In-situ calibration of Oxygen Optodes in the Southeast Pacific Oxygen Minimum Zone

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In-situ calibration:
Using the field measurements in combination with “known” environmental conditions to improve the calibration
Introduction Oxygen Optode

Characteristic:

- Long term stability
- Non-invasive (no oxygen consumption)
- NOT made for oceanographers seeking for decadal change of ~ 1 µmol/kg...
Introduction Oxygen Optode

Principle of operation:

- Oxygen luminescence quenching
- Foil is excited with a blue-green light → The phase shift of returning red luminescence is proportional to oxygen
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- Observed quantity:
  - $D_{\text{phase}} = \text{difference (Bphase / Rphase)}$
- where
  - Bphase – phase obtained with blue-green light
  - Rphase – phase obtained with red light (often set 0)
Introduction Oxygen Optode

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Introduction Oxygen Optode

From the Phase shift to oxygen:

- AADI purchases sensing foil from PreSense Incorporation (good for 100 optodes)
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- The sensing foil batch (good for 100 optodes) is “bulk” calibrated by finding an Dphase/oxygen relation which depends on temperature:
  - typically 5 temperatures (between 3° and 40°C) and 7 oxygen concentrations (0 to 400µmol/l)
Introduction Oxygen Optode

\[ [O_2] = C_0 + C_1 P + C_2 P^2 + C_3 P^3 + C_4 P^4 \]

where \( P = \text{Dphase} \) and each \( C \) is a 3\(^{rd}\) order polynom on temperature \( T \):

\[ C_x = C_{x,0} + C_{x,1} T + C_{x,2} T^2 + C_{x,3} T^3 \]

Results are reported in a data sheet that comes with each optode...
**Introduction Oxygen Optode**

### Calibration points and phase readings (degrees)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>3.04</th>
<th>10.78</th>
<th>20.35</th>
<th>30.00</th>
<th>39.56</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (hPa)</td>
<td>972.00</td>
<td>972.00</td>
<td>972.00</td>
<td>972.00</td>
<td>972.00</td>
</tr>
<tr>
<td>0.00</td>
<td>72.89</td>
<td>72.27</td>
<td>71.36</td>
<td>70.47</td>
<td>69.51</td>
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<tr>
<td>1.00</td>
<td>68.28</td>
<td>67.21</td>
<td>65.74</td>
<td>64.29</td>
<td>62.76</td>
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<tr>
<td>2.00</td>
<td>64.58</td>
<td>63.19</td>
<td>61.34</td>
<td>59.57</td>
<td>57.76</td>
</tr>
<tr>
<td>5.00</td>
<td>55.90</td>
<td>54.05</td>
<td>51.72</td>
<td>49.51</td>
<td>47.43</td>
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<tr>
<td>10.00</td>
<td>46.52</td>
<td>44.50</td>
<td>42.07</td>
<td>39.84</td>
<td>37.85</td>
</tr>
<tr>
<td>20.90</td>
<td>35.52</td>
<td>33.65</td>
<td>31.50</td>
<td>29.61</td>
<td>28.00</td>
</tr>
<tr>
<td>30.00</td>
<td>30.42</td>
<td>28.73</td>
<td>26.82</td>
<td>25.16</td>
<td>23.79</td>
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</table>

### Giving these coefficients

<table>
<thead>
<tr>
<th>Index</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0 Coefficient</td>
<td>4.60262E+03</td>
<td>-1.56352E+02</td>
<td>3.11002E+00</td>
<td>-2.63289E-02</td>
</tr>
<tr>
<td>C1 Coefficient</td>
<td>-2.56549E+02</td>
<td>7.84126E+00</td>
<td>-1.55660E-01</td>
<td>1.32344E-03</td>
</tr>
<tr>
<td>C2 Coefficient</td>
<td>5.79714E+00</td>
<td>-1.58265E-01</td>
<td>3.17570E-03</td>
<td>-2.71486E-05</td>
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<tr>
<td>C3 Coefficient</td>
<td>-6.10916E-02</td>
<td>1.48660E-03</td>
<td>-3.05830E-05</td>
<td>2.62173E-07</td>
</tr>
<tr>
<td>C4 Coefficient</td>
<td>2.46453E-04</td>
<td>-5.32422E-06</td>
<td>1.13945E-07</td>
<td>-9.73074E-10</td>
</tr>
</tbody>
</table>

Laboratory calibration

$C_{x,0, \ldots}$
Batch Calibration

- Example: Foil-batch no. 4804

Negative Oxygen...
Fine-tuning: Individual foil Calibration

- Two – point calibration for raw Dphase
  \( (1^{st} \text{ order polynom is derived}) \)

- Two – point calibration (see also Aanderaa manual)

  - \( O_2 = 0\% \)  \((\text{Temp. T1, pressure p1})\)
  - \( O_2 = 100\% \)  \((\text{Temp. T2, pressure p2})\)

for 0%: use sodium sulfite \((\text{Na}_2\text{SO}_3)\) to remove oxygen
for 100%: inject bubbles
Batch foil calibration + 2-point calibration

- $D\text{phase (corr)} = -7.4948 + 1.713 \times D\text{phase (raw)}$
Calibration problem

- Two-point calibration (0/100%) with only one temperature does not constrain well the correction
- Some laboratories calibrate the optode based on a range of temperature/oxygen/pressure situations
- Not always possible!! → in-situ calibration
Mission in the Southeast Pacific

- 20 days: Jan. 2009
- 185 profiles
- 560km section
Mission in the Southeast Pacific

- Observations in core of the oxygen minimum zone (150 to 500m depth range)
Mission in the Southeast Pacific

- Profiles:
  - Oxygen in Minimum <0
  - Hysteresis in gradient zone (oxycline)
Mission in the Southeast Pacific

- Profiles:
  - Oxygen in Minimum <0
  - Hysteresis in gradient zone (oxycline)
  - Optode temperature too slow → correct by using glider CTD temperature (& salinity)
Mission in the Southeast Pacific

- Good:
  two T/oxygen range with “known” concentration → OMZ~3µmol/l; surface=100% saturated
Optode data in “known” concentrations: OMZ (~ 3 mmol/l)

Batch foil calibration (2.8 - 3 µmol/l)

2-point lab & Batch foil calibration (2.8 to 3 µmol/l)

Observed (2.8 to 3 µmol/l)
Optode data in “known” concentrations

- Similar for 100% saturation

Phase Calibration at saturation Oxygen
Do a calibration

- Advantage of Pacific OMZ data: constant & known oxygen content over a wide temperature range → A robust least square fit is possible
- Different combinations of variables (T, S, p, O_2) in the constrained Dphase ranges (3µmol/l & 100%) are possible.
- We found a good overall agreement (Winkler & Optode) for a (p, T, T^2) fit.
Before & After

5th EGO Meeting
16. March 2011, Gran Canary, Spain
Before & After (with p, T, $T^2$ fit)
Recommendations

Before Deployment:

- Always record Dphase
- Do at least a 0% & 100% saturation calibration before deployment
- After 0% & 100% calibration:
  Read out ALL calibration from optode before glider deployment

Deployment:

- Sample 1 sec (SLOCUM glider software > V7.0)
- Record data (at least at some) up AND downcasts

After Deployment:

- Always use calibrated glider CTD temperature and salinity for conversion
  Dphase → Oxygen (µmol/l)
Thanks

In certain cases calibration is hopeless...
Manufacturer specification

Table A 2 Specifications for the Oxygen Optode 3830

<table>
<thead>
<tr>
<th></th>
<th>Channel1 Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂-Concentration</td>
<td>Air saturation</td>
</tr>
<tr>
<td>Measuring Range</td>
<td>0-500 μM³</td>
</tr>
<tr>
<td>Resolution</td>
<td>0 – 120%</td>
</tr>
<tr>
<td>Accuracy</td>
<td>&lt; 1 μM</td>
</tr>
<tr>
<td></td>
<td>0.4%</td>
</tr>
<tr>
<td></td>
<td>&lt; 8 μM or 5%⁴ whichever is greater</td>
</tr>
<tr>
<td></td>
<td>&lt; 5%⁴</td>
</tr>
<tr>
<td>Settling time (63%)</td>
<td>&lt; 25 sec</td>
</tr>
</tbody>
</table>