

Underway pH

An automated underway pH system was operated in the hydro lab of the R/V *Ronald H. Brown* during the A13.5 cruise in 2010. pH was measured every 30 seconds using a Durafet III pH combination electrode and an Orion Chloride Ion Selective Electrode (Cl-ISE). This combination allows for the calculation of pH using two reference electrodes: the internal reference electrode of the Durafet (pH_{int}) and the Cl-ISE directly submersed in seawater (pH_{ext}). pH is reported on 30 second intervals to provide the maximum flexibility for assessing precision and capturing small scale features in the ocean. Seawater continually flowed through a flowcell that housed the Durafet and Cl-ISE, then a SBE45 Micro Thermosalinograph. The temperature inside the flowcell was assumed to be the same as the SBE45. The salinity measurements from the SBE45 were not reliable on this cruise (based on comparisons with discrete bottle samples), therefore salinity from the SBE45 located next to the underway fCO_2 system [Wanninkhof, 2012] was interpolated onto the pH time stamp. Latitude, longitude, and sea surface temperature (SST) were also interpolated from the underway fCO_2 data set. All pH is reported on the total scale, and at SST. All data reported here are considered “good”. We recommend the use of pH_{ext} , as we believe this is more accurate than pH_{int} .

Details on the sensor theory and calculations can be found in [Martz *et al.*, 2010; Bresnahan *et al.*, 2014], but will be briefly described here. Computation of pH_{ext} requires knowledge of two sensor calibration coefficients, the sensor reference potential at 0 °C ($E_{ext,0°C}^*$) and the temperature coefficient ($\frac{dE_{ext}^*}{dT}$):

$$pH_{ext} = \frac{(E_{ext} - E_{ext}^*) + S \times \log(\gamma_H \gamma_{Cl} m_{Cl})}{S} \quad (1)$$

$$E_{ext}^* = E_{ext,0°C}^* + \frac{dE_{ext}^*}{dT} T \quad (2)$$

where E_{ext} is the electromotive force between the ISFET and the Cl-ISE, E_{ext}^* is the reference potential at in situ temperature, T is temperature in Celsius, γ is the activity coefficient of the respective ions, m_{Cl} is the molality of chloride, and $S = R \times T_K \times \ln(10)/F$ (R is the universal gas constant $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, T_K is temperature in Kelvin, and F is the Faraday constant 96485 C mol^{-1}). S , $\gamma_H \gamma_{Cl}$, and m_{Cl} are calculated from measurements of temperature and salinity [Khoo *et al.*, 1977; Dickson *et al.*, 2007; Martz *et al.*, 2010]. A linear regression between E_{ext}^* and T gives $E_{ext,0°C}^*$ (intercept) and $\frac{dE_{ext}^*}{dT}$ (slope). $\frac{dE_{ext}^*}{dT}$ was determined to be -957 ± 8 (95% CI) $\mu\text{V } ^\circ\text{C}^{-1}$.

Computation of pH_{int} requires knowledge of two sensor calibration coefficients, the sensor reference potential at 0 °C ($E_{int,0°C}^*$) and the temperature coefficient ($\frac{dE_{int}^*}{dT}$):

$$pH_{int} = \frac{(E_{int} - E_{int}^*)}{S} \quad (3)$$

$$E_{\text{int}}^* = E_{\text{int},0^\circ\text{C}}^* + \frac{dE_{\text{int}}^*}{dT} T \quad (4)$$

where E_{int} is the electromotive force between the ISFET and the internal reference electrode, E_{int}^* is the reference potential at in situ temperature, A linear regression between E_{int}^* and T gives $E_{\text{int},0^\circ\text{C}}^*$ (intercept) and $\frac{dE_{\text{int}}^*}{dT}$ (slope). $\frac{dE_{\text{int}}^*}{dT}$ was determined to be -1.127 ± 0.008 (95% CI) mV $^\circ\text{C}^{-1}$.

Both E_{int}^* and E_{ext}^* can be calculated by measuring E_{int} or E_{ext} in a solution of known pH. Here, we used the surface discrete sample for $f\text{CO}_2$ and dissolved inorganic carbo (DIC) from the rosette at each station to calculate the calibration coefficients ($n = 129$). $E_{\text{ext},0^\circ\text{C}}^*$ was determined to be -1.37370 ± 0.0003 (1σ) V. A non-linear drift in $E_{\text{int},0^\circ\text{C}}^*$ was observed, with a range of approximately 2 mV (Figure 1). In order to account for this drift, a piece-wise linear regression was performed over three sections: 1) before March 21st, 2) between March 21 and 28, and 3) after march 28. pH_{int} was calculated using this interpolated $E_{\text{int},0^\circ\text{C}}^*$. The cause of this drift is not known, but could be largely corrected for due to the large number of calibration samples.

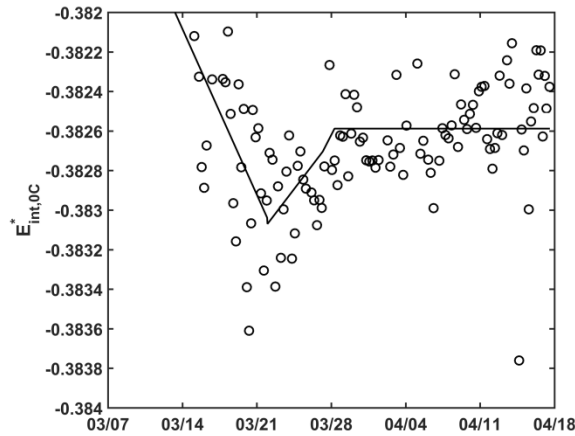


Figure 1: Time series of $E_{\text{int},0^\circ\text{C}}^*$ (open circles). Piece wise linear regression is shown in the solid black line.

All carbonate calculations were done using CO2SYS [van Heuven *et al.*, 2011], using carbonate equilibrium constants from [Mehrbach *et al.*, 1973] refit by [Dickson and Millero, 1987], salinity to boron ratios from [Uppstrom, 1974], and bisulfate equilibrium constants from [Dickson, 1990].

We believe the underway pH_{ext} is accurate to 0.007, based on the consistency of calibrating the pH sensors using multiple combinations of discrete samples (i.e. $f\text{CO}_2$, total alkalinity, DIC, and spectrophotometric pH). However, the short term precision (hours) and long term precision (weeks) of the underway pH_{ext} data is 0.0005 and 0.004, respectively. Details of the uncertainties associated with pH_{ext} can be found in [Takeshita *et al.*, 2017, in review].

Variable Descriptions

DATE.UTC_ddmmyyyy: Date in UTC, formatted as ddmmyyyy

TIME.UTC_hhmmss: Date in UTC, formatted as hh:mm:ss

LAT_dec_degree: Latitude in decimal degree, interpolated from the underway fCO₂ system

LONG_dec_degree: Longitude in decimal degree, interpolated from the underway fCO₂ system

Eint_volt: Voltage between the ISFET and internal reference electrode

Eext_volt: Voltage between the ISFET and the external reference electrode (CI-ISE)

TEMP_FLOWCELL_C: Temperature of the flow cell in Celsius

SALINITY_PSS_78: Sea surface salinity based on the PSS-78 practical salinity scale,, interpolated from the underway fCO₂ system

SEA_SURFACE_TEMPERATURE_C: Sea surface temperature in Celsius, interpolated from the underway fCO₂ system

pH_INT_TOT_AT_SST: pH on the total scale at sea surface temperature calculated using the internal reference electrode on the total scale, at SST

pH_EXT_TOT_AT_SST: pH on the total scale at sea surface temperature calculated using the external reference electrode on the total scale, at SST

References

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