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Feasibility of multifunction calibration of H^+ -responsive glass electrodes in seawater (IUPAC Technical Report)

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Abstract: Seawater pH values are of the highest relevance in marine chemistry studies, not only through being acidity indicators but also due to the control provided by $H^+(aq)$ over the various simultaneous equilibria occurring in seawater. Although the concept of $pH = -\lg a_{H^+} = -\lg (m_{H^+} \gamma_{H^+} / m^0)$, where m_{H^+} is the relative (molality basis) activity, γ_{H^+} is the molal activity coefficient of the hydrogen ion H^+ at molality m_{H^+} , and m^0 is the standard molality, was introduced in 1910 and reaffirmed on successive occasions by relevant bodies, different conceptual definitions and alternative measurement procedures have been adopted and are in use by some, namely among oceanographers, often leading to confusion. This leads to major difficulties with the use of data, e.g., on what concerns comparison of results in space and time. Primary pH values, the highest quality level in terms of the metrological chain, have been assigned to primary reference pH buffer solutions of low ionic strength, by a primary method based on measurements of the Harned cell potential in association with the Nernst equation, as well as on the adoption of extra-thermodynamic model assumptions for electrolyte solutions. Although equivalent types of recommendations dealing with standards and procedures based on metrological traceability are still lacking for higher ionic strength media, as it is in the case of seawater, reference Tris–Tris·HCl buffer solutions in artificial seawater have been suggested for use in the calibration of pH meter systems. In this work, Tris–Tris·HCl buffer saline solutions of three different molality ratios $m_{Tris}:m_{Tris \cdot HCl}$, $m/mol\ kg^{-1}\ H_2O$, have been assigned reference values for free $pH = -\lg a_{H^+}$ and total $pH^T = -\lg (m_{H^+}^*/m^0)$, where $m^0 = 1\ mol\ kg^{-1}$ and $m_{H^+}^* = \lim_{m \rightarrow m_{sw}} [m(H^+) + m(HSO_4^-)]$. Multi-point calibration of pH meters in terms of either pH or pH^T is thus possible and supports measurement of their respective values under routine conditions at a high metrological level.

Keywords: pH; pH^T ; potentiometric measurements; seawater; traceability; Tris–Tris HCl buffers in artificial seawater; analytical chemistry division.

1 Introduction

Measurement of pH and the study of hydron transfer reactions in seawater are critical areas of marine chemistry, requiring a proper metrological approach.

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Natural seawaters can be looked upon as multi-electrolyte solutions with typically high ionic strengths ($I_m \approx 0.67 \text{ mol kg}^{-1}$). Moreover, ion concentrations of the dissolved salts strongly influence the pH value, by changing both H⁺ concentration due to simultaneous equilibria (e.g., association with SO_4^{2-}) and activity coefficients due to the complexity of the saline matrix.

The most common and fastest way of measuring pH in routine analysis is the classical potentiometric method. Glass electrodes are sensitive to H⁺. An electrochemical potential difference between the electrode surface and the sample solution is measured potentiometrically against a reference electrode of constant potential, also called an electrode of second kind, typically a silver–silver chloride electrode:

The potential difference which occurs in the cell varies linearly with pH according to the analytical law that relates the measured potential, E_{cell} , with the activity, a , of the ion H⁺, a_{H^+} , which is the Nernst equation [1], Eq. (1):

$$E_{\text{cell}} = E_{\text{cell}}^0 - k' \cdot \lg(a_{\text{H}^+}) \quad (1)$$

Here, k' is the coefficient of $\lg(a_{\text{H}^+})$ (slope), most commonly sub-Nernstian, implying that there might be a discrepancy between theory and fit, obtained from calibration of the setup with reference pH buffer solutions. Theoretically, the Nernst coefficient equals $\frac{\ln 10 RT}{nF}$, where n represents the number of electrons exchanged per ion, F is the Faraday constant, R is the gas constant, and T is the thermodynamic temperature. E_{cell}^0 is the constant term (intercept), which corresponds to the sum of all constant terms that contribute to the cell potential and does not have the thermodynamic meaning of a standard potential, E^0 .

E^0 and k' are specific for each glass electrode and are determined through calibration with certified buffer solutions after linear regression of equation [1].

The cell potential is described by $E_{\text{cell}} = (E_{\text{ref}} + E_{\text{lj}}) - E_{\text{g,el}}$, where E_{ref} represents the reference electrode potential, E_{lj} is the liquid junction potential between the electrolytes of the two half-cells, and $E_{\text{g,el}}$ is the glass electrode potential.

Buffer solutions recommended for calibration of pH instruments cover only pH measurements in dilute solutions (ionic strength, $I_m \leq 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$) [2]. Such certified reference buffers are widely available, and practitioners tend to use them for all-purpose measurements, i.e., even when they are not fit for the purpose of the measurement. Since seawater has a high ionic strength and ocean water pH varies worldwide in a very narrow range, instruments with well-adapted calibration strategies need to be used if exemplar pH data are to be obtained. The development of a rigorous calibration methodology is based on the availability of appropriate buffers in a matrix having a composition representative of the real samples. In such a way, the residual liquid junction potential appearing when standard solutions used for calibration are replaced by the tested real solution is minimized, thus reducing the uncertainty of pH measurement results.

Assignment of reference pH values to dilute ($I_m \leq 0.1 \text{ mol kg}^{-1}$) primary standard solutions relies on the measurement of Harned cell potentials, in conjunction with the Nernst equation and chloride ion activity coefficients, γ_{Cl^-} , assessed using the Debye–Hückel electrolyte solution theory complemented by the Bates–Guggenheim convention [2]. For high ionic strengths, the model fails, hence requiring other valid approaches for the calculation of mean and single-ion activity coefficients that consider enhanced electrostatic effects plus specific interactions, such as the Pitzer model, associated with a seawater matrix [3, 4]. A procedure parallel to the one adopted for dilute solutions is being followed, and experimental and model approaches (Pitzer) are undergoing validation. To this end, studies conducted since 1948 [5–7] until now [8–10] have led to the preference of 2-amino-2-(hydroxymethyl)propane-1,3-diol (Tris)–Tris·HCl buffers in a saline background.

Despite the importance of pH, conceptually defined as $\text{pH} = -\lg a_{\text{H}^+}$ [2], measurement of seawater pH remains an issue for chemical oceanographers [1, 10, 11]. In this complex environment, various “pH” alternative quantities have been defined and measured in several ways by different users. Nevertheless the square quotes, “ ”, tend to be dropped and the same name, pH, has been mistakenly given to different measurands, e.g., $\text{pH}^T = -\lg(m_{\text{H}^+}^*/m^0)$, where $m^0 = 1 \text{ mol kg}^{-1}$ and $m_{\text{H}^+}^* = \lim_{m \rightarrow m_{\text{sw}}} [m(\text{H}^+) + m(\text{HSO}_4^-)]$. Here, $m_{\text{H}^+}^*$ represents the total hydrogen molality that is identical to the sum of the molalities of H⁺ and HSO₄[−] in the limit of the pure synthetic seawater. The molalities $m(\text{H}^+)$ and $m(\text{HSO}_4^-)$ are expressed in mol kg^{-1} seawater. Sample measurement procedures, other than potentiometry, are increasingly being adopted, consequently hindering metrological traceability, leading to serious problems of the lack of comparability of results in time and in space.

The pH^T measurement option using UV–Vis spectrophotometry with *m*-cresol purple indicator has gained support as an alternative measurement procedure which, contrary to potentiometry which simply senses H^+ (when electrodes have been properly selected in order to avoid interferences and mixed responses), senses both H^+ and HSO_4^- species, the latter resulting from the association of H^+ with SO_4^{2-} provided by the sodium sulfate Na_2SO_4 , existing in seawater.

For the sake of harmonisation of seawater acidity measurements and to ensure the quality of results, it is urgent to clarify which are the recommended methods and procedures, thus avoiding the current unfortunate situation of confusion among oceanographers, chemists, and other experts and practitioners on which parameter is being considered, measured, reported, etc.

The Guide to Best Practices for Ocean CO_2 measurements [12] contains a reference procedure, SOP6a, describing the method to be used for the potentiometric determination of the pH of seawater on the total hydrogen ion concentration pH scale. However, the cited document recommends using in-house prepared Tris–Tris·HCl buffer solutions, and a measurement precision (*i.e.*, not a total measurement uncertainty) that can reach 0.003 in pH^T is mentioned. Other studies [13] have been done using spectrophotometric calibration of electrodes but without an uncertainty statement. According to VIM [14], the metrological traceability is defined as a “*Property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.*” It is thus clear that in the absence of a traceability chain, a complete uncertainty budget cannot be evaluated. That is why, for example, in the IOC/UNESCO Sustainable Development Goal Indicators, Methodology for 14.3.1 related to “Average marine acidity (pH) measured at agreed suite of representative sampling stations” [15] such measurements were identified as having an undefined quality but nevertheless considered useful in the identification of coastal ocean acidification hot spots and prioritizing future monitoring plans [16].

This work presents a study which aims to demonstrate the feasibility of using potentiometry to determine pH^T values by transposing the method applied for aqueous dilute media including an uncertainty budget evaluation. The proposed practice will contribute to establish comparability for the potentiometric assignment of both pH and pH^T values in the routine analysis of seawater samples by calculating the conversion factors between the different scales and also the equivalence of pH^T measurement results obtained with different techniques. The study is based on the use of high-order Tris–Tris·HCl reference buffer solutions prepared in a seawater background [8] and traceable to the Laboratoire de Métrologie et d’Essais (LNE) pH^T standard measurement procedure.

The assignment of such pH and pH^T values to reference buffer standards falls in the mission and scope of action of National Metrology Institutes, NMIs, which can certify the buffers for these kinds of quantities and make them available to the users who can then easily perform calibration of the pH meter setups in terms of the acidity parameter of their choice, *E* vs. pH or pH^T .

2 Experimental

2.1 Reagents and solution preparation

In the present study, in order to allow a multi-point calibration for potentiometric measurements, three Tris–Tris·HCl buffers of different molality ratios, prepared in an artificial seawater matrix, were characterized by the pH primary method, covering a range of pH close to the expected values of seawater (7.8 to 8.3) [17]. These solutions were prepared in an artificial seawater (ASW) background representative of practical salinity [18], $S_p = 35$. A slightly different ASW formulation was used with respect to the reference solutions available from SCRIPPS [8]. According to K. Pratt [17] who focuses on an 0.04 equimolar Tris–Tris·HCl buffer solution, this difference modifies the pH^T value by 0.002 only.

Saline buffer solutions were prepared gravimetrically from stock solutions (see Table 1) with ultrapure water. Estimated conventional mass was corrected for buoyancy to estimate the real mass.

Table 1: Details on stock solutions used to prepare the buffer solutions.

Stock solution	Compound	Amount content/mol in 1 kg of stock solution	Remarks
1	KCl	0.049 56	Mass fraction of KCl based on halide content equals (99.877 ± 0.036) %
	CaCl ₂	0.050 45	Because of the hygroscopicity of solid salts, CaCl ₂ was added from stock solutions with an amount content of (0.510 66 ± 0.000 21) mol in 1 kg of solution
	MgCl ₂	0.2585	Because of the hygroscopicity of solid salt, MgCl ₂ was added from stock solutions with an amount content of (2.054 79 ± 0.000 77) mol in 1 kg of solution
2	NaCl	1.666	Mass fraction of salt based on halide content equals (99.916 ± 0.037) %
3	Na ₂ SO ₄	0.4117	Mass fraction of salt based on anion content equals (100.003 ± 0.027) %
4	HCl	0.105 16	Hydrochloric acid solution was prepared from commercial 30 % HCl solution purchased from Merck Amount content of chloride estimated by titrimetry with an uncertainty of 0.14 %
5	Tris*	0.6558	NIST SRM 723e

*Tris, 2-amino-2-(hydroxymethyl)propane-1,3-diol.

The various salts, sodium chloride, potassium chloride, magnesium chloride, calcium chloride, and sodium sulfate, were purchased from VWR and characterized by coulometry. Tris(hydroxymethyl)methylamine was purchased from NIST (SRM723e).

The composition of the artificial seawater matrix is given in Table 2 together with the target value for the three buffers used for this study.

Table 2: Reference calibration buffer solutions in the artificial seawater background composition. The total molality of Tris is 0.08 mol kg⁻¹. The molality of sodium chloride corresponds to $m - m_{\text{HCl}}$, where $m = 0.426\,64\text{ mol kg}^{-1}$. The chloride molality, m_{Cl^-} , is given with expanded uncertainty ($k = 2$). m_{Cl} is calculated based on the molalities of the component salts in the solution: $m_{\text{Cl}^-} = m_{\text{NaCl}} + m_{\text{HCl}} + m_{\text{KCl}} + 2(m_{\text{MgCl}_2} + m_{\text{CaCl}_2})$.

Buffer	$m_{\text{Tris}}:m_{\text{Tris,HCl}}$	$m/\text{mol kg}^{-1}$	Molality $m/\text{mol kg}^{-1}$						$m_{\text{Cl}}/\text{mol kg}^{-1}$
			HCl	NaCl	KCl	MgCl ₂	CaCl ₂	Na ₂ SO ₄	
Target			Fixed value	0.426 64 – m_{HCl}	0.010 58	0.055 16	0.010 77	0.029 26	
Buffer 1	0.035:0.045	0.034 99		0.3915	0.010 60	0.055 27	0.010 79	0.0292	0.5692 ± 0.0010
Buffer 2	0.04:0.04	0.040 00		0.3866	0.010 58	0.055 18	0.010 77	0.0293	0.5691 ± 0.0010
Buffer 3	0.06:0.03	0.060 00		0.3666	0.010 58	0.055 16	0.010 77	0.0293	0.5691 ± 0.0010

Minor deviations from target composition can be noticed for some individual components of artificial seawater but this does not significantly affect the molality of chlorides in the final buffer solution, which has an estimated expanded uncertainty ($k = 2$) of $1 \times 10^{-3}\text{ mol kg}^{-1}\text{ H}_2\text{O}$.

2.2 Calibration procedure

The calibration method described by the IUPAC [2] can be adapted to the desired quality of the measured value, *i.e.*, the aimed target uncertainty. A two-point calibration with buffer solutions bracketing the pH value of the analyzed solution is generally adopted, enabling obtaining pH data with an uncertainty ($k = 2$) of 0.02 to 0.03 in pH.

A Metrohm 867 pH Module and a new combination of pH glass electrodes, two Unitrode and two Primatrode electrodes, were used in conducting potentiometric measurements at $(25 \pm 0.05)^\circ\text{C}$. The two types of electrodes differ by the nature of their diaphragm that allows a slow constant flow of the reference electrolyte

solution into the sample, thus affecting the liquid junctions (interface that, for the establishment of the electrical circuit for measuring the potential of the electrochemical cell, allows electrolytic contact commonly between a saturated solution of KCl from the interior of the reference electrode and the solution to be analyzed). According to the manufacturer, Unitrode electrodes have a fixed ground-joint diaphragm [flow rate for $c(\text{KCl}) = 3 \text{ mol L}^{-1}$ between 3 and 30 $\mu\text{L h}^{-1}$], enabling them to be insensitive to contamination, whereas Primatrode electrodes have a ceramic diaphragm (flow rate for $c(\text{KCl}) = 3 \text{ mol L}^{-1}$ between 3 and 10 $\mu\text{L h}^{-1}$), thus a recommended usage in clear aqueous solutions.

The temperature of 25 °C is one of standardized conditions for spectrophotometric pH^T measurements and would enable obtaining equivalence between the two routine methods employed to obtained pH^T values, *i.e.*, potentiometry and spectrophotometry.

In order to check the electrode's performance, prior to pH measurements, each electrode was calibrated using three diluted standard buffer solutions traceable to SI (nominal pH 4, 7, and 10). The calibration parameters were also calculated manually using the operating principle of the pH meter. Thus, for each electrode, the measured potentials, E , were plotted as a function of the standard pH values used for calibration. Excellent agreement between the calculated and displayed calibration parameters (slope and pH(0)) was obtained. For all electrodes, the practical slopes were within 1 % with respect to the theoretical Nernst slope, indicating that the electrodes have a Nernstian behavior and the quality required to initiate measurements. Furthermore, pH values were assigned using the determined calibration parameters (*i.e.*, without resorting the pH meter's internal system software).

When measuring in unknown samples, the magnitude of the liquid junction potential cannot be quantified, and a rigorous bottom-up uncertainty budget cannot be established using the GUM approach. Hence, the uncertainty of pH and pH^T measurements was estimated based on the guidance proposed in the ISO 5725-2 document [19] that recommends using trueness, repeatability, and intermediate precision to calculate the uncertainty of a measured value. For this purpose, a standard buffer solution different from that used for calibration, namely of pH 9, was used.

The same methodology, *i.e.*, a two-point bracketing calibration procedure and one intermediate point as the control, was applied to perform pH and pH^T measurements of saline Tris–Tris·HCl buffer solutions. Accuracy was estimated based on the potentiometric measurements performed at the primary level with a Harned cell.

3 Results and discussion

Three Tris–Tris·HCl buffer solutions were prepared in artificial seawater, $S_p = 35$. These buffers were characterized in terms of pH and pH^T using a primary pH system.

The pH values were calculated based on the experimentally measured acidity function and the Pitzer-modeled activity coefficient of chloride, represented in Eq. (2) by the first and second terms of the right side.

$$\text{pH} = -\lg(a_{\text{H}^+} \gamma_{\text{Cl}^-}) + \lg(\gamma_{\text{Cl}^-}) \quad (2)$$

The free molalities of H⁺, HSO₄[−] and SO₄^{2−} needed to apply the Pitzer model have been determined using the stoichiometric dissociation constant of hydrogen sulfate, K_m^* , with the literature value of 0.103 93 [20]. The asterisk denotes the constant's representativeness for some specific ionic medium, here, the artificial seawater with the composition indicated in Table 2.

pH^T values were experimentally determined using the protocol described in the literature [17, 21], Eq. (3):

$$\text{pH}^T = \frac{E_{\text{cell}} - E^{0*}}{(RT \ln 10)/F} + \lg\left(\frac{m_{\text{Cl}}}{m^o}\right) - \lg(\omega_{\text{H}_2\text{O}}) \quad (3)$$

where E_{cell} is the potential of the Harned cell for the buffer, corrected to $p(\text{H}_2) = 1 \text{ atm}$ (101.325 kPa), the partial pressure of hydrogen gas used in electrochemistry in preference to 100 kPa; R and F are the gas and Faraday constants, respectively. E^{0*} represents the standard potential of the Ag/AgCl electrode in pure ASW of the same

nominal salinity. E^{0*} differs from the well-known E^0 defined as the standard potential of the Ag|AgCl electrode in pure water media and used for primary pH determinations. $\omega_{\text{H}_2\text{O}}$ represents the mass fraction of water and m^0 is the standard molality, 1 mol kg⁻¹.

Table 3 presents the primary pH and pH^T values reported with assigned overall expanded uncertainty ($k = 2$, for a confidence level of approximately 95 %) that includes contributions from the characterization, long-term stability, and homogeneity of buffer solutions. For primary pH, the uncertainty contribution related to characterization neglects contribution coming from the activity coefficient of chloride.

Table 3: Primary pH and pH^T values with associated expanded uncertainty, U ($k = 2$). These three buffers were used in two sets of experiments.

Buffer	Certified value	
	pH	pH ^T
Buffer 1	7.837 ± 0.005	7.622 ± 0.005
Buffer 2	8.313 ± 0.005	8.101 ± 0.005
Buffer 3	8.425 ± 0.005	8.209 ± 0.005

Experiment 1: The three Tris–Tris HCl buffers were treated as unknown samples and their pH was determined at 25 °C with different combination electrodes (Unitrode and Primatrode) after three-point calibration with classical buffer solutions of low ionic strength (nominal pH 4, 7, and 10). This experiment is representative of the current practice in use, in the absence of quality control standards for seawater pH measurements.

Experiment 2: Buffers 1 and 3 were used to calibrate the combination glass electrode setup, whereas Buffer 2 was treated as an unknown sample.

The expanded uncertainty ($k = 2$) assigned to the measured pH values was estimated based on the global approach with the ISO 5725-2 document [19] using a pH 9 standard buffer solution as QA/QC. The different sources of uncertainty together with their estimation are given in Table 4. Intermediate precision [14] was issued from measurements performed on three series of three measurements.

Table 4: Sources of uncertainty for pH measurements with Unitrode 1 based on the ISO 5725-2 approach, in which p corresponds to the number of series and N corresponds to the number of measurements for each series. E_i represents the result within each series, E is the reference value, s_W is variance of inter-series repeatability, and s_r is variance of intra-series repeatability.

	Formula	Value	Contribution to the overall uncertainty budget (%)
Standard	Based on standard uncertainty of the standard solution according to the certificate	2.5×10^{-5}	10.5
Trueness	$u_{\text{trueness}}^2 = \frac{1}{p-1} \sum_{i=1}^p (E_i - E_{\text{standard}})^2$	5×10^{-5}	20.9
Intermediate precision	$s_R^2 = s_W + \frac{p-1}{N} s_r^2$	1.5×10^{-4}	65.1
Resolution (number of digits displayed by the pH meter)	$u_{\text{resolution}}^2 = \frac{a^2}{12}$, where a is the resolution of the pH meter	8×10^{-6}	3.5
Overall estimation	–	2.4×10^{-4}	–
Expanded uncertainty, U ($k = 2$)	0.03		

Experiment 1: Table 5 presents a summary of the pH values obtained for the three saline buffer solutions and their associated expanded uncertainty obtained in the first set of experiments.

Table 5: pH value results for Tris–Tris-HCl in artificial seawater buffer solutions, treated as unknown samples, at 25 °C, with associated expanded uncertainty, U ($k = 2$).

Buffer	Certified pH value	pH Unitrode 1	pH Unitrode 2	pH Primatrode 1	pH Primatrode 2
Buffer 1	7.837 ± 0.005	7.72 ± 0.03	7.74 ± 0.05	7.71 ± 0.02	7.75 ± 0.01
Buffer 2	8.313 ± 0.005	8.20 ± 0.03	8.22 ± 0.05	8.20 ± 0.02	8.24 ± 0.01
Buffer 3	8.425 ± 0.005	8.32 ± 0.03	8.33 ± 0.05	8.30 ± 0.02	8.35 ± 0.01

The primary certified pH values were further compared with the results obtained using usual commercially available buffers with low ionic strength. This comparison revealed a difference greater than 0.1 pH, which is in good agreement with other published studies [22].

All pH values obtained with the pH meter are lower than the certified pH values, this difference being significantly greater than the expanded uncertainty. The existence of such a bias may come from an inappropriate calibration protocol and can be accounted for as a systematic error, due to the different ionic strengths affecting the liquid junction potential. Indeed, for calibration, several IUPAC documents recommend using buffer solutions that match the analyzed sample in terms of composition and ionic strength. However, when this is not possible, the users have two possibilities: (A) to integrate this bias into the result by performing the necessary correction or (B) to add it as a contribution to the overall uncertainty budget. The first option, (A), seems easier to apply, but in order to guarantee good data quality, several requirements must be satisfied:

- (i) ensure that the correction covers the range of seawater pH. To make this evaluation, measurements with solutions of different pH values need to be carried out.
- (ii) choose a certified reference material representative of the seawater media and possibly traceable to SI [23], in order to ensure the SI traceability of the final pH results.
- (iii) the operated correction has its own uncertainty that must be assessed and included in the overall pH uncertainty budget. The main sources contributing to the correction uncertainty would come from the standard solutions used to determine the correction, the reproducibility of measurement results, and the dispersion of the correction factors associated to their fluctuation in a studied pH range.

Table 6 summarizes the corrections to be applied for pH results in the seawater matrix and their associated expanded uncertainty ($k = 2$) for each studied glass electrode. The uncertainty of corrections is calculated with Eq. (4) and considers the uncertainty of the standard solution used to assess the value of correction and the repeatability obtained as standard deviation of the measured pH values.

$$u_{\text{correction}}^2 = u_{\text{standard}}^2 + u_{\text{repeatability}}^2 \quad (4)$$

Table 6 shows that for each studied electrode, the bias is constant within the studied range of pH between 7.8 and 8.4 and cannot be neglected as it is larger than the expanded uncertainty.

The second option, (B), applied mostly when the systematic errors are not completely understood or known, leading to much higher uncertainty, up to 0.2 pH, which is not fit for the intended purpose in several applications. The integration of the bias into the overall uncertainty budget could be done using the approaches described in different references [24–26].

Table 6: Corrections to be applied for pH results in the seawater matrix with their associated expanded uncertainty ($k = 2$) for each studied combined glass electrode.

Buffer	ΔpH Unitrode 1	ΔpH Unitrode 2	ΔpH Primatrode 1	ΔpH Primatrode 2
Buffer 1	0.12 ± 0.03	0.10 ± 0.05	0.13 ± 0.02	0.09 ± 0.01
Buffer 2	0.11 ± 0.03	0.10 ± 0.05	0.11 ± 0.02	0.07 ± 0.01
Buffer 3	0.11 ± 0.03	0.10 ± 0.05	0.13 ± 0.02	0.08 ± 0.01

A more rigorous approach would be to directly calibrate the pH meter with standard saline buffers, as recommended by the IUPAC. This was demonstrated with the second set of experiments.

Experiment 2: Buffer 1 and Buffer 3 have been used to perform two-point calibration manually, first using pH and, then, pH^T values. Figure 1 presents the measured potential values for dilute buffers and saline buffers recorded to establish the calibration curves for the Unitrode 1 electrode.

Fig. 1: Example of calibration curves for pH and pH^T potentiometric measurements with Unitrode 1. The symbols are used for (●) pH calibration with commercial dilute buffers, (○) pH calibration with Tris–Tris-HCl saline buffers and (□) pH^T calibration with saline Tris–Tris-HCl buffers. A zoomed version of the calibration curves is represented at the right-hand side of the figure.

The calibration slopes determined using this protocol showed that all the electrodes exhibit Nernstian behavior. To test the calibration efficiency, Buffer 2 solution was used as an unknown sample for pH and pH^T measurements.

Table 7 presents both pH and pH^T results obtained for Buffer 2 using the four electrodes and the associated expanded uncertainties calculated using the ISO 5725-2 document [19]. It shows excellent agreement between the values obtained with the combination electrodes for the reference primary values, which confirms that the selection of saline buffers to calibrate the pH electrode enables minimization of the systematic errors coming from liquid junctions. It has to be pointed out that measurements in the synthetic seawater matrix exhibit a good reproducibility, better than 0.002, and similar to the values attained for classical dilute buffers.

Table 7: pH and pH^T results of Tris–Tris-HCl Buffer 2 with the associated expanded uncertainty, U ($k = 2$), based on ISO 5725-2.

	Certified value	Buffer 2			
		Unitrode 1	Unitrode 2	Primatrode 1	Primatrode 2
pH	8.313 ± 0.005	8.31 ± 0.01	8.32 ± 0.01	8.32 ± 0.01	8.32 ± 0.01
pH ^T	8.101 ± 0.005	8.10 ± 0.01	8.10 ± 0.01	8.09 ± 0.01	8.10 ± 0.01

The consistency of the pH^T value with the reference primary pH^T value for this buffer documents the possibility to use the potentiometric method for direct determination of this quantity.

In 1988, an IUPAC recommendation [27] was published aiming at ensuring that measurements of different quantities used to assess seawater acidity, namely pH and pH^T, are comparable. Thus, it was recommended to calculate a parameter, $f_{H'}$, relating pH to pH^T, Eq. (5), that takes into account the systematic errors introduced by calibration with a low-ionic strength buffer solution.

$$\lg f_{H'} = \text{pH}^T - \text{pH} \quad (5)$$

In the present study, the dependency of the conversion factor between the acidity scales $f_{H'}$ to the electrode was evaluated.

Measurement results are sensitive to the type of liquid junction. The liquid junction potential is influenced by different factors, including the ionic strength (reflected by the difference of ionic strengths between reference buffer solutions and samples), geometry, and type of junction. Thus, the conversion factor should be calculated for each electrode, and based on the methodology proposed in the present work, a protocol can be relatively easily implemented for quality control of routine measurements.

Table 8 presents the f_H calculated based on the measurements done with the four combined glass electrodes and considering pH values obtained after calibration with saline buffers. The obtained values are represented graphically in Fig. 2.

Table 8: f_H values obtained by calibrating the combined glass electrodes used in this study with saline buffers together with their expanded uncertainty ($k = 2$).

Electrode	f_H
Unitrode 1	0.62 ± 0.02
Unitrode 2	0.60 ± 0.02
Primatrode 1	0.59 ± 0.02
Primatrode 2	0.60 ± 0.02

Fig. 2: f_H values obtained by calibrating the combined glass electrodes used in this study with saline buffers. Error bars are expanded uncertainties ($k = 2$).

Table 8 and Fig. 2 show that f_H values obtained for the tested electrodes are not statistically different. Both pH and pH^T values are reported with uncertainties explained inter-alia by the control of the liquid junction, by perfectly matching the salinity of solutions used to standardize the electrodes to the salinity of the sample. The present study was conducted with new well-behaved electrodes. Quality of results is expected to decrease if aged electrodes and electrodes with different types of liquid junctions are used.

4 Conclusions

pH is one of the master variables that characterize seawater, used as an indicator of ocean acidification. Nevertheless, measurement of pH is still of major concern due, on one side, to the lack of recommended commercial buffer solutions to establish fit for purpose calibration for routine measurements and, on the other one, as a consequence of the proliferation of values pertaining to different measurands and different measurement procedures, often without clear identification.

The calibration with saline buffers characterized in terms of pH and ionic strength has not been a generalized practice so far because there is not yet such a recommendation supported on data and due to the lack of commercially available suitable calibrants. Also, the often indiscriminate use of different kinds of quantities for “pH” as well as potentiometric and spectrophotometric measuring methods and procedures has

been hindering the traceability of values, hence making comparability of results in space and time impossible. The results of this study aim at overcoming these existing limitations.

For reliable QA/QC purposes, the availability of reference Tris–Tris HCl buffers in artificial seawater, of three different molality ratios, with assigned primary pH and pH^T values, provides the means for an adequate multi-point calibration approach to be used for pH meter setups, namely potentiometric devices equipped with quality assured, well-behaved glass electrodes. Conversion factors between the mentioned kinds of quantities can be applied to measurement results, thus solving the issues of comparability. Results with uncertainties of the same order of magnitude as those assessed for measurements in dilute solutions are reached.

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References

- [1] R. Bates. *Determination of pH – Theory and Practice*, New York: John Wiley & Sons Inc (1964).
- [2] R. P. Buck, S. Rondinini, A. K. Covington, F. G. K. Baucke, C. M. A. Brett, M. F. Camões, M. J. T. Milton, T. Mussini, R. Naumann, K. W. Pratt, P. Spitzer, G. S. Wilson. *Pure Appl. Chem.* **74**, 2169 (2002).
- [3] F. Camões, B. Anes, H. Martins, C. Oliveira, P. Físicaro, D. Stoica, P. Spitzer. *J. Electroanal. Chem.* **764**, 88 (2016).
- [4] B. Anes, R. J. N. Bettencourt da Silva, H. F. P. Martins, C. S. Oliveira, M. F. Camões. *Accred Qual. Assur.* **21**, 1 (2016).
- [5] R. G. Bates. *Chem. Rev.* **42**, 1 (1948).
- [6] M. F. Camões, A. K. Covington. *Anal. Chem.* **46**, 1547 (1974).
- [7] I. Hansson. *Deep Sea Res. Oceanogr. Abstr.* **20**, 479 (1973).
- [8] T. A. DelValls, A. G. Dickson. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **45**, 1541 (1998).
- [9] P. J. Brewer, D. Panagoulia, R.J.C. Brown, A. Tromans, A. Reyes, M. Arce, A. Vospelova, M. Rozikova, W. Pratt, T. Asakai, P.T. Jakobsen, M. F. Camões, C.S. Oliveira, I. Godinho, P. Spitzer, B. Sander, M. Mariassy, L. Vyskocil, P. Físicaro, D. Stoica, E. Uysal. *Meas.: J. Int. Meas. Confed.* **66**, 131 (2015).
- [10] A. G. Dickson, M. F. Camões, P. Spitzer, P. Físicaro, D. Stoica, R. Pawlowicz, R. Feistel. *Metrologia* **53**, R26 (2015).
- [11] G. M. Marion, F. J. Millero, M. F. Camões, P. Spitzer, R. Feistel, C. T. A. Chen. *Mar. Chem.* **126**, 89 (2011).
- [12] A. G. Dickson, C. L. Sabine, J. R. Christian. *PICES Spec. Publ.* **3**, 3, 191 (2007).
- [13] R. A. Easley, R. H. Byrne. *Environ. Sci. Technol.* **46**, 5018 (2012).
- [14] JCGM – Joint Committee for Guides in Metrology. *International Vocabulary of Metrology – Basic and General Concepts and Associated Terms (VIM)* Paris, (2012).
- [15] K. Isensee. *Update on SDG 14.3.1 Indicator and the Methodology*, Paris: IOC-UNESCO (2018).
- [16] J. Barbière, K. Isensee. *Update on IOC Custodianship Role in Relation to SDG 14 Indicators*, Paris (2018).
- [17] K. W. Pratt. *Mar. Chem.* **162**, 89 (2014).
- [18] IOC, SCOR, IAPSO. *Intergov. Oceanogr. Comm. Manuals Guide. No. 56*, 196, UNESCO, (2010).

- [19] ISO 5725-2:2019. *Accuracy (Trueness and Precision) of Measurement Methods and Results – Part 2: Basic Method for the Determination of Repeatability and Reproducibility of a Standard Measurement Method* ISO GENOVA, (2019).
- [20] A. G. Dickson, D. J. Wesolowski, D. A. Palmer, R. E. Mesmer. *J. Phys. Chem.* **94**, 7978 (1990).
- [21] J. D. Müller, G. Rehder. *Front. Mar. Sci.* **5**, 177 (2018).
- [22] B. Anes, R. J. N. Bettencourt da Silva, C. Oliveira, M. F. Camões. *Talanta* **193**, 118 (2019).
- [23] M. F. Camões, B. Anes. *Water* **7**, 8 (2015).
- [24] G. E. O'Donnell, D. B. Hibbert. *Analyst* **130**, 721 (2005).
- [25] I. H. Lira, W. Wöger. *Meas. Sci. Technol.* **9**, 1010 (1998).
- [26] K. Klauenberg, G. Wübbeler, C. Elster. *Meas. Sci. Rev.* **19**, 204 (2019).
- [27] A. K. Covington, M. Whitfield. *Pure Appl. Chem.* **60**, 865 (1988).