# Verifying ISFET Sensors

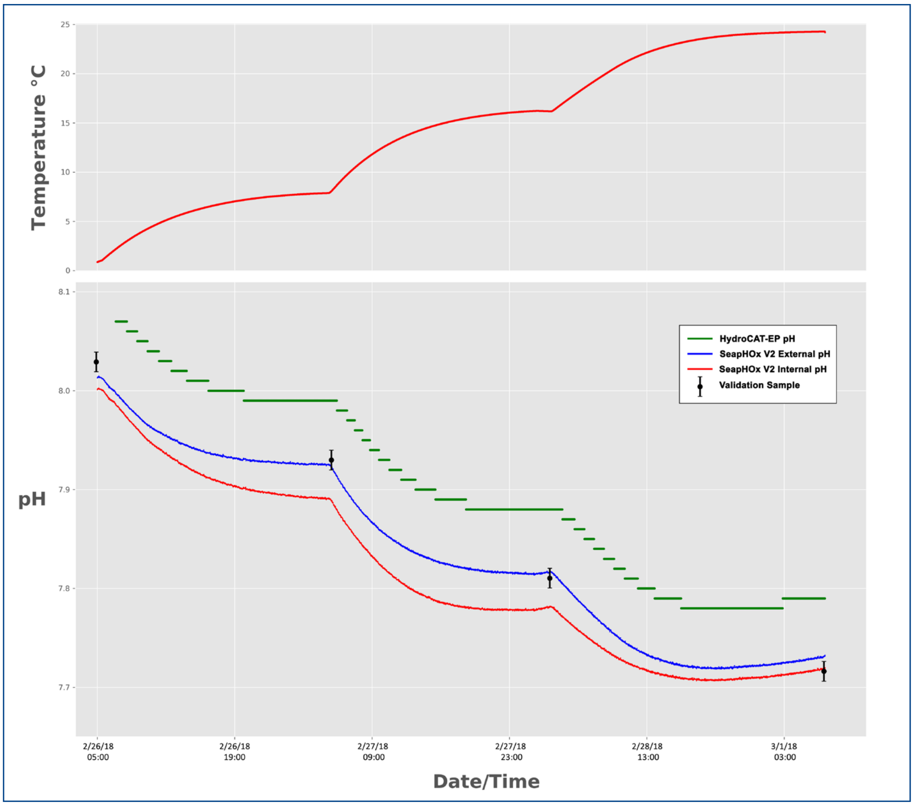
## *Test Bath, Field Experiments to Check Accuracy of pH Measurements*

**By Greg Ikeda**

An ocean mooring is like a small community: clusters of sensors huddle together, each measuring the ocean's pulse in a different way, sometimes chatting with one another about what they've seen. As the world's oceans become more acidic, it's becoming increasingly clear that pH sensors should be vital members of this community. However, the prevailing technology—glass-electrode pH sensors—is notoriously unstable in seawater, necessitating frequent calibration, reducing reliability of the sensors during long-term deployments.

Enter the Sea-Bird Scientific SeapHOx V2: part pH sensor, part CTD. It consists of the SeaFET V2, measuring pH with an ion-sensitive field-effect transistor (ISFET), and corrects data with temperature and salinity input from an SBE 37-SMP-ODO CTD. Unlike glass electrodes, the SeapHOx V2's ISFET and solid-state reference sensors do not undergo significant changes to their internal chemistry, allowing them to retain accuracy for long-term deployments without recalibration.

As part of ongoing efforts in pH sensor development, Sea-Bird Scientific conducted a basic comparison of pH data from the SeapHOx V2 to a HydroCAT-EP, a multiparameter moored CTD that uses a standard glass-electrode pH sensor. Simultaneously deployed in a stable test bath for approximately 72 hr., the response from the SeapHOx V2's ISFET sensor and the HydroCAT-EP's glass-electrode sensor highlighted the different capabilities of each sensor technology. While this test provided a snapshot of sensor performance under controlled, salinity-stable conditions, an experiment in a test bath is not an ideal test to characterize sensor differences: It fails to simulate rapidly changing field conditions and is not long enough




***The bath test of a SeapHOx V2 and a HydroCAT-EP. The test bath contained chilled natural seawater and retained a stable salinity of 36.63 to 36.90 psu. Temperature was increased at approximately 24-hr. intervals to stimulate changes in pH. Four pH validation samples were taken and analyzed on a spectrophotometer before each temperature change—the accuracy of this method with pure dye is approximately ±0.01 pH, as shown by the error bars on the figure.***

to capture drift rates of either pH sensor. Nonetheless, the experiment provided a useful baseline from which to evaluate the SeapHOx V2's overall accuracy and resolution relative to the prevailing glass-electrode technology.

To better characterize the SeapHOx V2's ability to withstand and perform in the field, Sea-Bird Scientific field scientists also deployed a Deep SeapHOx V2 in Puget Sound, a large estuary connected to the Pacific Ocean, with regular validation samples to determine sensor accuracy and drift over time.

### The SeapHOx V2

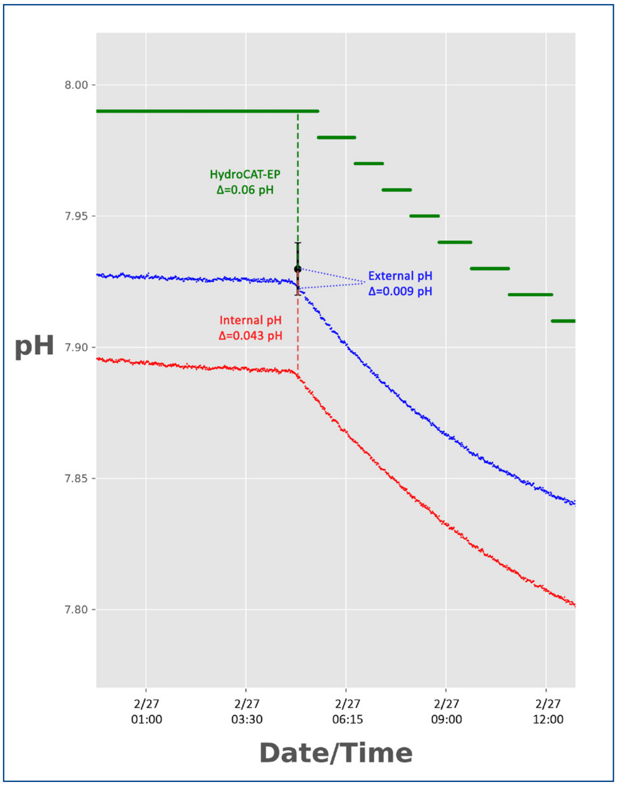
The SeapHOx V2 is an upgrade of the original Satlantic SeapHOx pH sensor, consisting of a SeaFET V2 pH sensor physically and electrically integrated with an SBE 37-SMP-ODO CTD. It measures pH with an ISFET as the primary sensor, providing two pH outputs from two separate reference electrodes. The internal pH value references an internal electrode submerged in saturated KCl solution. The external pH value references an Ag/AgCl electrode next to the ISFET. Unlike the internal electrode, this external electrode is directly in contact with seawater. Because this electrode is sensitive to chloride ions in seawater, it requires accurate salinity measurements from the CTD for proper corrections of the pH. Each output has unique sources of error, but external pH is generally more accurate when salinity data are available to correct pH data. The initial accuracy of both pH outputs is rated to 0.05 pH, expected to drift less than 0.003 pH/month.

The physical and electrical design of the SeapHOx V2 provides the ability to deploy the ISFET pH sensor in marine environments. Unlike the glass electrode, the ISFET and accompanying reference electrodes do not undergo rapid change in seawater, opening doors for long-term deployment of moored pH sensors.

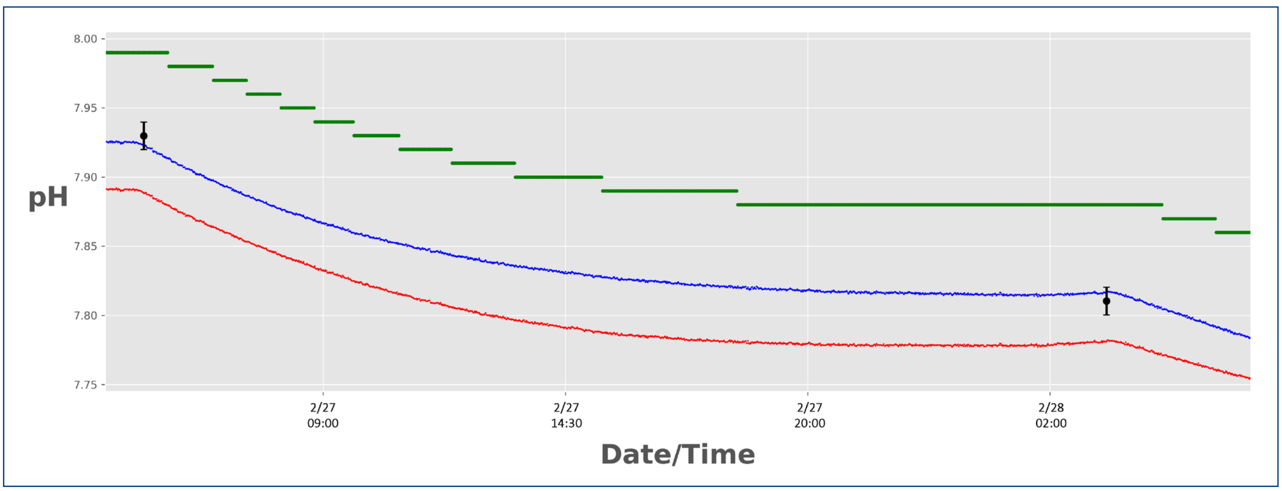
### The HydroCAT-EP

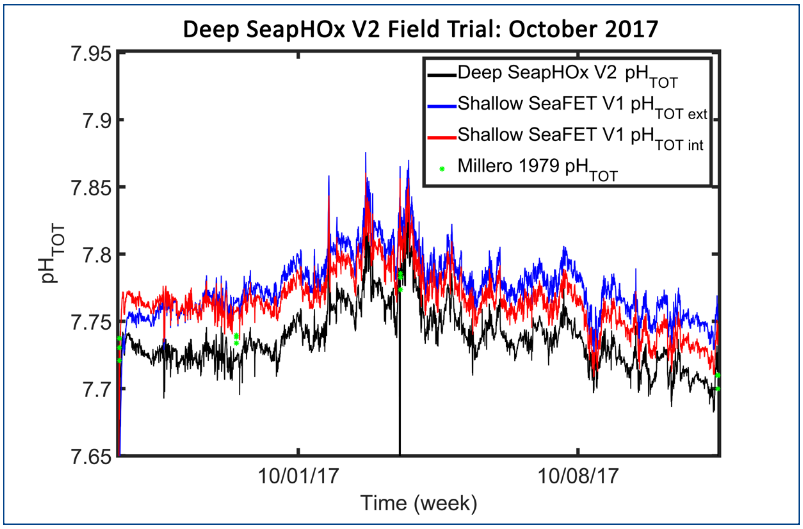
The HydroCAT-EP is a multiparameter moored CTD based on the SBE 37 CTD. It is capable of measuring temperature, conductivity, pressure, dissolved oxygen, pH, fluorescence and turbidity with integrated sensors. The HydroCAT-EP's "HC-pH" pH sensor is a standard glass electrode optimized for longer deployments, accurate to 0.1 pH and expected to retain accuracy for approximately 90 days.

Like all glass-electrode sensors, the HC-pH is subject to changes in internal chemistry that cause sensor drift over time. As such, it benefits from frequent recalibration. While useful for coastal monitoring applications,




***(Left) Enhanced view of the second validation sample, with the difference between pH from each sensor and the pH of the validation sample (Δ). All sensors are within their expected initial accuracy specification. (Bottom) Enhanced view of the second and third temperature changes, demonstrating how the HydroCAT-EP's pH resolution changes only in 0.01 pH increments. This is due to the pH sensor's resolution—it is unable to resolve changes below 0.01 pH. The SeapHOx is able to resolve very small changes in pH, producing a smooth line as pH drops.***






***A two-week time series of pH from a Deep SeapHOx V2 and Shallow SeaFET V1, deployed at Shilshole Marina in Seattle, Washington, October 2017. The black line is the pH from the Deep SeapHOx V2. The blue and red lines are the predicted pH from the external and internal reference of the Shallow SeaFET V1, respectively. Green represents the pH bottle samples.***

frequent recalibration is often unfeasible for long-term, open-ocean deployments where equipment is largely inaccessible and accuracy is paramount. Accuracy of the glass-electrode pH technology is often insufficient for ocean acidification research.

**The Bath Test**

A SeapHOx V2 and HydroCAT-EP were deployed simultaneously in a test bath in Sea-Bird Scientific's facility in Bellevue, Washington, February/March 2018. The bath contained clean, natural seawater from Hawaii and a chiller for temperature control.

At roughly 24-hr. periods, the temperature was increased to stimulate slight changes in pH. Salinity remained stable at approximately 36.63 to 36.90 psu.

To determine sensor accuracy, four pH validation samples were collected before each temperature change using standard pH indicator dye spectrophotometry (with an accuracy of ±0.01 pH).

The SeapHOx equilibrated to the test bath for 72 hr. prior to the experiment for optimal data quality and the HydroCAT-EP's pH sensor was calibrated before entering the bath.

**Accuracy**

As expected, the internal pH and external pH from the SeapHOx V2 were both significantly more accurate than the HydroCAT-EP. The SeapHOx V2 measured an average difference from the validation samples of 0.0108 pH (external) and 0.0253 pH (internal)—well within the rated accuracy spec of 0.05 pH—while the HydroCAT-EP retained an average difference of 0.062 pH from the validation samples (within the accuracy spec of 0.1 pH).

The improved accuracy of ISFET-based pH sensors is important for several applications, including ocean acidification research. Previous research that required accuracy finer than 0.1 pH generally relied on spectrophotometer analysis of water samples or glass electrodes that are extremely well designed and maintained. While spectrophotometer analysis still provides the greatest accuracy, reliance on analytical chemistry yields sampling challenges and lacks the speed and convenience of an in-situ sensor.

**Resolution**

Superior resolution from the SeapHOx V2 was immediately evident; it was capable of tracking minor changes within 0.002 pH, producing a smooth line as pH changed in the test bath. The HydroCAT-EP's pH sensor could only resolve changes of 0.01 pH, resulting in "stepwise" changes in pH data.

The resolution of the HydroCAT-EP's pH sensor is typical of glass-electrode pH sensors. Better resolution has obvious advantages for tracking ocean acidification, especially in deep-ocean environments where pH changes may be relatively small yet important to track.

**Test Bath Conclusion**

Overall, both the ISFET and glass-electrode pH sensors performed as expected in the test bath, with the ISFET achieving approximately three times better accuracy and five times better resolution than the glass electrode in a controlled seawater bath. However, as mentioned earlier, a comparison in a stable bath is not a strong representation of how each sensor will perform in the field. Rather, it verifies that each instrument is meeting its expected accuracy and resolution, and the SeapHOx V2 specs are indeed superior to the glass-bulb electrode on the HydroCAT-EP.

**Field Deployment**

In October 2017, Sea-Bird Scientific deployed a Deep SeapHOx V2 in Shilshole Bay Marina in Seattle, Washington. To benchmark the performance of the Deep SeapHOx V2, a Shallow SeaFET V1 was deployed simultaneously, plumbed to the exhaust outlet of the Deep SeapHOx V2 to ensure the instruments sampled the same parcel of water. Bottle samples were taken approximately twice a week, and the pH was measured using standard seawater pH spectrophotometric methods. The instruments recorded two weeks of data and then were returned to Sea-Bird for data analysis.

The resulting accuracy of the Deep SeapHOx V2 was found to be 0.0077 pH after salinity corrections, which was at least two times better than the Shallow SeaFET V1 and five times better than the current accuracy specification of 0.050 pH. After characterization and validation at Sea-Bird, the Deep SeapHOx V2 was redeployed in November 2017 for one week, with bottle samples at the beginning and end of this deployment. The resulting accuracy of the Deep SeapHOx V2 was found to be 0.0072 pH, approximately the same as the previous deployment.

This result demonstrates the excellent reproducibility of the new Deep SeapHOx V2. After the deployment, the Deep SeapHOx V2 performance was evaluated at Sea-Bird in seawater test baths. The post-field deployment accuracy of the instrument was found to be 0.0021 pH, three times better than the field performance.

The culmination of the results from these deployments demonstrates the improved accuracy of the Deep SeapHOx V2 in the field. **ST**

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