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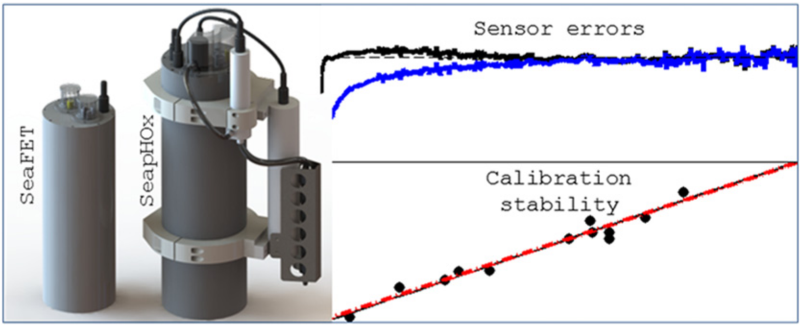
Best practices for autonomous measurement of seawater pH with the Honeywell Durafet

Philip J. Bresnahan Jr.[a], Todd R. Martz[a,*], Yuichiro Takeshita[a], Kenneth S. Johnson[b], Makaila LaShomb[a]

[a] *Scripps Institution of Oceanography, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA*

[b] *Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, Moss Landing, CA 95039, USA*

GRAPHICAL ABSTRACT



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ABSTRACT

Performance of autonomous pH sensors is evaluated by comparing *in situ* data to independent bench-top measurements of pH and to co-located pH, O_2, and pCO_2 sensors. While the best practice is always to deploy a properly calibrated sensor, the lengthy time period required for sensor conditioning and calibration often results in sensor deployment without comprehensive calibration. Quality control (QC) procedures are examined to determine the errors

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* Corresponding author. Tel.: +1 858 534 7466.
E-mail address: trmartz@ucsd.edu (T.R. Martz).

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associated with different *in situ* calibration approaches and lay a framework for best practices. Sensor packages employing the Honeywell Durafet remained stable across multiple deployments for over nine months. However, sensor performance was often limited by biofouling. Regional empirical relationships for estimating carbonate system parameters are shown to enable identification of otherwise indistinguishable sensor offset and drift when multiple sensor types are co-located. Uncertainty is determined by calibration approach and must be quantified on a case-by-case basis. Our results indicate that the Durafet is capable of accuracy, relative to a chosen reference, of better than 0.03 pH units over multiple months. Accuracy is improved when a robust shore-side calibration is performed, an independent means of QC is available throughout a deployment, and effective biofouling prevention measures are taken.

1. Introduction

A recent trend in ocean acidification (OA) research involves utilizing natural settings in order to incorporate the variability inherent in nature (Hofmann et al., 2011; Kline et al., 2012). Although Standard Operating Procedures (SOPs) have been established for CO_2 bottle analyses (Dickson, 2007) and laboratory-based OA experiments (Riebesell et al., 2010), no standard protocols are in place for calibration and validation of the sensors used to characterize the natural settings of *in situ* experiments, despite their increasing prevalence (e.g. Byrne et al., 2009; Cullison Gray et al., 2011; Easley et al., 2013; Frieder et al., 2012; Liu et al., 2006; Martz et al., 2010; Seidel et al., 2008; Yu et al., 2011). In addition to OA studies, a number of equally important applications for quantitative biogeochemical studies exist for pH sensors (e.g. Emerson et al., 2011; Martz et al., 2014) that would benefit from documented validation and quality control (QC) protocols. Furthermore, pH measurements used to investigate specific processes – from climate trends to organismal responses – should always carry a statement of the uncertainty in the number reported. Establishing data QC protocols is of paramount importance and must be addressed before the relationship between observed pH and biogeochemical thresholds or biological "tipping points" is reported.

The initial accuracy of a stable sensor is limited by the calibration approach. Trust in pre- and post-calibrations (i.e., setting calibration constants before sensors are deployed or after they are recovered) of any marine chemical sensor relies on two hard to satisfy criteria: (1) sensors must be calibrated in a similar physical setting (*viz.*, similar temperature, salinity, pressure) to that of the study location and (2) sensors must not undergo significant (re)conditioning in their new environments. It is always preferred to rigorously calibrate a sensor before deployment, but this may require facilities and time that are not available. Honeywell provides an initial factory calibration of every Durafet sensor on the NBS pH scale, but provides no statement of calibration accuracy or stability, recommending that the user perform the canonical NBS buffer standardization employed widely for all glass electrodes. Because the NBS pH scale is not recommended for seawater pH measurements (Marion et al., 2011), at minimum, the Honeywell factory calibration must be recalibrated on the appropriate pH scale (e.g., the seawater scale, total hydrogen ion scale) before use in most oceanographic applications. Examples of such conversions are provided in the Supplementary data (see Appendix A). Due to these complications, it is sometimes preferred to calibrate an operating Durafet to a field measurement after the sensor is deployed. This practice also serves to validate laboratory calibration. Clearly, the calibration sample must coincide in time and space with a sensor measurement—a challenging demand in dynamic environments. Here, we evaluate the utility of *in situ* calibrations via bottle samples as well as independent, co-located sensors linked through regional empirical relationships.