A Robust and Reliable ISFET Sensor for Measuring pH in the Deep Ocean

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1. ISFET is sensitive to Hydrogen Ion Concentration

2. CO2 is absorbed by the water and is converted to Hydrogen Ions

3. A Reference Voltage proportional to the H+ concentration is generated

4. To measure pH, we need the following:

   - $K_0$ [Standard Seawater Correction]
   - $K_2$ [Temperature Correction]
   - $f(p)$ [Pressure Correction]

The pH measurement equation is:

$$V_{rs} \propto [H^+]$$

Pressures, Temperature, and Salinity are measured and applied to the above equation along with $K_0$, $K_2$, and $f(p)$ to determine pH.
**pH Sensor Calibration**

**Interlaboratory Comparisons**

**SBE vs MBARI**

**Overall K2 Run-2-Run Results**
- $k_2 = -1.067E-3 \pm 6.773E-6$ V/C ($\pm0.1$ mPh/C)
- $k_0 = -1.3939\pm0.0056$ V

**Overall K0 Run-2-Run Results**
- No inflection at low pressure
- Good Correlation between sites

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*Spread in data is due to pressure response.*
Accuracy of SBS pH Reference Measurements

In the summer 2017 SBS participated in the 2017 Interlaboratory Comparison of CO2 Measurements lead by Andrew Dickson Group at Scripps.

All SBS samples were measured using standard cuvette based pH spectrophotometry methods utilizing purified m-cresol dye at 25C.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Scripps Measured pH</th>
<th>Sea-bird Measured pH</th>
<th>Sea-Bird pH - Scripps pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Scale, 25C</td>
<td>Total Scale, 25C</td>
<td>Total Scale, 25C</td>
</tr>
<tr>
<td>162</td>
<td>7.910</td>
<td>7.9031</td>
<td>-0.007</td>
</tr>
<tr>
<td>Std Dev</td>
<td>0.0005</td>
<td>0.0018</td>
<td></td>
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</tbody>
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<tr>
<td>164</td>
<td>7.5407</td>
<td>7.5463</td>
<td>0.0056</td>
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<tr>
<td>Std Dev</td>
<td>0.001</td>
<td>0.00085</td>
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Precision <0.0015 pH  Accuracy <0.006 pH

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Accuracy of pH Sensor in the Field

Experimental Design:

- A SeapHOxV2 (130) was deployed for 6 weeks
- The instrument was moored at a depth of 3.6 meters at the end of a pier within the marina
- pH validation bottle sample will be taken twice per week and measured using spectrophotometry at SBS

RMSEP = 0.015 pH
Accuracy specification is 0.050 pH
Results: HOT Data
pH Prototype Floats

Accuracy of the pH Sensor
• Our second prototype pH float was deployed off the eastern side of the big island in May 2017
• The float profiled daily and weekly
• When the pH is compared to the HOT series and PMEL bottle data from the Xprize, good correlation is observed
  — Similar accuracy performance to prototype pH Float 1 is observed

Reproducibility of pH Sensor
• Three prototype pH floats deployed at approximately the same location off the coast of Hawaii over a 3 years
• Correlation between the three floats at depths below 300m is remarkable
  — Reproducibility of the Float pH data!!
  — pH stability of the deep water surrounding the Hawaii islands!!
The pH at 2000m can be used to assess sensor drift
- At this depth pH should remain relatively constant

The stability of the pH sensor is better than 0.005 pH over a 9 month deployment.

An abruptlyed change in pH and STD pH is observed between profile 58-60
- This abrupt offset is due to the float moving from the shores of the Hawaiian Islands to much deeper Pacific Ocean that surround the island chain