Oxygen measurements: why and when?

Anders Tengberg (anderste@chem.gu.se) Associate Professor at the University of Gothenburg and at the Chalmers University of Technology, Sweden, Scientific Advisor/Product Manager at Aanderaa since 1997.
Outline

9:00-10:30
• Why should you measure Oxygen ($O_2$)?
• How is $O_2$ related to other parameters?
• Are we measuring at the right frequencies?
• Methods to analyze and measure $O_2$

11:00-13:00
• What affects $O_2$ sensors/methods to evaluate performance?
• How good is Winkler titration?
• Field data, value of combined measurements
• Summary
• Practical Demonstration and Hands-On
Why should you measure Oxygen?
1. Most important parameter and “easy” to measure
2. Crucial for higher organisms (fish, bottom living)
3. Crucial for biological, chemical & geological processes
4. Oceanographic tracer
5. Climate related, geologically has $O_2$ been constant?

How is Oxygen related to other parameters?
1. Temperature: higher Temp less $O_2$
2. Salinity: higher Sal lower $O_2$
3. Currents: higher currents more turbulence/more mixing
4. pH/p$CO_2$: depends on process in $O_2$ rich conditions in general higher pH $\Rightarrow$ lower p$CO_2$ $\Rightarrow$ higher $O_2$
5. ChlA $\Rightarrow$ higher $O_2$; Turbidity $\Rightarrow$ lower $O_2$; CDOM $\Rightarrow$ lower $O_2$
6. Light $\Rightarrow$ higher $O_2$
Salinity derived Alkalinity

pCO$_2$ optode and O$_2$ optode at the depth of 12.6

Net primary production (NPP) rates during spring bloom
- In 2012: 1.79 g C m$^{-2}$
- In 2013: 2.10 g C m$^{-2}$
Combining sensors gives increased understanding

Redfield ratios
-C:O$_2$

Atamanchuk, Kononets, Thomas, Hovdenes, Tengberg and Hall (2015)
Continuous long-term observations of the carbonate system dynamics in the water column of a temperate fjord.
Journal of Marine Systems 148, 272–284
Optode post-check in lab, air-bubbled water

- 16. SalComp02 (above ref) \([\text{uM}]\)
- 17. SalComp02 (1.1 m) \([\text{uM}]\)
- 18. SalComp02 (0.9 m) \([\text{uM}]\)
- 19. SalComp02 (4.8 m) \([\text{uM}]\)

Averaging: 1
What affects $O_2$ concentration?

1. Salinity and Temperature (Garcia and Gordon, 1992, L&O)
2. Primary production & bubbles, surface waters $\sim 105\%$
3. Decomposition of organic matter
4. Chemical oxidation, mainly at the bottom
5. Air pressure, at surface
6. Hydrothermal vents, lower $O_2$

All sensors (electrochemical & optical) measure partial pressure ($PO_2$)

Outside the photic zone there is now known process that produce $O_2$
Natural variations, are we measuring at the right frequencies?

With weekly sampling maximal difference from one week to another was 9°C
The average difference was 1.5°C.
Estimated that global warming increase temp with about 0.06°C/year
Autonomous Planar Optode deployed on Mini Lander
Tools: Autonomous Benthic landers

Our landers:
- 250-300 deployments
- About 800 incubations
- Deployed at 5-5600 m
- 40 water samples
- 15-25 sensors
- 95 % success rate

Measured Fluxes
- Oxygen
- Total Carbonate
- Silicate
- Phosphate
- Nitrate+Nitrite
- Ammonium
- DOC
- Alkalinity
- pH
- Fe and Mn
- Turbidity
- pCO_2
For phosphate fluxes: Oxygen concentration more important than resuspension.
Ways to measure Oxygen in Water

1. Chemical: Winkler titration (Winkler, 1888)
   Accuracy: about 2%; Precision: about 0.5%

2. Electro-chemical: By sensors (Clark, 1959)
   Accuracy: absolute measurements difficult, needs frequent calibration.
   Precision: about 0.5%

3A Optical: By sensors (Klimant et al., 1995)
   Intensity based: Accuracy: absolute measurements difficult, needs frequent calibration.
   Precision: about 0.5%

3B. Optical: By sensors (Holst et al., 1995)
   Lifetime based: Accuracy: about 1 %;
   Precision: about 0.5 %
Summary

9:00-10:30
- Why should you measure Oxygen (O$_2$)?
  Crucial parameter
- How is O$_2$ related to other parameters?
  Related to most other parameters
- Are we measuring at the right frequencies?
  Nyquist criteria: sample at twice the frequency as changes occur
- Methods to analyze and measure O$_2$
  Winkler, Electrochemical sensors, Optical foil based sensors

11:00-13:00
- What affects O$_2$ sensors/methods to evaluate performance?
  - How good is Winkler titration?
  - Field data, value of combined measurements
- Summary
  - Practical Demonstration and Hands-On
Oxygen measurements: how?

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## Ways to measure Oxygen in Water

1. **Chemical: Winkler titration (Winkler, 1888)**  
   Accuracy: about 2%; Precision: about 0.5%

2. **Electro-chemical: By sensors (Clark, 1959)**  
   Accuracy: absolute  
   Precision: about 0.5%

3A **Optical: By sensors (Klimant et al., 1995)**  
   Intensity based: Accuracy: absolute  
   Precision: about 0.5%

3B **Optical: By sensors (Holst et al., 1995)**  
   Lifetime based: Accuracy: about 1%;  
   Precision: about 0.5%

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Careful with manufacturer specifications! Do they give field or lab specifications? Is response time for air or water? Is accuracy for the whole range of O2 Concentration and Temperature? Can they show data to sustain claimed accuracy/precision and response time? What about publications from independent sources?

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<tr>
<th>Manufacturer</th>
<th>Model</th>
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<td>YSI</td>
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Which Parameters will influence the response of an Electro-chemical sensor?

- $O_2$: Yes
- pH: No Effect
- Sal: Yes, cross-term
- Temp: Yes, cross-term
- Pres: Yes, not fully reversible
- Stirr: Yes
- Aging=drift: Yes, electrolyte & membrane decompose

Counts = $-142 + \text{Fug} \times 716 + \text{Temp} \times 7.8 + \text{Stir} \times 1.9 + \text{Temp} \times \text{Fug} \times 27.8$

Fug = Fugacity = $O_2$ sample/$O_2$ saturation

Every sensor individual
Optode Measuring Principle
Based on Fluorescence Quenching
Detection of lifetime

**Note:** Oxygen Optodes are measuring partial pressure of oxygen.
- 100 % in sea water at 10°C and 35 ppt corresponds to 282 µM = 9.0 mg/l = 6.3 ml/l
- 100 % in fresh water at 10°C corresponds to 353 µM = 11.3 mg/l = 7.9 ml/l
→ **If salinity variable it should be measured and compensated for**

- **Fluorescence Quenching.** High O$_2$ gives shorter lifetime and lower intensity

Literature:
- Dynamic Fluorescence Quenching. Kautsky, 1939
Which Parameters will influence the response of an Oxygen Optode?

- $O_2$: Yes
- pH: No Effect
- Sal: Yes, simple formula
- Temp: No Effect
- Pres: Yes, about 4% per 1000 m, fully reversible
- Stirr: No Effect
- Aging=drift: No Effect

\[ y = 0.9956x + 2.4323 \quad R^2 = 0.9876 \]
\[ y = 0.9846x + 1.1039 \quad R^2 = 0.994 \]
\[ y = 1.0101x + 2.4262 \quad R^2 = 0.996 \]

Long term data from 69 Optodes on Argo floats


Conclusion: Optodes stable but gave lower values
Reason: Foils bleach in ambient light (especially fluorescent) and if sampling is done at high frequency

When storing sensors use black protection cap!
In air surface drift optode data from float 4900494

O₂ concentration (µM)

O₂ saturation (%)

Air temperature (°C)

Denis Gilbert et al., Argo Science Workshop 3, Hangzhou, China, March 27, 2009
Optode drift in relation to number of measurements and pre-treatment (with burn-in) or not

All Multipoint calibrated Foils are Pre-matured ➤ Better Accuracy
➤ Better Stability Drift < 0.15 µM/100,000 samples
If not mechanically damaged foils get better over time
Multipoint Calibration System

- Gas injection by use of mass flow controllers
- Automatic System 40 point calibration & 20 point subsequent verification
- Operational since August 2012
- 3 parallel reference optodes in system
- Automatic Winkler system from SI Analytics for frequent verification
- International inter-comparison of calibration facilities
- Absolute accuracy better than 1.5%/±2.5 µM
Validation

Accuracy over entire range of O₂ and Temp: ±2.5 µM or ±1.5%. Field resolution: ±0.2 µM

Multipoint Calibration + red LED referencing gives the highest accuracy on the market
Tools: Autonomous Benthic landers

Our landers:
- 250-300 deployments
- About 800 incubations
- Deployed at 5-5600 m
- 40 water samples
- 15-25 sensors
- 95% success rate

Measured Fluxes
- Oxygen
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- pCO₂
Plastic/Polycarbonate incubators dissolve high amounts of oxygen. Have to ventilated for hours prior to incubation in Hypoxic environments → Artifacts
Plastic Materials have “memory” effects on O2. Plastic materials should be avoided for profiling and if high accuracy/precision is needed.

Koljoe fjord observatory

- Installed April 2011
- Real time: http://koljofjord.cmb.gu.se
- 40-50 sensors
- Quality control by monthly sampling (SMHI)

Node cable for N1 (1)
>100 m, kevlar core, 10 pin Subcon
>2*RS com
>2*Power

Main Cable (Marum)
>500 m, armoured used ROV
>4 optical fibre
>3 copper lines for power
>Power max 200 W (160 V)
>Two way communication
>Ice protected at surface with tube

Distance 150 m
Examples of data: 18 months oxygen recordings, with monthly reference data from SMHI
About 1% O2 decrease in 11 months

Airpressure: +0.9%
Optode SG 137: +0.6%
Optode SG 136: +0.2%

Conclusion:
O2 decrease 0.3-0.7%
Oxygen Optodes
Examples of Scientific Papers


Gas Exchange Chamber
Sommer et al (2008)

Cabled CTD

Gliders

Incubators


Ferry boxes
Hydes et al (2009)

Argo floats
Johnson et al (2010, Nature)
Fiedler et al (2013)
Takeshita et al (2013)

Moorings

Boys
Jannash et al (2008), Bushinsky & Emerson (2013)

Gradients

Rivers/Hydrology/Hyporheic

Oxygen Optodes

Examples of Scientific Papers

- Sommer et al (2008)
- Jannash et al (2008), Bushinsky & Emerson (2013)
- Hydes et al (2009)
- Boys
- McGillis et al (2011)

- Long term stable
- Ferris boxes
- No O₂ consumption & Robust
- Argo floats
- Not freezing sensitive
- Gas Exchange Chamber
- Not sensitive to H₂S and most other chemicals
- Cabled CTD
- High accuracy & low noise
- Gliders
- Moorings
- No pressure hysteresis
- Boys
- Lower fouling sensitivity
- Rivers/Hydrology/Hyporheic

- Sommer et al (2008)
- Jannash et al (2008), Bushinsky & Emerson (2013)
- Hydes et al (2009)
- Boys
- McGillis et al (2011)
Contribution of the Elephant Seal to monitor the oxygen content of the Southern Ocean

Christophe Guinet, CEBC-CNRS
Mean Diving Depth: 500m
Mean Diving Duration: 21 mn
Mean Surface Interval: 3 mn
Mean number of dives per day: 60
0-2 km between dives
Summary

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• Why should you measure Oxygen (O$_2$)? Crucial parameter
• How is O$_2$ related to other parameters? Related to most other parameters
• Are we measuring at the right frequencies? Nyquist criteria: sample at twice the frequency as changes occur
• Methods to analyze and measure O$_2$ Winkler, Electrochemical sensors, Optical foil based sensors

11:00-13:00
• What affects O$_2$ sensors/methods to evaluate performance? Multivariate methods good tool for evaluation
• How good is Winkler titration? Depends on person, contamination at low O$_2$ from plastic bottles
• Field data, value of combined measurements Combined measurements gives better certainty, O$_2$ should always be combined with pCO$_2$, pH, ChlA
• Practical Demonstration and Hands-On