

Dissolved oxygen sensors

Calibration needs, current practices and alternatives

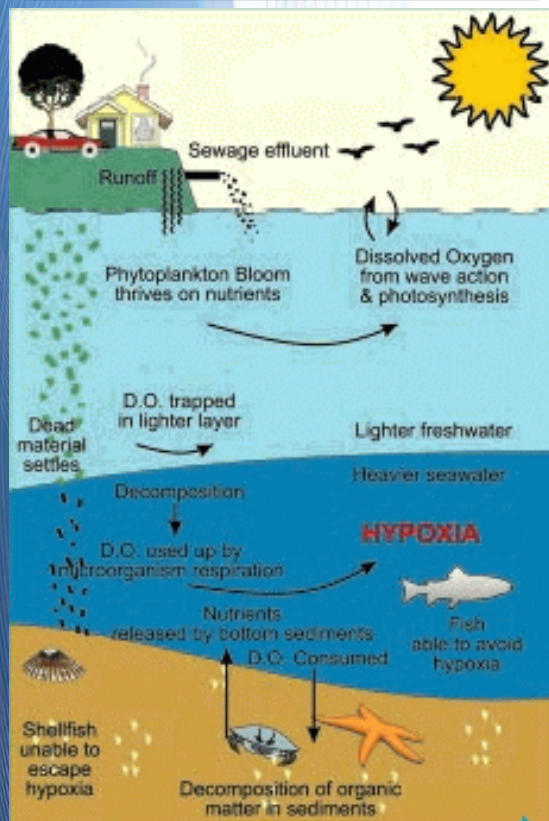
Florence Salvetat, Metrology Laboratory

- 1 – *Current status: needs, practices and lacks***
- 2 – *Up to date recommendations***
- 3 – *Alternatives***

Coastal waters

- Water quality index
- Biomass indicator

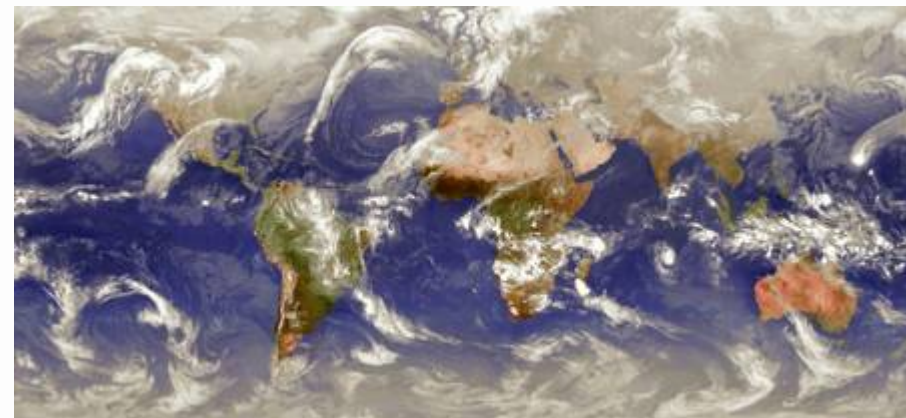
≈ 5 to 6 $\mu\text{mol/l}$



Open ocean

- Climatology
- Water masses
- Mixing processes
- Biogeochemical processes

≈ 1 $\mu\text{mol/l}$



Calibration common practices:

1- Manufacturer recommendations:

- Calibration at 100% (stirred water or humid air)
- Calibration at 0% (sodium sulphite)

2- Calibration lab recommendations:

- Winkler as reference measurement for 100%



Do not control sensor linearity

Maintenance sensor common practices:

- Membrane/foil life span (using conditions, ...)

Storage common practices:

- Storage condition effects

Using conditions:

- Biofouling effects
- Chemical interferents / Influence quantities (temperature, pressure, salinity, current, ... ?)

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Recent oceanographic calibration lab recommendations to reach best adjustment and uncertainties

Calibration common practices:

More recently, to reach best adjustment and uncertainties:

3- Oceanographic calibration lab recommendations:

- Multi-points calibration (*linearity control, temperature effects*)
- Adjustment following "H. Uchida, T. Kawano, I. Kaneko, M. Fukasawa, J. Atmos. Oceanic Technol., 25, 2271–2281 (2008)"

Existing multipoints calibration facilities for oceano:

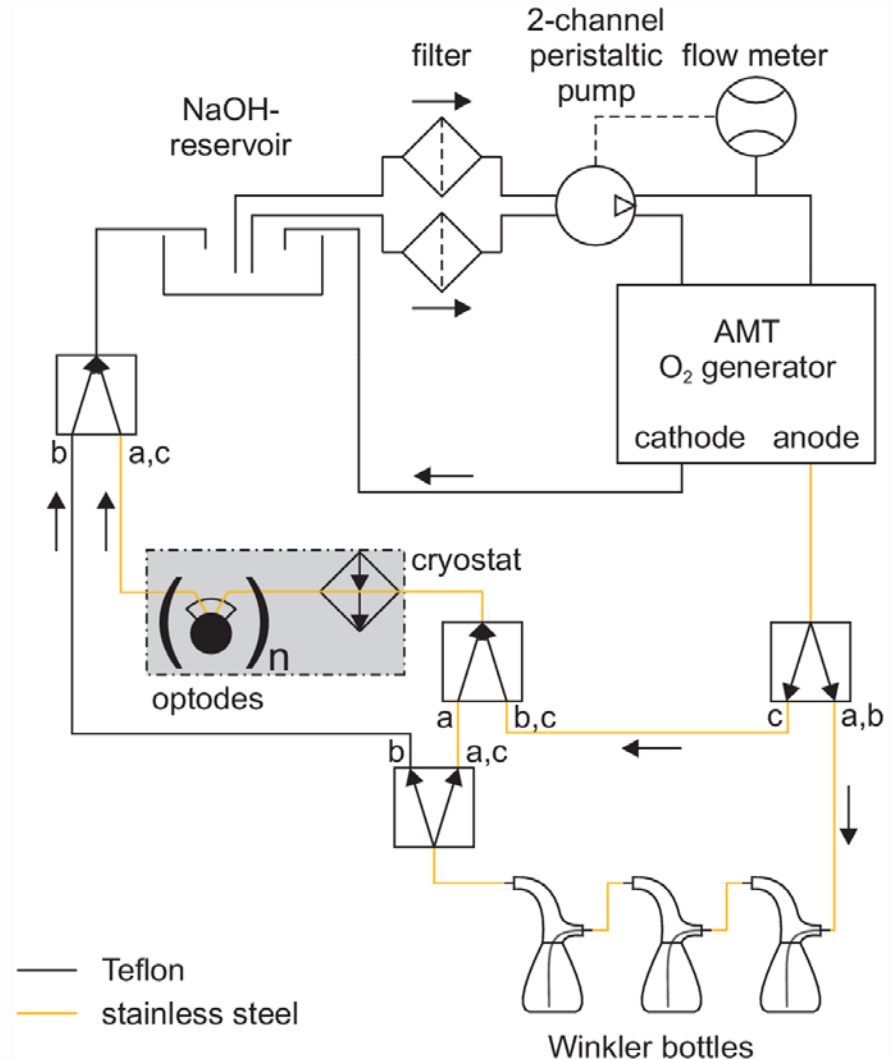
- Electrochemical systems:

GEOMAR (H. Bittig)

“A novel electrochemical calibration setup for oxygen sensors and its use for the stability assessment of Aanderaa optodes”

Henry C. Bittig, Björn Fiedler,
Tobias Steinhoff, Arne Körtzinger

Limnol. Oceanogr. Methods
10:921-933 (2012)



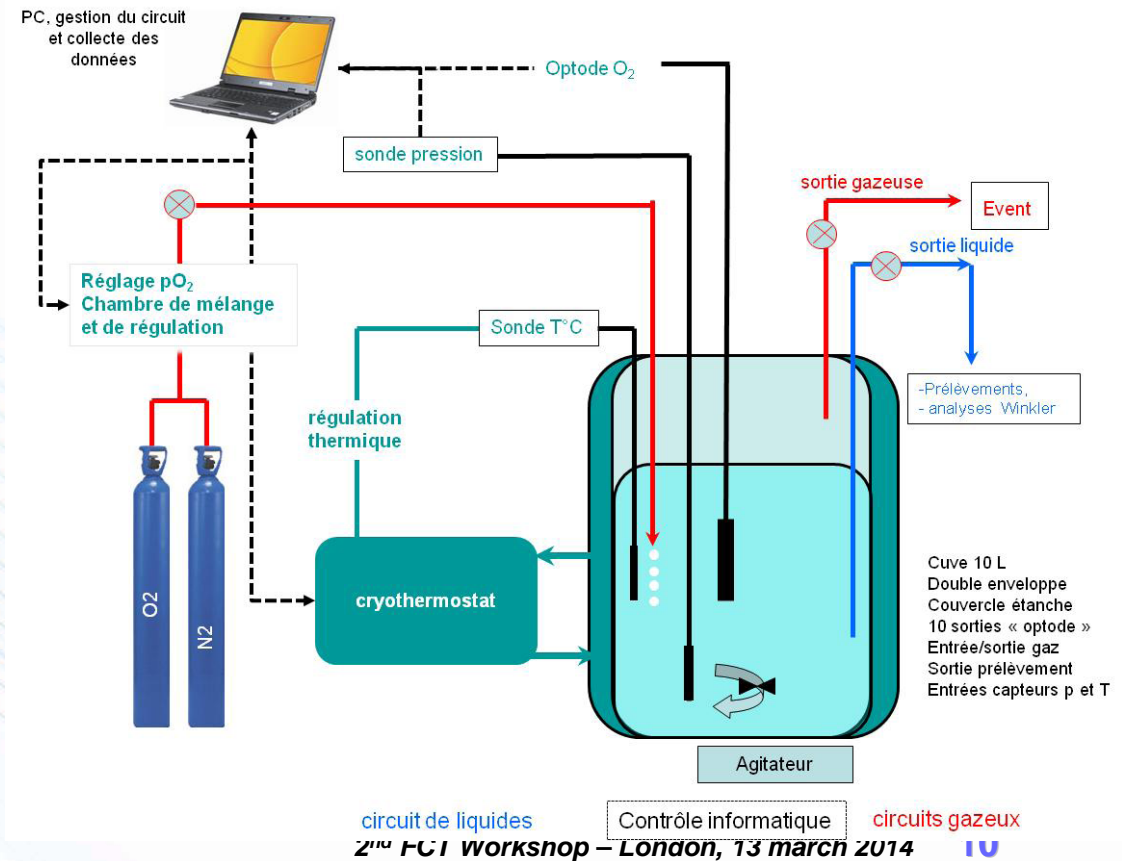
Existing multipoints calibration facilities for oceano:

- Bubbling systems:

- CSIRO (C. Neill) and AADI (J. Hovdenes)

Specific bench designed for optodes

- MIO (D. Lefèvre)



Existing multipoints calibration facilities for oceano:

- Bubbling systems:

- MPI (F. Janssen)

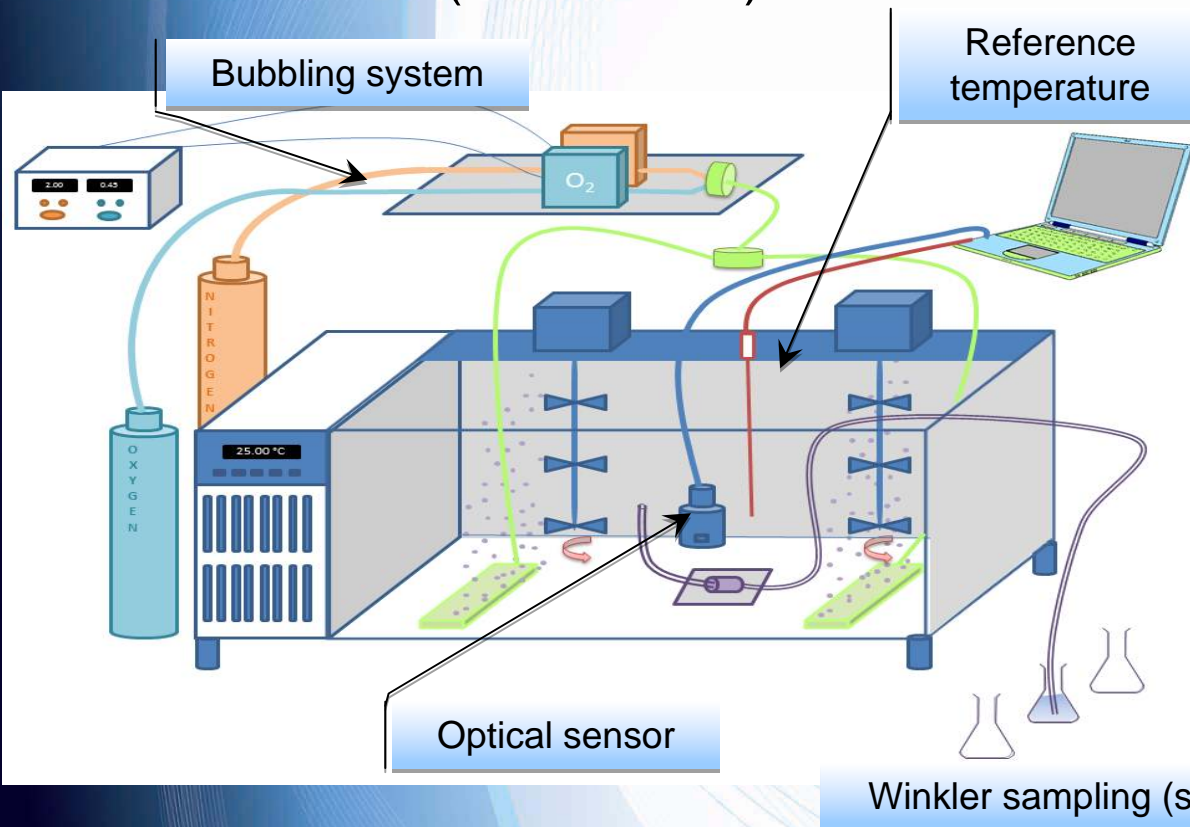


- JAMSTEC (H. Uchida)

Existing multipoints calibration facilities for oceano:

- Bubbling systems:

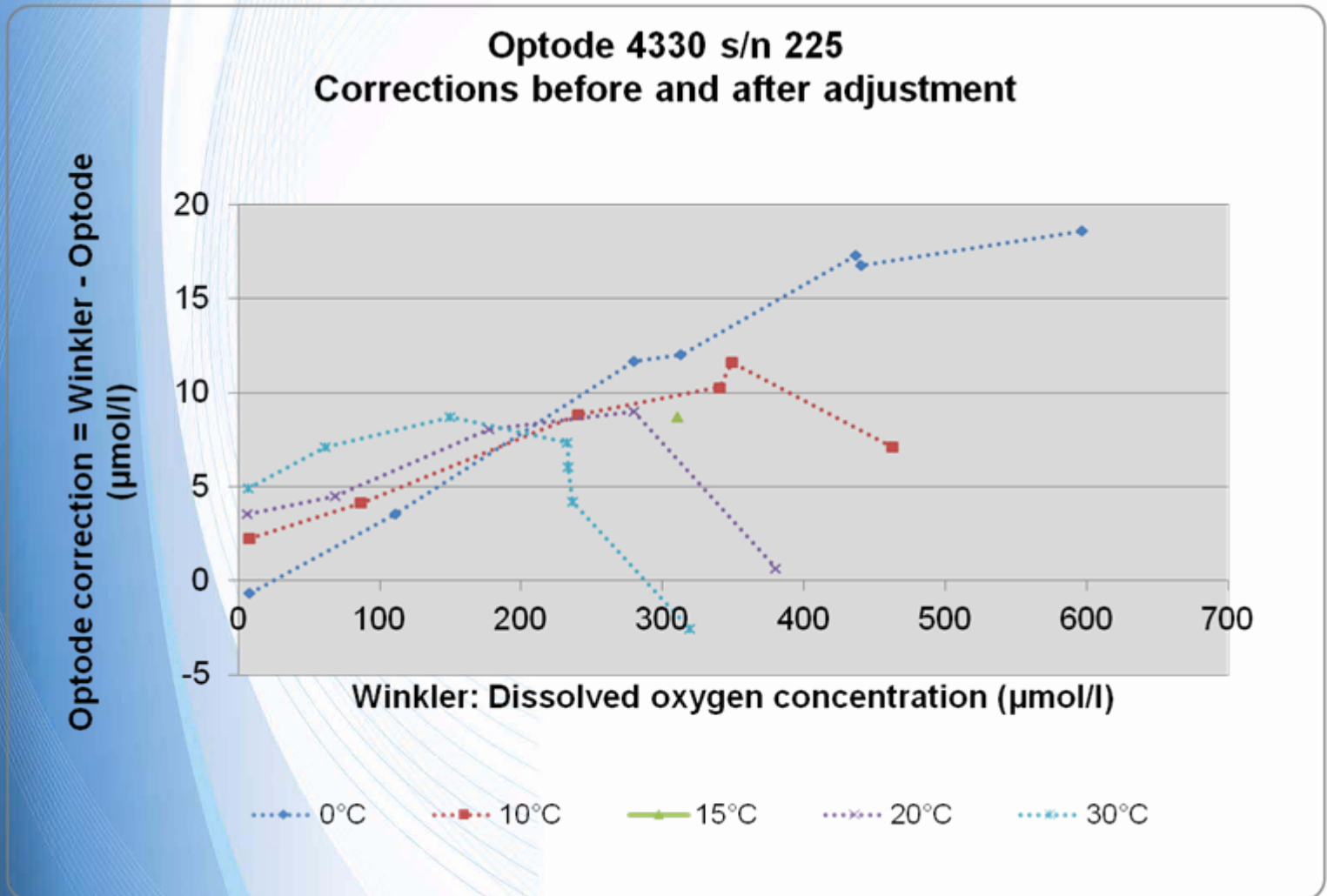
• Ifremer (F. Salvetat)



- Stability < 0.5 $\mu\text{mol/l}$
- Several hours stability
- Lowest level: nearly 0%
- O₂ homogeneity < 2 $\mu\text{mol/l}$

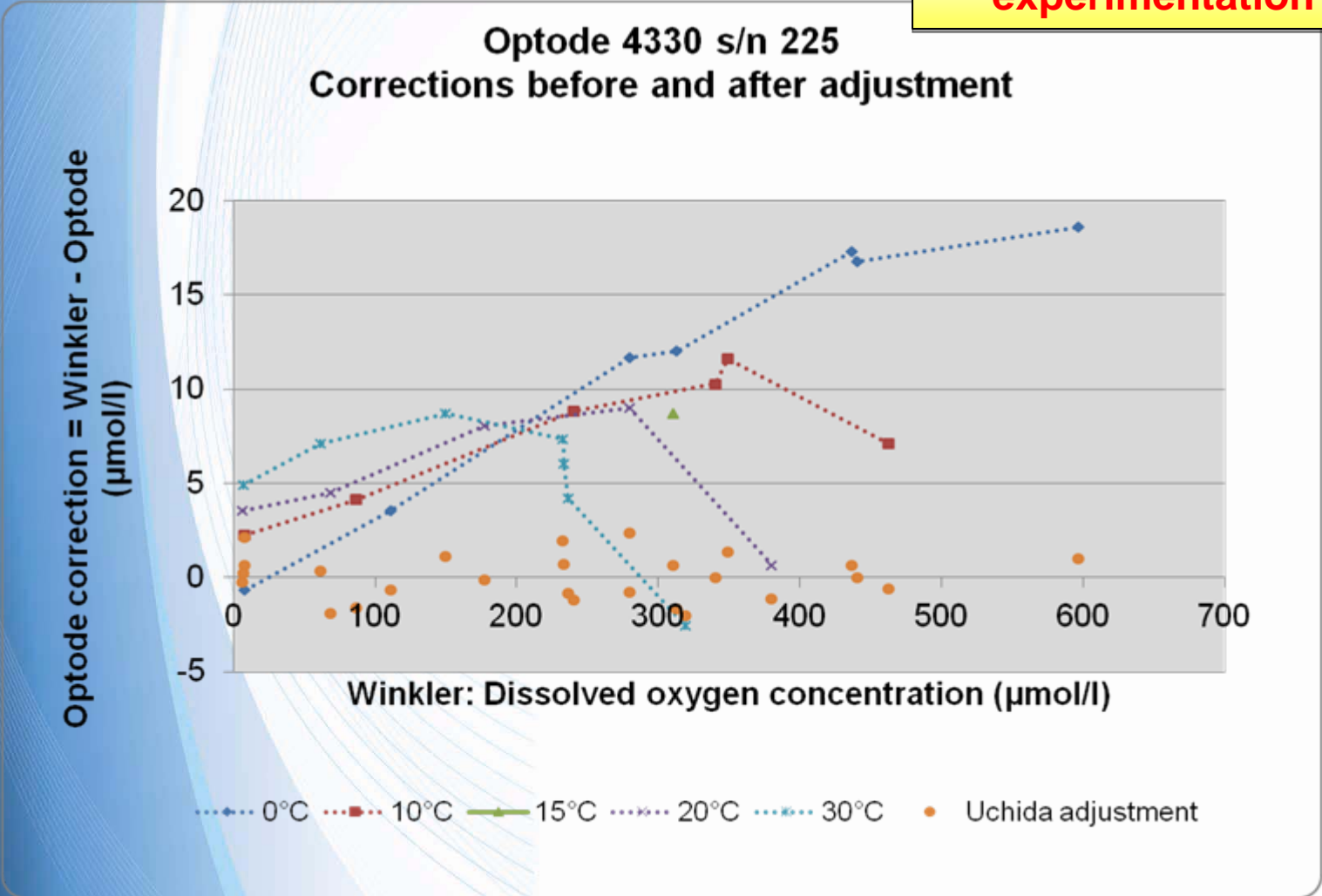
**Fulfill requirement:
a few $\mu\text{mol/l}$**

Results of a multipoints calibration



Results of a multipoints calibration

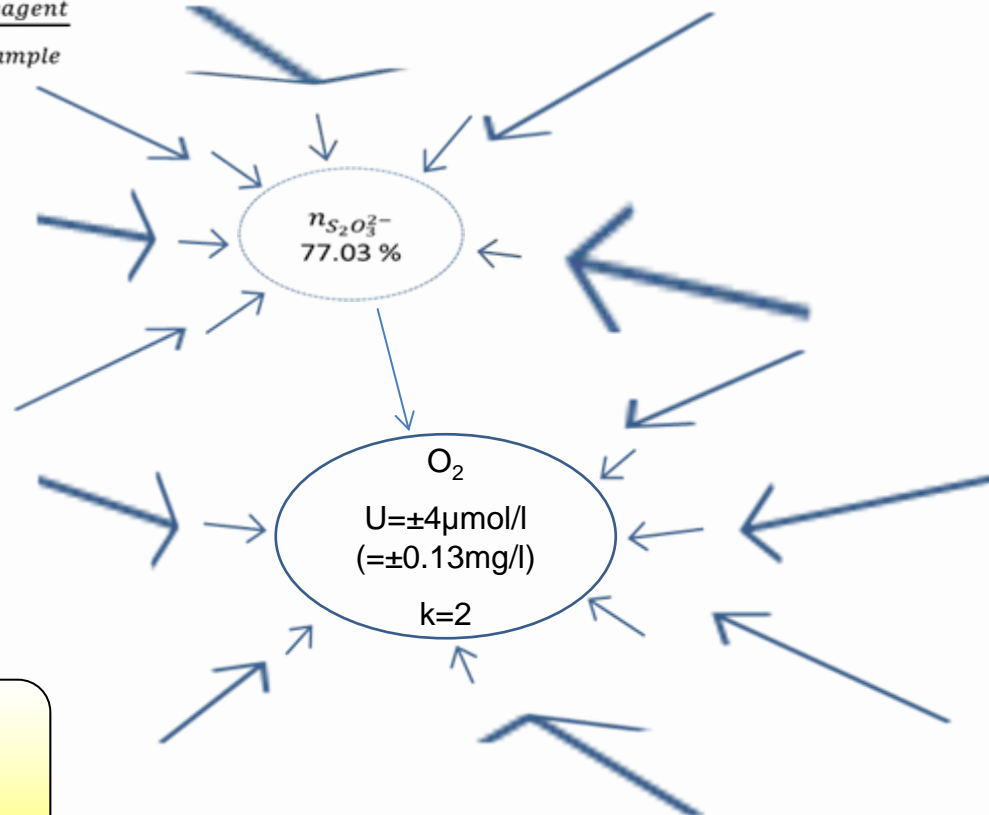
2 to 3 weeks experimentation



Results of a multipoint calibration

- Uncertainty calibration budget: $U \approx \pm 7 \mu\text{mol/l}$ (at 440 $\mu\text{mol/l}$) with U (Winkler) = 4 $\mu\text{mol/l}$

$$[O_2] \mu\text{mol/l} = \left[\begin{array}{l} \frac{n_{KIO_3} V_{KIO_3}}{(V_{S_2O_3^{2-} \text{-Cal}} - V_{S_2O_3^{2-} \text{-CalBlank}})} \\ \times \frac{(V_{S_2O_3^{2-} \text{-Sample}} - V_{S_2O_3^{2-} \text{-SampleBlank}})}{4} \\ \times \frac{1000000}{(V_{\text{Sample}} - V_{\text{Reagents}})} \end{array} \right] - 38 \times \frac{V_{\text{Reagent}}}{V_{\text{Sample}}}$$



Gravimetric Winkler: U/2
I.Helm, L.Jalukse, I. Leito, Anal. Chim. Acta. 741 (2012) 21-31.

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How to adapt metrology to needs ?

- Simplest to more complete calibration protocols
- Define the needs !
- *In situ* calibration
- Use of several non calibrated sensors and statistical post-processing the data → ...low cost sensors ?

How to be more efficient in metrology ?

- Rethink the roles or activities of oceano institutes, NMI, consultancy companies and manufacturers (! SME)
- Build collaborations, find ways/structures to exchange
- Propose trainings, audits, ILC, transfer of know-how

Thanks for your attention