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Traceability of pH_T values of equimolal TRIS buffered artificial seawater solutions in brackish waters

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***Abstract* – Assessment of seawater acidification can be achieved by the measurement of *pH*. A prerequisite for reliable and comparable *pH* values is traceability of *pH* measurement results to an agreed higher order *pH* standard. While this has already been established for low ionic strength aqueous solutions, traceability of *pH* measurement results for high ionic strength solutions is about to be realized for artificial seawater samples in the middle salinity range (5-20) on the so called total *pH* scale (pH_T). In the present work we show details of the pH_T measurement procedure for the measurement of TRIS (Tris(hydroxymethyl)-aminomethane) buffered artificial seawater solutions and the traceability of the measurement results to the SI system of units.**

I. INTRODUCTION

Anthropogenic CO_2 emission lead to a continuous acidification of the oceans with severe consequences for biological and biochemical processes. Therefore, spatial and temporal record of the acidification is particularly important. Acidification can be expressed by the *pH* of an aqueous solution. According to the IUPAC definition, *pH* is generally measured on low ionic strength buffer solutions ($I \leq 0.1$ mol·kg^{-1}) [1]. Traceability of this *pH* can only be achieved by taking the uncertainty of the Bates-Guggenheim convention (which is part of the *pH* definition) into account [1]. In this case the overall measurement uncertainty is increased by about 0.01 pH units.

In seawater media, however, ionic strength is usually higher than 0.1 mol·kg^{-1} and hence *pH* according to the IUPAC definition cannot be determined in seawater up to now [2]. Pitzer parameters allowing to determine *pH* in seawater media are part of current ongoing research. For seawater media it is convenient to determine pH on the total scale (pH_T). The concept of pH_T has originally been proposed by Sillén, was first used by Hansson and refined by Dickson [3,4,5,6]. pH_T is frequently determined on discrete samples on research vessels. While spectrophotometric pH_T measurements can be performed with very high precision under repeatability conditions, traceability of these pH_T measurement results has been hardly achieved so far due to questionable calibration of the spectrophotometric instruments leading to incompatible measurement results. In order to achieve traceability of spectrophotometric pH_T measurement results under these conditions, calibration of spectrophotometers is necessary using higher order pH_T standards. In this work we present details of the electrochemical pH_T measurement setup, the measurement procedure and the route of traceability of pH_T measurements in the salinity range 5-20.

II. DETERMINATION OF PH_T OF ARTIFICIAL SEAWATER SAMPLES IN THE SALINITY RANGE 5-20

A. Spectrophotometric pH_T determination

The spectrophotometric pH_T determination is based on the Henderson-Hasselbalch and the Lambert-Beer law, which can be expressed for spectrophotometry according to equation (1):

$$pH_T = pK(S,T) + \log\left(\frac{\varepsilon_1(HI^-)\cdot R - \varepsilon_2(HI^-)}{\varepsilon_2(I^{2-}) - \varepsilon_1(I^{2-})\cdot R}\right) \quad (1)$$

with the salinity (S) and temperature (T) dependent acid-base constant of the indicator dye *pK(S,T)*, the extinction coefficients ε for protonated (HI^-) and deprotonated (I^{2-}) forms of the indicator dye at wavelenghts 1 and 2 and R, which is the ratio of absorbance at wavelengths 1 and 2 [7]. Once *pK(S,T)* and the extinction coefficients been determined as a function of salinity and temperature, the purified indicator dye, can serve as a molecular standard allowing to determine pH_T of a seawater sample [8]. The

determination of *pK*, however, requires a series of initial measurements in solutions of stable and well-known pH_T, commonly TRIS buffered artificial seawater solutions.
Traceability of spectrophotometrically measured pH_T values can therefore only be achieved via traceability of *pK(S,T)* using independent measurement methods.

B. Electrochemical pH_T determination

According to the work of DelValls and Dickson (1998) pH_T of equimolal TRIS buffered artificial seawater solutions can be measured electrochemically according to equation (2) using the same Harned cell measurement system which is commonly used to determine *pH* values of low ionic strength buffers [9].

$$pH_T = \frac{(E - E^{0*})F}{RT\ln 10} + \lg(b_{Cl^-}) - \lg(\omega_{H_2O}) \quad (2)$$

with the measured electric potential E of the Harned cell filled with sample solution, the standard potential of the silver/silver chloride electrode (acting as the reference electrode in the Harned cell) in seawater medium E^{0*}, the Faraday constant F, the molar gas constant R, the absolute temperature T, the molality of chloride of the sample solution b_{Cl^-} and the specific water content of the sample solution ω_{H2O}.
pH_T determination with the Harned cell consists of two main steps.

1. Determination of the standard potential of the silver/silver chloride electrode E^{0*}:

Determination of E^{0*} can be achieved by variation of HCl in artificial seawater matrix without TRIS and quadratic extrapolation to zero HCl molality according to equation (3):

$$E^{0*} = \lim_{HCl \longrightarrow 0} E_{ASW/HCl} + \frac{RT\ln 10}{F} \cdot \lg(b_{HCl} \cdot b_{Cl}) \quad (3)$$

with the Harned cell potential of HCl added ASW solution $E_{ASW/HCl}$, the molality of chloride b_{Cl} and the molality of HCl in the solution b_{HCl}

2. Determination of the Harned cell potential E

In the second step the Harned cell potential E of the TRIS/TRISH$^+$ buffered artificial seawater sample solution is measured using the same setup as for step 1)
Finally pH_T is calculated according to equation (2).

pH_T values measured with the electrochemical measurement procedure are traceable to the international system of units (SI). Therefore, SI traceability of spectrophotometric pH_T measurement results can be achieved via buffer solutions characterized by electrochemical measurements.

pH_T values measured with the Harned cell are available for freshwater and high salinity (20-40) seawater but were missing for the middle salinity range of 5-20 particularly dominant in the Baltic sea [9,10,11].

C. Sample preparation

The variation of the HCl content in both the buffered artificial seawater solution and the solutions for the determination of E^{0*} must be compensated by reduction of other salts as to keep the ionic strength and salinity constant. At higher salinities this was previously achieved by reduction of NaCl alone leading to a rather moderate change of the cation ratios [9]. Towards lower salinites however the change of cation ratios by reduction of NaCl alone would be more pronounced. For a typical HCl concentration of 0.04 mol·kg^{-1}, NaCl would be entirely replaced at a salinity of around 4. In contrast, proportional reduction of all salt components keeps the composition of the artificial seawater solution closer to that of natural brackish waters.

III. EXPERIMENTAL SETUP

The potentials E and $E_{ASW/HCl}$ can be determined using a so called Harned cell which consists of a platinum hydrogen electrode and a silver silver chloride reference electrode placed into a measurement cell (e.g. U tube) without junction. It furthermore comprises a unit for humidification of the hydrogen gas. The utilized electrodes are in-house made. The platinum hydrogen electrode is prepared by weldering a platinum plate to the free end of a glass covered platinum wire. The resulting platinum electrode is platinized for 9 minutes with 45 mA·cm^2 in an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ and $Pb(CH_3COO)_2 \cdot 3H_2O$ and afterwards cleaned in distilled water. AgAgCl electrodes are prepared using the thermal-electrolytic method [12].
The Harned cells are filled with the solution to be measured and placed into a thermostatting bath controlled by a DLK 45 and a PV 36 thermostatting unit both from Lauda. The temperature inside the bath is measured at four positions using PT100 probes connected to a ASL F250 MKII thermometer, switched by a ASL Multi Switch SB250. The air surrounding the cells is temperature-controlled using a Lauda Proline RP 855 inside a temperation box. The temperature inside the thermostatting bath is kept constant by ± 0.005 K. The hydrogen gas used is of 6.0 purity. The cell voltage is measured using a A3458 Digital voltmeter from Agilent after temperature stability is reached. The cell voltage is corrected for the actual partial pressure of the hydrogen gas p_{H2} according to equation (4).

$$\Delta E = \frac{RT}{2F} \cdot \ln\left(\frac{p_{H_2}}{p^0}\right) \quad (4)$$

With p_{H2}: the partial pressure of hydrogen gas (Eq. 5) at the position of the electrode immersed into the measurement solution (Pa) and p^0: standard pressure (101325 Pa)

$$p_{H_2} = p_{atm} + p_{hydrostatic} + p_{water} \quad (5)$$

With p_{atm}: the hydrogen gas pressure outside of the measurement cell measured with a Setra Systems barometer

$$p_{hydrostatic} = 0.42 \cdot \rho \cdot g \cdot h \text{ (hydrostatic pressure)} \quad (6)$$

with ρ: Density of the measurement solution, g: gravity constant, h: immersion depth of the platinum hydrogen electrode

The factor 0.42 for the correction of the hydrostatic pressure was empirically found by Hills and Ives [13].

p_{water}: saturated vapor pressure of water calculated from the Clausius-Clapeyron equation

IV. TRACEABILITY OF ELECTROCHEMICALLY MEASURED PHT

According to the International vocabulary of Basic and General Terms in Metrology (VIM) metrological traceability is defined as the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of comparisons, each contributing to the measurement uncertainty [14].

A. *Traceability of the spectrophotometrical pH_T measurement procedure:*

According to this definition traceability of pH_T measured spectrophotometrically is achieved by directly linking the spectrophotometric measurement results to the primary pH_T measurement procedure described above. This can be achieved by characterizing the pK value of the indicator dye by absorption measurements in artificial seawater standard solutions with a electrochemically determined pH_T value. pK values of the indicator dye - once determined at different salinities and temperatures – then can serve as a molecular standard allowing to trace back spectrophotometrically measured pH_T values to the primary pH_T measurement procedure or even to SI.

In any case all uncertainty contributions from the input quantities of equation (1) have to be taken into account to obtain traceable spectrophotometrically measured pH_T values. Real traceability however is only achieved if the uncertainty arising from the different composition of natural seawater and the artificial seawater standards is taken into account. The differences are even more significant for lower salinities, where the contribution of the TRIS buffer to the overall ionic strength is more significant than for higher salinities. These issues are currently matter of further investigations.

B. *Traceability of the primary pH_T measurement procedure to the SI system of units:*

According to equation (2) pH_T can be expressed by input quantities which themselves are more or less directly traceable to the SI system of units. Table (1) gives an overview of the traceability routes of pH_T input quantities

Table 1: Input quantities of pH_T measurement equation (2) and their traceability to SI units

Input quantity	Unit	Traceable to SI unit
E	V	Ampere
p_{H2}	$kg \cdot m^{-1} \cdot s^{-2}$	Kilogram, meter, second
ω_{H2O}	1	Kilogram
$E_{ASW/HCl}$	V	Ampere
R	$V \cdot A \cdot s \cdot mol^{-1} \cdot K^{-1}$	-[1)]
T	K	Kelvin
F	$A \cdot s \cdot mol^{-1}$	-[1)]
b_{HCl}	$mol \cdot kg^{-1}$	Kilogram, Ampere, second
b_{Cl}	$mol \cdot kg^{-1}$	Kilogram

[1)] Fundamental constant

In order to consider electrochemically measured pH_T values of artificial seawater samples traceable to SI all uncertainties of the input quantities mentioned in Table 1 as well as the uncertainty of the non-linear regression for the determination of E^0* have to be taken into account (cf. equations (1) and (3)).

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