

O₂ optodes

Autonomous platforms (Argo and gliders): known issues, recommendations for implementation and qualification



LOW

Henry Bittig

IOW, Baltic Sea Research Institute Warnemünde

Workshop on Interoperability Technologies and Best Practices in Environmental Monitoring - Brest, 10-12 October 2018

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Known issues?

Best practice:

If you want to put your sensor in a given environment, know the behaviour of your probe beforehand (or know how to check).

What characterization?

(Equilibrium) response to O₂, to T, and to P (two-fold effect*)

→ Quite well known or 'straightforward' to obtain

Time delay τ ?

O₂ time response (reasonably-well known), no relevant pressure hysteresis

Change with time Δt ? If yes, in which way?

O₂ (strong 'storage' drift, small 'in-situ' drift, known), T (no evidence), P (possibly, not proven)

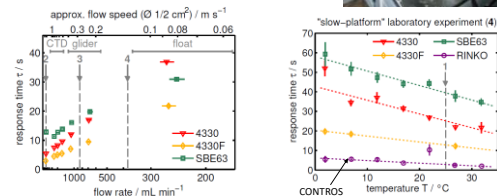
*Bittig et al. (2015) Pressure Response of Aanderaa and Sea-Bird Oxygen Optodes, JAO

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O₂ time response issue

Characterized in lab experiments: Step response O₂/N₂-bubbled baths

- (a) Changing flow at constant temperature
- (b) Constant flow with changing temperature



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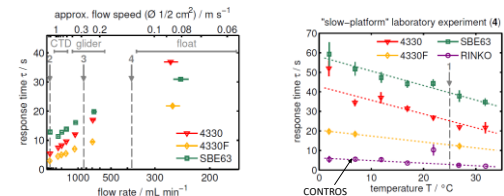
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- (a) Changing flow at constant temperature
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→ Two-layer stagnant film model to explain O₂ time response:

- (a) Flow determines liquid layer thickness l_L
 - (b) Temperature-dependent diffusivities/solubilities modify $\tau(T)$
- look up-table for $\tau = f(l_L, T)$



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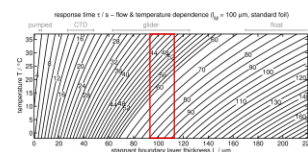
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Bittig et al. (2014) Time response of oxygen optodes on profiling platforms and its dependence on flow speed and temperature. Limnol. Oceanogr. Methods
Bittig and Körtzinger (2017) Technical note: Update on response times, in-air measurements, ... Ocean Sci.

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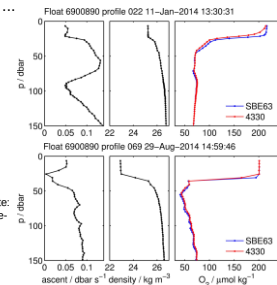
Transfer to field deployments:

→ velocity - l_L parameterization depending on platform & attachment

e.g., from dual-O₂ float (fast & slow O₂ optode on same float), dual-O₂ CTD, dual-O₂ glider, ...



Bitig and Körtzinger (2017) Technical note: Update on response times, in-air measurements, ... Ocean Sci.





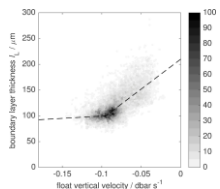
O₂ time response issue

Transfer to field deployments:

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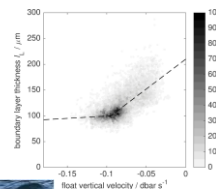
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O₂ response 'storage' drift

Strong O₂ sensitivity loss (O(5 % / year)), i.e.,

(1) Not recently calibrated optodes should be regarded as uncalibrated!

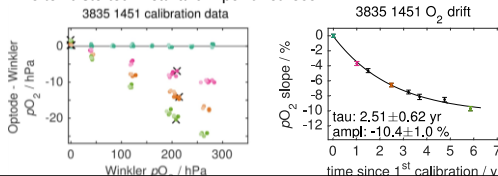
(2) Any deployment needs some way of referencing.

Linear with pO_2 , small (often negligible) zero intercept.

(3) Adjust with a **slope only** (or a slope and very small offset).

(4) Potentially easy to adjust (1 point at high pO_2), if base O₂-T characterization is good (i.e., lab multipoint!)

(5) Requires lab multipoint O₂-T calibration at some point; Batch-adjusted often distorted-linear and 1-point not recommended.



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Drift becomes less intense in older optodes / foils.

(6) Don't change foils unless mechanically damaged.



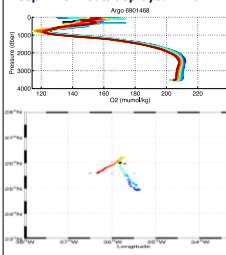
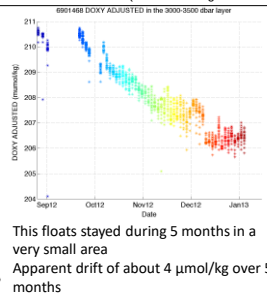
O₂ response 'in-situ' drift

From multi-year float deployments, e.g.,

• Change in deep O₂ (believed to be stable)

(Slide from Virginie Thierry)

Drift of the optode sensor ? Deep Arvor floats deployed in 2012



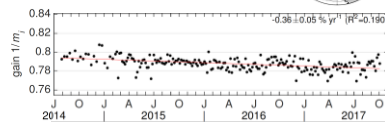
This floats stayed during 5 months in a very small area
Apparent drift of about 4 $\mu\text{mol/kg}$ over 5 months

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O₂ response 'in-situ' drift

From multi-year float deployments, e.g.,

- Change in deep O₂ (believed to be stable)
- Direct observations at surface 'in-air'



Order of 0(0.5 % / year) magnitude smaller than 'storage' drift (0(5 %/year))

- (7) Long-term deployments need long-term way of referencing, e.g. regular in-air measurements!



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O₂ response 'in-situ' drift – In-air observations

On floats: Established, becoming standard.



Bittig and Körtzinger (2015), Johnson et al. (2015), Bushinsky et al. (2016), SCOR WG 142 (2015)

Unclear fleet tendency (15 floats with multipoint calibration: slightly negative; 52 floats with batch calibration: both negative and positive), but individual ones drift significantly (correction needed) Bittig et al. (2018)

On gliders: Proven, but rare?

LIMNOLOGY and OCEANOGRAPHY: METHODS

Air calibration of an oxygen optode on an underwater glider

David P. Nicholson, Melodie L. Free

National Center for Environmental Modelling, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

University of California, San Diego, La Jolla, California, USA



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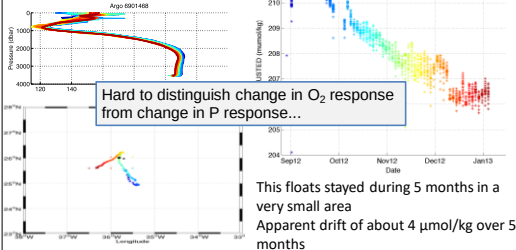
Pressure response drift

From multi-year float deployments, e.g.,

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Pressure response drift/conditioning

Surface O₂ drift only linear vs. deep O₂ drift curved – mismatch?

Pressure conditioning through pressure cycling?

But no hard clues. Still... watch out!

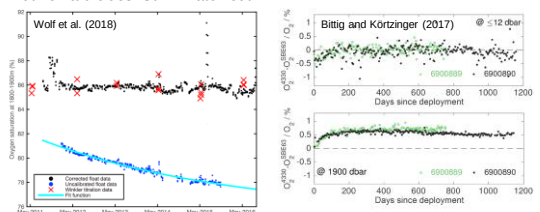


Figure 2. Float 1901210 corrected oxygen saturation (%) at 1,800 to 1,900 m (black dots) compared to the uncalibrated float data for the same depths used for the fit calculation (blue dots). The exponentially decaying fit function (light blue line) is calculated from equation (2). Winkler titration data from annual May surveys of the AR7W hydrographic line are shown in red "x". All floats shown in Figure S2.

Figure 6. Percent difference between O₂ from the Aanderaa 4330 optode and the SBE63 optode using time response corrected data (top) near the surface and (bottom) at depth for floats 6900880 (green) and 6900890 (black). There seems to be a conditioning effect on either one or both optodes during the first half-year / ~400 profiles, after which differences between optodes are stable.

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Summary

Two-fold pressure response, on luminophore and on quenching process.

(0) Pressure correction should be done in two steps.

Strong 'storage' O₂ sensitivity loss (O(5 % / year)), i.e.,

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- (5) Requires lab multipoint O₂-T calibration at some point; Batch-adjusted often distorted-linear and not recommended.

Drift becomes less intense in older optodes / foils.

(6) Don't change foils unless mechanically damaged.

Smaller but significant in-situ drift (O(0.5 % / year))

- (7) Long-term deployments need long-term way of referencing, (e.g., in-air if profiling or surface mooring)

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Further reading :-)

ORIGINAL RESEARCH ARTICLE

Front. Mar. Sci., 24 January 2018 | <https://doi.org/10.3389/fmars.2017.00429>



Oxygen Optode Sensors: Principle, Characterization, Calibration, and Application in the Ocean

Henry C. Bittig¹, Arne Körtzinger^{2,3}, Craig Neill⁴, Elkbert van Ooijen⁵, Joshua N. Plant⁶, Johannes Hahn⁷, Kenneth S. Johnson⁸, Bo Yang⁹ and Steven R. Emerson⁶

¹UMR 7093, Laboratoire d'Océanographie de Villefranche (LOV), Centre national de la recherche scientifique,

Sorbonne Universités, UPMC Université Paris 06, Villefranche-sur-Mer, France

²GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel, Kiel, Germany

³Christian-Albrechts-Universität zu Kiel, Kiel, Germany

⁴CSIRO Oceans and Atmosphere, Hobart, Australia

⁵Monterey Bay Aquarium Research Institute, Moss Landing, CA, United States

⁶School of Oceanography, University of Washington, Seattle, WA, United States