Traceability and Uncertainty of pHT Values of Artificial Seawater Standards over Wide Temperature and Salinity Ranges

Rieke Schäfer[1, S, C], Frank Bastkowski[1], Gaëlle Capitaine[2], Raquel Quendera[3], Olivier Pellegrino[3], Paola Fisicaro[2] and Steffen Seitz[1]

[1]*Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany*
[2]*Laboratoire national de métrologie et d'essais (LNE), Paris, France*
[3]*Instituto Português da Qualidade (IPQ), Caparica, Portugal*
rieke.schaefer@ptb.de

The need for traceable seawater pH_T measurements is increasing with the demand to monitor ocean acidification. As potentiometric pH_T measurements in seawater are not straightforward due to the high salinity, spectrophotometric measurements of pH_T are often used for this purpose. However, those optical measurements must be linked to the electrochemical definition of pH_T to establish metrological traceability. The SapHTies project has established, for the first time, a traceability route and an appropriate uncertainty budget for spectrophotometric pH_T measurements of primary pH_T measurement standards over temperature and salinity ranges relevant in oceanography.

In our presentation, we will present one of the main outcomes of the project. A 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS) buffered artificial seawater (TRIS-ASW) solution was selected as primary standard for seawater pH_T measurements. The measurement model to assign pH_T values using Harned cell measurements to this primary standard has been specified in detail, involving all relevant input quantities, such as salinity, temperature, and TRIS concentration. Primary pH_T measurements of TRIS-ASW at salinities from 5 to 40 and temperatures from 5 to 30 °C were conducted. In this way, temperature and salinity ranges most relevant in oceanography were covered with a single measurement model. Most important, uncertainties have been assigned to pH_T values based on the model. The uncertainty contributions were determined by classical uncertainty propagation of input variables. A Monte Carlo Simulation was used to determine the uncertainties of the coefficients of the regression model of pH_T depending on temperature and salinity.

The pH_T values of TRIS-ASW and their uncertainties have been used in the same temperature and salinity range in a next step as metrological reference for spectrophotometric pH_T measurements, which use the indicator dye meta-Cresol Purple. This characterization of the standard, together with associated uncertainties, is crucial to quantify the uncertainty of subsequent routine seawater pH_T measurement results.