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

Todd Martz
Scripps Institution of Oceanography

Presented to C-CAN
Ocean Acidification Roundtable Discussion
31 March 2015
Topics

• Overview of recent progress toward documenting best practices: Bresnahan et al. (2014); Martz, McLaughlin, Weisberg (2015)
• Summary of OA technology
Outline (will loosely follow protocols)

Recommended Protocols

1. Preceding deployment, operate sensors in natural seawater until initial sensor drift due to conditioning ends (approx. 5-10 days), with daily samples in order to observe the pre-deployment conditioning period; repeat this process following deployment for validation. Power the ISFET continuously during this period.

2. Collect a careful shore-side calibration point based on discrete sample(s) following the conditioning period.

3. Store sensors in seawater between deployments.

4. Prevent biofouling as permitted, especially within the euphotic zone.
   i. Utilize an actively flushed flow scheme that minimizes light.
   ii. Incorporate a Sea-Bird instrument with tributyltin plugs into the flow scheme.
   iii. Wrap sensor housings with tape (McMaster-Carr P/N 6029T98) and paint with EP-8N1 or similar antifouling paint.
   iv. When using passively flushed SeaFET sensors, incorporate a 70:30 Cu-Ni alloy tube into a flow stream around DuraFet and ISE.

5. When practical, take frequent discrete samples alongside a sensor throughout a deployment in order to establish an error estimate in the sensor data. At minimum collect one bottle sample alongside an operating deployed sensor.

6. Deploy co-located, independent sensors such as redundant pH, pCO₂, and O₂ sensors.

7. Estimate pH from regional empirical and/or thermodynamic relationships.

8. Assess and control pH sensor data quality with discrete pH and estimated pH using the following plots:
   i. time-series anomaly to first identify and then eliminate periods of ostensible sensor conditioning, drift, and failure.
   ii. property-property to examine agreement between sensor pH and an independent reference pH (through the intercept, c₀, & slope, c₁). Property-property plots are useful for quality assessment; that is, if c₀ is significantly different from 0 and/or c₁ from 1 indicates bias in the sensor and/or reference pH used for comparison.

9. Apply a single calibration point, chosen to minimize the anomaly relative to a trustworthy reference pH throughout the deployment. In particular, it is not recommended to force sensor data to agree with multiple individual bottle samples as this imparts sampling error to the sensor time series.

10. Establish an error envelope for the sensor time-series. The accuracy of the sensor time-series can be no better than the reference to which it is calibrated or validated.
Background

- **2007**: Durafet operated underway adjacent pCO$_2$ on MBARI cruise.
- **2008-2009**: SeaFET developed at MBARI, refined at SIO, commercialized by Satlantic.
- **2010**: SeapHOx developed at SIO to expand measurement suite and extend the duration of moored deployments.
- **2014**: WavepHOx designed for surface mapping in specialized applications (Waveglider and Stand Up Paddleboards).
Other groups are now building their own Durafet-based pH data loggers independent of the SeaFET family of sensors. Hundreds operating in the various (overlapping) sensor networks.

Figure from G. Hofmann

http://omegas.science.oregonstate.edu/
NOAA has installed several SIO SeaFETs configured as underway systems for repeat hydrography cruises.

The Ocean Acidification Environmental Laboratory (OAEL) at U. Washington Friday Harbor operates 12 Durafet sensors in mesocosms.

(photo: http://electronicbiology.org)
Underway multi-parameter measurement systems

- Some Burkelator systems have integrated Durafet sensors, allowing measurement of 3 variables (pH, pCO$_2$, TCO$_2$)
- CalCOFI and CCE-LTER now have a pH-pCO$_2$ system (below).

**pH + pCO$_2$ system for CalCOFI**

**Left**
(UDA Display)

**Front**
(Electronics: UPS, UDA, SUPER-CO$_2$, laptop)

**Right**
(Wet components: Shower head equilibrator
Sea Bird 37 Thermosalinograph)

**Back**
(Wet components: Honeywell Conductivity Sensor & Durafet pH Sensor)

Photos: Kylee Chang
Underway multi-parameter measurement systems

Martz et al. (2010)
Commercially-available instruments designed to measure seawater CO$_2$ system variables, categorized by level of autonomy. Although custom systems have been developed for all cases shown, only commercially-available instruments are displayed here; the criteria for inclusion being a manufacturer/vendor website with purchasing information as of March 2015.

<table>
<thead>
<tr>
<th>DIC</th>
<th>UNDERWAY</th>
<th>AUTONOMOUS</th>
</tr>
</thead>
</table>
| VINDTA 3D/3C  
Marianda | AS-C3  
APOLLO SCITECH |  
HydroFIA  
Contros |
| AIRICA  
Marianda |  
 |  
 |
| VINDTA 3S/3C  
Marianda | AS-ALK2  
APOLLO SCITECH |  
 |  
 |
| TA |  
 |  
 |
| pH | AFT-pH  
Sunburst Sensors | SAMI-pH  
Sunburst Sensors | SeaFET  
Satlantic |
| pCO$_2$ |  
 |  
 |
| pCO$_2$ | GO 8050  
General Oceanics | MOG 701  
Kimoto | Seaology  
Battelle |
|  
 | SuperCO2  
Sunburst Sensors | OceanPack  
SubCtech |  
 |
|  
 | AFT-CO2  
Sunburst Sensors | AS-P2  
APOLLO SCITECH | HydroC  
Contros |
|  
 | SUNDANS  
Marianda | OceanPack  
SubCtech |  
 |
|  
 |  
 | C-Sense  
Turner Designs |  
 |

$^1$Benchtop: discrete bottle, auto-assisted.  
$^2$Underway: flow-thru, automated, externally powered.  
$^3$Autonomous: automated, internally powered, in situ.

Martz et al. (2015)
2014 summer workshop on pH sensor best practices

Venue: Scripps Institution of Oceanography
Dates: August 4-8, 2014
Hosts: Todd Martz, Andrew Dickson, Gretchen Hofmann

Topics covered will include: (1) Introduction to seawater pH; (2) Introduction to pH sensors (theory of operation, principles of calibration); (3) Practical deployment of autonomous sensors; (4) Collection and analysis of discrete seawater samples for sensor validation; (5) Use of measurements on discrete samples for calibration and quality control of in situ pH sensor data; (6) Assessment of the overall uncertainty of resulting seawater pH measurements.
1. Preceding deployment, operate sensors in natural seawater until initial sensor drift due to conditioning ends (approx. 5-10 days), with daily samples in order to observe the pre-deployment conditioning period; repeat this process following deployment for validation. Power the ISFET continuously during this period.

2. Collect a careful shore-side calibration point based on discrete sample(s) following the conditioning period.

3. Store sensors in seawater between deployments.

4. Prevent biofouling as permitted, especially within the euphotic zone.
   i. Utilize an actively flushed flow scheme that minimizes light.
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5. When practical, take frequent discrete samples alongside a sensor throughout a deployment in order to establish an error estimate in the sensor data. At minimum collect one bottle sample alongside an operating deployed sensor.

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7. Estimate pH from regional empirical and/or thermodynamic relationships.

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Green = pH_{O_2}^{est}
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Complete L20 pH anomaly time-series beginning 12-Jul-2010: the lines represent anomaly relative to the stable SeapHOx pH\textsuperscript{INT}. Shown are four independent sensors: SeaFET0, SeaFET1, SeaFET2, and a SAMI-pH. A SAMI-pH failure on day 2 was fixed after which it operated until day 30. pH\textsuperscript{EXT} values for the three SeaFETs overlap their corresponding pH\textsuperscript{INT} time-series at this resolution and are therefore not displayed.
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![Graphs showing electrode conditioning, biofouling, electrode drift, and discrete sampling mismatch over time](image-url)
How well should bottle samples agree with in situ sensors?

Common metrics used to answer this question include relative accuracy and the standard deviation of the residual plot (same as RMSE).

Relative accuracy reflects overall quality of calibration; useful for applying corrections in post-processing.

\[-0.003 \pm 0.004 \text{ (n = 16)}\]

RMSE reflects sample collection errors (spatiotemporal mismatch) plus bottle measurement errors.
How well should bottle samples agree with in situ sensors?

<table>
<thead>
<tr>
<th>RMSE</th>
<th>description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>±0.0007 (n = 6)</td>
<td>Shipboard underway vs. mooring - Not from bottles. (pH derived from pCO$_2$).</td>
<td>Friederich et al (1995)</td>
</tr>
<tr>
<td>±0.002 (n = 12)</td>
<td>small boat collecting samples at a near shore mooring (L20, previous slides)</td>
<td>Bresnahan et al. (2014)</td>
</tr>
<tr>
<td>±0.004 (n = 16)</td>
<td>SAMI pH in a river</td>
<td>Martz et al. (2003)</td>
</tr>
<tr>
<td>±0.008 (n = 86)</td>
<td>SAMI pH at an ocean reef</td>
<td>Cullison et al. (2012)</td>
</tr>
<tr>
<td>±0.007 (n = 107)</td>
<td>ACT test for SeaFET at CBL</td>
<td>ACT (2015)</td>
</tr>
<tr>
<td>±0.029 (n = 84)</td>
<td>ACT test for SeaFET at MLML</td>
<td>ACT (2015)</td>
</tr>
<tr>
<td>±0.02-0.10</td>
<td>ACT test for various glass electrodes</td>
<td>ACT (2015)</td>
</tr>
</tbody>
</table>
How well can we expect to do when using bottle measurements to validate in situ sensors?

ACT results from MLML test for SAMI and SeaFET. ACT reports

SeaFET
-0.008 ± 0.029

SAMI
0.039 ± 0.003

0.03?
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Pressure

The commercial version of the Honeywell Durafet is not designed for pressure cycling (i.e. profiling applications).

Pressure is not addressed in the 10 recommended protocols, but might be summarized by the following:

**11. Operate Durafet-based sensors at a constant depth or pressure in the range 0 – 70 m (0 - 100psi).** Pressure cycling of the Durafet is not recommended due to sensor-specific, non-repeatable, hysteresis of the sensor response with pressure.
Salinity

- The SeaFET has not yet been characterized over the full salinity range (0 to >36).
- Therefore, calibration protocols for the sensor do not apply to freshwater.
- Existing data suggest that the present calibration protocol is adequate to a salinity of 30.
- For $S = 30-36$, when the sensor is properly functioning, the two pH signals agree to better than 0.005 (bottom figure at left). Therefore, we do not apply a salinity correction for the pH signal based on the internal reference in this salinity range.
- As seen here, it is critical to correct the external reference signal (using established thermodynamic relationships).
- If left uncorrected, $\text{pH}_{\text{ext}}$ error will be: 0.013 pH Salinity$^{-1}$. 
1.3.2 The total hydrogen ion concentration scale

the total hydrogen ion scale for seawater be defined as

\[ [H^+] = [H^+]_T (1 + S_T / K'_S) \]  \hspace{1cm} (1.33)

where \( S_T \) is the total amount of sulphate ion present in the seawater and this is the current definition. At pH > 5, equations (1.32) and (1.33) are essentially equivalent.

1.3.5 Other pH scales (that are not recommended for use)

Two other pH scales have been used for seawater measurements in the past:

1. The so-called NBS scale (more correctly now referred to as the IUPAC scale) was based originally
   on recommendations and primary buffer standards from the US National Bureau of Standards (NBS),
   renamed the National Institute of Standards and Technology in 1988.

2. The seawater pH scale (SWS) which includes fluoride ion in the ionic medium (in addition to sulphate)
   and thus includes the species HF in the definition of the SWS hydrogen ion concentration:

\[ [H^+]_{SWS} = [H^+]_F + [HSO_4^-] + [HF] \]  \hspace{1cm} (1.40)

or, more strictly,

\[ [H^+]_{SWS} = [H^+]_F (1 + S_T / K'_S + F_T / K'_F) \]  \hspace{1cm} (1.41)

where \( F_T \) is the total concentration of fluoride ion in the seawater, and \( K'_F \) is the dissociation constant
for HF with hydrogen ion concentration expressed as the free concentration.
I decided to include this note because most publications explain pH scales using the minimum number of equations and usually as concentration rather than $-\log(\text{concentration})$ (e.g. previous page). This often leads to confusion for non experts when converting among the scales because it requires multiple arithmetic steps. The equations below explicitly express each scale in terms of one other scale, which is convenient for programmers and engineers not familiar with chemical terminology.

Note 1: pH Scale

For data reporting purposes a pH scale must be specified. The pH is commonly calculated on the free, total (tot), and seawater (SWS) scales. A pH value, reported on a particular scale is converted to another scale as follows:

\[
\begin{align*}
\text{pH}_{\text{tot}} &= \text{pH}_{\text{free}} - \log \left( 1 + \frac{S_T}{K_S} \right) \\
\text{pH}_{\text{tot}} &= \text{pH}_{\text{SWS}} - \log \left( 1 + \frac{S_T}{K_S} \right) + \log \left( 1 + \frac{S_T}{K_S} + \frac{F_T}{K_F} \right) \\
\text{pH}_{\text{SWS}} &= \text{pH}_{\text{free}} - \log \left( 1 + \frac{S_T}{K_S} + \frac{F_T}{K_F} \right) \\
\text{pH}_{\text{SWS}} &= \text{pH}_{\text{tot}} + \log \left( 1 + \frac{S_T}{K_S} \right) - \log \left( 1 + \frac{S_T}{K_S} + \frac{F_T}{K_F} \right) \\
\text{pH}_{\text{free}} &= \text{pH}_{\text{tot}} + \log \left( 1 + \frac{S_T}{K_S} \right) \\
\text{pH}_{\text{free}} &= \text{pH}_{\text{SWS}} + \log \left( 1 + \frac{S_T}{K_S} + \frac{F_T}{K_F} \right)
\end{align*}
\]

where $S_T$, $F_T$, $K_S$, $K_F$ are functions of temperature and salinity. Further details on these calculations may be found in (Riebesell et al., 2010) and recommended software programs include CO2SYS (Lewis and Wallace, 1998) and CO2calc (Robbins et al., 2010)

For ease of comparability, C-CAN recommends that all pH data be reported on the total scale.
Note 2: Data processing functions for sensors based on the Honeywell Durafet

The functions below are provided for users with access to raw voltages from Durafet-based sensors. Durafet users without access to raw voltages may still follow the recommended protocols listed above, by processing all data in the pH domain.

**getDurafetTemp.m** returns temperature (tempC, °C) from the Durafet’s thermistor voltage (VTherm, V) when an independent conductivity/temperature sensor is not available. Note that Durafet thermistors are accurate to ±0.5 °C, making it necessary to perform a calibration to a known reference temperature in order to retrieve an offset value (TCOffset, °C).

```matlab
function tempC = getDurafetTemp(VTherm, TCOffset)
```

**pHCalib.m** has inputs of discrete $E_{\text{INT}}$ (V), $E_{\text{EXT}}$ (V), pH, temperature (°C), and salinity at time of calibration and returns the calibration coefficients $E_{\text{INT,25}}^*$ and $E_{\text{EXT,25}}^*$.

```matlab
function calib = pHCalib(calEint, calEext, calpH, calT, calsal)
```

**pHCalc.m** uses the calibration coefficients to calculate pH given the full $E_{\text{INT}}$, $E_{\text{EXT}}$, temperature, and salinity time-series. Note that the term $E_0$ written in the code below is referred to as $E^*$ in text and what is here written as $E$ (e.g., $E_{\text{INT}}$, $E_{\text{EXT}}$) has often been referred to in its engineering units as V ($V_{\text{INT}}$, $V_{\text{EXT}}$).

```matlab
function calc = pHCalc(Eint, Eext, E0int25, E0ext25, tempC, salt)
```