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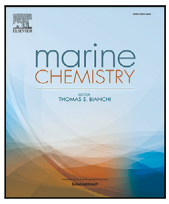

# $pH_T$ measurements of TRIS buffer solutions in artificial seawater matrix in the salinity range 5–40 and temperature range 5–40 °C. Part 2: Uncertainty of $pH_T$ values

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## ABSTRACT

In the first part of this study, we determined a fit function which allows the calculation of the total pH ($pH_T$) value of an artificial seawater/2-amino-2-(hydroxymethyl)-1,3-propanediol (TRIS) buffer, extrapolated to 0 mol $kg^{-1}$ $H_2O$ TRIS molality (i.e. to a true $pH_T$ scale), in terms of temperature and practical salinity. In this second part, we present a method to quantify the uncertainty of that function. The uncertainty plays an important role in the characterization of the indicator dye used for the routine spectrophotometric $pH_T$ measurement in seawater. However, it has not been determined previously. We assigned uncertainties to measured input quantities, and propagated them through the calculation steps described in the first part. Both, analytical uncertainty calculation and Monte Carlo simulations have been applied to adequately consider the various steps of the procedure needed to calculate $pH_T$ values of artificial seawater. The combined standard uncertainty of $pH_T(S, T, b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ for artificial seawater/TRIS buffers was 0.0011 over the practical salinity range 5 to 40 and temperature range 5 °C to 40 °C. This uncertainty can now be used to determine, the uncertainties of the characterization of the indicator dye used for seawater $pH_T$ measurements.

## 1. Introduction

In part 1 of this study (Capitaine et al., 2025), we presented $pH_T$ primary measurements of artificial seawater (ASW)/2-amino-2-(hydroxymethyl)-1,3-propanediol (TRIS) buffers in the nominal practical salinity $S$ range from 5 to 40 and temperature $T$ range from 5 °C to 40 °C. The results were used as a basis to fit a function describing the dependence of $pH_T$ on temperature and salinity in artificial seawater. This function can be used for the characterization of meta-Cresol Purple, an indicator dye for seawater $pH_T$ measurements. With the uncertainties associated with the $pH_T$ reference material used for the characterization, uncertainties can be propagated to the final $pH_T$ measurements of seawater. This topic is of interest because anthropogenic emissions of $CO_2$ decrease the pH value of the ocean (Calvin et al., 2023; Friedlingstein et al., 2023) which needs to be monitored. Reliable measurements with adequately determined measurement uncertainties are essential to accurately assess ocean acidification (Newton et al., 2015).

The Harned cell measurement of $pH_T$ in artificial seawater at different temperatures $T$ and salinities $S$ with a TRIS buffer of molality $b$(TRIS) (see Buck et al., 2002 for detailed information on primary pH measurements), and the determination of the fit function involve a variety of measurements and calculation steps. This makes the determination of appropriate uncertainties a difficult and complex task. In this part 2, we demonstrate and discuss in detail how the uncertainties of the measured $pH_T$ values were quantified and how these uncertainties are considered to assign an uncertainty to the fit function. In the future,

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**Table 1**
Overview of the key packages and package bundles used in R with their version number and respective main use. A full list of package versions is included with the code (doi:10.5281/zenodo.14964817).

| Package | Use | Version | Citation |
|---|---|---|---|
| `MASS` | stepwise model selection by AIC[a] | 7.3.65 | Venables and Ripley (2002) |
| `metafor` | uncertainty of extrapolations | 4.8.0 | Viechtbauer (2010) |
| `metRology` | uncertainties following (BIPM et al., 2008a) | 0.9.29.2 | Ellison (2018) |
| `mltools` | weighted RMSE[b] | 0.3.5 | Gorman (2018) |
| `tidymodels` bundle | leave-one-out cross-validation | 1.3.0 | Kuhn and Wickham (2020) |
| `tidyverse` bundle | data processing | 2.0.0 | Wickham et al. (2019) |

[a] AIC – Akaike Information Criterion.
[b] RMSE – root-mean-squared error.

those uncertainties can be used to determine the uncertainties in the characterization of the indicator dye meta-Cresol Purple (specifically the uncertainty of $pK_2^T e_2$) which is used in seawater $pH_T$ measurements. As far as we are aware, the uncertainty of the fit function was not available previously thus interrupting the uncertainty propagation for spectrophotometric seawater $pH_T$ measurements. As such the uncertainty value presented in this work, constitutes an important step on the way to establishing full metrological traceability for those measurements.

The complete model to determine the fit function from the measured input quantities involved a variety of steps. While the uncertainties of some of the intermediate results were better calculated by uncertainty propagation according to the "Guide of the expression of uncertainty in measurement" (GUM) (BIPM et al., 2008a), the use of a Monte Carlo approach (BIPM et al., 2008b) was more suitable for others, i.e., the involved fitting procedures. The main challenges to address were: (i) the determination of reasonable uncertainties of extrapolated values; and (ii) the determination of the uncertainty of a $pH_T$ value at a specific temperature and salinity calculated from the fit function. To tackle these challenges, we have employed a step-wise approach in which we calculated the uncertainties of each step individually by different methods. This approach combined analytical and numerical methods from the GUM and its supplements.

## 2. Uncertainty of primary $pH_T(S, T, b(\text{TRIS}))$ values of ASW/TRIS buffers

The measurement model used to determine the fit function $pH_T(S, T, b(\text{TRIS}))$ has been detailed in part 1 (Capitaine et al., 2025). From that model, the $pH_T(S, T, b(\text{TRIS}) = 0\,\text{mol}\,\text{kg}^{-1}\,H_2O)$ value of a given artificial seawater standard at nominal practical salinity $S$ and temperature $T$, referred to a TRIS molality of $0\,\text{mol}\,\text{kg}^{-1}\,H_2O$, was calculated. In summary, the model involved the following fundamental steps:

1. calculation of water mass fraction, $\omega_{H_2O}$, of the buffer and equimolal TRIS and TRIS hydrochloride (TRIS.HCl) molality, $b(\text{TRIS})$, in water,
2. determination of the standard potential, $E^{0*}$, of the silver-silver chloride electrodes in artificial seawater media,
3. calculation of the ASW/TRIS buffer $pH_T(S, T, b(\text{TRIS}))$ value and
4. fitting of the function.

Each step required a specific approach to determine the associated uncertainties which are needed to propagate the uncertainties of the measured input quantities to the combined uncertainty of $pH_T(S, T)$. In the following section, the uncertainty calculation and data processing are described and discussed for each step to determine the primary $pH_T(S, T, b(\text{TRIS}))$ value of the ASW/TRIS buffer. The next section describes the uncertainty determination for the last step, the fitting of the function.

Calculations were done in R version 4.3.2 (R Core Team, 2023). Table 1 lists key packages with their versions. The data and code can be found in doi:10.5281/zenodo.14964822 and doi:10.5281/zenodo.14964817, respectively. Additionally, a custom R package was developed to combine many of the main functions needed. It is available as part of the code.

### 2.1. Uncertainties of ASW/TRIS buffer preparation

Stock solutions for ASW/TRIS buffer and HCl solutions were prepared gravimetrically at the Physikalisch-Technische Bundesanstalt (PTB, Germany). The purities of all salts were measured by coulometric titration at the Slovak Institute of Metrology (purities are shown in Table 2). The HCl solutions were characterized with coulometry at the Danish National Metrology Institute (under DANAK accreditation reg. No. 255). The ASW/TRIS buffer solutions were prepared at PTB, while the ASW/HCl solutions needed to determine the standard potential of the silver-silver chloride electrodes in artificial seawater, $E^{0*}$, were prepared from the stock solutions by Instituto Português da Qualidade (IPQ, Portugal), Laboratoire National de Métrologie et d'Essais (LNE, France) and PTB individually. The measured masses were corrected for air buoyancy (for details see Supplementary Material 1). The water mass fraction, $\omega_{H_2O}$, was calculated from the nominal practical salinity, $S$, as defined in part 1 section 2.3 (Capitaine et al., 2025) with

$$\omega_{H_2O} = 1 - 0.0010047 \cdot S \quad (1)$$

(Clegg et al., 2022). This was used to convert from the molality-based to the amount-content-based $pH_T$ scale based on the reference composition of seawater and its practical salinity. The factor with the value of 0.0010047 was established by Clegg et al. (2022) (as opposed to 0.00106 used by DelValls and Dickson (1998)). The uncertainty of the nominal practical salinity was calculated as the combined uncertainty of the mass measurements needed for the preparation of stock solutions and subsequent preparation of ASW/TRIS buffers, as well as the difference between the measured mass and the target mass of the artificial seawater recipe (for details see Supplementary Material 2). The uncertainties of the TRIS molality were determined from the uncertainties of the measured masses and their impurities. Propagation of uncertainties was performed within the GUM (BIPM et al., 2008a) framework, using the `metRology` package (Ellison, 2018) with the uncertainties of the molar masses assumed to be $0\,\text{kg}\,\text{mol}^{-1}$ (Meija et al., 2016).

Table 3 shows an example uncertainty budget for a nominal practical salinity of 35. The main uncertainty contributors were the molalities of NaCl and $MgCl_2$. A visual summary of the uncertainty calculation and the relative contribute of the different components is given in Supplementary Material 3.

### 2.2. Uncertainties of potential and temperature measurements

At IPQ, the potential difference between the electrodes was measured using a Keithley 2700 digital multimeter (Keithley Instruments, Solon, United States) and recorded with XLinx software. Measurements were recorded every minute. $pH_T$ calculations were based on the mean

**Table 2**
Characterization of salts and solutions by the Slovak Institute of Metrology and the Danish National Metrology Institute.

(a) Purity characterizations of salts and solutions with their absolute standard uncertainty.

| Substance | Purity / % | Standard uncertainty / % |
|---|---|---|
| KCl | 99.880 | 0.018 |
| NaCl | 99.842 | 0.018 |
| $Na_2SO_4$ | 99.999 | 0.0135 |
| TRIS | 99.925 | 0.027 |

(b) Amount contents of solutions.

| Substance | Amount content / mol $kg^{-1}$ | Standard uncertainty / mol $kg^{-1}$ |
|---|---|---|
| $CaCl_2$ | 0.51586 | 0.00009 |
| HCl | 0.106494 | 0.000019 |
| | 0.106470 | 0.000019 |
| $MgCl_2$ | 1.42292 | 0.00029 |

Two different batches of HCl were used.

**Table 3**
Example uncertainty budget for an ASW/TRIS buffer of nominal practical salinity 35 and $b$(TRIS) = 0.025 mol $kg^{-1}$ $H_2O$, made from stock solutions (PTB). The uncertainty of the molality already includes both the weighing uncertainty and the component from the difference to target weight. The last column shows the individual uncertainty contributions to the combined standard uncertainty of the nominal practical salinity (in the last row). A visual summary of the uncertainties is given in Supplementary Material 3. For the equation to calculate the salinity, see Supplementary Material 2. The shown numbers were rounded for presentation. For precise numbers, please see the original calculations provided in doi:10.5281/zenodo.14964817.

| Substance | Molality / mol $kg^{-1}$ $H_2O$ | Standard uncertainty / mol $kg^{-1}$ $H_2O$ | Sensitivity coefficient / kg $H_2O$ $mol^{-1}$ | Uncertainty contribution |
|---|---|---|---|---|
| NaCl | 0.40253 | $2.2 \cdot 10^{-4}$ | 46.74431 | 0.010086 |
| $MgCl_2$ | 0.054736 | $3.0 \cdot 10^{-5}$ | 140.2329 | 0.004182 |
| $Na_2SO_4$ | 0.029262 | $1.5 \cdot 10^{-5}$ | 140.23294 | 0.0021464 |
| HCl | 0.025097 | $4.2 \cdot 10^{-5}$ | 46.74431 | 0.0019647 |
| $CaCl_2$ | 0.010501 | $5.7 \cdot 10^{-6}$ | 140.23294 | 0.0008060 |
| KCl | 0.0105793 | $5.8 \cdot 10^{-6}$ | 46.74431 | 0.0002701 |
| combined standard uncertainty for the nominal practical salinity | | | | 0.011 |

potential data collected over one hour, after reaching a stable potential (standard deviation below $5 \cdot 10^{-5}$ V).

The potential difference between the electrodes at LNE was measured using an Agilent 34972 A data acquisition system (Agilent, Santa Clara, United States) and recorded with Agilent Benchlink Data Logger software (Agilent, Santa Clara, United States). Measurement results were recorded every 2 min. $pH_T$ calculations were made from the mean of potential data acquired over one hour with a stable potential signal (i.e., standard deviation below $2 \cdot 10^{-5}$ V).

At PTB, the potential was measured with a digital multimeter (3458 A, Agilent, Santa Clara, United States). The system was stabilized for 45 min. The potential was recorded every five minutes and averaged over 50 min once a stable potential (standard deviation below $5 \cdot 10^{-5}$ V over 11 measurements) was reached.

Potentials were measured with a mean standard uncertainty of $5.4 \cdot 10^{-6}$ V (IPQ), $6.1 \cdot 10^{-6}$ V (LNE) and $2 \cdot 10^{-5}$ V (PTB) after the correction to a hydrogen pressure of 1 atm. The main uncertainty components were the uncertainty of the electrode potentials, the uncertainty of the multimeter and the repeatability of the measurement.

At IPQ, Harned cell measurements were performed at 20 °C, 25 °C, and 30 °C. The cells were placed in a Lauda Proline PV36 thermostatic bath with the temperature measured by three Pt100 probes.

Harned cell measurements at LNE were conducted at 15 °C, 25 °C, and 30 °C. Cells were placed in a TAMSON thermostatic bath with five Pt100 probes to measure temperature. Measurement results were recorded every 2 min. The temperature was averaged within each condition across the time the potential was measured and then averaged across the five temperature probes.

At PTB, temperature was measured with four PT100 temperature probes connected to a F250 MKII thermometer (Automatic Systems Laboratories (ASL), Sevenoaks, United Kingdom) evenly distributed inside the temperature bath. The temperature result was averaged within each condition across the time the potential was measured and then averaged across the four temperature probes. Calibration uncertainty and stability of the temperature measurement (standard deviation) had similar values of 0.0017 K and 0.0014 K. Their combined contribution was about one order of magnitude smaller (mean of 0.000692 K) than the value of the temperature inhomogeneity within the bath (mean of 0.00776 K).

Temperatures were measured with a mean standard uncertainty of 0.021 °C (IPQ), 0.011 °C (LNE) or 0.0045 °C (PTB).

As mentioned in part 1, the $pH_T$ values at a nominal practical salinity 20 were excluded from the analysis. As can bee seen in figure 2 in part 1 especially for a TRIS molality of 0.025 mol $kg^{-1}$ $H_2O$, they were lower compared to the values of the adjacent salinities. As a consequence, the residuals from the fit are likewise unusually large at nominal practical salinity 20. The deviation has been measured by PTB and LNE. Therefore, a defect of the measurement system can be excluded. However, a similar anomaly was not seen in the works of DelValls and Dickson (1998) and Müller et al. (2018). Therefore, and because PTB and LNE have measured samples from the same batch, it is much more likely that an unnoticed error occurred during the preparation of salinity 20 solutions than that an unusual physicochemical effect caused the observed anomaly, for which there is no explanation. Therefore, we decided to exclude the values at nominal practical salinity 20. We have conducted repeated fits in which we

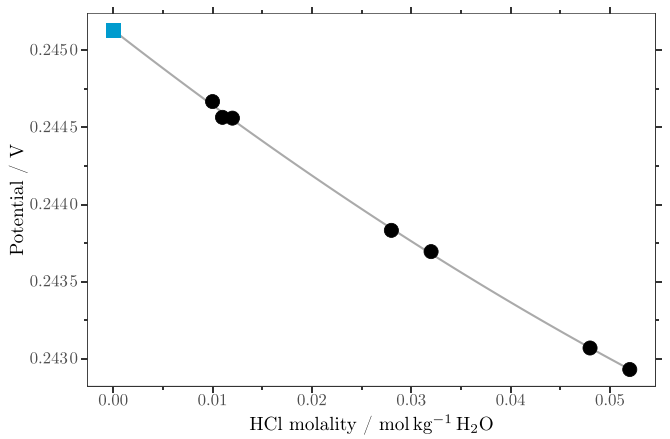


**Fig. 1.** Example extrapolation of measured potentials ($E'$, black points) to determine an extrapolated value for $b$(HCl) equal to zero ($E^{0*}$, blue square) at 25 °C, nominal practical salinity 25 from measurements carried out at PTB. The thin black line shows the quadratic fit used to determine the extrapolated value.

have removed the data at a single condition to investigate the effect on the fit function. They showed that the fit was robust against removal, especially for salinities in the middle of the salinity range.

### 2.3. Uncertainties of the standard potential $E^{0*}$

$E^{0*}$ values (see equations (7) and (8) in part 1) have been determined for each salinity and temperature condition from the potential measurements of the corresponding ASW/HCl solutions. They were calculated from a quadratic extrapolation of the measured potentials to 0 mol kg$^{-1}$ H$_2$O HCl molality as in Dickson (1990) (see Fig. 1 as an example). The extrapolation and uncertainty of this extrapolated value were determined with the `metafor::rma` function (Viechtbauer, 2010). We chose this method because we wished to propagate the uncertainties of the potential to the extrapolated value. The `metafor::rma` function uses the covariance matrix the uncertainties of the input potentials to include them in the determination of the uncertainty at 0 mol kg$^{-1}$ H$_2$O. The distribution of HCl molalities was chosen to minimize the expected uncertainty of the extrapolated value.

The uncertainties of $E^{0*}$ and residuals of the fit did not vary significantly across measurement conditions. The average uncertainty was $2.9 \cdot 10^{-5}$ V, and the root-mean-squared error (RMSE) of all residuals was $3.4 \cdot 10^{-5}$ V. For the measurements at PTB, the RMSE of the residuals of the fit was always smaller compared to the uncertainty determined for $E^{0*}$. For the measurements at LNE and IPQ, the residuals were generally higher compared to the uncertainty, and also compared to the residuals of the PTB data (absolute residual up to $2.3 \cdot 10^{-4}$ V compared to the maximum of $5.7 \cdot 10^{-5}$ V in PTB measurements).

### 2.4. Uncertainties of measured $pH_T(S, T, b(TRIS))$ values

Uncertainties of the measured $\mathrm{pH_T}(S, T, b(\mathrm{TRIS}))$ values at nominal practical salinity $S$, temperature $T$ and TRIS molality $b$(TRIS) were calculated according to the GUM framework (BIPM et al., 2008a) by propagating the uncertainties of the above-mentioned input quantities through

$$\mathrm{pH_T} = \frac{E - E^{0*}}{(R \cdot T \cdot \ln(10)) \cdot F^{-1}} + \log\left(\frac{b(\mathrm{Cl^-})}{b_0}\right) - \log(\omega_{\mathrm{H_2O}}). \quad (2)$$

$E$ is the measured potential of the ASW/TRIS buffer corrected to 1 atm $H_2$ pressure, $R$ is the molar gas constant, $T$ is temperature in kelvin, $F$ is the Faraday constant, $b(\mathrm{Cl^-})$ is the molality of $Cl^-$ ions, $b_0$ is the standard molality ($b_0$ = 1 mol kg$^{-1}$ H$_2$O and $\omega_{\mathrm{H_2O}}$ is the water mass fraction (Clegg et al., 2022, equation 1). The `metRology` package (Ellison, 2018) was used for the uncertainty propagation.

Table 4 shows an exemplary uncertainty budget of a $\mathrm{pH_T}(S, T, b(\mathrm{TRIS}))$ value. The uncertainty components with the highest contribution were those of $E$ and $E^{0*}$, followed by temperature, molality of $Cl^-$ and $\omega_{\mathrm{H_2O}}$. A visual summary of the uncertainty calculation is given in Fig. 2 and the relative contribution of the different components is shown in Supplementary Material 3.

The uncertainty contribution of $E$ to $\mathrm{pH_T}$ was almost constant across the temperature and salinity range with only a slight decrease at higher temperatures. The uncertainty contribution of $E^{0*}$ showed little variation but had some outliers with higher uncertainties at nominal practical salinity 5 and 30 and lower uncertainties at nominal practical salinity 35. The uncertainty contribution of the molality of $Cl^-$ increased for all temperatures with increasing salinity from around $4.8 \cdot 10^{-5}$ mol kg$^{-1}$ H$_2$O to $5.7 \cdot 10^{-5}$ mol kg$^{-1}$ H$_2$O. The uncertainty contribution of the temperature increased slightly with increasing temperature and decreasing salinity. And the uncertainty contribution of $\omega_{\mathrm{H_2O}}$ was constant across temperatures but decreased with increasing salinity. The combined uncertainty of $\mathrm{pH_T}(S, T, b(\mathrm{TRIS}))$ values was stable across all conditions with a few outliers resulting from variations in the uncertainties of $E^{0*}$.

### 2.5. Uncertainties of consensus $pH_T(S, T, b(TRIS))$ values

If measured $\mathrm{pH_T}(S, T, b(\mathrm{TRIS}))$ values were provided by more than one institute for a combination of (nominal) salinity, temperature and TRIS molality, we calculated the weighted mean of the $\mathrm{pH_T}(S, T, b(\mathrm{TRIS}))$ results and their uncertainties using the Graybill-Deal estimator with dispersion (CCQM, 2013). We chose the uncertainty-weighted mean to account for different uncertainties of the individual measurements and included dispersion correction to include interlaboratory differences. This step was not necessary and therefore skipped if the condition was measured by only one institute.

Fig. 3 illustrates the distribution of the standard uncertainties of the $\mathrm{pH_T}(S, T, b(\mathrm{TRIS}))$ measurement results as a function of temperature and salinity. The uncertainty of $\mathrm{pH_T}(S, T, b(\mathrm{TRIS}))$ for conditions where measurements were taken at more than one institution was between $1.2 \cdot 10^{-5}$ and $2 \cdot 10^{-3}$ in $\mathrm{pH_T}$ units. If only measurements from PTB were available, the uncertainties were between $2.8 \cdot 10^{-4}$ and $1.6 \cdot 10^{-3}$ in $\mathrm{pH_T}$ units.

As uncertainties of the $\mathrm{pH_T}$ values for TRIS buffer solutions have not been routinely determined previously, limited literature is available for comparison. The uncertainties for the measurements by Müller et al. (2018) were mostly in the range between $1 \cdot 10^{-3}$ to $2.1 \cdot 10^{-3}$ in $\mathrm{pH_T}$ units. Our maximum uncertainties had similar values. However, our minimum uncertainties were lower. This was caused by the combination of measurements from different institutes and, in the case of PTB, lower uncertainties of the determined $E^{0*}$.

In the data by Müller et al. (2018), a tendency for higher uncertainties at higher temperatures and lower salinities can be observed. We did not observe this trend. This is likely due to improved temperature stability of the measurement set-up and the correction of the ASW/TRIS buffer composition.

## 3. Uncertainty of the fitted equation $\mathrm{pH_{T,c}}(S, T, b(\mathrm{TRIS}) = 0$ mol kg$^{-1}$ H$_2$O)

### 3.1. Fitting procedure

We used the equation proposed by Müller et al. (2018) to calculate a fit function describing the dependence of $\mathrm{pH_T}$ on salinity, temperature and TRIS molality. However, since we have omitted the $\mathrm{pH_T}(S, T, b(\mathrm{TRIS}))$ results at TRIS molality $b(\mathrm{TRIS}) = 0.01$ mol kg$^{-1}$ H$_2$O

**Table 4**
Example uncertainty budget for nominal practical salinity 35, temperature 25 °C and TRIS molality 0.025 mol kg$^{-1}$ $H_2O$ at PTB, before averaging. The last column shows the uncertainty contribution of the individual components to the combined uncertainty. A visual summary of the uncertainties is given in Fig. 2 with the relative contributions of each visualized in Supplementary Material 3. The shown numbers were rounded for presentation. For precise numbers, please see the original calculations provided in doi:10.5281/zenodo.14964817.

| Component | Value | Standard uncertainty | Sensitivity coefficient | \|Uncertainty contribution\| |
|---|---|---|---|---|
| $E$ | 0.738154 V | $2.0 \cdot 10^{-5}$ V | 16.902875 V$^{-1}$ | $3.38 \cdot 10^{-4}$ |
| $E^{0*}$ | 0.245972 V | $2.0 \cdot 10^{-5}$ V | −16.902875 V$^{-1}$ | $3.377 \cdot 10^{-4}$ |
| $T$ | 298.16 K (25.01 °C) | $4.7 \cdot 10^{-3}$ K | −0.0279 K$^{-1}$ | $1 \cdot 10^{-4}$ |
| $b(Cl^-)$ | 0.569177 mol kg$^{-1}$ $H_2O$ | $7.7 \cdot 10^{-5}$ mol kg$^{-1}$ $H_2O$ | 0.763022 kg $H_2O$ mol$^{-1}$ | $5.83 \cdot 10^{-5}$ |
| $\omega_{H_2O}$ | 0.964836 g/kg sol | $1.1 \cdot 10^{-5}$ g/kg sol | −0.4501228 kg sol g$^{-1}$ | $5.12 \cdot 10^{-6}$ |
| combined standard uncertainty of the $pH_T$ value | | | | $4.993 \cdot 10^{-4}$ |

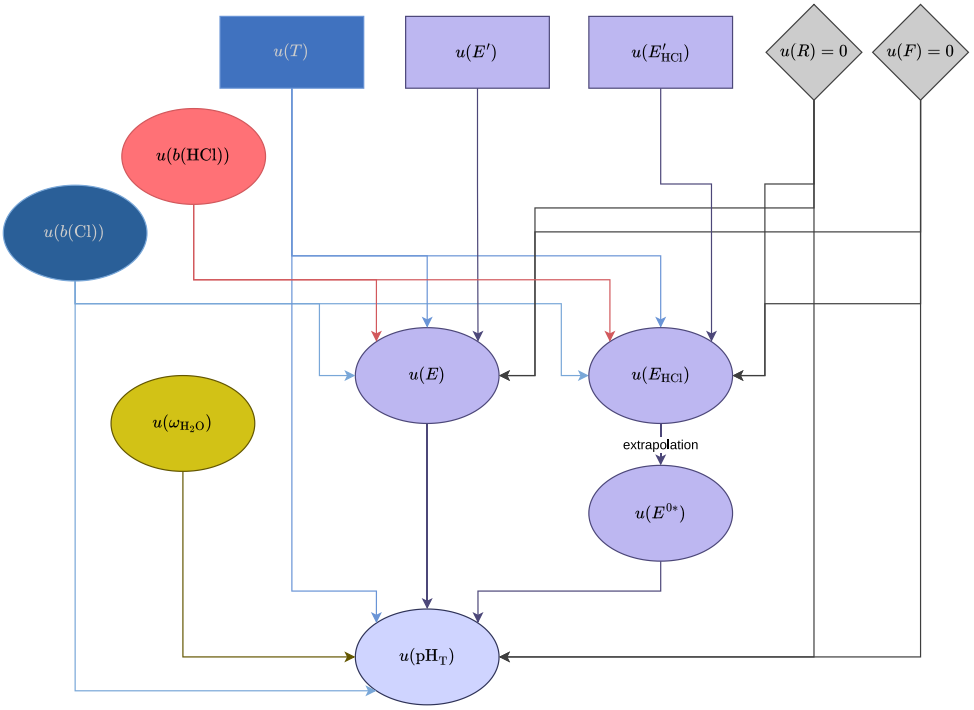


**Fig. 2.** Contributions to the uncertainty of a single $pH_T$ value. Gray boxes indicate constants. The blue and green reference the corresponding contributions in Supplementary Material 3. The lighter the blue/purple, the larger the contribution.

and expected a linear relationship across TRIS molalities, we have considered only the linear term of TRIS molality in the equation:

$$\begin{aligned} pH_{T,c}(S,T,b(\text{TRIS})) = {} & g + h_1 \cdot S + h_2 \cdot S^2 + h_3 \cdot S^3 + i_1 \cdot T_d + i_2 \cdot \ln(T_d) \\ & + i_3 \cdot \frac{1}{T_d} + j_1 \cdot S \cdot T_d + j_2 \cdot S^2 \cdot T_d + j_3 \cdot S^3 \cdot T_d \\ & + j_4 \cdot S \cdot \ln(T_d) + j_5 \cdot S^2 \cdot \ln(T_d) + j_6 \cdot S^3 \cdot \ln(T_d) \\ & + k_1 \cdot S \cdot \frac{1}{T_d} + k_2 \cdot S^2 \cdot \frac{1}{T_d} + k_3 \cdot S^3 \cdot \frac{1}{T_d} \\ & + l_1 \cdot b_d(\text{TRIS}) + l_2 \cdot b_d(\text{TRIS}) \cdot S \\ & + l_3 \cdot b_d(\text{TRIS}) \cdot T_d + l_4 \cdot b_d(\text{TRIS}) \cdot S \cdot T_d, \end{aligned} \tag{3}$$

where temperature and TRIS molality are of dimension one, given as

$$T_d = \frac{T}{T_0} \tag{4}$$

and

$$b_d(\text{TRIS}) = \frac{b(\text{TRIS})}{b_0} \tag{5}$$

and with nominal practical salinity $S$, temperature $T$ in kelvin, standard temperature $T_0 = 1$ K, TRIS molality $b$(TRIS) in mol kg$^{-1}$ $H_2O$ and standard molality $b_0 = 1$ mol kg$^{-1}$ $H_2O$. We have fitted the equation to the dataset with TRIS molalities of 0.025 and 0.04 mol kg$^{-1}$ $H_2O$. The $pH_{T,c}(S,T,b(\text{TRIS}))$ value of artificial seawater at 0 mol kg$^{-1}$ $H_2O$ TRIS molality was then calculated by inserting $b$(TRIS) = 0 mol kg$^{-1}$ $H_2O$.

We used a generalized linear model with the `glm` function (R Core Team, 2023) to fit the data and weighted them with the uncertainty of the $pH_T(S,T,b(\text{TRIS}))$ values: $\frac{1}{u(pH_T)^2}$. The `stepAIC` function was used to perform a stepwise model selection based on the Akaike Information Criterion (AIC) (Venables and Ripley, 2002). The numbers of relevant digits of the coefficients were determined by checking with how many digits the calculated $pH_{T,c}(S,T,b(\text{TRIS}))$ value of the function stabilized compared to the standard uncertainty.

### 3.2. Uncertainty determination

The uncertainty of $pH_{T,c}(S,T,b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ was determined from the weighted RMSE of the fit ($u_{RMSE}$) and from the variation of the $pH_{T,c}(S,T,b(\text{TRIS}))$ values at 0 mol kg$^{-1}$ $H_2O$ TRIS molality in three Monte Carlo simulations ($u_{MC}$). This combination allowed us to consider the goodness of fit and the robustness of the extrapolation with respect to uncertainty.

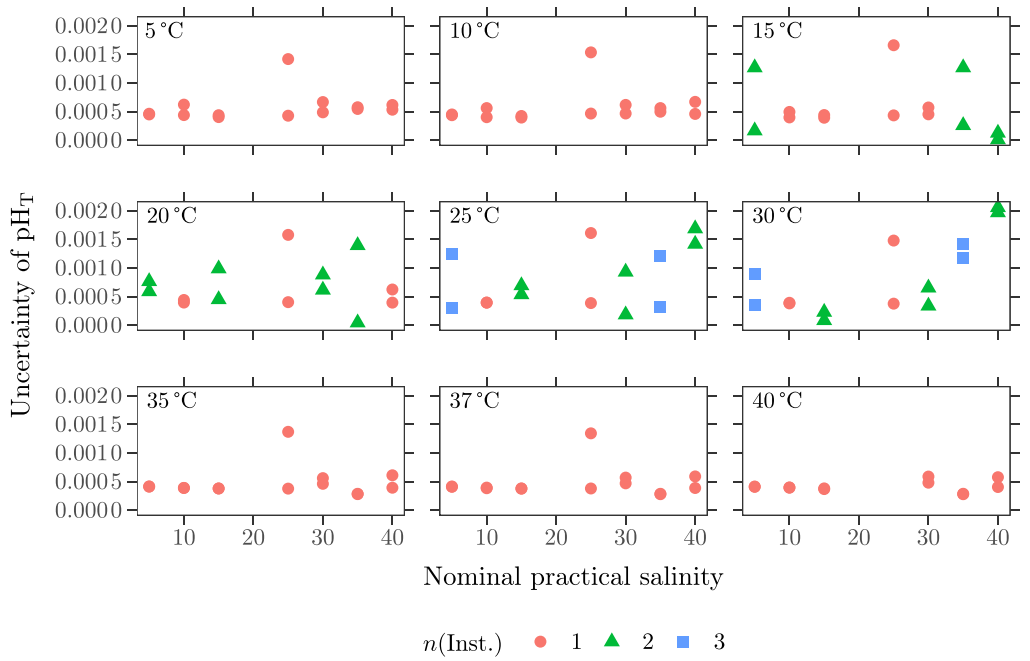


**Fig. 3.** Standard uncertainties of the $pH_T(S,T,b(\text{TRIS}))$ values calculated from the measurements of the individual institutes. The differently colored shapes indicate how many institutes ($n$(Inst.)) measured under the specific condition. The two TRIS molalities did overall not differ in their uncertainties significantly and are not distinguished here, therefore, there are two points for each salinity-temperature combination (though sometimes so similar in value that they are indistinguishable). Each plot shows the data for the temperature indicated at the top.

The weighted RMSE of the fit was calculated with the `mltools::rmse` function (Gorman, 2018). The weights were the same as for the fit: $\frac{1}{u(pH_T)^2}$. The weighing of the RMSE with uncertainties meant that values with a higher uncertainty contributed less to the RMSE. This was chosen to adequately account for the different levels of confidence in the values as indicated by the uncertainties.

In each Monte Carlo simulation run, a new dataset was generated by random draws from the measurement value distributions of $pH_T$, temperature, salinity and TRIS molality data. The starting points of the simulations were $pH_T$ data at 0.025 mol $kg^{-1}$ $H_2O$ and 0.04 mol $kg^{-1}$ $H_2O$ TRIS molality, with their respective temperature, salinity and TRIS molality data. We assumed normal distributions for all input data. Since the main contribution to uncertainties of the $pH_T(S,T,b(\text{TRIS}))$ values are the statistical variation of the potential measurements and the interlaboratory reproducibility, correlation of the input data have not been considered in the determination of the uncertainty of the fit.

We used the function coefficients from the stepwise selected model of the original fit in the Monte Carlo simulation. It was fitted in each run to the generated dataset. Using the fit function of a single run, the $pH_{T,c}(S,T,b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ values for all nominal temperatures and salinities were calculated and saved. For each combination of temperature and salinity, the standard deviation of the $pH_{T,c}(S,T,b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ values was finally calculated across all runs. A Monte Carlo simulation involved 30,000 runs, which was sufficient to let the standard deviations of the three independent simulations converge. The uncertainty component $u_{MC}$ for the variation of $pH_{T,c}(S,T,b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ was calculated as the average standard deviation from three independent Monte Carlo simulations.

The combined uncertainty $u_c$ was then calculated as

$$u_c = \sqrt{u_{RMSE}^2 + u_{MC}^2}. \tag{6}$$

$u_c$ estimates the uncertainty of the $pH_{T,c}(S,T,b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ value of an artificial seawater standard at a given salinity and temperature.

### 3.3. Uncertainty of $pH_{T,c}(S,T,b(TRIS) = 0\,mol\,kg^{-1}\,H_2O)$

We have presented the fit function describing $pH_T$ depending on salinity and temperature in part 1 (Capitaine et al., 2025). Fig. 4 visualizes the fit function with the uncertainty. The two uncertainty contributions had values in the same order of magnitude: 0.000 42 from the RMSE of the fit ($u_{RMSE}$) and 0.000 99 from the variation of the extrapolated values in the Monte Carlo simulation ($u_{MC}$; the variations for other molalities up to 0.04 mol $kg^{-1}$ $H_2O$ were smaller than this value for 0 mol $kg^{-1}$ $H_2O$). $u_{RMSE}$ is smaller than the goodness-of-fit value reported by DelValls and Dickson (1998) which was 0.000 71. As the RMSE is calculated across the whole salinity, temperature and TRIS molality range and the extrapolated values did not show a relevant pattern across all conditions either, we have decided to use a single uncertainty estimate for $pH_{T,c}(S,T,b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ for all temperature and salinity conditions. Thus, the combined standard uncertainty of the $pH_{T,c}(S,T,b(\text{TRIS}))$ value at 0 mol $kg^{-1}$ $H_2O$ TRIS molality ($u_c$) is 0.001 1 in $pH_T$ units.

To assess the quality of the fit function, we have applied a leave-one-out cross-validation, which showed less variation (maximum: 0.000 11) than the uncertainty we have assigned to $pH_{T,c}(S,T,b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ (Fig. 5). This demonstrates the stability of the fit. It further justifies that leaving out the results at salinity 20 for the reason mentioned in part 1 (see section 2.6.1) has little effect on the reliability of the fit function.

In this work, we have decided to fit a function through the measured $pH_T(S,T,b(\text{TRIS}))$ values and calculate $pH_{T,c}(S,T,b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ at zero TRIS molality. Alternatively, it would have been possible to extrapolate $pH_T(S,T,b(\text{TRIS}))$ for each temperature-salinity combination to 0 mol $kg^{-1}$ $H_2O$ TRIS molality first, and use the extrapolated results to calculate the $pH_T$ at 0 mol $kg^{-1}$ $H_2O$ TRIS molality as a function of salinity and temperature. The weighted RMSE was 0.001 4. However, even though that function did represent the extrapolated values well the dependence on salinity and temperature seen at 0.025 mol $kg^{-1}$ $H_2O$ and 0.04 mol $kg^{-1}$ $H_2O$ TRIS molality was not well reflected. This was due to variations in the measurement data that were amplified in the extrapolation to 0 mol $kg^{-1}$ $H_2O$

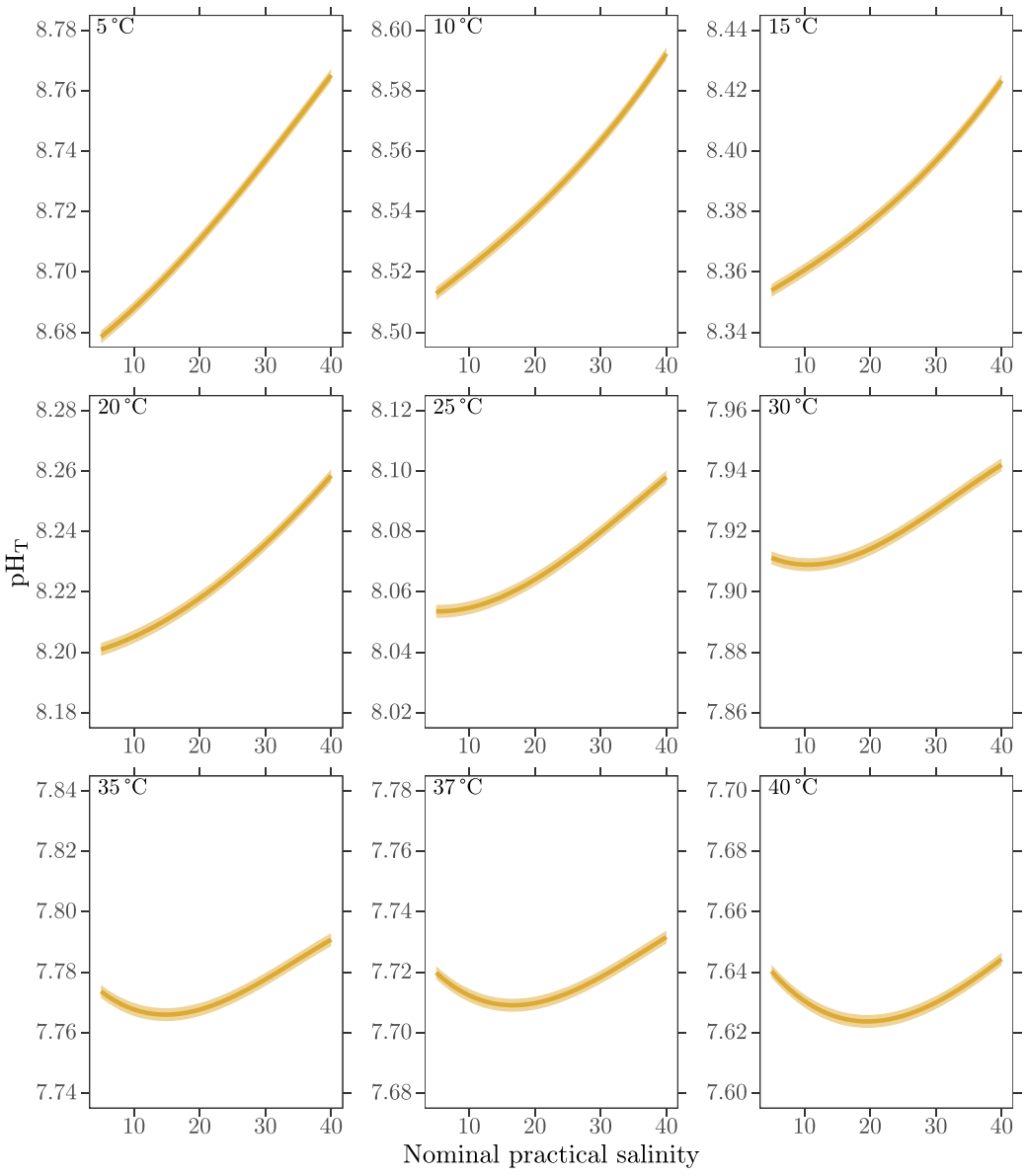


**Fig. 4.** Fit function at 0 mol kg$^{-1}$ $H_2O$ TRIS molality with uncertainty. The lines show the fit function at 0 mol kg$^{-1}$ $H_2O$ TRIS molality, the shaded area is the expanded uncertainty ($k = 2$). Each plot shows the data for the temperature indicated at the top. Note that the y-axis ranges are different between the individual plots.

TRIS molality. Locally extrapolated values amplified the effect of the measurement variation on the extrapolation, while global extrapolation smoothed local variations. For example, in some cases the $pH_T(S, T, b(\text{TRIS}))$ value for 0.04 mol kg$^{-1}$ $H_2O$ TRIS molality was lower than for 0.025 mol kg$^{-1}$ $H_2O$, which does not comply with the expectation that it should be the other way round (Clegg et al., 2022). As a consequence, the fit function was distorted to some extent. In contrast, the fit presented in this work smoothed such irregularities and did not affect the dependence on salinity and temperature seen at 0.025 mol kg$^{-1}$ $H_2O$ and 0.04 mol kg$^{-1}$ $H_2O$ TRIS molality significantly.

## 4. Role of ASW/TRIS buffer standards for the characterization of the indicator dye meta-Cresol Purple and its uncertainty

We have described the uncertainty of the $pH_T$ value of ASW/TRIS buffers, having a nominal practical salinity between 5 and 40, a temperature between 5 °C and 40 °C and for $b(\text{TRIS}) = 0$ mol kg$^{-1}$ $H_2O$. Currently, such ASW/TRIS buffers are used to characterize the $pK_2^T e_2$ value of the indicator dye meta-Cresol Purple (Liu et al., 2011; Müller and Rehder, 2018). This characterization is essential for conducting spectrophotometric $pH_T$ measurements. Traceability of spectrophotometric $pH_T$ measurement is basically given through published $pK_2^T e_2$ values of meta-Cresol Purple, or rather through a function of $pK_2^T e_2$ depending salinity and temperature. The uncertainties described here can henceforth be used to also assign uncertainties to the $pK_2^T e_2$ values of the indicator dye, which was not possible before because the uncertainty of the $pH_T(S, T, b(\text{TRIS}) = 0$ mol kg$^{-1}$ $H_2O)$ was not known. This is needed to establish, by propagation, a complete uncertainty budget of the spectrophotometric measurement of $pH_T$ for a seawater sample.

Due to the time-consuming experimental process, $pK_2^T e_2$ values are currently not determined for each new batch of meta-Cresol Purple, instead, published values are used for each batch, independently from the actual provider. Therefore, uncertainties in the replicability, mainly because of varying unknown impurities, increase the uncertainty of the assigned $pK_2^T e_2$ values and, consequently, of subsequent $pH_T$ measurements to an unknown extent. Ideally, each new batch of meta-Cresol Purple should be calibrated by measuring the $pH_T$ of

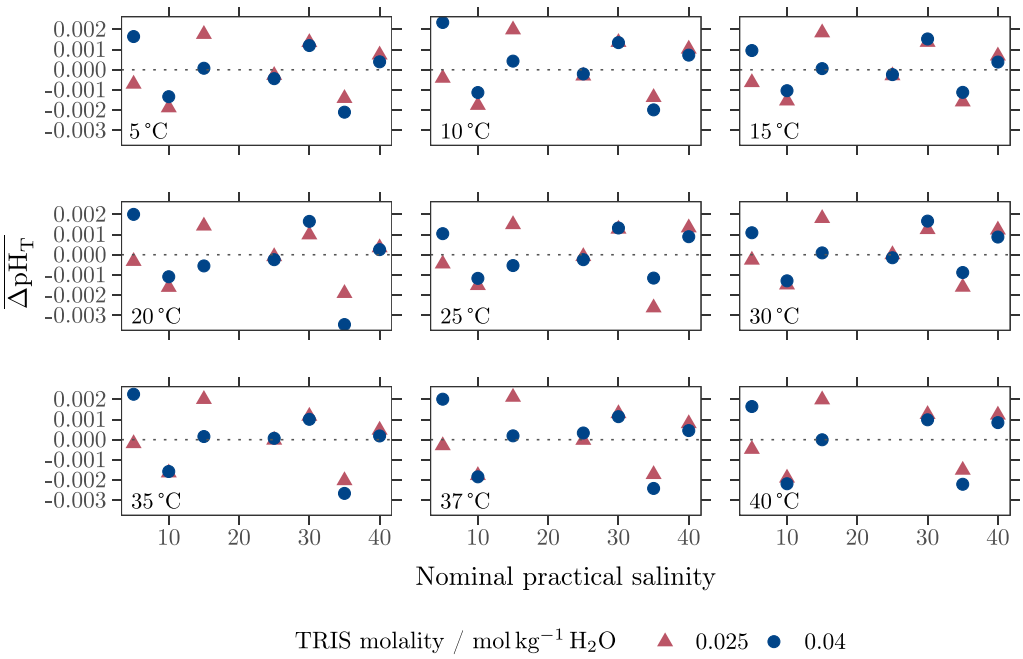


**Fig. 5.** Mean residuals under each condition from the leave-one-out cross-validation. Each point represents the mean of the results from the 124 runs (triangular for 0.025 mol kg$^{-1}$ H$_2$O and round for 0.04 mol kg$^{-1}$ H$_2$O). Standard deviations were below $1.15 \cdot 10^{-4}$ in pH$_T$ units and are not shown here. The dotted line indicates a difference of 0 in pH$_T$ units. Each plot shows the data for one temperature shown in the bottom left.

certified ASW/TRIS buffer standards with a spectrophotometer. The $pK_2^T e_2$ can be calculated from the spectrophotometrical measurement of an ASW/TRIS buffer standard, its certified pH$_T$ value, and the temperature measurement following the procedure in Müller and Rehder (2018). The fit function $pH_{T,c}(S, T, b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ presented here can be used to calculate the pH$_T$ value of the reference material (i.e., ASW/TRIS buffer standard) and its uncertainty directly impacts the uncertainty the determined $pK_2^T e_2$.

Ideally, each batch of meta-Cresol Purple should be accompanied with a certificate stating its $pK_2^T e_2$ value and its uncertainty for a range of salinity and temperature relevant for oceanographic measurements. In this way, batch to batch variations due to impurities could be compensated for. Such a certified meta-Cresol Purple can then be used by oceanographers to do their measurements on unknown samples, with adequate uncertainty calculations. However, such certification of meta-Cresol Purple demands time and resources as ASW/TRIS buffers over a wide range of salinity need to be analyzed by spectrophotometry for a wide range of temperature. Alternatively, it could be recommended for meta-Cresol Purple producers to determine $pK_2^T e_2$ at a specific salinity (i.e., for only one ASW/TRIS buffer) and temperature. This would allow a limited quantification of the variations due to impurities.

The uncertainty goal for seawater pH$_T$ measurements is a standard uncertainty of 0.003 for climate research (Newton et al., 2015). The standard uncertainty of 0.0011 for artificial seawater presented here, is a valuable step towards this goal. It provides important insight into the attainable accuracy of spectrophotometric pH$_T$ measurements. The uncertainty of the $pK_2^T e_2$ term, as well as other terms coming from the characterization of the molar extinction coefficients of the dye, still need to be assessed.

However, the uncertainty of the function presented here applies only if the uncertainties of salinity and temperature from the original measurements (the electrochemical measurements of the artificial seawater) are achieved in the calibration measurements. If that is not the case, these uncertainties should be considered in the calculation. This could, for example, be done by propagating them through the functions. In essence, this would lead to an additional uncertainty contribution $u_{TS}$ of

$$u_{TS} = \sqrt{\left(\frac{\partial pH_{T,c}(S,T,b(\text{TRIS}))}{\partial T}\right)^2 \cdot u(T)^2 + \left(\frac{\partial pH_{T,c}(S,T,b(\text{TRIS})}{\partial S}\right)^2 \cdot u(S)^2}. \quad (7)$$

The uncertainty of temperature has a much larger effect on the combined uncertainty compared to the uncertainty of salinity since the sensitivity of pH$_T$ on temperature is higher. An increase of the uncertainty of temperature by 0.01 °C results in an increase of the uncertainty of pH$_T$ by about 0.00004 (at 25 °C and nominal practical salinity 35) while the effect of a salinity uncertainty increase of 0.01 is about two orders of magnitude lower. Sensitivity is somewhat affected by temperature and salinity, but the overall pattern remains. We estimate that uncertainties in temperature below 0.015 °C and in salinity below 0.1 are negligible. Fig. 6 shows how much the uncertainty of $pH_{T,c}(S, T, b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ is affected by the uncertainty of salinity and temperature for one example condition.

This is in agreement with the results from the sensitivity analysis method where we found that the primary source of uncertainty was the uncertainty of the temperature with more than 99 % of the value of the combined uncertainty. In this method the minimum and maximum value of salinity, temperature and TRIS molality are calculated based on their uncertainties (value minus or plus the uncertainty) (Bernardini et al., 2024). We used the fitted coefficients to calculate a pH$_T$ value at zero TRIS molality for those conditions, and then estimated an uncertainty from the resulting variation of the result. The resulting standard uncertainties for $pH_{T,c}(S, T, b(\text{TRIS}) = 0\,\text{mol kg}^{-1}\,H_2O)$ were between 0.00020 and 0.00028 in pH$_T$ units if the mean uncertainties for all three input quantities were used. Which is lower than the uncertainty we propose because only the effect of input uncertainties is determined and not the effect of the fitting. However, it does reveal the sensitivity of the function towards temperature.

While our measurements covered most of the oceanographically relevant temperature and salinity range, we were unable to measure

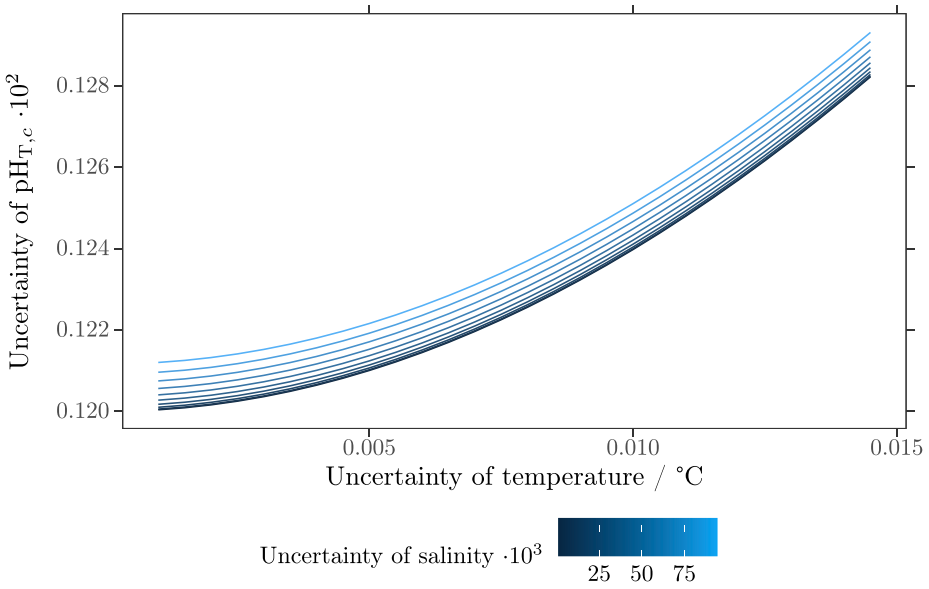


**Fig. 6.** Dependence of the combined uncertainty of $pH_T$ on the uncertainties of temperature ($u(T)$) and practical salinity ($u(S)$) ($S = 35$ and $T = 25\,°C$). In the calibration where the ASW/TRIS buffer is used, temperature and salinity might be known with a larger uncertainty than in our measurements. The effect of a larger temperature uncertainty is higher than a larger salinity uncertainty. The plot gives an indication how high the uncertainty of the calculated $pH_T$ value of the ASW/TRIS buffer is when the uncertainty of the temperature increases. It also shows that the effect of an increase in salinity uncertainty has a smaller effect (though for a given buffer the salinity should be known from the preparation).

at 0 °C due to technical constraints. Application of the results to values below 5 °C should therefore be carefully considered and the extrapolation added in the uncertainty budget. Similar caution should apply to higher temperatures and salinities outside the range covered by our measurements.

As discussed in part 1, the artificial seawater is the best approximation of the acid-base equilibria in natural seawater available for the measurements. Even so, artificial seawater does not exactly represent the behavior of acid-base equilibria in natural seawater and this should be taken into account when determining the uncertainty of a measurement of natural seawater when the calibration was done with artificial seawater.

## 5. Conclusion

After determining the fit function to describe the $pH_T$ value of an ASW/TRIS buffer at $b(\text{TRIS}) = 0\,\text{mol}\,\text{kg}^{-1}\,H_2O$ in a practical salinity range from 5 to 40 and temperature range from 5 °C to 40 °C in Capitaine et al. (2025), this study added the uncertainty determination for the final values. This value is an important step towards traceable spectrophotometric $pH_T$ measurements of seawater because with it, the indicator dye can be characterized with uncertainties. We determined that the combined standard uncertainty is 0.001 1 in $pH_T$ units with analytical procedures following GUM (BIPM et al., 2008a) and a Monte Carlo simulation (BIPM et al., 2008b). This is an important step towards the climate measurement objective established by Newton et al. (2015).

The main open questions regarding the uncertainty of spectrophotometric $pH_T$ seawater measurements remain in the context of the uncertainties related to the impurities in meta-Cresol Purple and the effect of practical salinity not being traceable to the International System of Units (SI) (Seitz et al., 2011). However, the results in this paper present a first step towards fully traceable seawater $pH_T$ measurements.

## CRediT authorship contribution statement

**Rieke Schäfer:** Writing – original draft, Visualization, Software, Formal analysis, Data curation. **Gaëlle Capitaine:** Writing – review & editing, Investigation, Formal analysis. **Frank Bastkowski:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Daniela Stoica:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Olivier Pellegrino:** Writing – review & editing, Investigation. **Raquel Quendera:** Writing – review & editing, Investigation. **Eric P. Achterberg:** Writing – review & editing, Supervision. **Simon L. Clegg:** Writing – review & editing. **Paola Fisicaro:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Steffen Seitz:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization.

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The color scheme used in Figs. 4 and 5 was created by Paul Tol (https://personal.sron.nl/~pault/).

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## Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.marchem.2025.104573.

## Data availability

Data (DOI: 10.5281/zenodo.14964822) and code (DOI: 10.5281/zenodo.14964817) are shared on Zenodo.

## References


Bernardini, L., McLinden, M.O., Yang, X., Richter, M., 2024. How accurate are your experimental data? A more accessible GUM-based methodology for uncertainty evaluation. Int. J. Thermophys. 45, http://dx.doi.org/10.1007/s10765-024-03446-9.

BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OIML, 2008a. Evaluation of measurement data — Guide to the expression of uncertainty in measurement. JCGM URL: https://www.bipm.org/documents/20126/2071204/JCGM_100_2008_E.pdf/cb0ef43f-baa5-11cf-3f85-4dcd86f77bd6, jCGM 100:2008, GUM 1995 with minor corrections.

BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OIML, 2008b. Evaluation of measurement data — Supplement 1 to the guide to the expression of uncertainty in measurement — Propagation of distributions using a Monte Carlo method. JCGM URL: https://www.bipm.org/documents/20126/2071204/JCGM_101_2008_E.pdf/325dcaad-c15a-407c-1105-8b7f322d651c. jCGM 101:2008.

Buck, R.P., Rondinini, S., Covington, A.K., Baucke, F.G.K., Brett, C.M.A., Camoes, M.F., Milton, M.J.T., Mussini, T., Naumann, R., Pratt, K.W., Spitzer, P., Wilson, G.S., 2002. Measurement of pH. Definition, standards, and procedures (IUPAC recommendations 2002). Pure Appl. Chem. 74, 2169–2200. http://dx.doi.org/10.1351/pac200274112169.

Calvin, K., Dasgupta, D., Krinner, G., Mukherji, A., Thorne, P.W., Trisos, C., Romero, J., Aldunce, P., Barrett, K., Blanco, G., Cheung, W.W., Connors, S., Denton, F., Diongue-Niang, A., Dodman, D., Garschagen, M., Geden, O., Hayward, B., Jones, C., Jotzo, F., Krug, T., Lasco, R., Lee, Y.Y., Masson-Delmotte, V., Meinshausen, M., Mintenbeck, K., Mokssit, A., Otto, F.E., Pathak, M., Pirani, A., Poloczanska, E., Pörtner, H.O., Revi, A., Roberts, D.C., Roy, J., Ruane, A.C., Skea, J., Shukla, P.R., Slade, R., Slangen, A., Sokona, Y., Sörensson, A.A., Tignor, M., van Vuuren, D., Wei, Y.M., Winkler, H., Zhai, P., Zommers, Z., Hourcade, J.C., Johnson, F.X., Pachauri, S., Simpson, N.P., Singh, C., Thomas, A., Totin, E., Alegría, A., Armour, K., Bednar-Friedl, B., Blok, K., Cissé, G., Dentener, F., Eriksen, S., Fischer, E., Garner, G., Guivarch, C., Haasnoot, M., Hansen, G., Hauser, M., Hawkins, E., Hermans, T., Kopp, R., Leprince-Ringuet, N., Lewis, J., Ley, D., Ludden, C., Niamir, L., Nicholls, Z., Some, S., Szopa, S., Trewin, B., van der Wijst, K.I., Winter, G., Witting, M., Birt, A., Ha, M., 2023. IPCC, 2023: Climate change 2023: Synthesis report. In: Core Writing Team, Lee, H., Romero, J. (Eds.), Contribution of Working Groups I, II and III To the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. IPCC, Geneva, Switzerland, http://dx.doi.org/10.59327/ipcc/ar6-9789291691647.

Capitaine, G., Schäfer, R., Bastkowski, F., Pellegrino, O., Quendera, R., Achterberg, E., Wagener, T., Seitz, S., Fisicaro, P., 2025. $pH_T$ measurements of TRIS buffer solutions in an artificial seawater matrix in the salinity range 5–40 and temperature range 5–40 °C. Part 1: Measurements and data fitting Mar. Chem. 273, 104551. http://dx.doi.org/10.1016/j.marchem.2025.104551.

CCQM, 2013. CCQM guidance note: Estimation of a consensus KCRV and associated degrees of equivalence. Version 10.

Clegg, S.L., Humphreys, M.P., Waters, J.F., Turner, D.R., Dickson, A.G., 2022. Chemical speciation models based upon the pitzer activity coefficient equations, including the propagation of uncertainties. II. tris buffers in artificial seawater at 25° C, and an assessment of the seawater 'total' pH scale. Mar. Chem. 244, 104096. http://dx.doi.org/10.1016/j.marchem.2022.104096.

DelValls, T., Dickson, A., 1998. The pH of buffers based on 2-amino-2-hydroxymethyl-1, 3-propanediol ('tris') in synthetic sea water. Deep. Sea Res. Part I: Ocean. Res. Pap. 45, 1541–1554. http://dx.doi.org/10.1016/s0967-0637(98)00019-3.

Dickson, A.G., 1990. Standard potential of the reaction: AgCl(s)+1/2 $H_2$(g)=Ag(s) + HCl(aq), and the standard acidity constant of the ion $HSO_4^-$ in synthetic sea water from 273.15 to 318.15 K. J. Chem. Thermodyn. 22, 113–127. http://dx.doi.org/10.1016/0021-9614(90)90074-z.

Ellison, S.L.R., 2018. metRology: Support for metrological applications. URL: https://CRAN.R-project.org/package=metRology. R package version 0.9-28-1.

Friedlingstein, P., O'Sullivan, M., Jones, M.W., Andrew, R.M., Bakker, D.C.E., Hauck, J., Landschützer, P., Le Quéré, C., Luijkx, I.T., Peters, G.P., Peters, W., Pongratz, J., Schwingshackl, C., Sitch, S., Canadell, J.G., Ciais, P., Jackson, R.B., Alin, S.R., Anthoni, P., Barbero, L., Bates, N.R., Becker, M., Bellouin, N., Decharme, B., Bopp, L., Brasika, I.B.M., Cadule, P., Chamberlain, M.A., Chandra, N., Chau, T.T.T., Chevallier, F., Chini, L.P., Cronin, M., Dou, X., Enyo, K., Evans, W., Falk, S., Feely, R.A., Feng, L., Ford, D.J., Gasser, T., Ghattas, J., Gkritzalis, T., Grassi, G., Gregor, L., Gruber, N., Gürses, O., Harris, I., Hefner, M., Heinke, J., Houghton, R.A., Hurtt, G.C., Iida, Y., Ilyina, T., Jacobson, A.R., Jain, A., Jarníková, T., Jersild, A., Jiang, F., Jin, Z., Joos, F., Kato, E., Keeling, R.F., Kennedy, D., Klein Goldewijk, K., Knauer, J., Korsbakken, J.I., Körtzinger, A., Lan, X., Lefèvre, N., Li, H., Liu, J., Liu, Z., Ma, L., Marland, G., Mayot, N., McGuire, P.C., McKinley, G.A., Meyer, G., Morgan, E.J., Munro, D.R., Nakaoka, S.I., Niwa, Y., O'Brien, K.M., Olsen, A., Omar, A.M., Ono, T., Paulsen, M., Pierrot, D., Pocock, K., Poulter, B., Powis, C.M., Rehder, G., Resplandy, L., Robertson, E., Rödenbeck, C., Rosan, T.M., Schwinger, J., Séférian, R., Smallman, T.L., Smith, S.M., Sospedra-Alfonso, R., Sun, Q., Sutton, A.J., Sweeney, C., Takao, S., Tans, P.P., Tian, H., Tilbrook, B., Tsujino, H., Tubiello, F., van der Werf, G.R., Ooijen, E.van., Wanninkhof, R., Watanabe, M., Wimart-Rousseau, C., Yang, D., Yang, X., Yuan, W., Yue, X., Zaehle, S., Zeng, J., Zheng, B., 2023. Global carbon budget 2023. Earth Syst. Sci. Data 15, 5301–5369. http://dx.doi.org/10.5194/essd-15-5301-2023.

Gorman, B., 2018. mltools: Machine learning tools. URL: https://CRAN.R-project.org/package=mltools. R package version 0.3.5.

Kuhn, M., Wickham, H., 2020. Tidymodels: a collection of packages for modeling and machine learning using tidyverse principles. URL: https://www.tidymodels.org.

Liu, X., Patsavas, M.C., Byrne, R.H., 2011. Purification and characterization of meta-cresol purple for spectrophotometric seawater pH measurements. Environ. Sci. Technol. 45, 4862–4868. http://dx.doi.org/10.1021/es200665d.

Meija, J., Coplen, T.B., Berglund, M., Brand, W.A., De Bièvre, P., Gröning, M., Holden, N.E., Irrgeher, J., Loss, R.D., Walczyk, T., Prohaska, T., 2016. Atomic weights of the elements 2013 (IUPAC technical report). Pure Appl. Chem. 88, 265–291. http://dx.doi.org/10.1515/pac-2015-0305.

Müller, J.D., Bastkowski, F., Sander, B., Seitz, S., Turner, D.R., Dickson, A.G., Rehder, G., 2018. Metrology for pH measurements in brackish waters—part 1: Extending electrochemical pHT measurements of TRIS buffers to salinities 5–20. Front. Mar. Sci. 5 (176), http://dx.doi.org/10.3389/fmars.2018.00176, URL: https://www.frontiersin.org/article/10.3389/fmars.2018.00176.

Müller, J.D., Rehder, G., 2018. Metrology of pH measurements in brackish waters—part 2: Experimental characterization of purified meta-cresol purple for spectrophotometric pHT measurements. Front. Mar. Sci. 5 (177), http://dx.doi.org/10.3389/fmars.2018.00177, URL: https://www.frontiersin.org/article/10.3389/fmars.2018.00177.

Newton, J., Feely, R.A., Jewett, E.B., Williamson, P., Mathis, J., 2015. Global ocean acidification observing network: Requirements and governance plan. URL: http://www.goa-on.org/docs/GOA-ON_plan_print.pdf. GOA-ON.

R Core Team, 2023. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, URL: https://www.R-project.org/.

Seitz, S., Feistel, R., Wright, D.G., Weinreben, S., Spitzer, P., Bièvre, P.D., 2011. Metrological traceability of oceanographic salinity measurement results. Ocean. Sci. 7, 45–62. http://dx.doi.org/10.5194/os-7-45-2011.

Venables, W.N., Ripley, B.D., 2002. Modern Applied Statistics with S, fourth ed. Springer, New York, ISBN: 0-387-95457-0, URL: https://www.stats.ox.ac.uk/pub/MASS4/.

Viechtbauer, W., 2010. Conducting meta-analyses in R with the metafor package. J. Stat. Softw. 36, 1–48. http://dx.doi.org/10.18637/jss.v036.i03.

Wickham, H., Averick, M., Bryan, J., Chang, W., McGowan, L.D., François, R., Grolemund, G., Hayes, A., Henry, L., Hester, J., Kuhn, M., Pedersen, T.L., Miller, E., Bache, S.M., Müller, K., Ooms, J., Robinson, D., Seidel, D.P., Spinu, V., Takahashi, K., Vaughan, D., Wilke, C., Woo, K., Yutani, H., 2019. Welcome to the tidyverse. J. Open Source Softw. 4 (1686), http://dx.doi.org/10.21105/joss.01686.