



Seawater pH measurements with a combination glass electrode and high ionic strength TRIS-TRIS HCl reference buffers – An uncertainty evaluation approach



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ABSTRACT

The comparison of pH measurements in seawater collected at different locations or occasions, is meaningful if the same measurand (i.e. the quantity intended to be measured) is determined, if adequate measurement procedures are used, including the selection of calibrators, and if the measurement uncertainty is known. Depending on the purpose of this evaluation, the measurement uncertainty should be smaller than a defined target value. The measured pH should have a sound physical-chemical meaning to allow the adequate assessment of its impacts.

In the present procedure TRIS-TRIS HCl solutions, of different molality ratios, prepared in artificial seawater with reference values estimated by primary measurements, were used to obtain proper calibrators for the pH meter used for the analysis of seawater samples.

This work presents the uncertainty evaluation of pH measurements in seawater, performed by potentiometry using a combination glass electrode, from the interpolation uncertainty evaluated by the Least Squares Regression Model and by Monte Carlo Simulations of measured potentials and reference values. The uncertainty evaluation was critically assessed.

The developed algorithms were implemented in a user-friendly MS-Excel file available as Electronic Supplementary Material.

Seawater pH was measured with an expanded uncertainty of 0.019 enabling discriminating differences of pH of two samples larger than 0.029.

1. Introduction

pH, as a master variable for the CO₂ system, is of fundamental importance to the study of the oceans.

The most common and fastest way of measuring pH in routine analysis is the classical potentiometric method that consists on measurements of the electromotive force, e.m.f., of a cell, often with a combination glass electrode selective to hydrogen ions.

The potential difference which occurs in the cell varies linearly with pH according to the Nernst equation [1]. The relationship is achieved through linear regression which, in case of multipoint calibration, is given by the calibration function described by Eq. (1) [4]:

$$E_{\text{std}} = E_a - k' \text{pH}_{\text{std}} \quad (1)$$

where E_{std} is the potential difference measured in the standard buffer solution with the assigned pH_{std} reference value, E_a is the intercept, and

k' is the practical slope determined by the linear regression.

The pH value of a sample, $\text{pH}_{(x)}$, is obtained from the measured potential difference, $E_{(x)}$ through Eq. (2):

$$\text{pH}_{(x)} = \frac{[E_a - E_{(x)}]}{k'} \quad (2)$$

To measure the pH of seawater – a complex matrix with high ionic strength of approximately 0.67 mol dm^{-3} – appropriate calibration buffer solutions must be adopted [16,5,8]. Since the commercially available pH buffer solutions are characterized by their low ionic strength, $I (< 0.1 \text{ mol dm}^{-3})$ [4], hence inadequate for these specific measurements, appropriate calibrators have to be produced by the analyst.

TRIS-TRIS HCl buffers have been studied for pH measurements in seawater since 1964 and in 1973 have been proposed as primary pH standards for oceanic pH measurements [10]. More recently, reference

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Table 1
Target reference calibration buffers solution in ASW background composition.

Buffer solutions composition	Molality (mol kg ⁻¹)							
	TRIS	HCl	NaCl	KCl	MgCl ₂	CaCl ₂	Na ₂ SO ₄	
1	0.03 TRIS-0.05 TRIS-HCl in ASW	0.08	0.05	0.37753	0.01058	0.05574	0.01075	0.02926
2	0.04 TRIS-0.04 TRIS-HCl in ASW		0.04	0.38753				
3	0.05 TRIS-0.03 TRIS-HCl in ASW		0.03	0.39753				

calibration pH buffer solutions were prepared in Artificial Seawater, ASW [7], in order to approach seawater conditions. To allow a multi-point calibration for potentiometric measurements, three TRIS-TRIS HCl buffers in ASW matrix of different molality ratios were characterized covering a range of pH close to the expected values of seawater (7.8–8.3) [17].

In this work, three TRIS-TRIS HCl solutions, in ASW matrix, of molality ratios of 0.03:0.05, 0.04:0.04 and 0.05:0.03 were prepared using high purity grade reagents ($\geq 99.99\%$ *m/m*) in order to establish proper calibration for pH measurements of seawater samples in routine conditions.

In order to assess if the Least Squares Regression Model, LSRM, can be applied to establish the calibration of the pH meter with no restrictions, the measured potentials of the potentiometric measurements, expressed in mV, were tested for the normality of the distribution, for the homogeneity of variance and for linearity of the variation with the pH value. It was also evaluated if the uncertainty of the pH value of reference buffers (i.e. the calibrators) is negligible given the precision of the measured potentials, assuming this as the fourth assumption of the LSRM [2].

If the assumptions of the LSRM are valid, the uncertainty from quantifications performed by interpolating the sample potential in the calibration curve is evaluated by combining the standard deviation of the interpolation, estimated by the regression model, with the uncertainty from the calibration values. Alternatively, the impact of the statistical interpolation of the sample potential in a calibration curve, built from the measured potentials of the calibrators and from the uncertainty of calibrators values on the performed quantifications, can be estimated by the Monte Carlo Method (MCM).

In MCM, the actual values and measured potentials of calibrators and samples, are randomly generated in a computer to estimate the subsequent dispersion of the pH value of the sample which will represent the measurement uncertainty. The use of the MCM requires defining Probability Density Functions, PDF, of all input variables.

This approach uses extensive computing resources but can run on few experimental data values. However, if they are too few, the variability of estimated parameters of the PDF will increase the measurement uncertainty.

In this work, a natural Atlantic Ocean water, IAPSO Standard Seawater, commercially provided by the Ocean Scientific International Ltd, OSIL, with salinity, $S = 35$, and seawater samples from the Portuguese Coast were analyzed by this procedure. The measurement uncertainty was evaluated through a bottom up approach based on the LSRM and on the MCM.

For routine pH measurements in seawater samples for the purpose of ocean monitoring, the defined target (i.e. maximum admissible) uncertainty is ± 0.02 in pH [14].

2. Experimental

2.1. Reagents and solution preparation

Solid reagents of high purity were used according to instructions from the producers.

TRIS (hydroxymethyl) methylamine ($\geq 99.8\%$ purity by mass, Sigma-Aldrich), sodium chloride ($> 99.999\%$ *m/m* Sigma-Aldrich),

potassium chloride (99.9995% *m/m* Sigma-Aldrich) and anhydrous sodium sulfate ($\geq 99.99\%$ *m/m* Alfa Aesar) were dried over night at 105°C . Calcium chloride (99.99% *m/m* Sigma-Aldrich) and magnesium chloride (99.995% *m/m* Sigma-Aldrich) were desiccated before use.

Hydrochloric acid solution was prepared from commercial 30% HCl solution (31.1% *m/m* Sigma-Aldrich).

TRIS-TRIS HCl solutions in ASW background of three different nominal compositions, presented in Table 1, were prepared using 5 target stock solutions previously prepared:

- Stock Solution A: containing the “minor” salts with a constant molality in all the solutions: 0.05 mol kg^{-1} KCl; 0.05 mol kg^{-1} CaCl₂ and 0.25 mol kg^{-1} MgCl₂.
- Stock Solution B: 0.1 mol kg^{-1} HCl solution standardized by titration against a TRIS solution according to reference procedures [3]
- Stock Solution C: 2 mol kg^{-1} NaCl
- Stock Solution D: 0.7 mol kg^{-1} TRIS
- Stock Solution E: 0.4 mol kg^{-1} Na₂SO₄

All solutions were prepared with ultrapure water with resistivity higher than $18.2\text{ M}\Omega\text{ cm}$ supplied by a Milli-Q Academic water system from Millipore®.

All solutions were prepared gravimetrically. Estimated conventional mass was corrected for buoyancy to estimate the real mass.

2.2. Sample collection

Seawater samples from the Portuguese Coast were collected in “Praia do Paraíso” in Zambujeira do Mar at the SW coast of Portugal (GPS positions: Latitude, $\varphi = 37^\circ 31' 3\text{N}$; Longitude, $L = 008^\circ 47' 2\text{W}$).

The samples were collected into clean plastic bottles fitted with tight-fitting caps. The bottles were filled completely up to the top and closed immediately ensuring absence of air bubbles. Care was taken to prevent agitation of the sample and exposure to air.

After collection, the samples were kept at $(5 \pm 3)^\circ\text{C}$ until analysis.

2.3. Procedure

The pH system consisted of a Metrohm 848 with an Electrode Plus Glass electrode and a temperature probe.

Seawater samples were brought up to room temperature prior to analysis.

The electrode response was evaluated using two commercial buffer solutions produced by Metrohm of certified pH 7 and pH 9 traceable to the value of a standard produced by the National Institute of Standards and Technology, NIST.

Measurement results of the three different TRIS-TRIS HCl buffers solutions previously prepared and seawater samples were conducted at the same temperature.

Results were recorded in mV and performed in duplicate.

2.4. Evaluation of the measurement uncertainty

The evaluation of the measurement uncertainty was conducted by two different methods:

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