

# Reliably Measuring pH In the Ocean

## Deep SeaFET Maintains Accuracy over Broad Temp, Pressure Ranges

By Charles W. Branham • David J. Murphy • Ian D. Walsh

The development of autonomous vehicles capable of performing hundreds of profiles in the ocean from depths of 1 to 2 km has led to a dramatic shift in the collection of deep-sea data from shipboard, often hands-on measurements to remote robotic collection. Dissolved oxygen is the first chemical parameter to see this transformation.

The potential for pH to be the second chemical parameter to see this shift is considerable as high-resolution in-situ measurements of pH in the ocean are now possible with innovative adaptations of ion sensitive field-effect transistors (ISFET). Oceanographic instruments based on the ISFET technology have been in development for more than a decade, but, as with most technologies, have had significant hurdles to overcome. Current instruments have depth limitations or significant drift and environmental constraints that have limited their adoption. Here, we present field and laboratory research results with the Sea-Bird Scientific Deep SeaFET, an ISFET-based pH sensor that demonstrates the technology has reached the stability and robustness necessary for a similar transformation in the source of quality pH measurements.

The ocean is buffered with respect to pH over long time scales, which for most of the history of oceanography meant that the fact that the measurement tools for pH are either relatively unstable (glass bulb) or laborious (dye spectrophotometry) didn't significantly impact research and monitoring. Recently, the importance of pH in the ocean has been recognized because, on short time scales relevant to biological productivity, the food chain and carbon fluxes, pH is dynamic and potentially controlling across critical scales. Given that atmospheric loading of carbon dioxide from anthropogenic sources will feedback as a decrease in oceanic pH, the need for robust and reliable in-situ, oceanographic-quality pH sensors is urgent and has led to many development paths spurred by

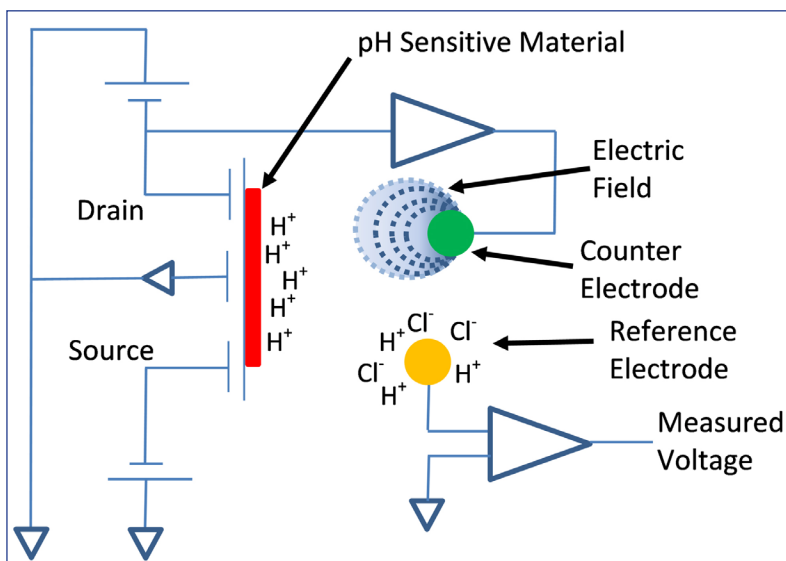


the obvious need and encouraged by global competitions such as the Wendy Schmidt Ocean Health XPRIZE in 2015 (<http://oceanhealth.xprize.org>).

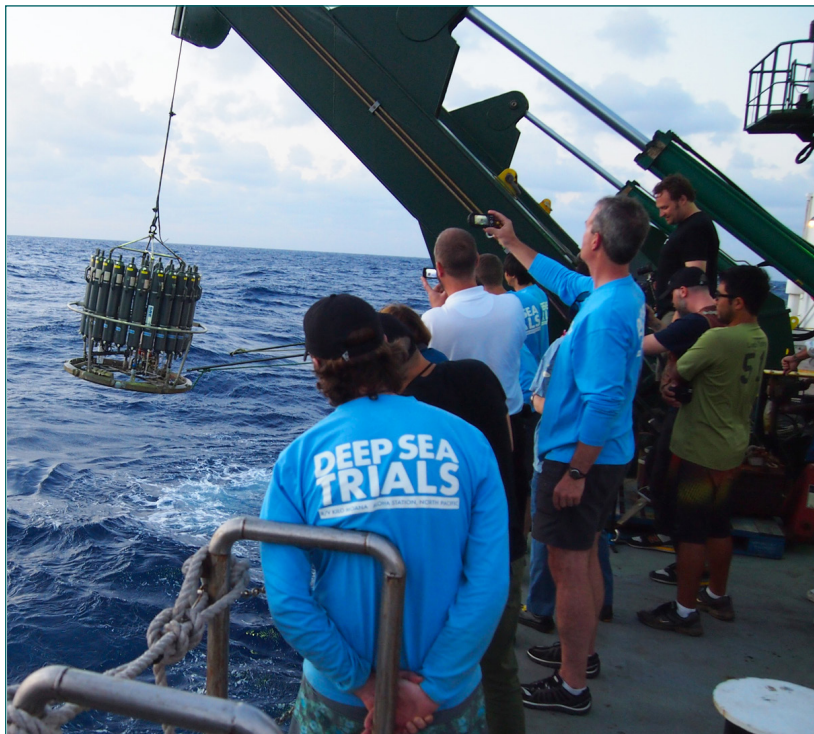
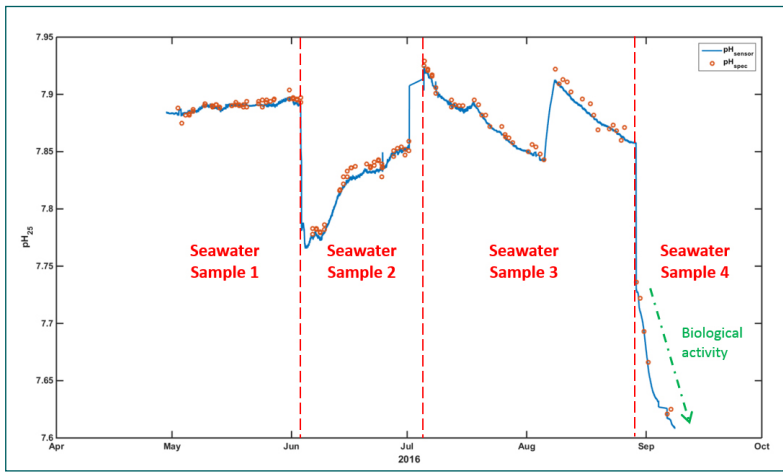
### The Technology

The Sea-Bird Scientific Deep SeaFET is based on the Honeywell Durafet, an ISFET that was originally developed to replace the glass electrode in industrial applications where chemical robustness and dependable long-term measurements are necessary. The chief concern in the development of the deep-ocean-capable Durafet is the maintenance of the accuracy of the sensor over sufficiently broad ocean temperature and pressure ranges. To reach this goal, the liquid/gel Ag/AgCl

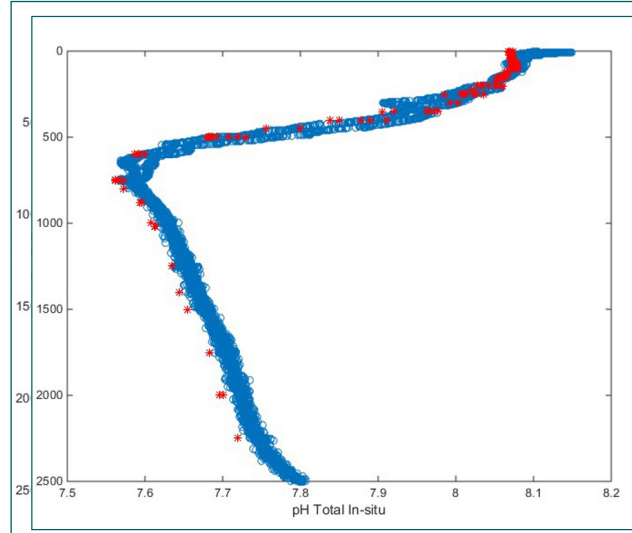
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(Top) The Deep SeaFET. (Bottom) Schematic representation of the ISFET, counter electrode, reference electrode and operating components.



(Top) The stability of the Deep SeaFET in filtered seawater over a four-month period in Sea-Bird Scientific's pH laboratory. The blue line is the pH measured by the Deep SeaFET, and the orange circles are the pH validation samples measured using dye spectrophotometry. The red dash lines indicate when the seawater was exchanged from the system. (Middle) Participants in the Wendy Schmidt Ocean Health XPRIZE test cruise off Hawaii, watching the deployment of the instruments on the rosette during sea trials May 2015. (Photo Credit: XPRIZE) (Bottom) A profile of pH measured by the Deep SeaFET from the final side-by-side XPRIZE competition in 2015 off Hawaii. The red asterisks are the pH measured from bottle samples by NOAA's PMEL Laboratory. The y-axis is depth in meters.



reference electrode used in the original Durafet design has been replaced with a solid state Ag/AgCl reference electrode. The use of a solid state reference electrode and a custom-designed pressure-tolerant housing for the Durafet chip extends the pressure rating of the sensor from 100 to 3,000 psi.

The sensing element of the Deep SeaFET is an ISFET pH sensor, which is a type of metal oxide semiconductor field-effect transistor (MOSFET) where the gate terminal is an ion-sensitive material exposed to the analyte of interest, in this case, the hydronium ions in seawater. The ISFET pH sensor has three major components: the counter electrode, the pH-sensitive material of the ISFET and the reference electrode. For the sensor to function properly, all three of these components need to be exposed to seawater. Once exposed to seawater, these three components can be considered as two half cells of a solid state electrochemical cell. One half cell is the combination of the counter electrode and pH-sensitive material of the ISFET. The counter electrode applies a small electric field to maintain a constant current across the ISFET, and the pH-sensitive material is used to detect the hydronium ions in the seawater. Since chloride ions are relatively constant in deep seawater, a solid state chloride ion selective electrode was chosen to be the reference electrode and the other half of the electrochemical cell. The chloride ion selective electrode is an Ag/AgCl puck that has an electrical potential proportional to the concentration of chloride ions in seawater. When these two half cells are combined, the voltage that forms on the chloride ion selective electrode is proportional to the pH in seawater and is the signal that is measured by the sensor. The solid state electrochemical cell exhibits a Nernstian response to pH, but presents the added complexity of being sensitive to chloride activity.

### Design, Calibration and Stability Considerations

The Deepsea DuraFET's specified operational ranges for temperature and pressure are 5 to 35° C and 50 to 3,000 psi. The original Durafet was developed for low-pressure industrial conditions and could not achieve this pressure range. All three of the major components of the sensor needed to be modified from the original Durafet design to achieve the needed pressure tolerance: the

conductive polymer counter electrode was replaced with a titanium tube that surrounded the reference electrode; the ISFET die was placed in a stress-minimizing polyetherether-



ketone (PEEK) housing; and the liquid/gel Ag/AgCl reference electrode was replaced with a solid state Ag/AgCl reference electrode.

Calibrating the Deep SeaFET presents challenges in that the stability of the instrument over the ranges of temperature and pressure expected while deployed on a profiling float has to be demonstrated at the same time. To achieve the necessary accuracy and precision, it is not sufficient to characterize the instrument in separate temperature and pressure regimes. Thus, in addition to the Durafet design, a custom temperature-controlled pressure vessel had to be designed and built. Calibrations are performed in a computer-controlled titanium calibration vessel filled with a 0.01 N HCl acid solution of known thermodynamic properties to allow for correction of the sensor response to both temperature and pressure. The calibration procedure runs through a matrix of four temperature and seven pressure points over the range of 5 to 35° C and 0 to 3,000 psi to build the calibration equations for each instrument.

One of the key limitations of standard glass electrode pH sensors is their insufficient measurement stability in all media. The Durafet technology by contrast has been proven to be stable in a variety of industrial processes, however, little work had been done to demonstrate its stability in seawater. To determine the measurement stability in seawater, a Deep SeaFET was placed in a continuous-flow tank filled with filtered seawater over a four-month period (May to September 2016). The Deep SeaFET was run continuously and delivered pH measurements every 20 seconds throughout the experiment.

Validation samples were taken daily and pH was determined in the grab samples using standard pH indicator dye spectrophotometry. The coherence throughout the experiment was excellent, with the average difference between the Deep SeaFET and the validation samples within  $\pm 0.005$  pH over the entire four-month experiment. The response of the instrument to rapid changes in pH was demonstrated by exchanging the seawater three times over the course of the experiment. Each exchange exposed the instrument to a new seawater sample with a different salinity, temperature and dissolved gas concentration. Inadvertently, we also demonstrated the response of the instrument to the effect of biological activity as the fourth batch of seawater was contaminated. While pH declined much more rapidly over the last week of the experiment, the Deep SeaFET measurements tracked the grab samples as well as it had during the earlier, more stable periods.

## Field Validation

Our laboratory work has demonstrated that the Deep SeaFET is stable in seawater for much longer periods than previous methods. One consideration to achieve this stability in the field is that the solid state Ag/AgCl reference electrode requires conditioning in seawater for at least one week prior to deployment to maintain the accuracy of the sensor in natural seawater.

The Deep SeaFET has been used in field validation on floats during the development process. It was also evaluat-

ed during the Wendy Schmidt Ocean Health XPRIZE competition in a field trial off the coast of Hawaii in May 2015.

In the surface ocean and across the thermocline, the Deep SeaFET performed extremely well, to within  $\pm 0.005$  pH units of the validation measurements. In the deep ocean, however, the sensor was less accurate, measuring pH to  $\pm 0.02$  of the validation measurements. Overall, the Deep SeaFET performed extremely well in comparison to other technologies tested and was awarded second prize for accuracy by the XPRIZE award committee in 2015. Efforts to improve the modeling of the pressure response of the sensor in the deep ocean have continued, with updated designs and additional field testing by scientists at both Sea-Bird Scientific and MBARI.

## Conclusion

Laboratory and field tests of the Deep SeaFET have demonstrated the stability and accuracy of ISFET technology necessary for incorporation of pH sensors into routine ocean monitoring on autonomous vehicles.

Further work by Sea-Bird Scientific engineers and scientists will be directed toward improving the calibration methodology, mechanical robustness and manufacturability.

In the coming year, the improved Deep SeaFET prototypes will be evaluated and validated in the field.

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## References

For a list of references, contact Charles W. Branham at [cbranham@seabird.com](mailto:cbranham@seabird.com). **ST**

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