Routine $O_2$ optode in air measurements on Argo floats

SCOR WG 142:
Quality Control Procedures for Oxygen and Other Biogeochemical Sensors on Floats and Gliders

Recommendation for Oxygen Measurements from Argo Floats: Implementation of In-Air-Measurement Routine to Assure Highest Long-term Accuracy

Situation
As Argo has entered its second decade and chemical/biological sensor technology is improving constantly, the marine biogeochemistry community is starting to embrace the successful Argo float program. An augmentation of the global float observatory, however, has to follow rather stringent constraints regarding sensor characteristics as well as data processing and quality control routines. Owing to the fairly advanced state of oxygen sensor technology and the high scientific value of oceanic oxygen measurements (Gruber et al., 2010), an expansion of the Argo core mission to routine oxygen measurements is perhaps the most mature and promising candidate (Freeland et al., 2010).

In this context, SCOR Working Group 142 “Quality Control Procedures for Oxygen and Other Biogeochemical Sensors on Floats and Gliders” (www.scor-int.org/SCOR_WGs_WG142.htm) set out in 2014 to assess the current status of biogeochemical sensor technology with particular emphasis on float-readiness, develop pre- and post-deployment quality control metrics and procedures for oxygen sensors, and to disseminate procedures widely to ensure rapid adoption in the community.
Background: Optical $O_2$ sensors (= $O_2$ optodes)

Fundamentals of optical $O_2$ sensing:
- Immobilized luminescent chemical ("luminophore", "sensing foil/coating")
- LED excitation, luminescence detection
- Sensor response depends on temperature, hydrostatic pressure, $O_2,_{lum}$ at luminophore

Examples:
- Aanderaa (AADI) Optode 4330
- Sea-Bird Optode SBE 63
- JFE Advantech ARO-RINKO III
- CONTROS HydroFlash $O_2$
Background: Optical O₂ sensors (= O₂ optodes)

Fundamentals of optical O₂ sensing:
- immobilized luminescent chemical ("luminophore", "sensing foil/coating")
- LED excitation, luminescence detection
- sensor response depends on temperature, hydrostatic pressure, O₂,lum at luminophore
- O₂ equilibrium between O₂,lum at sensing foil and ambient medium (sea water O₂,sw or air O₂,air)
  - every optical O₂ sensor can measure in air
  - equal pO₂ as equilibrium condition
  (→ in seawater: response also dependent on salinity)
- O₂,lum needs to be translated to O₂,sw or O₂,air

\[
\text{not } cO₂,lum \neq cO₂,sw \quad \text{and} \quad cO₂,lum \neq cO₂,air \\
\text{but } pO₂,lum = pO₂,sw \quad \text{and} \quad pO₂,lum = pO₂,air
\]
Challenge: Long-term stability

Optodes tend to drift: Field offsets of ~10% to factory calibr. not uncommon

- Drift is systematic

- Drift rate decreases with time

\[ \Delta pO_2 / \text{mbar} \]

\[ \text{Winkler } pO_2 / \text{mbar} \]

\[ \text{Apr 2011} \quad \text{Dec 2011} \quad \text{Apr 2012} \quad \text{Feb 2014} \]

\[ \text{Optode Bias from Factory Calibration at 100% Saturation} \]

\[ 3 \text{ optodes all with foil 1707} \]

→ measurement at one reference value sufficient to (1) correct drift and (2) to track time evolution in-situ

Bittig & Körtzinger (2015)

Field demonstrations

In-situ calibration: accuracy ≤1 % similar to Winkler-based hydrocast calibration

• Fiedler et al. 2013, J. Atm. Ocean. Techn. 30:112–126
• Bittig and Körtzinger 2015, J. Atmos. Oceanic Techn. 32:1536–1543
• Johnson et al. 2015, J. Atmos. Oceanic Techn., in press
• Bushinsky 2015, PhD thesis

In-situ drift indication: drift rates of –0.2 to –0.5 % yr⁻¹ or higher detectable

• Bushinsky 2015, PhD thesis
• Bittig and Körtzinger 2015, E-AIMS deliverable D2.1.2. report
In air implementations

- Optode on 10 cm stalk
- 5 samples @ 20 s before air bladder inflation
- 10 samples @ 30 s after air bladder inflation
- At end of every profile

In air implementations

Steve Riser/Ken Johnson (UW/Webb Apex): 1 spot sample during telemetry cycle
Björn Fiedler/Arne Körtzinger (NEMO): 5 samples @ 90 s after air bladder inflation
Henry Bittig/Arne Körtzinger (SBE Navis): 10 samples @ 30 s after air bladder inflation (in air)
5 samples @ 20 s before air bladder inflation just below the surface (in water)
Seth Bushinsky/Steve Emerson (UW Apex): 60 samples @ 120 s

Figure. Oxygen optodes mounted on the top caps of floats: (a) APEX float with pole-mounted Aanderaa optode 3830, (b) PROVOR CTS3 DO float with pole-mounted Aanderaa optode 3830, (c) NAVIS float with pole-mounted Aanderaa optode 4330, and NEMO float with cable-mounted Aanderaa optode 4330.
Correction principle

For each surfacing, optode $pO_{2,\text{optode}}$ in air, optode $pO_{2,\text{water}}$ in the surface water, and reference air $pO_{2,\text{air}}$ are compared.

Why so complicated??

TEMP\_DOXY_{air}  \rightarrow pO_{2,\text{optode}}

PHASE_{air}  \rightarrow pO_{2,\text{water}}

surface DOXY  \rightarrow \text{water vapour}

SSS  \rightarrow \text{humidity}

SST  \rightarrow \text{atm. pressure}

optode height

Location and time of profile
Correction principle

For each surfacing, optode $pO_2_{\text{optode}}$ in air, optode $pO_2_{\text{water}}$ in the surface water, and reference air $pO_2_{\text{air}}$ are compared.

Why so complicated??

Because float “in air” (red) read a mixture of air (black) and water (blue) $O_2$:

after Bittig and Körtzinger 2015

Johnson et al. 2015: 47 floats: about 75 % air & 25 % water, too

Bushinsky 2015: maybe additional effects
Time evolution → Perspective for RT-QC

(Average) correction factor can be computed in RT.

→ Perspective to include this into RT QC procedures
   Alternative: Preserve interpretation of in air data to DM QC

There is some (first) indication that the correction factor might change:
Correction principle

For each surfacing, optode $pO_{2,\text{optode}}$ in air, optode $pO_{2,\text{water}}$ in the surface water, and reference air $pO_{2,\text{air}}$ are compared.

TEMP_{DOXY}_{air} \quad \rightarrow \quad pO_{2,\text{optode}}

PHASE_{air} \quad \rightarrow \quad pO_{2,\text{optode}}

surface DOXY \quad \rightarrow \quad pO_{2,\text{water}}

SSS \quad \rightarrow \quad water \ vapour

SST \quad \rightarrow \quad pO_{2,\text{air}}

optode height \quad \rightarrow \quad humility

Location and time of profile \quad \rightarrow \quad atm. \ pressure
SCOR WG 142 recommendations

Requirements:

• Optode mounted in an elevated position so that it is exposed to the air during surfacing. A minimal elevation of 20 cm above the water line is recommended.
  → Track optode height in metadata!

• For the in-air cycle, 5-10 measurements over a few minutes (optode sample interval ≥15 s) are required.
  → In air readings are the prime source of uncertainty → ensure adequate S/N within sequence

Recommendations:

• Include a short measurement sequence with the optode still submerged in seawater. → Truly get sub-surface vs. ~6 dbar end-of-profile observation for in-water part

• Measure in-air at every surfacing. → ensure optimal statistics of long-term corr.

• Preference for nighttime surfacings to avoid potential warming by direct sunlight and to obtain lower noise in the measurements.
Data Management Preparations

- What data to store?
- Where to store the data?
- Perspective: RT or DM correction
What data to store?

Once:
• Optode height (above water line, above CTD top cap, ...?)

At every profile: 5 – 10 measurements
• Optode raw data, i.e., TEMP_DOXY, PHASE
• Derived partial pressure (new variable: PPOX?)
• Pressure data PRES (optional?)
• Measurement time (optional?)

Other float data used:
• Predeployment calibration
• Location and time of the surfacing
• Shallowest profile {TEMP, PSAL, DOXY} or {TEMP_DOXY, PHASE}
Where to store the data?

Once:
• Optode height (above water line, above CTD top cap, ...?) → Metadata?

At every profile: 5 – 10 measurements
• Optode raw data, i.e., TEMP_DOXY, PHASE → Trajectory vs. Profile
• Derived partial pressure (new variable: PPOX?)
• Pressure data PRES (optional?)
• Measurement time (optional?)

Other float data used:
• Predeployment calibration
• Location and time of the surfacing
• Shallowest profile {TEMP, PSAL, DOXY} or {TEMP_DOXY, PHASE}