Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

Comparison Measurement
2019

Measurement of Practical Salinity of Seawater

Technical Protocol

Version 03.04.2019

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Alfred Wegener Institute
Sandra Tippenhauer
Helmholtz Centre for Polar and Marine Research
Am Handelshafen 12
27570 Bremerhaven, Germany

Background

This comparison measurement is conducted to demonstrate the capabilities of the participating laboratories to measure the Practical Salinity of a seawater sample. Successful participation provides evidence for the quality assurance of measurement results within the meaning of ISO/IEC 17025.

The comparison measurement is organized and evaluated by the Working Group 3.13 "Electrochemistry" of the Physikalisch-Technische Bundesanstalt (PTB), which is the national metrology institute of Germany. It is conducted within the framework of European Metrology Network for Ocean and Climate Observation.

The participants have to measure a seawater sample which has a Practical Salinity value in the range of 30 to 35.

Coordinating laboratory and contact persons

First contact

Beatrice Sander

Physikalisch-Technische Bundesanstalt (PTB)

3.13 Elektrochemie

Bundesallee 100

38116 Braunschweig

Tel: + 49 (0) 531 592 3132

E-mail: beatrice.sander@ptb.de

Second contact

Steffen Seitz

steffen.seitz@ptb.de

Description of the samples

The seawater samples have been prepared from surface seawater collected from the North Atlantic and stored in a 100 L PE barrel under cool and half-light conditions. The seawater has been filtered with a 0.4 µm filter. A portion of the seawater has been diluted with distilled water to adjust Practical Salinity to a value between 30 and 35 and filled into a 20 L PE barrel. Afterwards, the seawater has been homogenized, filled into 200 mL bottles of boron-silicate glass and sealed with crimped rubber stoppers.

Five bottles were chosen from all over the filling sequence to verify homogeneity. To this end their conductance ratios have been measured with a Guildline 8400B salinometer under repeatability conditions. Stability of the samples will be verified every 2-4 weeks over the period of the comparison measurement.

Each bottle has a label indicating "S_P comparison", the filling date and a bottle number. Each participating laboratory will receive 2 bottles. In case of need, more bottles can be sent upon request. Shipment to all the participating laboratories will be performed at the same time on the beginning of April 2019. The participants will be informed about the shipment. Unless a special request is made, the bottles are shipped in one cardboard box by courier. The content will be marked "natural seawater for analysis" with no commercial value.

Actions before measurements

Do not open the bottles until you start the measurements!

Please conduct the following actions after receipt of the bottles:

- Confirm the receipt by sending an email to the coordinating laboratory.
- Inspect the bottles for damage, leakage or visible contaminants in the solution
- Weigh the bottles to check their integrity. To this end, leave the bottles overnight in the weighing room. **Do neither remove the labels, the metallic crimp nor the rubber**. Weigh each bottle and correct the balance reading for air buoyancy, using the Excel-file that will be sent by the time of sample dispatch. Compare the result with the mass noted by the coordinating lab in that file. If the discrepancy is larger than 0.2 g, please investigate for possible leakage and inform the coordinating lab immediately, so that it can send replacement bottles.
- The bottles should be stored in a dark and cool place until the measurement starts.

Measurement instructions

Perform the measurements by 31 May 2019.

If you intend to use the results of this comparison as evidence for accreditation, conformity or other quality assurance purposes you must use the measurement method and measurement procedures related to this purpose.

Turn the bottle a few times upside down to homogenise the solution. However, you must not shake the bottle to avoid formation of microbubbles.

Measure Practical Salinity of the seawater sample according to your work instructions.

Instructions for reporting

You must provide the following information in terms of a measurement report:

- Address of your institute and name and email address of the contact person.
- Sample specification (bottle number, date received, date measured and bottle masses).
- Practical Salinity results, its standard uncertainty, coverage factor and expanded uncertainty, calculated according to GUM [1]
- A short, but comprehensive description of the measurement, including method, devices, measurement procedure, measurement temperature and other intermediate results, including their uncertainties.
- Calculation of measurement uncertainty, including contributions from measurement stability, measurement temperature and measurement standards in particular. The calculations should be verifiable on the basis of the description and the submitted data.

You should use the attached *Measurement Report* form for reporting. Please send the measurement report as a pdf-file by email by the end of May. The project coordinator will send a confirmation message to the participant within one week after receipt of the report. If a participant does not receive the confirmation message, the participant must contact the coordinating laboratory.

Measurement reports should be received by the coordinating laboratory

by 15 June 2019 at the latest

Evaluation of the results

The coordinating laboratory will verify the measurement reports with respect to the requirements stated in this *Technical Protocol*. Furthermore, it will calculate a comparison reference value (CRV) that is based on the results of the participants. The CRV and its uncertainty will be calculated using common statistical methods.

If a result shows a significant deviation from the expected CRV the coordinating institute will inform the corresponding participant before it publishes the results to check for typing errors. No information will be given on the sign or magnitude of the deviation.

A draft report on the comparison will be sent to the participants for review. The draft report will be accordingly revised, and a final report will be sent to the participants after all participants have agreed to the results and the evaluation.

[1] *GUM, "Guide to the expression of uncertainty in measurement", JCGM, JCGM 100:2008, available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf*

Validity range

This comparison can be used to prove the capability of the participating lab to measure Practical Salinity of natural seawater in the Salinity range 2 to 42, assuming that the laboratory has used agreed measurement standards to calibrate the measurement system in the salinity range of the measurement.

Timetable

Registration	by 15 March 2019
Sample dispatch	3 April 2019
Measurement period	until 31 May 2019
Deadline for reporting	15 June 2019
Draft report	by 13 July 2019
Final Report	4 weeks after agreement on final results

Measurement Report

Laboratory

Institute	Alfred Wegener Institute
Contact person	Sandra Tippenhauer
Address	Helmholtz Centre for Polar and Marine Research Am Handelshafen 12 27570 Bremerhaven, Germany
Phone	+49 471-4831-1816
Email	stippenh@awi.de

Sample data

Bottle No	Date received	Date measured	Mass (g) at coordinating lab [(i)]	Mass (g) after receipt [(i)]
16	8. April 2019	10. April 2019	335,296	335,292
34	8. April 2019	10. April 2019	345,367	345,360

add rows if needed
(i) corrected for air buoyancy

Measurement result

Practical Salinity	Standard uncertainty u_c(y)	Coverage factor k	Expanded Uncertainty U [(ii)]
#16 30,9974	0.00216	2	0.00432
#34 30,9973	0.00216	2	0.00432

(ii) Corresponding to a 95% coverage interval according to GUM. Usually a coverage factor of 2 can be used, if an infinite number of degrees of freedom can be reasonably assumed for all individual standard uncertainty contributions.

Description of the measurements

Instrument

- Optimare Precision Salinometer System SN 003, equipped with SBE3 precision thermometer (SN 3P5159) and modified SBE4 conductivity cell (SN 043688 with modified liquid cell)

Conductivity measurements are performed with an Optimare Precision Salinometer (OPS) System. The OPS aims mainly at high accuracy onboard reference salinity measurements for samples from the deep ocean. It consists of a pre and a main bath, the former used to temperature-preadjust the sample roughly (to within 0.1K of the main bath temperature). The main bath contains the conductivity cell (modified SBE4) and a precision thermometer (SBE3). Both SBE3 and SBE4 have a frequency output (Wien-Robinson Oscillator). The conductivity cell is a three-electrode design, which avoids an external electrical field. The platinum electrodes are melted into a glass cell and are covered by platinum black.

A key element to achieve the high accuracy of the OPS is outstandingly excellent thermal control. This includes the introduction of a pre bath, which effectively decouples the main bath from the original temperature of the water sample. A second aspect is the realisation of heater and cooler in the baths. A stirring element serves as the heat source in the main bath (Patent K. Ohm). This distributes its heat input rapidly and evenly throughout the entire bath volume. The cooling is realised by a Peltier Element with a specially shaped surface and a controlled heat resistance across the element. These measures result in a very homogeneous temperature distribution in the bath with very small fluctuations. As even seemingly modest amounts of heat exchange with the environment are adverse to the measurements on the precision level achieved here, lights in the bath are switched off during measurements.

The flow diagram of the Precision Salinometer illustrates the sample treatment (figure 1). The bottle containing the water sample to be analysed (or, during calibration, the Standard Sea Water) is located underneath the intake. The intake is inserted into the bottle automatically when a new measurement starts. The filling pump sucks the sample water into the instrument. It is pushed through a heat exchanger and leaves the pre bath with a temperature very close to that of the main bath. The Peltier Element is located at the bottom of the pre bath. Here, the temperature sensor is a Platinum thermometer.

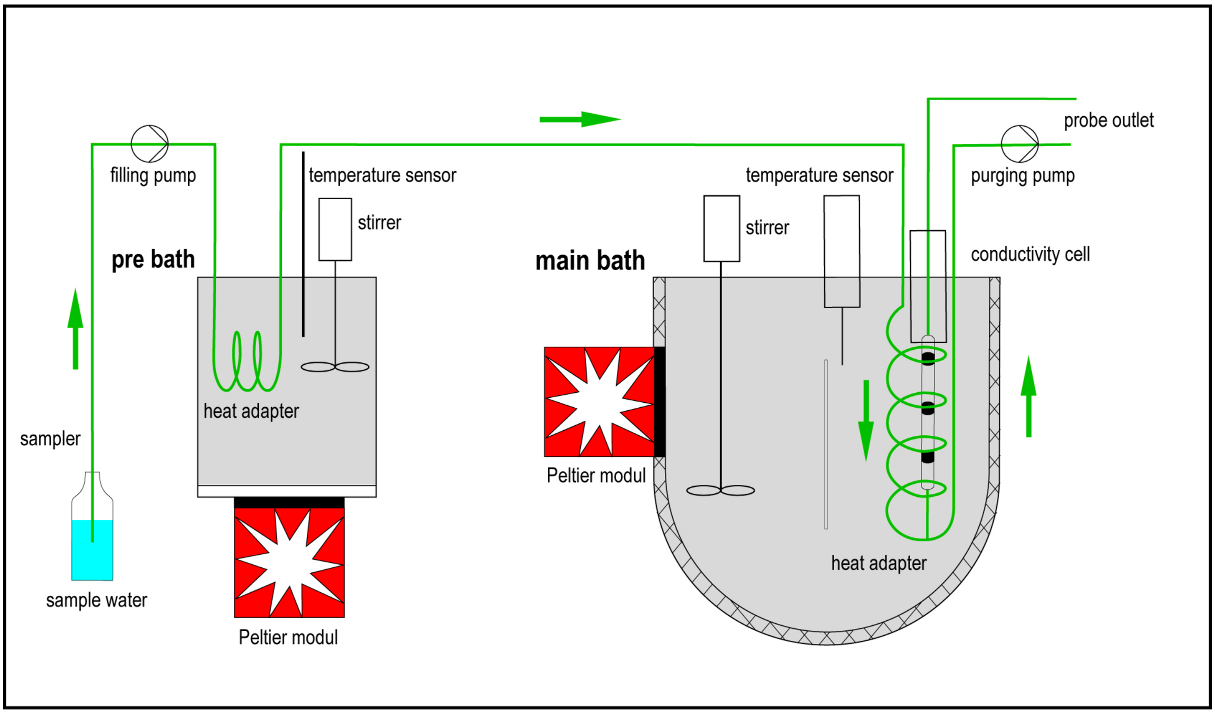

Figure1: Flow diagram of the sample water in the Precision Salinometer.

The temperature adjusted water sample is pushed through a second heat exchanger, residing in the main bath, and into the conductivity cell. For the conductivity measurements, the flow is halted for a few seconds, the Residence Time (typical: 10 s). A fraction of this, at the end of the Residence Time, is used for the actual measurement (typical: 3 s). After the measurement, the water sample leaves the conductivity cell at the opposite side of its entrance, so that a flow-through from the lower to the upper end of the cell is established. The water of the next sample replaces that of the previous one. The entire measurement is automated to establish a controlled heat flow.

Methods

Measurements were performed at 21.4°C room temperature. The samples were kept in the lab two days prior to the measurement.

The nonlinear characteristic of the conductivity cell was determined immediately before the measurements. Readily available IAPSO standard seawater (SSW) of S=38, S=35, S=30, S=20, and S=10 was used for linearization. Also the zero-reading of an empty cell was used. From the known salinity and the bath temperature, the sample conductivity is determined according to PSS78 (including conversion from IPT90 to IPTS68) using the Seabird Software SBE Data Processing Version 7.26.0.7 Step 21 SeaCalc III. A third order polynomial fit is performed to relate frequencies to conductivities.

We used two different linearity sets, one new one and another one that was already old and expired. Some irregularities were observed during the measurement so that some samples hat to be repeated or even discarded.

Samples had been stored in the same room for 2 days. Bottles were shaken repeatedly, and vigorously before measuring their content in order to overcome stratification of the liquid. At least 3 min before the measurement, they were placed upright and were kept still to allow gas bubbles to escape through the liquid surface. This is a well-established method and does not produce micro bubbles.

By using the OPS method of measuring salinity we do not need to switch the measurement range. Thus we do not need to account for uncertainties due to switching ranges.
Continuously monitoring the measurement of the salinometer we can assure that no contaminations such as air bubbles or other substances contaminate the sample. If a measurement is suspicious we abort and restart the measurement.
Inhomogeneities or fluctuations of the temperature are estimate to be below 0.2 mK. The uncertainty of the absolute temperature is not relevant as the calibration (linearization) with standard seawater of the OPS prior the measurement corrects for a possible offset of the temperature sensor.
The uncertainty of the salinity measurements is thus dominated by the accuracy given by the standard seawater, which is 0.002 (https://osil.com/wp-content/uploads/2019/01/OSIL-Seawater-and-Salinometers-Brochure-2014_Web-Version.pdf).
Estimating the effect of temperature fluctuations of 0.2 mK by calculating the difference in conductivity we found an uncertainty of 0.0002 mS/cm. Conversion to salinity results in an uncertainty of less than 0.00016 in salinity.

Uncertainty of temperature measurement

Source	
Inhomogeneity of bath	0.2 mK
Uncertainty of salinity due to temperature fluctuations of 0.2 mK	0.00016
Uncertainty of Standard Seawater	0.002
Sum	**0.00216**

Here, include:

- *A short, but comprehensive description of the measurement, including method, devices, measurement procedure, measurement temperature and other intermediate results, including their uncertainties.*
- *Measurement uncertainty in accordance with GUM, including contributions from measurement stability, measurement temperature and measurement standards in particular. The calculations should be verifiable on the basis of the description and the submitted data.*