_{\text{H}^+}$$

Modern use of the pH concept is widespread, largely because it can be measured easily using a relatively straightforward potentiometric technique, however important aspects are often not adequately taken into account. Over the past decades, due to technical issues, a variety of related but different operationally defined 'pH' quantities have been introduced. However seawater studies can be particularly problematic for pH for two main reasons; firstly, seawater has a high ionic strength, which causes problems when using conventional pH calibration standards. Secondly, current research in marine science requires an extremely small standard uncertainty in pH measurements (of the order of 0.004), over a fairly narrow range of pH, which is far smaller than the difference between many of the available operationally defined 'pH' quantities. To deal with these issues, recently, more and more of the oceanographic community has adopted spectrophotometric techniques for measuring seawater pH using an indicator dye. However, the main problem with this technique is that the measurand is not expressed in terms of hydrogen ion activity but in terms of total hydrogen ion concentration (pH<sub>T</sub>), which creates problems for metrological traceability and the comparability of measurement results.

To address these issues the project aimed to produce a primary reference procedure for pH measurements in seawater, as well as harmonised and validated pH measurement procedures for both potentiometric and spectrophotometric pH measurements. The first step was to choose a representative matrix for seawater acidity measurement, which was done based on the reference composition established by IAPSO for a seawater of practical salinity of 35. Next, in order to represent the pH value as close as possible to that of real seawater but to avoid the issues related to the presence of carbonates, a Tris-Tris·HCl buffer was selected. This Tris-Tris·HCl buffer solution in artificial seawater was then characterised by a Harned cell, i.e. the primary system for pH measurements, with the aim of determining the acidity function value and the pH<sub>T</sub> value. Finally, these procedures were validated by an intercomparison between 3 of the project partners (INRIM, LNE and PTB) and 2 NMI collaborators (NMIJ and NIST).

The results obtained at 25°C for the acidity function are shown in Figure 3.3.1 and show a good agreement between the results of the intercomparison with uncertainties of 0.004 (for  $k=2$ ) for most participants, similar to results for pH measurements obtained in low ionic strength solutions.



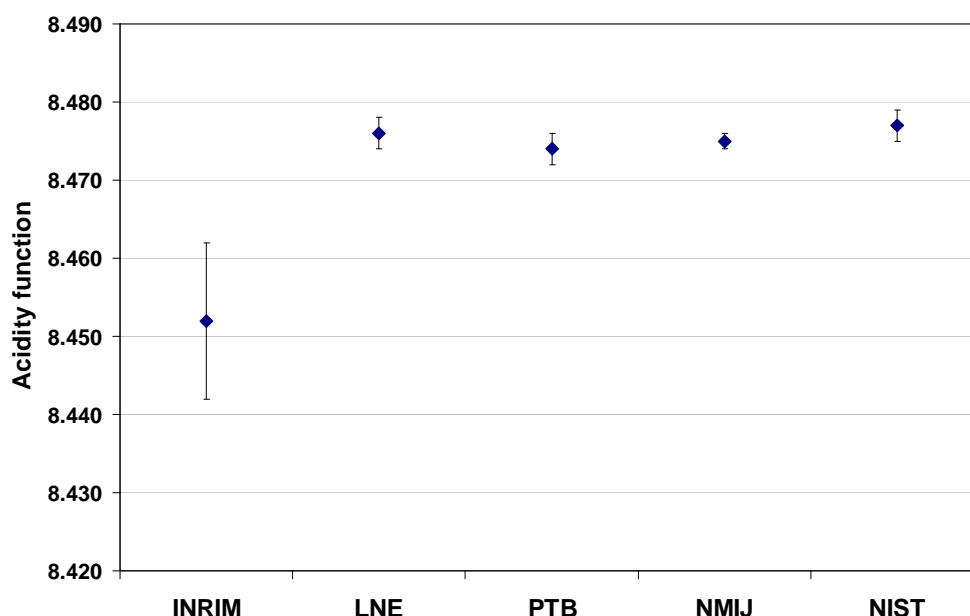


Figure 3.3.1 Intercomparison results for the acidity function at 25 °C.

In order to convert the acidity function into pH, the activity coefficient was calculated. However this calculation is based on thermodynamics assumptions, which are valid only for aqueous buffers at low ionic strength. Therefore, the project produced an experimental approach which was then compared to a modelling approach (Pitzer model) in order to determine the best approximation representing a complex matrix (i.e. seawater). The project then compared the values expressed in pH and in  $\text{pH}_T$  which showed a discrepancy of about 0.2 pH between pH and in  $\text{pH}_T$  values (as expected by the project), and supports the fact that there is a lack of comparability when different concepts are used (i.e. pH and  $\text{pH}_T$ ).

In order to produce a complete uncertainty budget and create a link between different pH measurement procedures used in the field (i.e. in situ), the project used the same Tris-Tris·HCl buffer solution with analysis by glass electrodes and by spectrophotometry, in collaboration with The Institut français de recherche pour l'exploitation de la mer (IFREMER). This work was conducted in parallel to a comparison organised by ISO for validating the ISO standard ISO/CD 18191 "Water quality — Determination of pH in sea water — Method using the indicator dye m-cresol purple".

## Conclusion

### 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  $\text{pH}_T$  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  $\text{pH}_T$  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  $\text{pH}_T$  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  $\text{pH}_T$  value to the conceptual pH value was tested but further research and experimentation are necessary before stating its applicability for the aforementioned purposes.

### 3.4 Major and minor component and micronutrient elements determination

#### Introduction

The aim of this work was the provision of new, robust, and validated methods for the determination of important seawater components such as strontium, nitrate, phosphate, silicate and iron traces (objective 9).

#### Results

The complexity of the marine environment introduces an additional difficulty into measurements due to the effects of the matrix, which makes it difficult to determine the mass fraction of important seawater components such as strontium, nitrate, phosphate, silicate and iron (Fe) traces. Furthermore, the results of analytical instruments can be affected by spectroscopic interferences, which can have severe repercussions on component quantification. Micronutrient/component variations in seawater are consistent in deep ocean waters over a few mK. However, the quantification of components in seawater poses a number of difficulties, particularly in terms of matrix interference and calibration. Therefore the project set-out to develop new methods based on isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS) for the determination of important seawater components such as strontium, nitrate, phosphate, silicate and iron (Fe) traces.

Currently, there are several methods for the shipboard and laboratory determination of Fe in seawater but the discrepancies between results from different methods and different laboratories differs significantly at the 95 % confidence level. Such discrepancies are due to a variety of factors; (i) efficiency of the extraction of Fe from the matrix during preconcentration (resulting in different methods measuring different fractions of Fe); (ii) errors in the quantification of the analytical blank, and (iii) inaccuracies in the calibration of the system. The uncertainties from these previous intercomparisons also appear to be underestimated, and signal blanks are often significantly larger than the signals from seawater with sub-nanomolar Fe concentrations. Hence Fe data for the same water mass is inconsistent in these intercomparisons. Reliable determination of important micronutrient components in marine waters are essential for our understanding of their impact on ocean productivity and processes and therefore the project set out to develop new, robust and validated measurement procedures for the determination of important seawater components. Project partner JRC worked with REG(UoP) on this.

JRC and REG(UoP) began by reanalysing a dataset of existing flow injection – chemiluminescence (FI-CL) results. This reanalysis had two aims; firstly to estimate the typical combined uncertainties, and secondly to identify the main factors affecting the results and uncertainties. From this reanalysis a set of equations was proposed for uncertainty propagation according to the GUM. The set of equations included equations for data processing and equations for the quantification of standard uncertainties associated with individual input quantities. The reanalysis of the FI-CL data also showed a dependence on a range of assumptions, therefore the project developed, a phased experimental plan to confirm them. Following this a procedure was developed for measuring the dissolved Fe concentration in <0.2 µm filtered and acidified seawater samples by ID-ICPMS. The ID-ICPMS method involved concentration via off line solid phase extraction (using Titanium oxide nanoparticles) and ICPMS sample introduction at less than 10 µL min<sup>-1</sup> flow rate. From the results of this ID-ICPMS method a set of mathematical equations was produced covering the entire ID-ICPMS measurement procedure.

Based on these results, the project held a training school for early career researchers, organised by the REG(UoP) in conjunction with an international GEOTRACES study as part of COST action EOS0801, on the measurement of dissolved metals and radionuclide concentration in seawater samples. The discussions at the training school were very positive and supported the production of reliable data using validated measurement procedures, as per the requirements of ISO/IEC 17025.

#### Conclusions

##### 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<sup>+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) 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<sub>2</sub>. 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 GUM. A measurement procedure for measuring the dissolved Fe concentration in <0.2 µm filtered and acidified seawater samples by isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS) was developed.

### 3.5 Determination of Dissolved Oxygen (DO)

#### Introduction

The aims of this work were:

- 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) (objective 10).
- 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) (objective 11).

#### Results

DO content in natural waters is an indispensable quantity whenever data is collected for hydrobiological, ecological or environmental protection investigations. The majority of DO measurements are made with the use of amperometric and optical sensors and the performance of these sensors has dramatically improved over the years. Nevertheless, accurate DO measurement with sensors is not easy as it is influenced by numerous uncertainty sources. Therefore, agreement between sensor-based DO data from different laboratories has long been an issue and has caused a negative perception of the sensor-based DO data in the oceanography community. Because of this, the recent issue of the World Ocean Atlas was compiled taking into account only those DO concentrations obtained with chemical titration methods (e.g. the Winkler titration method). A similar decision was also made in a recent study of DO decline rates in coastal oceans. However, oceanographers need large amounts of DO data, collected continuously and over long time periods (e.g. months), often at locations that are far away from any human settlements. Therefore only sensor-based automatic DO measurements can meet this need and thus it is vital to improve the quality of such sensor-based DO measurements.

The most common chemical titration method for DO concentrations is the Winkler titration method, however like DO sensor-based measurements the Winkler titration method has a number of issues. For example Nordtest TR 537 (the handbook for environmental testing laboratories in Nordic countries) pointed out a 'long-term' uncertainty due to variation in the calibration of the method, as no stable reference material currently exists for DO measurement. The method suggested in Nordtest TR 537 for Winkler titration was to therefore calibrate the same thiosulfate solution several times during a few days and use the variation between the results for the uncertainty estimation. However, this suggestion in Nordtest TR 537 is an estimation and cannot be considered to fully address any bias in the uncertainty.

Therefore this project aimed to address these issues in two ways, in order to provide traceability to DO measurements;

- 3.5.1. an improvement of the Winkler titration method, and
- 3.5.2. the development of a coulometric titration method for DO measurement.

#### 3.5.1 Improved of Winkler titration method for DO measurement

An improvement (i.e. high-accuracy modification) of the Winkler titration method was developed by the project for determination of DO concentration <http://www.ut.ee/EACH/report-on-improved-high-accuracy-winkler-method-for-determination-of-dissolved-oxygen-concentration/>. Careful analysis of all uncertainty sources relevant to the Winkler method was carried out including: (i) oxygen introduced with the reagents; (ii) oxygen diffusing into the sample solution through the ground glass joint; and (iii) iodine volatilisation. The Winkler titration method was also optimised for minimising all uncertainty sources as far as practically possible. The key factors for improving the Winkler titration method were:

- gravimetric (as opposed to volumetric) preparation of all solutions and measurement of the titrant amount by weighing, as well as the possibility of adding very small amounts of titrant;
- careful investigation of the effect of iodine evaporation from the solutions and correcting the result for this evaporation; use of pre-titration to minimise this effect;
- using Winkler reagents with well-defined oxygen content and correcting for this content;
- amperometric determination of the titration equivalence point.



The improved of Winkler titration method is possibly the most accurate method of determining DO concentration currently available. Depending on the measurement conditions and on the DO content the expanded uncertainty ( $k = 2$ ) of the method is in the range of  $0.023 - 0.035 \text{ mg/dm}^{-3}$  ( $0.27 - 0.38\%$ , relative). To the best of our knowledge this is the most comprehensive uncertainty analysis of the Winkler method published to date.

### 3.5.2 Coulometric titration method for DO measurement

For the coulometric titration method, setups for coulometry at stable potentials and constant currents were assembled. The coulometry setup at stable potentials was satisfactorily tested using electrogenerated iodine. However, the coulometry setup at constant current, was thought to be more promising based on the available literature. Two auxiliary systems were described in the literature as suitable for oxygen determination: firstly, bipyridilium cation/bipyridilium radical cation and secondly, Copper ( $\text{Cu/Cu(I)}$ ) system in an ammonia EDTA solution. The second system was rejected based on current efficiency data. For the first system, a current efficiency generation of viologen radical cation was studied and conditions were found for current efficiency losses as small as  $0.03\%$ , well below the target uncertainty of  $0.5\%$ . However, further work detected hydrogen peroxide as an intermediate product in the electrolyte medium. This formation could not be avoided and gave a negative error in the oxygen determination, therefore the work had to be discontinued.

### 3.5.3 Intercomparison of DO measurements

Typically the calibration of electrochemical and optical sensors is done using the saturation method and the reference values for DO saturation concentrations are determined using the Benson and Krause equation. However, in order to obtain accurate results an accurate barometer, an accurate thermometer and a very stable thermostat are needed. Even with accurate equipment the saturation method is tricky to use and prone to errors. One of the main issues is super- or undersaturation. The smaller the bubbles used for saturation are, the faster the saturation conditions are achieved. But at the same time smaller bubbles may lead to supersaturation. In contrast, the use of the larger bubbles avoids supersaturation, but increases the time necessary for saturation. If uncertainty due to possible super- or undersaturation is carefully taken into account then the resulting uncertainty can be 2-3 times higher than the uncertainty of the project's improved Winkler titration method.

When measuring DO content with an optical or amperometric sensors in high salinity water samples, e.g. seawater, calibration should be carried out in water with a similar salinity. However, this is very difficult to rigorously do with the saturation method as the available saturation values of DO content in seawater are significantly less accurate than the respective values in pure water. An alternative approach is to calibrate in water and apply a salinity correction, but this also introduces a substantial uncertainty from the correction. In contrast, the dissolved salts commonly found in seawater do not hinder usage of the Winkler titration method and therefore two intercomparisons were organised to examine the performance of the project's improved Winkler titration method for DO measurements.

It is extremely difficult to organise DO intercomparisons that involve sending samples to participants (as usually done with most intercomparisons), as no stable samples of DO exist that are suitable for distribution. As an alternative and, given that most DO measurement instruments can be transported, the project organised in situ intercomparisons instead. In situ intercomparisons are where all participants (with their own equipment and experience) measure the same sample at the same time, and on the same site. This arrangement also provides the best possibility for assessing participant performance in DO measurements.

The first of the project's DO intercomparisons was an international in situ intercomparison of DO measurement (ESTDO-2012) which took place at project partner UT with 13 participants from 4 countries (Estonia, Finland, France, Germany) <http://www.ut.ee/EACH/in-situ-interlaboratory-comparison-of-dissolved-oxygen-at-university-of-tartu/>.

The results of the in situ intercomparison fully support the fact that the physical and chemical processes underlying DO measurements are complex and are not at all as robust as often considered by routine laboratories. In total 63 measurement results of DO obtained by the 33 participants in the intercomparison, which is  $52\%$ , were unacceptable according to the En numbers. Based on the analysis of the results of the in situ intercomparison a set recommendations were given to the participants how to improve the quality of their

results and from this a Good Practice Guide for Improving Accuracy of Dissolved Oxygen Measurements was produced by the project

[http://www.ut.ee/EACH/wp-content/uploads/2012/03/Dissolved\\_Oxygen\\_Sensor\\_Calibration\\_Good\\_practice\\_guide\\_Final.pdf](http://www.ut.ee/EACH/wp-content/uploads/2012/03/Dissolved_Oxygen_Sensor_Calibration_Good_practice_guide_Final.pdf)

This Good Practice Guide will help laboratories to better estimate their measurement uncertainty and bias and thus improve comparability of DO measurements. The main suggestions in the Good Practice Guide were:

- Optical sensors are in general more robust and require less skill in usage than the amperometric sensors. The latter need more maintenance (replacement of the membrane and electrolyte solution) and are more sensitive to stirring of the solution and temperature.
- The sensors should be regularly calibrated.
- The temperature compensation and the salinity compensation should be verified
- The zero current of the sensors should be periodically checked.
- The flow dependence of sensors should be checked; and a procedure for checking the sensor state was given in the Good Practice Guide
- Use of “in-house” reference materials and routine sample replicate results together with control charts should enable laboratories to estimate the measurement uncertainty of DO measurements with the Nordtest TR 537 approach more easily and more reliably.
- Control charts should be set up for daily quality control
- Participation in interlaboratory comparisons or proficiency tests should be used to check if the self-declared uncertainty estimate is realistic
- Participation in interlaboratory comparisons or proficiency tests should be used in the estimation of measurement uncertainty.

The second of the project's in situ intercomparisons on DO measurement (FIELDOXY 2014) was organised on board the research vessel Aranda in 2014 in the Gulf of Finland at depths from 5 m to 40 m (location “LL7”: 59°50.79', 24°50.27'). The aim of this in situ intercomparison was to enable the participants to assess their performance in measuring DO content in seawater under field conditions. The intercomparison was jointly organised by project partners SYKE and UT and it differed from the in situ intercomparison carried out by UT in 2012 (ESTDO-2012); by measuring a real seawater sample instead of pure water, by making measurements in the field instead of in a laboratory, and by the fact that water movement was achieved by the movement of natural water currents and the ship due to waves, instead of by stirring the water.

A total of 21 participants from 10 institutes in Finland, Estonia, France, Germany and Sweden participated in the SYKE and UT intercomparison on board the research vessel Aranda. In total, 13-18 oxygen sensors were tested depending on the test depth and 6 different Winkler titrimetric setups were used. The traceable/reference Winkler titration result (the assigned value) was measured using the setup of UT on board the research vessel.

In total, 88 % of the results were satisfactory when total deviation of 8 % from the assigned values were accepted. Only three results were questionable and five results were unsatisfactory. A possible reason for the unsatisfactory results could be problems with the calibration of electrochemical (amperometric) oxygen sensors. The electrochemical sensors need water movement and if this is not sufficient then lower readings are observed. The movement of the water during the intercomparison may have been insufficient for the electrochemical sensors, and thus it cannot be reliably concluded that the electrochemical measurement principle is inferior to the optical one.

In general the share of satisfactory results was very good and was higher than the in situ intercomparison of UT in 2012. Both in situ intercomparisons (ESTDO-2012 and FIELDOXY 2014) showed that the most number of unsatisfactory results were obtained with electrochemical sensors. In fact most of the participants in the ESTDO-2012 intercomparison were using electrochemical sensors, which could explain why there was a lower

number of successful results. In contrast, in the FIELDOXY 2014 intercomparison most participants used optical sensors which performed better. <http://www.ut.ee/EACH/dissolved-oxygen-intercomparison-measurement-fieldoxy-2014/>

#### Conclusions:

##### 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 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 project partners SYKE and 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.

## 4 Actual and potential impact

### 4.1 Dissemination activities

#### Publications and presentations

The project has generated 10 high impact publications in key journals, two pH thesis and one Good Practice Guide. A review paper: Metrological challenges for measurements of key climatological observables: Oceanic salinity and pH, and atmospheric humidity has also been published by *Metrologia*. The review paper is written by 20 leading specialist, six of which are from the project consortium. The review paper summarises the results obtained in the project for the observables salinity and pH, and examines the metrological history of these observables, the problems with their current definitions and measurement practices, and options for future improvements in conjunction with the recent seawater standard TEOS-10. The review paper concludes that BIPM, in cooperation with the International Association for the Properties of Water and Steam (IAPWS), along with other international organisations, can make significant contributions to long standing metrological problems in climatology by developing and recommending state-of-the-art solutions.

In total more than 60 presentations were given by the project partners at conferences such as Euroanalysis, XX IMEKO World Congress, 6<sup>th</sup> International Congress on Metrology, 4<sup>th</sup> International Union of Pure and Applied Chemistry (IUPAC) Congress, IAPWS annual meetings, the 16 ICPWS (Greenwich, UK, September 2013), 2<sup>nd</sup> Symposium on Thermodynamic Properties for Technical Thermodynamics and the General Assembly European Geosciences Union (EGU Vienna, April 2013). Project partners were also highly involved in the organisation of the 16<sup>th</sup> ICPWS and two sessions were chaired by them.

The project's work on the potential of acoustic temperature measurements using time-of-flight sensors was presented at the national Temperatur 2013 conference (June 2013, Berlin, Germany) and the international TEMPMEKO conference (October 2013, Madeira, Portugal). As well as being important for oceanography these results are also relevant for thermometry applications in industrial processes. The results were also presented by PTB at the ICPWS conference (September 2013, London, UK) and by INRIM at the European Construction Technology Platform (ECTP) Conference (September 2014, Porto). Further to this, an invited lecture entitled "Flow injection inductively coupled plasma mass spectrometry: A powerful combination for trace element measurements in seawater" was given at the 18<sup>th</sup> International Conference on Flow Injection Analysis, Porto, Portugal, September 2013.

Presentations of the project's outcomes have also been given to EURAMET Technical Committee of Metrology in Chemistry (TC-MC) and BIPM-CCQM Working Group on Electrochemical Analysis (EAWG) and Working Group on Inorganic Analysis (IAWG). Based on this, a future pilot study is expected on seawater pH, and a key comparison on electrolytic conductivity on seawater has been conducted K105, in order to demonstrate the feasibility of ensuring SI traceability for salinity measured by conductivity and ensure metrological traceability to the stated references for seawater pH.

Indeed, an expert group has been endorsed by the EAWG to investigate the unexpectedly poor interlaboratory reproducibility of conductivity ratios. The outcome (i.e. the unexpectedly poor interlaboratory reproducibility of conductivity ratios) of the first conductivity ratio comparison has startled both, the oceanographic and the metrological community, as good reproducibility is essential for the replicability of SSW as well as for secondary conductivity cell calibration.

#### Stakeholder Engagement, Training and Workshops

The results of the project have also been disseminated to relevant international (e.g. ISO TC 147 Water quality sub-committee 2 Physical, chemical and biochemical methods) and national standardisation bodies, such as DIN Committee NMP pH Messtechnik NA 062-09-21 AA, AFNOR Committee Eaux - physico-chimie de base T91B and BSI Committee, Glass electrodes and pH scale LBI/16, as well as to the IAPWS sub-committee on Seawater and the IUPAC Analytical Chemistry division.

A Good Practice Guide for Improving the Accuracy of Dissolved Oxygen Measurements in the field (i.e. in situ) was compiled as a result of an interlaboratory comparison organised by project partners SYKE (a Proficiency Testing scheme provider) and UT. The Good Practice Guide contains recommendations for improving the performance of field laboratory measurements and testing, as well as an analytical method, with a low enough

level of uncertainty for the high-level calibration of DO sensors at variable oxygen concentrations. In addition, the project established and successfully tested methodology for in situ and interlaboratory comparisons of DO.

Further to this, a training school covering the metrology of dissolved metals concentration in seawater samples was conducted for early career researchers by the REG(UoP) in conjunction with an international GEOTRACES study as part of COST action EOS0801.

Four stakeholder workshops were also held by the project, of which two – one on salinity and one on pH – were organised in conjunction with the 16<sup>th</sup> ICPWS (Greenwich, 2013) and the JCS. The first stakeholder workshop was held during the project's kick-off meeting in Berlin in September 2011. About 30 participants attended, including stakeholders from the seawater standardisation body (IAPWS), academia, seawater reference laboratories and the producer of IAPSO SSW. Five invited speakers from IAPWS sub-committee on Seawater, Ocean Scientific International Ltd (OSIL), The Institut français de recherche pour l'exploitation de la mer (IFREMER), Leibniz Institute of Marine Sciences-Helmholtz Centre for Ocean Research Kiel (IFM-GEOMAR), and Helmut Schmidt University (HSU), gave presentations at the workshop on their solutions to outstanding problems in the measurement of oceanic observables and thermodynamic quantities.

The second and third stakeholder workshops – one on salinity and one on pH – were organised in conjunction with the 16<sup>th</sup> ICPWS (Greenwich, UK, 2013). ICPWS16 was organised on behalf of the IAPWS by the British & Irish Association for the Properties of Water and Steam (BIAPWS) and the Institution of Mechanical Engineers. About 30 stakeholders from seawater standardisation bodies, academia, seawater reference and monitoring laboratories and producer of sensors and seawater reference materials attended the 2 workshops, entitled "Seawater pH" and "Seawater Salinity". Invited speakers at the workshops came from Scripps Institution of Oceanography, US, MARUM (Center for Marine Environmental Sciences) University of Bremen, Baltic Sea Research Institute Warnemuende (IOW), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Anton Paar, and the University of British Columbia). During the workshops the consortium discussed with stakeholders how the project's outcomes could be transferred to future seawater standards and disseminated for use in the field and these discussions were summarised and reported to the IAPWS by the JCS convener.

The fourth stakeholder workshop was organised in conjunction with the project's final meeting in Berlin in June 2014. More than 30 participants attended the workshop and discussed the project's results and potential future work. Presentations on the wider impact of the project's results were also given by four invited speakers from IFM-GEOMAR, the University of British Columbia, Scripps Institution of Oceanography, US, and the Helmholtz-Centre for Environmental Research (UFZ).

At all 4 workshops, stakeholders showed very positive interest in the outputs of the project, in particular the development of the metrological traceability for oceanic observables, needed to ensure the comparability of their measurements.

## 4.2 Effective cooperation between JRP-Partners

Ten NMIs/DIs and two Researcher Excellence Grants from 10 different countries took part in this project, which was one of the first collaborative projects involving partners with expertise from both chemical and physical metrology and with contacts to the oceanographic end-user community.

A variety of research exchanges occurred between project partners during the project, for example researchers from project partner JRC- spent time at REG(UoP) (and vice versa) on work involving oceanic micronutrients. Researchers from project partners LNE and IPQ visited PTB for work on pH and salinity and researchers from project partners SYKE and UT jointly organised two in situ interlaboratory comparisons on DO measurements (ESTDO-2012 and FILEDOXY-2014). Finally, a researcher from UT visited project partner SMU to study coulometry for DO measurement.

This project has also benefitted from collaborative working between project partners, as demonstrated by several joint publications and by the new calibration facilities which have been developed. These calibration facilities include: DO content at both SYKE and UT, density, speed of sound and pH at PTB, and pH at both LNE and IPQ. These new primary calibration facilities are available for other NMIs as well as for use by end-users not only from oceanographic laboratories but also from environmental laboratories.



### 4.3 Examples of early impact

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 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.

## 5 Website address and contact details

Project website <http://www.ptb.de/emrp/env05.html>

The contact for traceability of practical salinity is  
([steffen.seitz@ptb.de](mailto:steffen.seitz@ptb.de))

Dr Steffen Seitz, PTB

The contact for traceability of density measurements under pressure is  
([henning.wol@ptb.de](mailto:henning.wol@ptb.de))

Dr Henning Wolf, PTB

The contact for speed of sound and temperature is  
([s.lago@inrim.it](mailto:s.lago@inrim.it))

Dr Simona Lago, INRIM

The contacts for harmonised seawater pH measurements are  
([daniela.satoica@lne.fr](mailto:daniela.satoica@lne.fr)) and Dr Paola Fisicaro, LNE ([paola.fisicaro@lne.fr](mailto:paola.fisicaro@lne.fr))

Dr Daniela Stoica, LNE

The contact for calibration methods for DO measurements is  
([michal.mariassy@smu.gov.sk](mailto:michal.mariassy@smu.gov.sk))

Dr Michal Mariassy, SMU



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