

## Collection and processing of benchmark water samples for DuraFET type pH sensors

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### Overview and Background:

Continuously recording pH sensors are field-calibrated with discrete water samples, which are analyzed in the lab for salinity, pH, and total alkalinity. Honeywell Durafet-based pH sensors include SeaFET and ipHat. This protocol describes collection and processing of those benchmark samples.

### Methods:

*Field Collection:* Discrete bottles samples are collected as physically close to the pH sensor as possible and approximately in concurrence with the sensor's voltage measurement by a SCUBA diver using a Niskin bottle, or by hand, as appropriate for the site (moored underwater or near-surface intertidal). Water samples are poisoned with saturated mercuric chloride immediately after collection, sealed, and stored in a cool, dark place until analysis.

*Laboratory Processing:* Salinity, pH, and total alkalinity in the water samples are measured in the laboratory. Seawater pH was measured using a spectrophotometric method with indicator dye, unpurified m-cresol purple (Sigma-Aldrich, SOP 6b, Dickson et al. 2007). Total alkalinity (AT) was measured using an automated, open-cell potentiometric titration (SOP 3b, Dickson et al. 2007) with a Mettler-Toledo T50 titrator and a DG115-SC pH probe (Mettler-Toledo). The probe was calibrated using a Tris buffer (A. Dickson Laboratory, Scripps Institution of Oceanography). Titrations were performed using certified acid titrant (~0.1M HCl, 0.6 M NaCl; A. Dickson Laboratory, Scripps Institution of Oceanography). Certified reference materials (CRMs) from A. Dickson Laboratory, Scripps Institution of Oceanography, were used to determine the accuracy and precision of the titrations daily before experimental samples were measured. Analyzed CRMs were accurate within 10 micromol kg<sup>-1</sup>.

*Data Processing:* The suite of carbonate chemistry parameters was calculated using the CO2CALC program. Along with temperature and salinity, CO2calc algorithms produce a suite of carbonate system parameters using only two measured variables (of five potential inputs); the remaining three possible inputs are also calculated as algorithm outputs. In our samples, pH, TA and/or TCO<sub>2</sub> are routinely measured, and precedence of use is: 1) measured pH and TA (total alkalinity), 2) measured pH and TCO<sub>2</sub> (total dissolved inorganic carbon). Use of TA and TCO<sub>2</sub> is not recommended (Hoppe et al, 2012). In situ carbonate system parameters were also calculated using temperature recorded in the field (“adjusted” outputs), per Robbins et al. (2010), with CO<sub>2</sub> constants K<sub>1</sub>, K<sub>2</sub> from Mehrbach et al. 1973 refit by Dickson and Millero, 1987 and pH expressed on the total scale (mol kg<sup>-1</sup>-SW-1).

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