

Measurement of pH_T values of Tris buffers in artificial seawater at varying mole ratios of Tris:Tris·HCl

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ABSTRACT

Measurements of total pH, pH_T , in Harned cells are reported for 2-amino-2-hydroxymethyl-1,3-propanediol (Tris) buffers in artificial seawater (ASW) of salinity 35 at three molality ratios of Tris to Tris·HCl: 0.03:0.05, 0.04:0.04, and 0.05:0.03. The ASW formulation was derived from the 2008 International Association for the Physical Sciences of the Oceans (IAPSO) composition of seawater (Millero et al., 2008). The pH_T value of each buffer was measured at 288.15 K, 298.15 K, and 308.15 K (15 °C, 25 °C, and 35 °C). Measurement uncertainties compliant with the ISO GUM (JCGM, 2008) are provided for each buffer. These new formulations extend the available data for Tris buffers in ASW to pH_T values that bracket the pH_T range of natural surface seawaters at 298.15 K. The data provide a framework for future multiple-point calibrations of spectrophotometric and potentiometric pH_T measurements traceable to these new buffers.

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1. Introduction

The traceability of pH measurements of seawater to accepted standards is of critical importance in studies of climate change. The de facto standard for the pH of seawater at the present time is an equimolal buffer that consists of 2-amino-2-hydroxymethyl-1,3-propanediol ('Tris') and Tris hydrochloride, Tris·HCl, each at a molality of 0.04 mol/kg, in artificial seawater (ASW) (DelValls and Dickson, 1998; Nemzer and Dickson, 2005). The pH of this standard is obtained from measurements in $H_2|H^+$ electrochemical cells without transference (Harned cells). The result is expressed as total pH, pH_T (Dickson, 1993a; Millero et al., 1993), the sum of the contributions from free H^+ and from HSO_4^- . Such Harned cell measurements are at the highest metrological level. They form the foundation for all other seawater pH_T measurements and are thus of fundamental importance to the field.

The current state of seawater pH metrology is currently deficient in that pH_T values derived from Harned cell measurements have not been reported in the literature for Tris·H⁺:Tris buffers with mole ratios other than 1:1. Furthermore, rigorous uncertainty estimates, essential for metrological traceability (JCGM, 2012), are lacking. Although the

0.04 mol/kg equimolal pH buffer is available as a certified reference material (CRM) (Dickson, 2011), that CRM and previous research (DelValls and Dickson, 1998; Ramette et al., 1977) only provide pH_T values for the equimolal formulation, with no uncertainty compliant with the International Standards Organization *Guide to the Expression of Uncertainty in Measurement* (ISO GUM) (JCGM, 2008).

Owing to this lack of multiple buffers with values assigned through Harned cell measurements, multi-point calibrations of secondary measuring systems for seawater pH_T at a high metrological level have not been possible. The spectrophotometric determination of pH_T using m-cresol purple (mCP) (Clayton and Byrne, 1993) is currently the most precise (standard deviation: 0.0004) secondary method for pH_T values in seawater. The measurement is traceable to the absorbance measurements and to the pK_a ($= -\lg K_a$, acid dissociation constant) of the mCP, which is determined in a parallel, single-point calibration using the 0.04 mol/kg Tris equimolal standard buffer. The method was originally validated (Byrne, 1987) over a range of ± 0.04 pH. This range is smaller than the pH_T range of open-ocean seawater. Measurements over the entire range of pH_T applicable to seawater, using multiple standards value-assigned in Harned cells, would provide a more rigorous verification of the spectrophotometric technique and could independently confirm the reduced bias observed using mCP purified by high-pressure liquid (Liu et al., 2011) (HPLC) or flash (Patsavas et al., 2013) chromatography. Single-point calibrations of secondary potentiometric pH measurements also suffer from analogous shortcomings (Buck et al., 2002): multi-point calibrations offer similar advantages here also.

The present work is the first step in this process: characterization of the Tris buffers themselves. This paper reports measurements of the pH_T

Abbreviations: ASW, artificial seawater; CA, concentrated acid; CB, concentrated buffer; CRM, certified reference material; CASW, concentrated ASW; ERB, buffer prepared to the EMRP recipe; EMRP, European Metrology Research Programme; ISO GUM, International Standards Organization *Guide to the Expression of Uncertainty in Measurement*; SRM, Standard Reference Material®; Tris, 2-amino-2-hydroxymethyl 1,3-propanediol.

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values of three Tris buffers in ASW that cover the range of pH_T currently applicable to open-ocean surface seawater samples. Each buffer was measured in a parallel series of measurements in Harned cells. Uncertainty calculations compliant with the ISO GUM are provided for each temperature. The paper also presents a general protocol for preparing an arbitrary number of Tris buffer solutions in an identical ASW matrix.

Fig. 1 summarizes in schematic form the contributions of the present article.

2. Experimental

2.1. Composition of reference ASW

In 2008, the International Association for the Physical Sciences of the Oceans (IAPSO) published an internationally-agreed reference composition for seawater (Millero et al., 2008). The molalities cited in Table 4 of that work were used as the basis for the ASW formulation used here.

The following substitutions were made to yield the reference ASW composition used for the Tris buffers. First, Cl^- replaced the buffering anions (HCO_3^- , $\text{B}(\text{OH})_4^-$, CO_3^{2-} , F^- , and OH^-) and the Br^- in the IAPSO reference composition, according to Eq. (1):

$$b_{\text{Cl}^-} = b_{\text{Cl}^-, \text{IAPSO}} + \sum_i |z_i| b_{i, \text{IAPSO}} + b_{\text{Br}^-, \text{IAPSO}}. \quad (1)$$

In Eq. (1), b_{Cl^-} is the molality of chloride in the ASW, i is the index for the above-stated buffering anions, z_i and b_i are the ionic charge and molality of the i th buffering ion, and IAPSO denotes the IAPSO reference composition. The symbol b for molality (Mills et al., 1993) avoids conflict with m , mass, used in the supplementary material.

Second, Ca^{2+} replaced Sr^{2+} in the IAPSO reference composition:

$$b_{\text{Ca}^{2+}} = b_{\text{Ca}^{2+}, \text{IAPSO}} + b_{\text{Sr}^{2+}, \text{IAPSO}}. \quad (2)$$

The molalities of the added salts in the ASW were calculated from Eq. (3a) through Eq. (3e), where the subscript refers to the given salt or ion. The added subscript ASW in Eq. (3a) indicates that the molality of NaCl is that of the reference ASW.

$$b_{\text{NaCl, ASW}} = b_{\text{Cl}^-}, \quad (3a)$$

$$b_{\text{MgCl}_2} = b_{\text{Mg}^{2+}, \text{IAPSO}}, \quad (3b)$$

$$b_{\text{CaCl}_2} = b_{\text{Ca}^{2+}}, \quad (3c)$$

$$b_{\text{KCl}} = b_{\text{K}^+, \text{IAPSO}}, \quad (3d)$$

$$b_{\text{Na}_2\text{SO}_4} = b_{\text{SO}_4^{2-}, \text{IAPSO}}. \quad (3e)$$

The formal ionic strength (molality basis) of the ASW, I_{ASW} , is calculated from Eq. (4):

$$I_{\text{ASW}} = b_{\text{NaCl, ASW}} + b_{\text{KCl}} + 3(b_{\text{MgCl}_2} + b_{\text{CaCl}_2} + b_{\text{Na}_2\text{SO}_4}). \quad (4)$$

Eq. (5) gives b_{Cl^-} in terms of the molalities of the component salts:

$$b_{\text{Cl}^-} = b_{\text{NaCl, ASW}} + b_{\text{KCl}} + 2(b_{\text{MgCl}_2} + b_{\text{CaCl}_2}). \quad (5)$$

This IAPSO-derived ASW composition served as the basis for the three Tris buffers.

Two separate equimolar Tris buffers, each based on a slightly different ASW formulation, served as controls in the present work. The first control was the CRM, based on the formulation of (DelValls and Dickson, 1998). The second control, based on older work (Millero, 1986; Millero et al., 1993), was prepared at NIST using separately-sourced and independently-assayed salts provided by the European Metrology Research Programme (EMRP) Project ENV05 OCEAN (Spitzer, 2012), which adopted this recipe for their work. This second control is denoted here as the “EMRP recipe buffer” (ERB).

Table 1 lists the molalities of the five component salts; I_{ASW} ; b_{Cl^-} ; the mass fraction of water, $w_{\text{H}_2\text{O}}$; and $-\lg w_{\text{H}_2\text{O}}$ for these three ASW formulations.

The ionic strength of the ASW based on the IAPSO reference composition agrees to within 1 part in 7000 with that of the formulation used in the CRM but is about 5 parts in 7000 lower than that in the ERB. The main difference in the ERB formulation is in the molality of MgCl_2 , which originated (Millero; personal communication; July 11, 2011) from different titration data for $b_{\text{Mg}^{2+}}$.

2.2. Target compositions and preparation of Tris buffers and HCl solutions in ASW

To produce a set of J Tris + Tris·HCl buffers in ASW, Tris and HCl are added to the ASW such that the desired molality ratio of Tris to Tris·HCl is attained. To maintain a constant ionic strength and molality of chloride in each buffer, $b_{\text{NaCl, ASW}}$ is reduced (Dickson, 1993b) by $b_{\text{HCl}, j}$, the added molality of HCl in the j th buffer:

$$b_{\text{NaCl}, j} = b_{\text{NaCl, ASW}} - b_{\text{HCl}, j}. \quad (6)$$

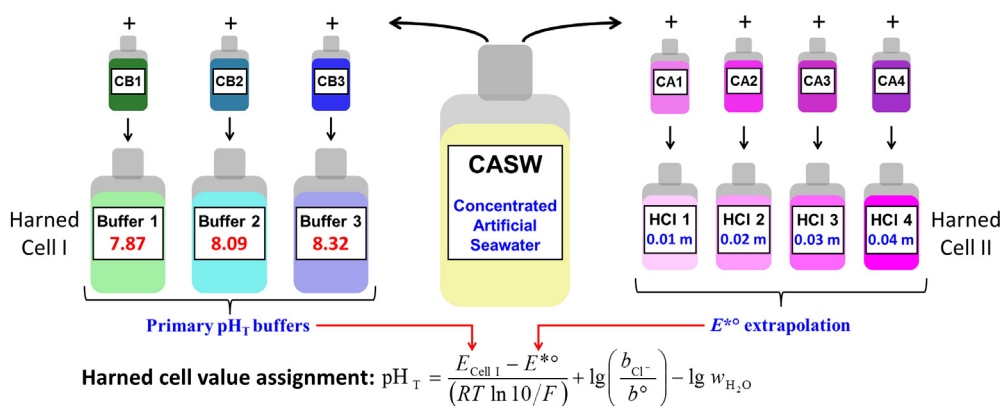


Fig. 1. Summary of synthesis protocol^a and measurement procedure^b. ^aCA = concentrated acid solution; CB = concentrated buffer (see text). Symbol m in the HCl solutions denotes molality of HCl in $\text{mol} \cdot \text{kg}^{-1}$. Cited pH_T values of buffers and molalities of HCl solutions are nominal. ^bEquation yields the final pH_T value assignment from the Harned cell measurement of each buffer. See text, Eqs. (9) and (10).

Table 1
Reference compositions of artificial seawater (ASW) for Tris buffers.

ASW	IAPSO ^a	CRM ^b	ERB ^c
Component <i>i</i>	Molality $b_i/(\text{mol} \cdot \text{kg}^{-1})$		
NaCl	0.427531	0.42762	0.42664
Na ₂ SO ₄	0.029264	0.02927	0.02926
KCl	0.010580	0.01058	0.01058
MgCl ₂	0.054742	0.05474	0.05518
CaCl ₂	0.010751	0.01075	0.01077
Ionic strength	0.72238	0.72248	0.72285
b_{Cl^-}	0.569097	0.56918	0.56912
$w_{\text{H}_2\text{O}}$ ^d	0.964937	0.964932	0.964945
$-\lg w_{\text{H}_2\text{O}}$	0.015501	0.015503	0.015497

^a IAPSO = based on International Association for the Physical Sciences of the Oceans (Millero et al., 2008).

^b CRM = certified reference material formulation (DelValls and Dickson, 1998).

^c ERB = buffer prepared to the recipe (Millero, 1986; Millero et al., 1993) adopted by European Metrology Research Programme.

^d $w_{\text{H}_2\text{O}}$ = mass fraction of water.

From Eq. (6), $b_{\text{NaCl},j} + b_{\text{HCl},j} = b_{\text{NaCl,ASW}}$. Thus, Eqs. (4) and (5) still yield the ionic strength and b_{Cl^-} of each buffer.

The nominal molalities (neglecting hydrolysis) of Tris·HCl (Tris·H⁺) and of Tris in buffer *j* after addition of the HCl are given by Eqs. (7a) and (7b), where b_0 is the initial added molality of Tris, prior to its reaction with the HCl:

$$b_{\text{Tris} \cdot \text{HCl},j} = b_{\text{HCl},j} \quad (7a)$$

$$b_{\text{Tris},j} = b_0 - b_{\text{HCl},j} \quad (7b)$$

The value of b_0 in Eq. (7b) is set at 0.08 mol/kg to maintain consistency with the existing Tris buffer. For $b_{\text{HCl},j} = b_0/2$, the additions yield exactly the equimolal buffer used in previous work (neglecting the small difference in the composition of the reference ASW). Other values of $b_{\text{HCl},j}$ yield buffers with different Tris:Tris·HCl ratios but with a constant I_{ASW} and constant b_{Cl^-} , as given by Eqs. (4) and (5), respectively.

Prior to preparing the buffers, it is necessary to select preliminary values of $\text{pH}_{\text{T},j}$, the pH_{T} of each buffer *j*. The exact $\text{pH}_{\text{T},j}$ of each buffer is subsequently assigned in the Harned cell measurements. The preliminary $\text{pH}_{\text{T},j}$ estimates are obtained via the Henderson–Hasselbalch equation for the Tris buffer system, which yields the molality-based total pH of the *j*th Tris buffer, $\text{pH}_{b,j}$:

$$\text{pH}_{b,j} = \text{p}K_{\text{a,Tris} \cdot \text{H}^+}^* + \lg \frac{b_0 - b_{\text{HCl},j}}{b_{\text{HCl},j}} \quad (8)$$

In Eq. (8), $K_{\text{a,Tris} \cdot \text{H}^+}^*$ is the molality-based K_{a} of Tris·H⁺ in ASW. At $T = 298.15$ K and $S = 35$, $\text{p}K_{\text{a,Tris} \cdot \text{H}^+}^* = 8.0736$ for $b_0 \rightarrow 0$ mol/kg (DelValls and Dickson, 1998). At $b_0 = 0.08$ mol/kg, the apparent value

of $\text{p}K_{\text{a,Tris} \cdot \text{H}^+}^*$, denoted $\text{p}K_{\text{a,Tris} \cdot \text{H}^+}^{**}$, is roughly 0.002 greater [see Fig. 1 of (DelValls and Dickson, 1998)]. Use of $\text{p}K_{\text{a,Tris} \cdot \text{H}^+}^{**}$ in place of $\text{p}K_{\text{a,Tris} \cdot \text{H}^+}^*$ in Eq. (8) yields the estimated $\text{pH}_{b,j}$ of the Tris buffers in ASW at $b_0 = 0.08$ mol/kg.

The estimated $\text{pH}_{b,j}$ from Eq. (8) are converted to corresponding values of $\text{pH}_{\text{T},j}$, the pH_{T} of the *j*th buffer, by Eq. (9):

$$\text{pH}_{\text{T},j} = \text{pH}_{b,j} - \lg w_{\text{H}_2\text{O},j} \quad (9)$$

The pH_{T} is calculated (DelValls and Dickson, 1998; Dickson, 2011; Nemzer and Dickson, 2005) on an amount content (Cvitaš, 1996; Máriássy et al., 2009; Rigg et al., 1991) basis, “moles per kilogram of solution” (DelValls and Dickson, 1998); $w_{\text{H}_2\text{O}}$ converts molality to amount content (see supplementary material).

Table 2 presents the values of $b_{\text{NaCl},j}$, $b_{\text{HCl},j}$, the estimated pH_{T} , $w_{\text{H}_2\text{O}}$, and $-\lg w_{\text{H}_2\text{O}}$ for each of the buffers studied. Corresponding values for a generic IAPSO-based Tris buffer, *j*; for the ERB; and for the CRM buffer are also shown.

Measurements in Harned cells also require knowledge of the standard potential of the Ag|AgCl electrodes in ASW, E° . These E° measurements are performed in solutions that contain a known b_{HCl} added to the same ASW matrix used for the Tris buffers. As with the Tris buffers, $b_{\text{NaCl,ASW}}$ in these solutions is also reduced by the added b_{HCl} (Eq. (6)). The I_{ASW} and b_{Cl^-} for the HCl solutions in ASW are also given by Eqs. (4) and (5) above.

Central to the present work is the accurate preparation of a set of multiple Tris + Tris·HCl buffers in ASW and multiple HCl solutions in the same ASW, all of which conform to the target molalities for the ASW obtained above. To minimize the required effort, the protocol for the synthesis of the solutions should minimize unnecessary duplication of weighings, especially of exact masses of solid compounds.

These goals were met through the development of a protocol based on mutual gravimetric dilution based on amount content. A single concentrated ASW solution (CASW) is diluted with *J* concentrated buffer (CB) solutions to yield *J* Tris buffers and with *K* separate concentrated acid (CA) solutions to yield the *K* solutions of HCl in ASW for the E° measurements. The CASW contains all the minor components of the ASW and most of the NaCl. Each CB_{*j*} contains all the HCl and Tris for buffer *j*, along with the balance of the NaCl needed for that buffer. Each CA_{*k*} contains all the HCl for solution *k* of HCl in ASW, along with the balance of the NaCl needed for that HCl solution. The dilutions are performed such that Eq. (3b) through Eq. (6) are fulfilled for each buffer and HCl solution, i.e., the *J* Tris buffers and the *K* HCl solutions in ASW all have the identical ionic strength given by Eq. (4) and the identical b_{Cl^-} given by Eq. (5). The detailed protocol is described in the supplementary material.

For the present work, three Tris buffers (i.e., *J* = 3) were investigated, with $b_{\text{HCl}} = (0.05, 0.04, \text{ and } 0.03)$ mol/kg. These b_{HCl} values yield buffers with Tris:Tris·HCl molality ratios of 0.03:0.05, 0.04:0.04, and 0.05:0.03, respectively. The buffers are denoted Buffer 1, Buffer 2, and Buffer 3 (corresponding to *j*) in this work. The estimated pH_{T} values at

Table 2
Compositions and approximate total pH (pH_{T}) values of Tris buffers in ASW at 298.15 K.

Buffer	1	2	3	<i>j</i>	CRM	ERB
Component <i>i</i>	Molality $b_i/(\text{mol} \cdot \text{kg}^{-1})^a$					
NaCl	0.377531	0.387531	0.397531	$b_{\text{NaCl,ASW}} - b_{\text{HCl},j}$	0.38762	0.38664
Added Tris	0.08	0.08	0.08	b_0	0.08	0.08
Added HCl	0.05	0.04	0.03	$b_{\text{HCl},j}$	0.04	0.04
Tris (final)	0.03	0.04	0.05	$b_0 - b_{\text{HCl},j}$	0.04	0.04
Tris · HCl (final)	0.05	0.04	0.03	$b_{\text{HCl},j}$	0.04	0.04
Estimated pH_{T}	7.87	8.09	8.32	see Eqs. (8) and (9)	8.0924 ^b	8.09
$w_{\text{H}_2\text{O}}$	0.957004	0.956802	0.956602	Variable	0.956797	0.956810
$-\lg w_{\text{H}_2\text{O}}$	0.01909	0.01918	0.01927	Variable	0.01918	0.01917

^a Molalities of remaining ASW components are the same as those in reference ASW (see Table 1).

^b Certified value of CRM (Dickson, 2011).

25 °C for these three formulations as calculated from Eq. (8) are 7.87, 8.09, and 8.32. The accompanying measurements of E° were performed with four HCl solutions in ASW (i.e., $K = 4$) with target molalities of (0.04, 0.03, 0.02, and 0.01) mol/kg (corresponding to k). The IAPSO-derived reference composition was used for all of these solutions.

The ERB control was synthesized using the protocol for Buffer 2 and a separate ERB CASW prepared at NIST from the EMRP salts. The ERB thus provided an independent verification of the preparation protocol.

2.3. Determination of pH_b in Harned cells

The Tris buffers and controls were each value-assigned using Harned cell measurements, yielding $pH_{b,j}$ for each buffer j and each control buffer. The four HCl solutions in ASW were concurrently measured in Harned cells, yielding E° . Measurements were performed at thermodynamic temperatures, T , in the order: 298.15 K (initial), 288.15 K, 308.15 K, and a second time at 298.15 K (final). Details are given in the supplementary material.

Measurements of each Tris buffer j and the control buffers were performed in Cell I:



Concurrent measurements of the k HCl solutions in ASW were performed in Cell II:



The $pH_{b,j}$ are given (DelValls and Dickson, 1998; Ramette et al., 1977) by Eq. (10):

$$pH_{b,j} = \frac{E_{\text{Cell I},j} - E^{\circ}}{(RT \ln 10/F)} + \lg\left(\frac{b_{\text{Cl}^-}}{b^{\circ}}\right). \quad (10)$$

In Eq. (10), $E_{\text{Cell I},j}$ is the potential of Cell I for buffer j corrected (Clark, 1928; Dickson, 1987; Millero and Leung, 1976) to pressure of $\text{H}_2 = 101.325$ kPa; R and F are the gas and Faraday constants; and b° is the standard molality, 1 mol/kg.

In the present work, the E° determinations were performed concurrently (in the same measurement runs) with the pH_T measurements of the Tris ASW buffers, using the same Harned cells and electrodes. The resulting E° values were directly used in Eq. (10). In contrast, the previous pH_b measurements (DelValls and Dickson, 1998; Dickson, 2011; Nemzer and Dickson, 2005; Ramette et al., 1977) relied (Dickson; personal communication [e-mail] to Pratt; June 13, 2013) on separate E° values (Dickson, 1990; Khoo et al., 1977). In the previous work, values of E° , the standard potential of the Ag, AgCl electrodes in pure water, were measured both at the time of the pH_T and of the E° measurements. These E° were each normalized (Dickson, 1987; Ramette et al., 1977) to reference E° values (Bates and Bower, 1954). The E° measurements thus provided the only link between the previously measured E° values and their subsequent use in the calculation of pH_b . The present approach improves the traceability of E° and hence, of pH_T , at the cost of additional E° measurements.

2.4. Conversion of pH_b to pH_T

The measured values of $pH_{b,j}$ (molality basis) from Eq. (10) above were converted to pH_T (amount content basis) for each buffer using Eq. (9) and the $-\lg w_{\text{H}_2\text{O}}$ values shown for the respective buffers in Table 2.

The $w_{\text{H}_2\text{O}}$ values for the buffers differ slightly from each other and, to a greater extent, from those for the corresponding reference ASW compositions. The ranges of $-\lg w_{\text{H}_2\text{O}}$ among the three IAPSO-based Tris buffers, 0.00018; between the original IAPSO reference seawater (Millero et al.,

2008) ($-\lg w_{\text{H}_2\text{O}} = 0.015547$) and the IAPSO-based ASW, 0.00005; and among the three ASW formulations, 0.000008; are each smaller than the Type A uncertainty of the replication of the pH_b measurement (0.00023 to 0.00098, see supplementary material). However, the difference of 0.00368 ± 0.00009 between the Tris buffers and the IAPSO reference ASW composition is on the order of 0.004, the estimated uncertainty for the CRM measurement (Dickson, 2011). The dominant factor in this difference is the added mass of the Tris, which reduces $w_{\text{H}_2\text{O}}$ in the Tris buffer.

If the pH_b values are taken as true, this variation between $-\lg w_{\text{H}_2\text{O}}$ for the reference ASW and for the Tris buffers in ASW constitutes a significant bias in pH_T . Therefore, the selection of which $w_{\text{H}_2\text{O}}$ value to use in the conversion of pH_b to pH_T is significant. The pH_T is measured in the Tris buffer in ASW, not in the unbuffered ASW. Hence, the respective $w_{\text{H}_2\text{O}}$ for the given Tris buffer would seem to be the better option.

Previous work (Clayton and Byrne, 1993; DelValls and Dickson, 1998; Dickson, 1993b) used $w_{\text{H}_2\text{O}} = 1 - 0.00106$ S, which yields $-\lg w_{\text{H}_2\text{O}} = 0.01642$ at $S = 35$. This value is 0.0009 greater than $-\lg w_{\text{H}_2\text{O}}$ $\lg w_{\text{H}_2\text{O}}$ $w_{\text{H}_2\text{O}} = 0.01550$ calculated for the reference ASW formulation from its stated composition (see Table 1). This difference does not constitute a significant bias in pH_T if the ASW reference is selected for the conversion of pH_b to pH_T . However, if the buffer compositions are used in the conversion calculation, the residual difference of 0.00276 ± 0.00009 from 0.01642 is significant.

3. Results and discussion

3.1. Results

Table 3 summarizes the results of the pH_T measurements of Buffers 1 through 3 and the two control buffers at the three temperatures. Table 3 also presents the pH_b values directly obtained from the Harned cell measurements. It is emphasized that the pH_T values derive from the Harned cell measurements (Eq. (10)), not from the preliminary values obtained in the initial estimates (Eq. (8)).

The pH_T conversions from pH_b to pH_T (Eq. (9)) were performed using the $-\lg w_{\text{H}_2\text{O}}$ values from Table 2 for the respective buffers.

For Buffer 2 and the ERB, Table 3 presents the differences, ΔpH_T or ΔpH_b , referred to the respective CRM result obtained in the present work at the same temperature. The ΔpH_T and ΔpH_b facilitate rapid comparison of the three equimolar buffers. To simplify Table 3, ΔpH_T and ΔpH_b are not shown for the non-equimolar Buffer 1 and Buffer 3.

The results noted in these same columns for the CRM buffer at 298.15 K in **bold italics** are referred to the certified value of the CRM. The ΔpH_T for the CRM at 298.15 K is referred to the certified pH_T of the CRM, 8.0924. The ΔpH_b is referred to 8.07598, the pH_b value calculated by subtracting 0.01642 (see above) from the certified pH_T . This back-calculation yields the value of pH_b that was obtained in the CRM certification.

Table 3 also presents experimental values for $pK'_{a,\text{Tris-H}^+}$, calculated at $b_0 = 0.08$ mol/kg using Eq. (8) solved for $pK'_{a,\text{Tris-H}^+}$ and corrected for hydrolysis [Eq. (16) of (DelValls and Dickson, 1998)]. The ninth column gives $\Delta pK'_{a,\text{Tris-H}^+}$, referred to the $pK'_{a,\text{Tris-H}^+}$ calculated from $pH_T = f(T)$ [Eq. (18) of (DelValls and Dickson, 1998) at $S = 35$]. These pH_T were converted to pH_b ($-\lg w_{\text{H}_2\text{O}} = 0.01642$) and also corrected for hydrolysis.

The right column of Table 3 presents the expanded uncertainty, U , for each pH_T measurement of each buffer, calculated using the ISO GUM (JCGM, 2008). The respective values of U for pH_b and $pK'_{a,\text{Tris-H}^+}$ are substantially the same as those shown. The detailed analysis of uncertainty is given in the supplementary material.

4. Discussion

The values of pH_T and pH_b listed in Table 3 for Buffer 2 and the ERB agree with the measured pH_T and pH_b for the CRM within the expected uncertainty of the measurement at each temperature.

Table 3Results for Total pH on amount content (pH_T) and molality (pH_b) basis; $pK_{a,Tris-H^+}^* = -\lg K_{a,Tris-H^+}^*$, differences from literature values; and expanded uncertainty, U , of pH_T, pH_b and $pK_{a,Tris-H^+}^*$.

T/K	Buffer	b_{Tris}/b_{Tris-H^+}	pH _T	ΔpH_T vs CRM	pH _b	ΔpH_b vs CRM	$pK_{a,Tris-H^+}^*$	$\Delta pK_{a,Tris-H^+}^*$ ^b	U
Initial 298.15 (25 °C) ^c	Buffer 1	0.03:0.05	7.8712		7.8521		8.0740	−0.0032	0.0072
	Buffer 2	0.04:0.04	8.0948	0.0006	8.0756	0.0006	8.0756	−0.0015	0.0071
	CRM	0.04:0.04	8.0941	0.0017	8.0750	−0.0010	8.0750	−0.0022	0.0072
	ERB	0.04:0.04	8.0943	0.0002	8.0752	0.0002	8.0752	−0.0020	0.0071
	Buffer 3	0.05:0.03	8.3158		8.2966		8.0747	−0.0023	0.0071
288.15 (15 °C)	Buffer 1	0.03:0.05	8.1932		8.1741		8.3960	−0.0018	0.0041
	Buffer 2	0.04:0.04	8.4166	0.0009	8.3974	0.0009	8.3974	−0.0003	0.0040
	CRM	0.04:0.04	8.4158	Reference	8.3966	Reference	8.3966	−0.0011	0.0045
	ERB	0.04:0.04	8.4162	0.0004	8.3970	0.0004	8.3970	−0.0007	0.0042
	Buffer 3	0.05:0.03	8.6373		8.6180		8.3962	−0.0014	0.0041
308.15 (35 °C)	Buffer 1	0.03:0.05	7.5675		7.5484		7.7703	−0.0018	0.0023
	Buffer 2	0.04:0.04	7.7906	0.0021	7.7714	0.0021	7.7714	−0.0006	0.0022
	CRM	0.04:0.04	7.7885	Reference	7.7693	Reference	7.7693	−0.0027	0.0056
	ERB	0.04:0.04	7.7907	0.0022	7.7715	0.0022	7.7715	−0.0005	0.0022
	Buffer 3	0.05:0.03	8.0115		7.9922		7.7703	−0.0015	0.0022
Final 298.15 (25 °C) ^b	Buffer 1	0.03:0.05	7.8722		7.8531		8.0749	−0.0022	0.0027
	Buffer 2	0.04:0.04	8.0954	0.0020	8.0762	0.0020	8.0762	−0.0009	0.0024
	CRM	0.04:0.04	8.0934	0.0010	8.0742	−0.0018	8.0742	−0.0029	0.0042
	ERB	0.04:0.04	8.0955	0.0021	8.0763	0.0021	8.0763	−0.0008	0.0024
	Buffer 3	0.05:0.03	8.3162		8.2969		8.0750	−0.0020	0.0026

^a $K_{a,Tris-H^+}^*$ – apparent acid equilibrium constant of Tris·H⁺ at total molality, $b_0 = b_{Tris} + b_{Tris-H^+} = 0.08$ mol/kg.^b Referred to $pK_{a,Tris-H^+}^*$ values reported in DelValls and Dickson (1998).^c Values in **bold italics** are referred to certified pH_T or to the pH_b back-calculated (see text) from the CRM certified value.

The ΔpH_T and ΔpH_b for Buffer 2 agree to better than 0.0001, as do the corresponding values for the ERB. This agreement results because the $-\lg w_{H_2O}$ values used to convert the measured pH_b to pH_T for Buffer 2, the ERB, and the CRM are all within 0.000005.

For the CRM at 298.15 K, the listed ΔpH_T and ΔpH_b values show the effect of $-\lg w_{H_2O}$ on the calculated pH_T. The ΔpH_T value includes the contribution of $-\lg w_{H_2O}$. The ΔpH_b value excludes this effect. The ΔpH_T is larger than ΔpH_b by 0.00276, i.e., the difference in $-\lg w_{H_2O}$ between the value used in the present work (0.01918, Table 2) and 0.01642, the value used (DelValls and Dickson, 1998) to calculate pH_T in the CRM certification.

The values of $pK_{a,Tris-H^+}^*$ from the present work are constant to within the measurement uncertainty at each T , both as a function of the Tris: Tris·HCl molality ratio (i.e., among Buffers 1, 2, and 3) and among the three equimolal buffers from different sources. These $pK_{a,Tris-H^+}^*$ values also agree with values calculated from the published $pH_T = f(T)$ to within the uncertainty of the present pH_T (hence, $pK_{a,Tris-H^+}^*$) measurement for all three Tris:Tris·H⁺ molality ratios investigated. In the absence of literature pH_T data for non-equimolal Tris buffers in ASW, Quantity ($pK_{a,Tris-H^+}^*$) should remain on a single line (split between p and K in the .pdf proof). These $pK_{a,Tris-H^+}^*$ values show that the pH_T values reported in this work for the non-equimolal formulations are consistent with previous results for equimolal Tris buffers. These results thus extend the validity of Eq. (18) of (DelValls and Dickson, 1998) at $S = 35$ to non-equimolal Tris buffers in the T range studied here.

The E^* values in the present work (see Table S-4 in the supplementary material) are on the order of 310 μV lower than those reported in previous work (Campbell et al., 1993; Dickson, 1990). The concurrent measurement of E^* used in the present protocol minimizes the effect from any such difference. Any electrode-specific shift cancels out in the quantity $E_{Cell 1} - E^*$ in Eq. (10), and the pH_b result is unchanged. Similarly, the CCQM key comparisons show pH results of high quality for different participants, even though differences in E^* of more than 300 μV are reported (CCQM, 2006a, 2006b; Pratt, 2009; Spitzer et al., 2011) by the participants.

Negative shifts were noted in the E^* measurements performed before and after the measurements in the ASW matrix. Fig. 2 shows $-\Delta E^*$ as a function of the chronological order of the E^* measurement runs. The error bars (discussed in the Uncertainty section) give the standard deviation of the mean of the post-ASW E^* values. Fig. 2 reveals that

superimposed long-term and short-term effects are present. The long-term shift affects the set of Ag, AgCl electrodes as a whole. The short-term effect (discussed in the Uncertainty section) is associated with equilibration of the individual Ag|AgCl electrodes and decreases in magnitude during the progression of temperatures in the final E^* measurements.

The long-term shift in E^* likely resulted from the Br[−] present in the NIST salts. The ASW composition (Table 1) and the assay data (Table S-8, supplementary material) indicate that 83% of the Br[−] in the ASW arises from the NaCl, 10% from the MgCl₂, 4.2% from KCl, and 2.4% from CaCl₂. Therefore, a given reduction of w_{Br-} in NaCl will decrease w_{Br-} in the ASW to a greater extent than will reduction of w_{Br-} in the other ASW salts. NaCl with low w_{Br-} is available commercially. However, its cost is prohibitive for use in preparing large batches of ASW solutions. Literature methods (Pinching and Bates, 1946) to reduce w_{Br-} in reagent-grade NaCl are also not well suited to purifying the large quantities of NaCl required for large CRM batches of ASW.

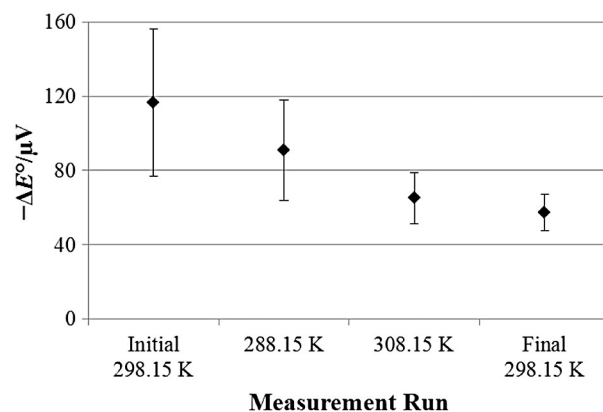


Fig. 2. Measured difference in standard potential, ΔE^* , of Ag, AgCl electrodes after exposure to ASW, referred to E^* before exposure^a. Error bars show standard deviation of the mean of the E^* measurement after exposure to ASW.

4.1. Uncertainty analysis

The expanded uncertainties, U , reported in Table 3 for Buffers 1, 2, and 3 at 288.15 K, 308.15 K, and 298.15 K (final), 0.0022 to 0.0041, are comparable to or lower than the preliminary uncertainty “of the order of 0.004” (Dickson, 2011). The uncertainties for the initial measurements at 298.15 K were larger, 0.0071 to 0.0072. Values at 308.15 K and 298.15 K (final) were smaller than those at 288.15 K.

The larger U values obtained in the initial 298.15 K measurement derive predominantly from the larger deviations of the eight measured E' values from Eq. (12) in the least-squares E^{*o} determination. The corresponding Type A uncertainty at each T is included in the reported U for each buffer at that T . Exposure of the Ag, AgCl electrodes to the ASW solution at $T = 288.15$ K and $T = 308.15$ K significantly reduced this Type A uncertainty of the E^{*o} curve fit. The reduced uncertainty was retained in the subsequent final measurements at 298.15 K.

A parallel decrease is noted in the standard deviation of the mean of the E^o measurements in aqueous 0.01 mol/kg HCl following exposure to ASW (see error bars in Fig. 2). Equilibration was again complete at the 308.15 K measurements. This conclusion is supported by the agreement in the standard deviation of the mean for the set of Ag, AgCl electrodes in the pre- and post-ASW E^o measurements at 308.15 K and 298.15 K (final). The standard deviation of the mean E^o was 14 μ V in both the pre- and post-ASW measurements at 308.15 K. The corresponding values for the final 298.15 K measurements were each 10 μ V.

These results indicate that the pre-measurement equilibration period for the Ag/AgCl electrodes (≈ 16 h at $T \approx 295$ K, see above), which suffices for the low ionic strength International Union of Pure and Applied Chemistry (IUPAC) buffers (Buck et al., 2002), was insufficient to attain the final equilibrium state of the Ag, AgCl electrodes, both on transfer to the high ionic strength ASW matrix and following return to 0.01 mol/kg HCl. In both cases, the electrodes attain their equilibrium potentials at the time of the 308.15 K measurement.

The effect of the ΔE^o (both the long- and the short-term effects) was assessed by including a run-specific Type B (JCGM, 2008) component in the uncertainty of the pH_T measurement (see supplementary material).

Measurements of the low-ionic-strength IUPAC pH buffers in key comparisons (CCQM, 2001, 2003, 2006a, 2006b; Pratt, 2009; Spitzer et al., 2011) at NIST have attained U values for pH [neglecting the uncertainty (Buck et al., 2002) of the Bates–Guggenheim convention (Bates and Guggenheim, 1960)] on the order of 0.001 at $T \leq 298.15$ K and 0.003 at $T > 298.15$ K. The optimal U values for Tris buffers in ASW in the present work are similar to these values.

5. Implications

The present work reports Harned cell measurements of pH_T of non-equi-molal Tris buffers in artificial seawater (ASW) for the first time. The pH_T values for these buffers bracket the values for pH_T of open-ocean seawater, enabling multi-point calibration or verification of secondary spectrophotometric and potentiometric pH_T measurements of natural seawater that presently depend on single-point calibrations. Optimal expanded measurement uncertainties, U , calculated according to the ISO GUM, are reported. These U are on the order of those attained in CCQM pH key comparisons, provided that the Ag, AgCl electrodes have reached equilibrium with the ASW matrix. The best estimates of pH_T and U for each buffer are given in Table 3.

The present work was performed on a pilot batch of buffers and does not represent the pH_T values for a specific batch of CRMs. As with the IUPAC pH buffers, batch-to-batch variations on the order of 0.003 can be expected (Buck et al., 2002). Hence, for a set of CRM buffers, it is recommended to use Harned cell characterization of the pH_T for each component buffer following the protocol described here, rather than relying on recipe preparation. The preparation protocol is readily scaled to large batches and facilitates production of multiple Tris buffers in ASW with a minimum number of exact weighings.

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Appendix A. Supplementary material

Details of the multi-buffer preparation protocol, Harned cell protocols, measured E_{cell} values, uncertainty analysis, and assays of the ASW component salts are in the supplementary material. Supplementary material associated with this article can be found, in the online version, at doi: <http://dx.doi.org/10.1016/j.marchem.2014.03.003>.

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