Oxygen data in water column: scientific issues and needs

Laurent Coppola, Virginie Thierry, Francois Baurand, Henry Bittig, Pierre Branellec, Emilie Brion, Sophie Cravatte, Solenn Fercoq, Jonathan Fin, Claire Gourcuff, Jacques Grelet, Nolwenn Lamande, Caroline Le Bihan, Christian Le Gail, Dominique Lefèvre, Aurélien Paulmier, Anne Piron, Virginie Racapé, Gilles Reverdin, Pierre Rousselot, Florence Salvetat, Carole Saout-Grit, Pierre Testor, Thibaut Wagener

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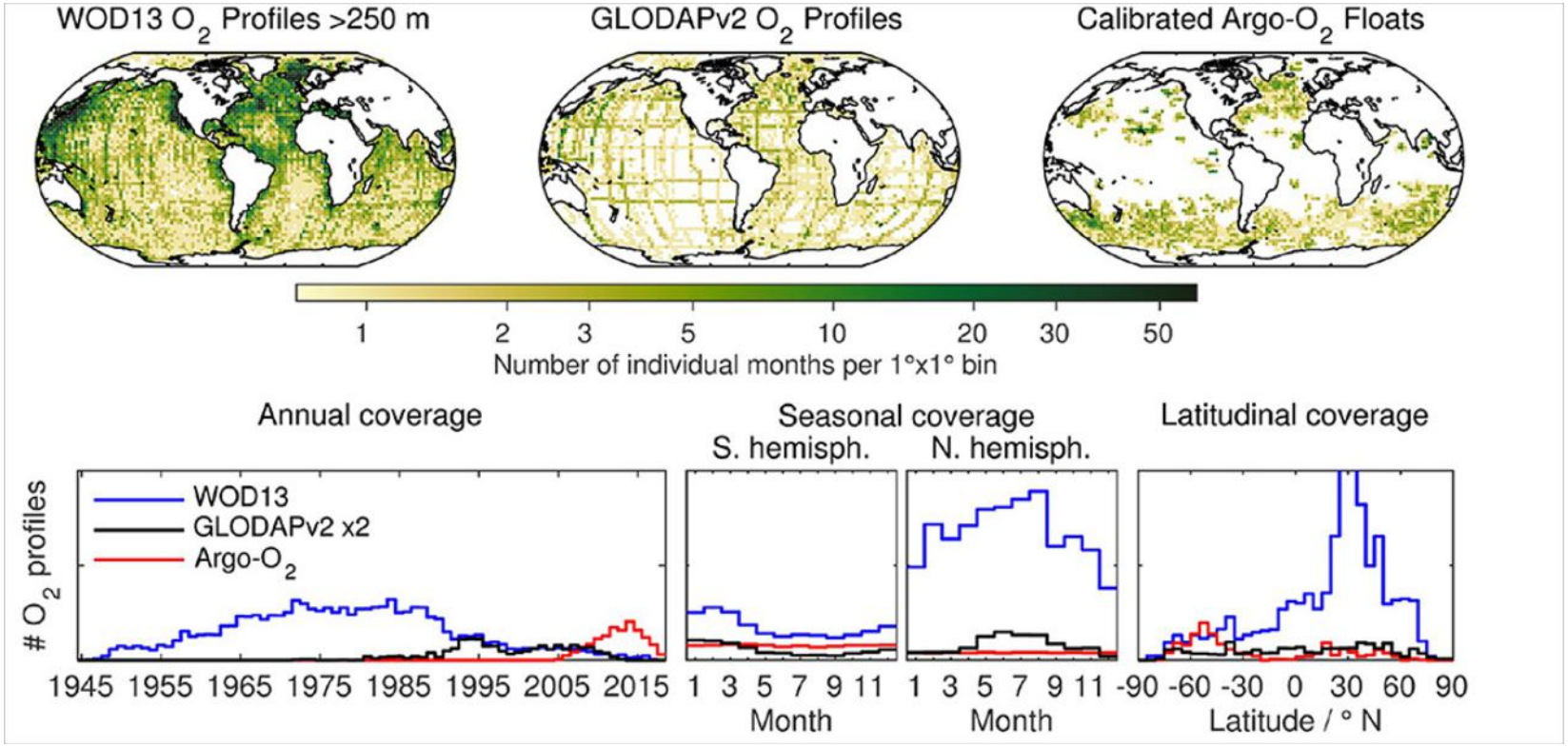
O_2 is the most measured oceanic biogeochemical variable

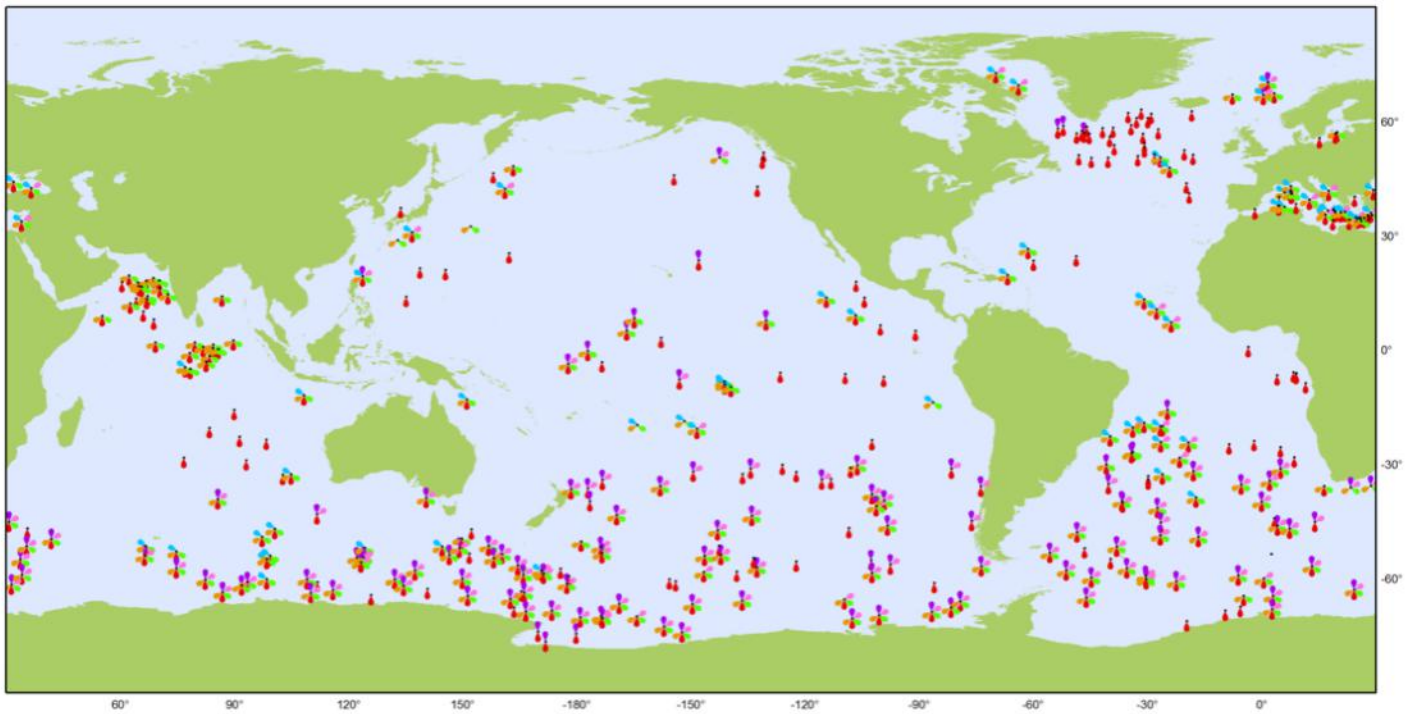
Bittig et al. (Frontiers 2018)



Argo-O2: accuracy lower than 5 µmol/kg (+/- 2 µmol/kg) with objective to achieve an accuracy of 1 µmol/kg (+/- 0.5 µmol/kg) for open sea studies (Gruber et al., 2010)

Data quality and accuracy are often unsatisfactory: sensor and data treatment are not always easy to apply and/or sensor characteristics are not adequately taken into account

Oxygen seawater spatial coverage from Argo



biogeochemical Argo

166194

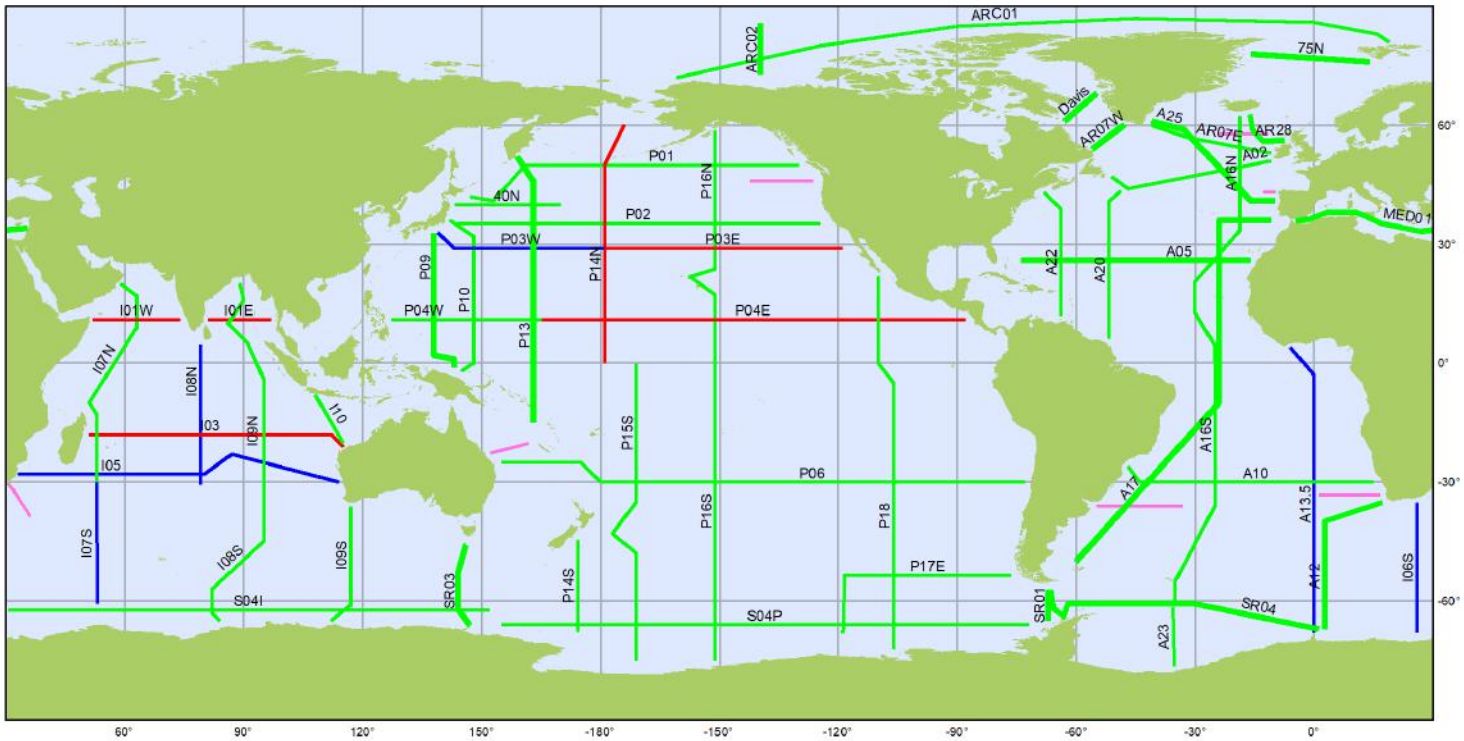
TOTAL NUMBER OF **OXYGEN** PROFILES ACQUIRED BY BGC-ARGO FLOATS

1044

PROFILES ACQUIRED IN 2019

342 Argo-O_2 floats acquisition in real-time

Oxygen seawater spatial coverage from GO-SHIP



GO-SHIP **Status of 2012-2023 Survey (62 Lines)** **October 2018**

Bold lines: High Frequency (reduced requirements) Thin lines: Decadal GO-SHIP (full requirements)

completed | at sea | funded | planned | not planned yet | associated & completed

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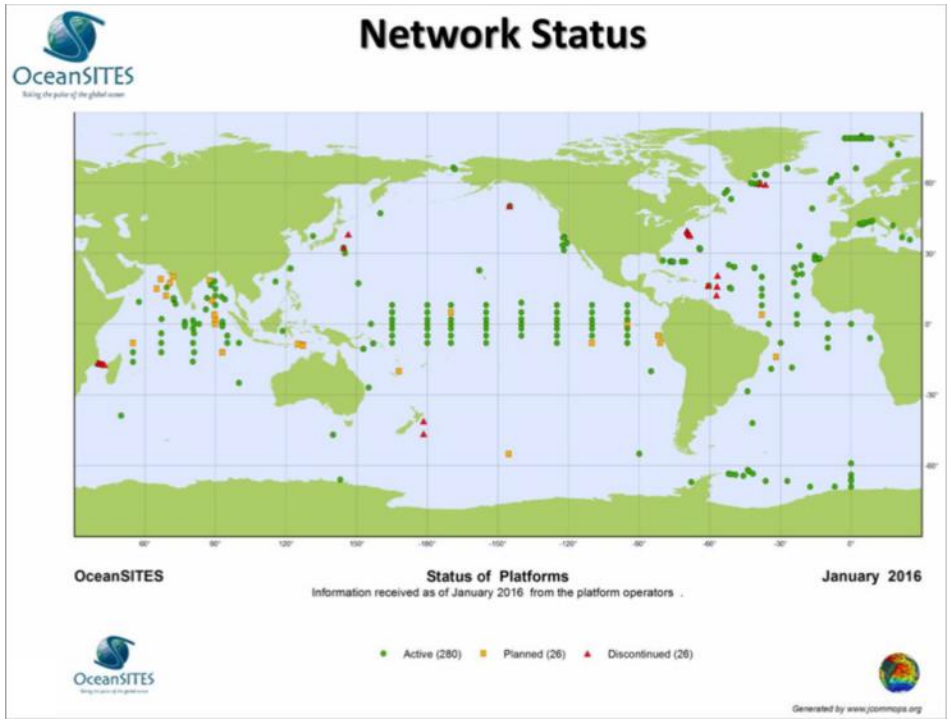
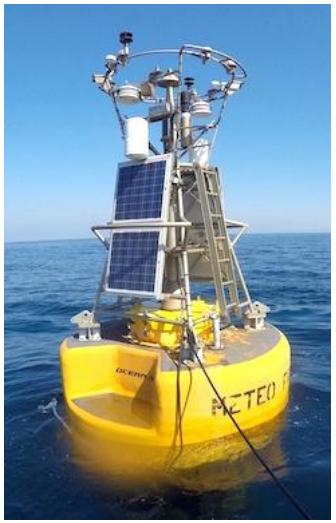
O_2 is a core parameter measured systematically during GO-SHIP cruises (full cruise every 10 years)

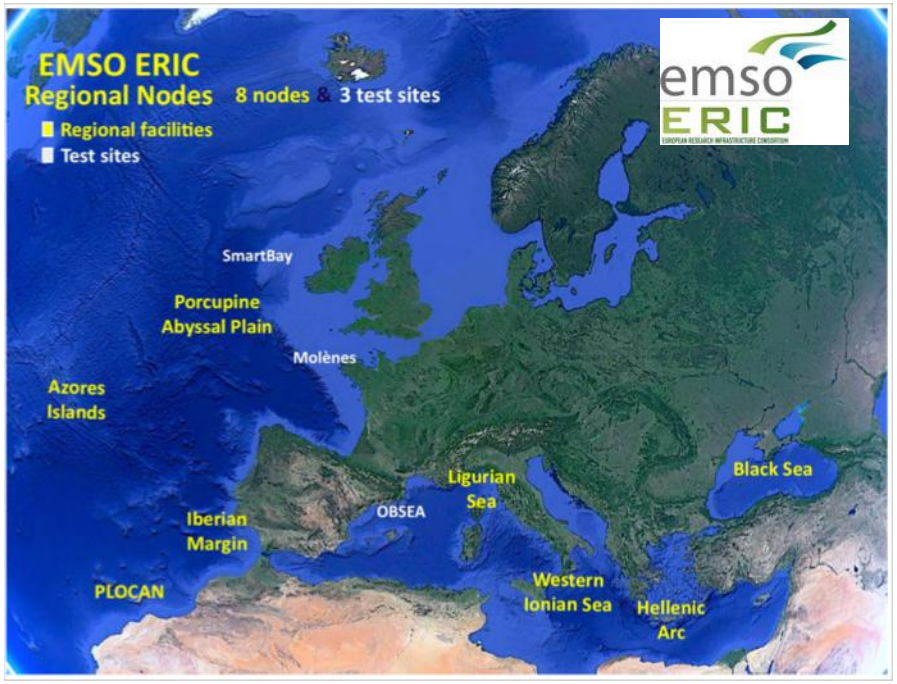
Oxygen seawater spatial coverage from OceanSites/EMSO



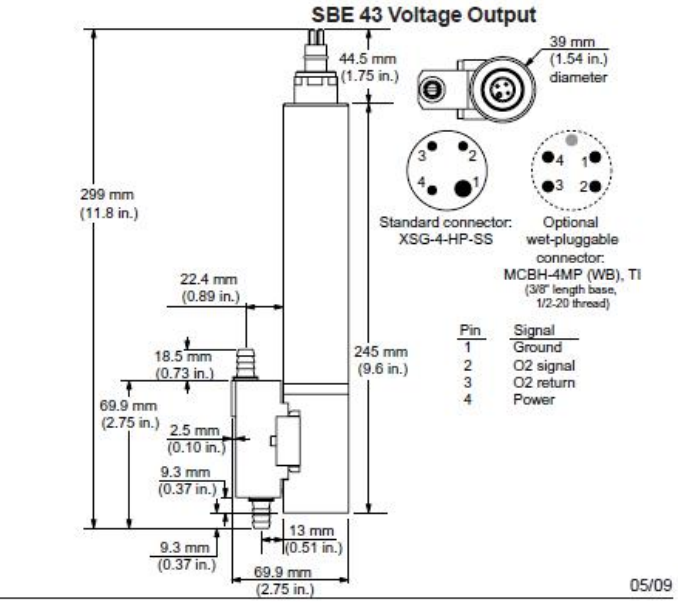


Oxygen is not measured everywhere (RT & DM)

Distributed from surface (pCO2) to intermediate and deep waters (mixing, ventilation, biological activity)



SBE43 Dissolved Oxygen sensor



Clark-cell sensor (electrochemical)
Most common sensor used to measure DO concentrations during CTD profiles (fast response)

Specifications

Measurement range:	120% of surface saturation in all natural waters, fresh and salt
Initial accuracy:	2% of saturation
Typical stability:	0.5% per 1000 hours (clean membrane)

Known issues with SB43 sensor

Advantages:

- automatic measuring system
- generating continuously data
- acceptable resolution/accuracy (on average 4-5 µmol/kg uncorrected)

Disadvantages:

- extensive calibration/maintenance work before installation necessary
- long-term stability is limited to the reaction of the electrolytical liquid
- susceptible to bio-fouling

Need to use Winkler measurements as reference values to correct SBE43 drift during the cruise

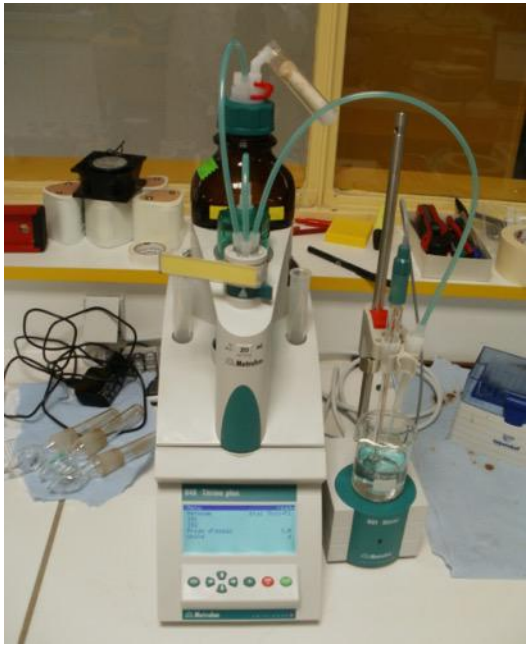
Follow SBE cleaning procedure and respect SBE43 response time during CTD cast (closing Niskin bottle after 30s)

$$Oxygen\ (ml/l) = \left\{ Soc * \left(V + Voffset + tau(T,P) * \frac{\partial V}{\partial t} \right) \right\} * Oxsol(T,S) * \left(1.0 + A*T + B*T^2 + C*T^3\right) * e^{\left(\frac{E*P}{K}\right)}$$

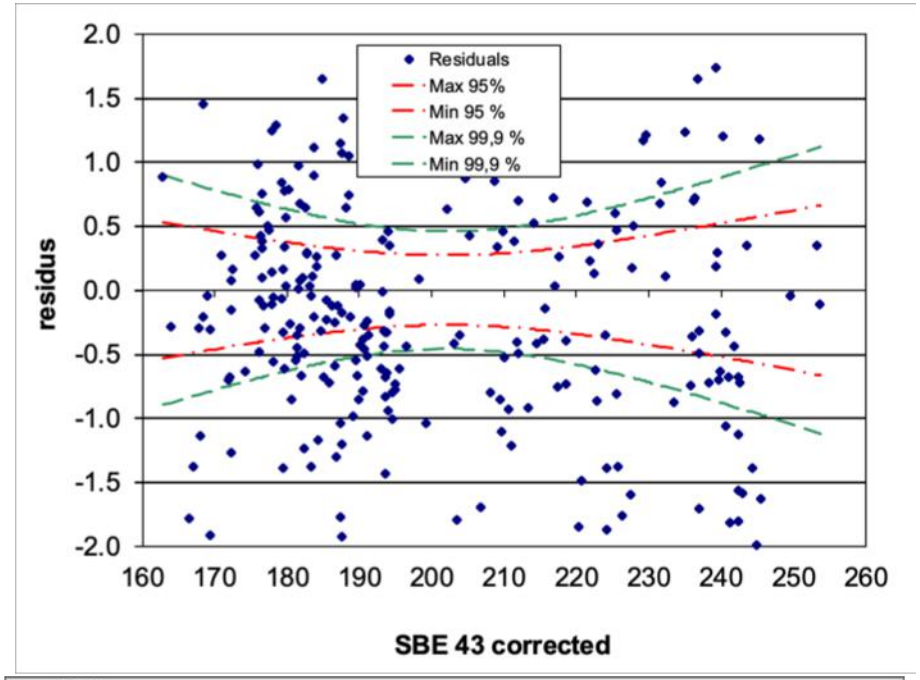
$$Oxygen(ml/l) = Soc * (V + Voffset) * \phi$$

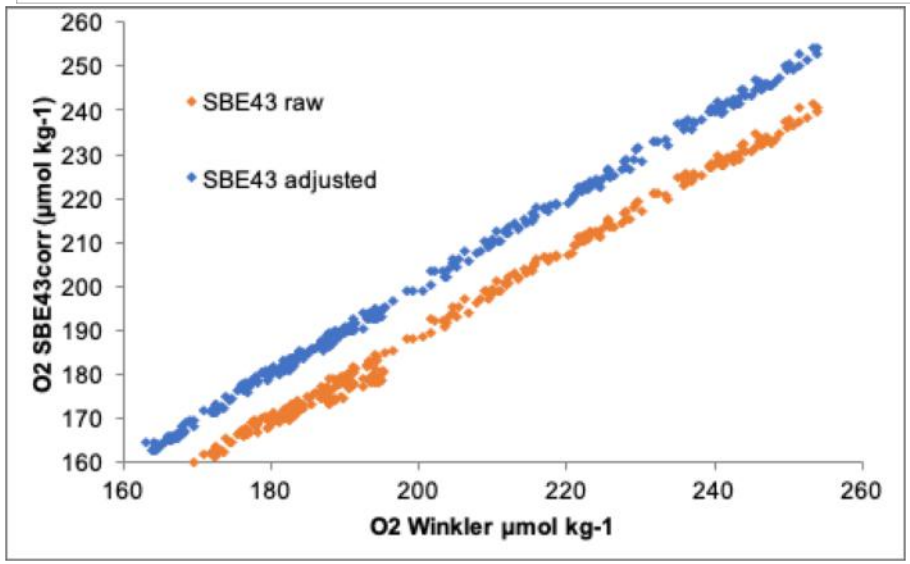
WINKLER measurements cautions

- **Careful when using reagents** : one bubble of 50 mm3 (50 µL) represents an input of 1.5 µmol of O2 which corresponds to an error of 4 µM on O2 concentrations !
- **Need to calibrate the volume of Winkler bottles**: for 150ml vials, an error of 50 mg induces an uncertainty of O2 concentrations around 0.15 µM
- Need regular **inter-labs comparisons** (e.g. SOMLIT, WINKLEX,…)



Example with PEACETIME cruise (MED SEA)

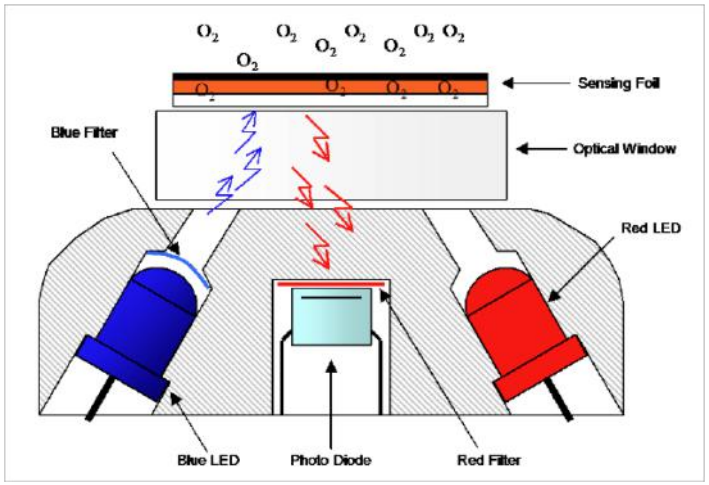


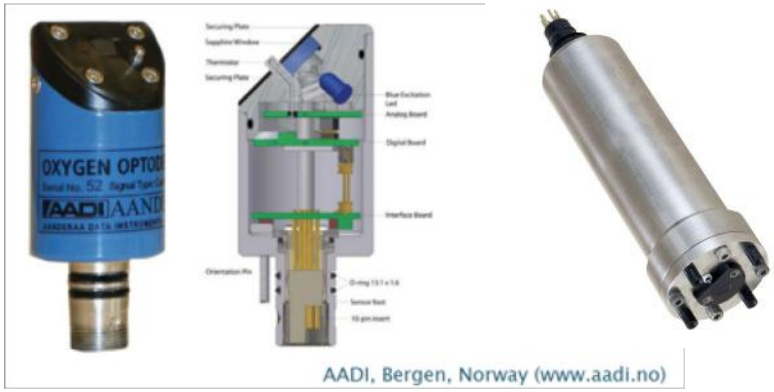


- Perform Winkler measurements from surface to bottom on 34 stations (1 profile per day = 365 data)
- SBE43raw - Winkler = 10-15 µmol/kg
- Adjust SOC, Voffset and E
- After fitting R = +/- 2 µmol/kg
- SBE43adj - Winkler < 1.5 µmol/kg

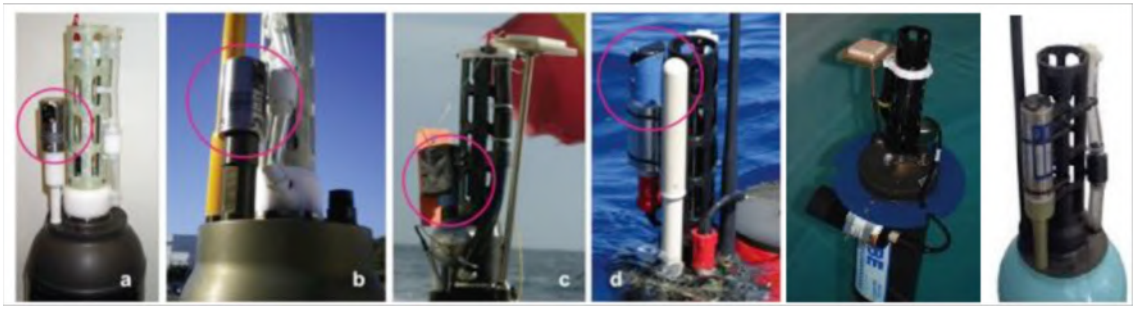
Optical sensors

- The sensor is based on the dynamic luminescence quenching of an oxygen-sensitive fluorochrome embedded in the tip
- Long time stability, no pressure hysteresis, fast response, compact, better accuracy (< 5 µmol/kg; Bittig et al., 2018)
- Adapted for Argo floats, gliders, ferry boxes, moorings, plankton incubators





From Argo-O2 & BGC-Argo community



- **Strong 'storage' O_2 sensitivity** (loss 5 % / year): not recently calibrated optodes should be regarded as uncalibrated!
- Any deployment needs some way of **referencing** (pO2): adjusted CTD or WOA
- Adjust with a ***slope only*** (or very small offset).
- Necessary to adapt **O_2-T calibration** (lab multi-points with 35-40 points)
- Don't change foils unless mechanically damaged.
- **In situ drift,** order of O(0.5 % / year) : long-term deployments need long-term way of referencing: **apply in-air correction** (SAGE-O2, LOCODOX) and surface mooring or adjusted CTD casts is possible

SLOPE = mean ratio PPOX_WOA/PPOX_FLOTTEUR, OFFSET = 0, DRIFT in % PPOX per year

Correction WOA = error +/- 10 µmol/kg
Correction adjusted CTD casts = error +/- 2 µmol/kg

Details in Bittig et al., 2018 (Frontiers)

Best practices for data analysis O_2 : where are we now ?

- White book in JERICO (2011-2015)
- Argo-O2 cookbook v.2.0 Oct 2018
- Reports Gallian Marine, Thierry Virginie (2018): Argo-O2 + LOCODOX
- OceanObs2019 paper “Evolving and Sustaining Ocean Best Practices and Standards for the Next Decade” Pearlman et al., 2019
- Handbook EMSO_Link D2.2 (first release)

Some recommendations:

1. Ship community (GO-SHIP,…)

- Long history about SBE43 data validation with Winkler data
- Winkler analysis onboard is mandatory to correct sensor drift and offset (min. one profile per day)
- Least square adjustment method to correct SBE calibration coefficients (SOC, offset and E)
- Regular inter-calibration between labs is also recommended

2. Argo-O_2 community

- Strong experiences from the last 10 years with optode
- Multi-points calibration for optode using Sterm-Volmer equation is necessary
- Bittig et al. 2018 method is the best practices suggested with pO2, slope correction and optode-air calibration

3. Fixed platforms community (EMSO, OceanSites):

- Recent experiences on O_2 sensor deployment
- SBE63 seems to be the best sensor so far (pumping system)
- Inter-calibration with CTD ship based is mandatory during mooring maintenance
- Cross-reference with in situ sampling and Winkler is also recommended
- Data processing and adjustment are not matured yet (on going…)

4. Glider community (OceanGliders)

- Follows Argo recommendations. In addition, a temperature correction and a time lag correction based on phase measurements are applied that minimize the differences between up- and down-casts
- Multi-points calibration and optode storage are now used

5. Ultra-Low concentration & high O_2 gradients (ship & other autonomous platforms)

- Require specific measurements, sampling and data adjustments (AMOP O2 reports)