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GEOMAR LOV UPMC SORBONNE UNIVERSITES
DFG O_2-Floats remOcean AtlantOS cnrs

O_2 optodes

Data acquisition, state of the art of sensor knowledge, implementation and recommendations

Best practices:
(1) Know your sensor!
(2) Get to know your sensor in the lab first under controlled conditions.

Henry Bittig
IOW, Baltic Sea Research Institute Warnemünde

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Slide 2

O_2 sensors

Variety of dimensions:
  self-logging – online, cabled – autonomous, fixed – profiling, electrochemical – luminescence quenching
Variety of implications:
  endurance (power, fouling), needed stability, time response, characterization of the probe
Variety of implementations

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O_2 sensors

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  self-logging – online, cabled – autonomous, fixed – profiling, electrochemical – **luminescence quenching**
Variety of implications:
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Variety of implementations

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How do O_2 optodes work?

Dynamic luminescence quenching by O_2
  = presence / absence of O_2 modifies luminescence lifetime of a chemical

ALL O_2 *optodes sense the* **seawater O_2 partial pressure, pO_2,** ***NOT*** *the seawater O_2 concentration. No matter what they claim!* It's in their sensing principle.

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How do O_2 optodes work? – pO_2 probes

Dynamic luminescence quenching by O_2
All textbooks say: Quenching ~ O_2 concentration, i.e., #O_2 per vol.?
  Right! But O_2 concentration around the luminescent chemical.
Is that in Seawater?

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How do O_2 optodes work? – pO_2 probes

Dynamic luminescence quenching by O_2
All textbooks say: Quenching ~ O_2 concentration, i.e., #O_2 per vol.?
  Right! But O_2 concentration around the luminescent chemical.
Is that in Seawater?
  No. It's immobilized. (In a sensing foil / membrane / coating / polymer)

For the luminescent chemical to sense the seawater's O_2, O_2 molecules have to exchange with foil / membrane / coating / polymer until there is an equilibrium.
→ Equal partial pressures!

→ What the luminescent chemical 'sees' is the membrane O_2 concentration $c(O_2)^M$ is the **seawater's partial pressure pO_2**!

O$_2$ optodes – pO$_2$ probes

Who cares?

(1) O$_2$ conc. / pO$_2$ / O$_2$ saturation are (distinctly) different sides, albeit of the same thing.

But their relation is modified by

– Temperature T $\quad T_{Corr} = 44.6596 \cdot \exp(A_0 + A_1 \cdot T_s + A_2 \cdot T_s^2 + A_3 \cdot T_s^3 + A_4 \cdot T_s^4 + A_4 \cdot T_s^5)$

– Salinity S $\quad S_{Corr} = \frac{1013.25 - pH_2O(T,0)}{1013.25 - pH_2O(T,S)} \quad S_{corr} = \exp(S \cdot (B_0 + B_1 \cdot T_s + B_2 \cdot T_s^2 + B_3 \cdot T_s^3) + C_0 \cdot S^2)$

– Hydrostatic pressure P $\quad \exp\left(\frac{V_m \cdot P}{R \cdot T_{abs}}\right)$

– Atmospheric pressure p_{air} $\quad \frac{\varepsilon_m - pH_2O(T,S)}{1013.25 \, mbar - pH_2O(T,S)}$

Not all conversions impacted by all impact factors.

*T$_{corr}$ and S$_{corr}$ from Garcia and Gordon (1992), Benson and Krause refit P from Enns et al. (1965)

O$_2$ conversions – not a stumbling block!

SCOR WG 142: Recommendations on O$_2$ quantity conversions (incl. Matlab functions) → google or DOI:10.13155/45915

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(2) To get the characterization right.

What characterization?

• (Equilibrium) response to O$_2$, to T, to S and to P.
• Is there a delay τ for these responses?
  (e.g., O$_2$ time response, pressure hysteresis)
• Do these responses change over time Δt? If yes, in which way?

Best practice:
If you want to put your sensor in a given environment (O$_2$, T, S, P, maybe τ, maybe Δt), know the behaviour of your probe beforehand (or know how to check).

At best from lab experiments, where you can vary environment one variable at a time. Tedious, but rewarding!

O$_2$ and Temperature response

O$_2$ and T response well-recognized; typically done

• 2D matrix of varying O$_2$ and T while tracking sensor response Φ
• Subsequent fit of mathematical model to data pO$_2$ = F(T,Φ)

Non-linear Stern-Volmer (& non-linear O$_2$) behaviour

Salinity response

O$_2$ optodes do **not have a salinity response**, if the foil / membrane / coating / polymer is inert / impermeable to salt. (Typically the case.)

Wait: What about all these "Salinity corrections" à la $S_{Corr} = \frac{1013.25 - pH_2O(T,0)}{1013.25 - pH_2O(T,S)}$ that I see elsewhere??

Only for optodes that claim to measure O$_2$ concentration, right?!

Example: 200 μmol/L at 25 °C and	S=0	S=20	S=35
pO$_2$ is	159 hPa	179 hPa (+12 %)	195 hPa (+22 %)
"c(O$_2$)" optode gives	200 μmol/L	224 μmol/L (+12 %)	244 μmol/L (+22 %)
"pO$_2$" optode gives	159 hPa	179 hPa (+12 %)	195 hPa (+22 %)

• O$_2$ optodes see the ambient pO$_2$, see the ambient pO$_2$, and see the ambient pO$_2$, no matter whether at S=0, S=20, or S=35.
• "Salinity correction" comes only from pO$_2$ □ c(O$_2$) (fresh/salty) conversions needed if assumed to 'sense' seawater O$_2$ concentration.
  → Avoid in the first place, no need to salinity-'correct' afterwards.
• Hard to spot on 'xx μmol/L' whether salinity-'corrected' or not → Errors

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Hydrostatic pressure response

Why does P affect pO$_2$ sensing?
From fundamental thermodynamics: □ $\quad \frac{p\mathrm{O}_2(P)}{p\mathrm{O}_2(0\ dbar)} = \exp\left(\frac{V_m \cdot P}{R \cdot T_{abs}}\right)$

V$_m$ – partial molar volume

In words: "higher outgassing tendency"; pO$_2$ increases & O$_2$ solubility decreases under pressure due to solute–solvent interactions

V$_m$ of O$_2$ in silicone:
~42 mL/mol → ~+20 % / 1000 dbar

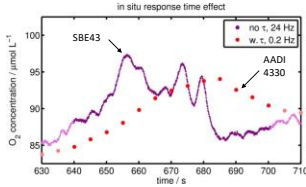V$_m$ of O$_2$ in water:
31.7 mL/mol → ~+15 % / 1000 dbar

ratio ('seen' by luminescene quenching due to re-equilibration between foil / water):
~4-5 % / 1000 dbar

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Response delays τ?

✓ ✓ ✗ ✓ ✓

O_2 molecules need time to diffuse in/out of sensing foil. Causes "lag" and "smearing". Reasonably-well understood → Corrections possible.

O_2 time response is faster:

- with faster flow in front of foil (liquid boundary layer)
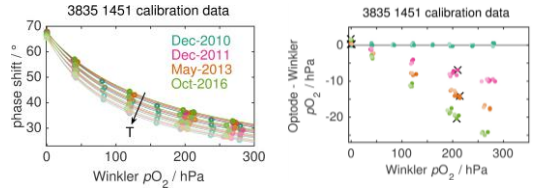- at higher T (diffusivity & solubility T-dependence)

No (/rare?) observations of a P time response (pressure hysteresis).

Slide 2:

Response changes (long-term)?

✓ ✓ ✗ ✓ ✓ ✓/?

All of the above, but in repeated intervals (after / during deployment)!
Figure out what's happening and use knowledge.

Example: O_2 – T response evolution of PreSens foils

Gets at character of drift / stability. Can be different for different implementations (e.g., PyroScience, JFE Advantech, ...)!

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Take Home

(1) Know your sensor!
E.g. Sensing principle renders O_2 optodes seawater pO_2-sensitive. And not depending on salinity.

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

(2b) Get to know your sensor in the lab first under controlled conditions, where you can vary environment one variable at a time. Tedious, but rewarding!

(3) O_2 conversions no stumbling block: SCOR WG 142 recommendations.

More details on O_2 optodes: Frontiers paper and references therein.

Bittig et al.. (2018) Oxygen Optode Sensors: Principle, Characterization, Calibration, and Application in the Ocean. Front. Mar. Sci. 4, 429