FIELD PERFORMANCE OF AN ISFET BASED PROFILING PH SENSOR

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Introduction
Project Goal: Assess the field performance of an ISFET based Profiling pH Sensor for use with shipboard CTDs, like SBS 25S and SBS 5.

- The Profiling pH Sensor is a device based on a board and firmware from the SeaFET V2 and the hardware was modified from the SBS 39.
- The Profiling pH Sensor was calibrated using the standard calibration methods developed by Sea-Bird Electronics for their ISFET pH sensor line.
- The evaluation was performed in May 2019 during the Central California Currents, pH, and Oxygen (CICO) research cruise, operated by MBARI.

The predicted pH values from the sea were validated against bottle samples measured using spectrophotometry.

Why is this important?
Historically, ocean pH on a shipboard CTD cast was either measured using spectrophotometry or with a glass electrode. Spectrophotometry using HCl is the gold standard to measure seawater pH, but this method is expensive, labor intensive, and can only be measured at depths where bottle samples were taken. This greatly reduces the pH data density obtained from a given cast. The glass electrode can provide more data density when used in conjunction with a CTD, but suffers from depth limitations (<1200m), calibration drift, offsets caused by undetermined local ion functions, and interferences. However, with the introduction of robust and stable ISFET pH sensors for use in ocean applications, a paradigm shift has occurred to acquire reliable high density pH data has occurred. Due to this technological advancement, pH is beginning to be recognized as critical for the understanding of long and short time scale biological productivity, food chain cycles, and carbon fluxes.

Technology:
Sensor was designed around existing SBE technology:
- Sensor: Deep ISFET pH sensor sub-assemblies
- Board: SeaFET V2 Board Set
- Housing: SBS 3 Ti Housing (12 in length by 2 in diameter)

Integrating with current SBE shipboard profiling CTDs was made possible by modifying the SeaFET V2 Firmware:
- Enabled DAC to take samples at 1Hz by optimizing board level sampling methods and reducing number of variables recorded (only pH, Temp, and Humidity are load values).
- Enabled DAC to output in analog mode 0-2.5V.
- Created transfer function from 12-bit counts to V (V) to pH data into integrated data stream from the CTD, making data analysis easier and reducing the barrier of entry to scientists who want shipboard profiling pH data.

Sensing Mechanism Basics:
The ISFET is a type of MOSFET (Fig. 2).

- The gate of an ISFET acts like a micron-sized electrode and selects to the anode of the ion, here the pH.
- Current (K) is drawn from the ISFET via pH and the counter electrode voltage, which creates a feedback loop.
- The anode is maintained between 7 and 9, to SBS Ti Ti bias for data collection.
- When the gate is removed, and the voltage is driven over to a pH.

Experimental Setup
The Profiling pH Sensor was installed next to the SBS 9 on the lower section of the canister water sampler on the RV Rachel Carson operated by MBARI, shown in Figure 3A. Integration with the CTD package was achieved by using a wet pluggable Y-cable with the distal section connected to one of the SBS 5% analog in channels (Vdc). The proximal Y sections were split between the titanium ST pump and the titanium Profiling pH Sensor. A trap was constructed from two pieces of black tubing, one connected to the ST pump outlet, and the titanium Profiling pH sensor inlet. This shows the pH response of the Profiling pH Sensor during 30 casts performed during the CICO research cruise with depth ranging from 3000m to 500m against pressure.

Calculating pH

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pH = -\log[H^+]
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- Khs is the potential that forms on the reference electrode when the two half cells are combined. It is proportional to pH and is the signal that is measured.
- Ck is the chloride concentration and is calculated from salinity.
- Vref is the activity of H2O and is calculated from salinity and temperature.
- Vref is calculated using temperature and pressure calibration coefficients.
- pOH can be calculated from Vref with an H2O temperature, pressure, and salinity.

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\text{pH Sensor Calibration}
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- Note, the last term compensation for the proportionality of seawater and is set to zero for calibration in H2O.

Results
The evaluation of the Profiling pH Sensor was performed as part of the research cruise (CICO) operated by MBARI off the continental shelf of central California. This research cruise’s purpose was to validate the in situ calibration performance of their pH enabled glider (also using SBS pH sensor technology). During this cruise 33 casts were performed with depths ranging from 200m to 500m with +300 bottle samples taken to be analysed by spectrophotometry. Figure 3C shows the response of the Profiling pH Sensor during 30 casts performed during the CICO research cruise. Two casts were removed due to human sampling errors. The repeat performance of the Profiling pH Sensor is exceptional in the thermocline (500m). While hysteresis is observed between the ascending and descending cast in the lower depths (300-1200m). This hysteresis is theorized to be an artifact of osmotic/electric response of the ISFET die. Overall, the performance of the Profiling pH Sensor was excellent and work is being performed to mature this sensor into a future product.

Accuracy Performance
- The accuracy of the Profiling pH Sensor was assessed against bottle samples at each cast during the CICO research cruise. The pH of these bottle samples were evaluated with a spectrophotometer. Figure 4 shows the distribution of the pH predicted by the Profiling pH Sensor and the pH measured from the bottle samples taken from the 30 casts with surface outliers removed. While the sensor remains within SeaFET V2 specification (+0.05 pH) through the entire cruise. This drift could be from many sources, but filtering is the most probable cause. The sensor was not protected from fouling before being filtered between cast and the sensor showed evidence of fouling when returned to SES for evaluation. SES is working on new methods to mitigate fouling in future field evaluations.

Conclusions
The initial field tests of the Profiling pH Sensor have demonstrated that it is a stable and accurate pH sensor for shipboard ocean acidification monitoring. These field tests have also laid the foundation to establish the Profiling pH Sensor as an essential tool for understanding one of the critical parameters that controls many of the biological and chemical cycles in our ocean. Currently, Sea-Bird (Senors and systems) is in conjunction with the MBARI Chemical Sensor Group are working closely to evaluate this sensor's analytical performance in the hopes of maturing it into a future product.

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References:
- Johnson et al, Deep-Sea DuneFET: A Pressure Tolerant pH Sensor

Fig. 1: a) A picture of the SBS 3 Ti, B) Shows the difference between the Profiling pH Sensor and the spectrophotometric pH solution in a 1:1000 dilution, (C) Shows the pH response of the Profiling pH Sensor during 30 casts performed during the CICO research cruise with depth ranging from 3000m to 500m against pressure.

Fig. 2: Schematic representation of the ISFET, counter electrode, reference electrode and operating components.