Metrology for oceanography :

Main issues and Ifremer's actions

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The metrology laboratory:

Dedicated to physical and physico-chemical parameters:

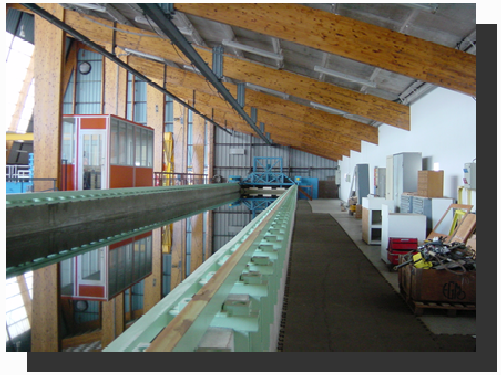
Temperature, pressure, salinity (conductivity), velocity, ocean current, dissolved oxygen, pH, turbidity, fluorescence.

The chemical laboratory: (A. Laes)

Ammonia, nitrates/nitrites, silicates.

Salinometer

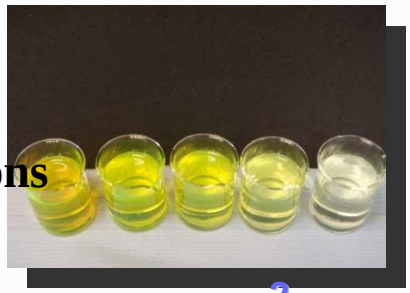
Fresh water or seawater bath (800l)



Towing canal

Formazin solutions

Fluorescein solutions

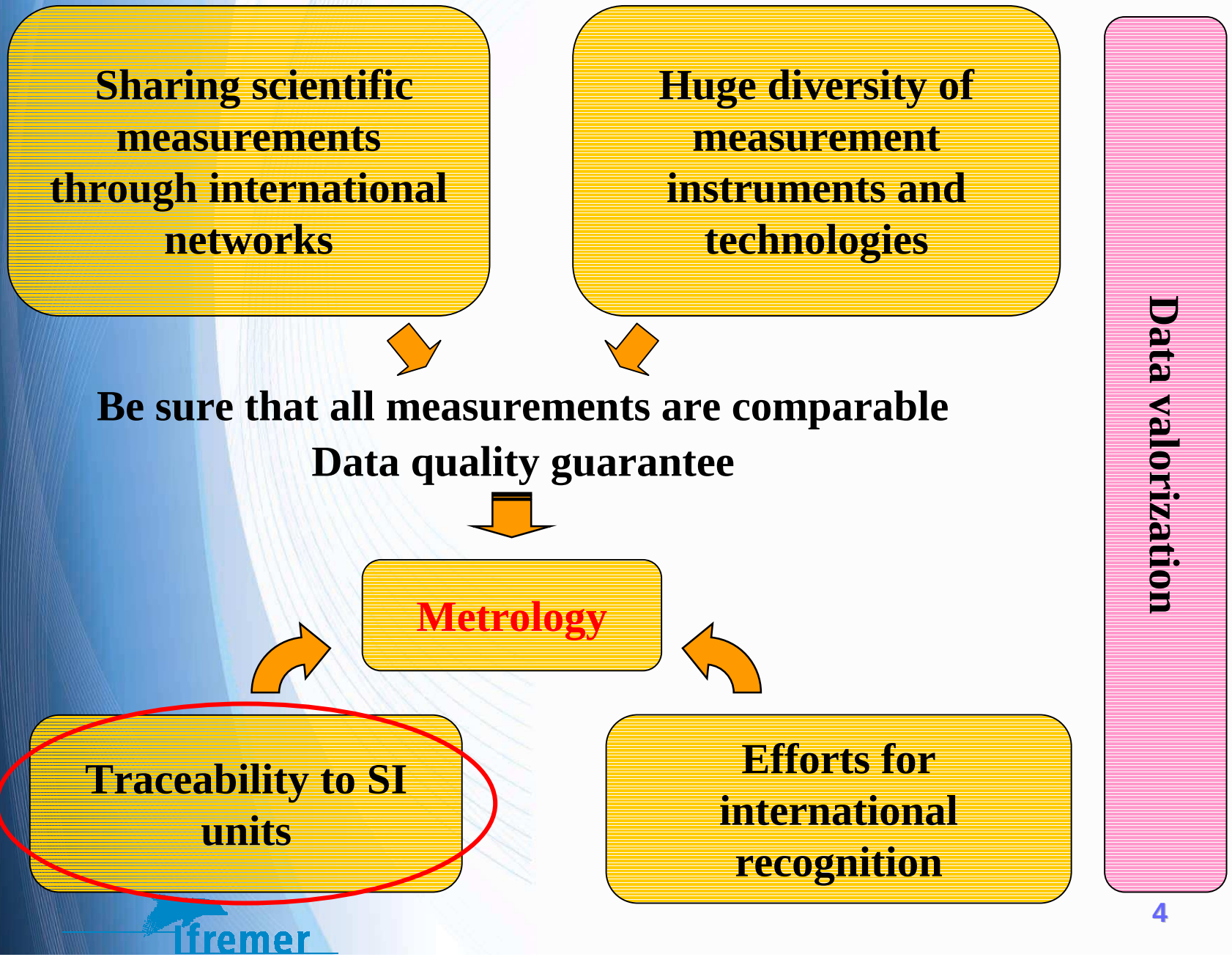


1 – Context

2 – Main issues

3 – On going studies

Context


Sharing scientific measurements through international networks
Huge diversity of measurement instruments and technologies
Be sure that all measurements are comparable
Data quality guarantee
Metrology
Traceability to SI units
Efforts for international recognition
Data valorization

1 – Context

2 – Main issues

3 – On going studies

Main issues

Temperature calibration: (Cofrac)

- **Range: -10°C to +60°C**

  with U= +/- 4m°C to 13m°C

- **Current procedure:**

  comparison in temperature regulated bath for different values of temperature

Fresh water or seawater bath (800l)

Issues:

Reduce uncertainties (few m°C)

Main issues

Pressure calibration: (Cofrac)

- **Gauge P: Range: 0.1 MPa to 80MPa**

  with $U \# 1.10^{-4} \times P_{Gauge}$

- **Current procedure:**

  comparison for different values of pressure with a pressure balance

Issues:

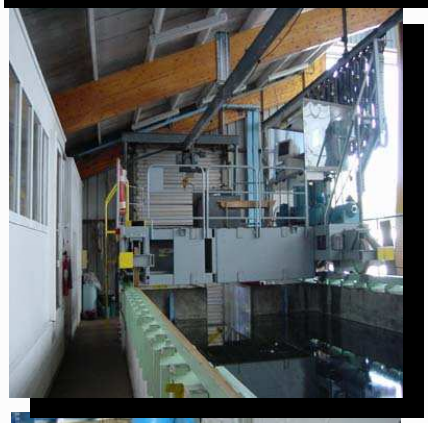
Absolute pressure measured, sea pressure delivered, gauge pressure calibrated

Main issues

Current calibration:

- Range: 0.1m/s to 1m/s
- Current Procedure:

  comparison for different values of current (mechanical current meter)



➡ **Issues:**

Acoustic Doppler current meter:

- Wall reflexion of the beam
- Particles spreading needed

Main issues

Dissolved oxygen calibration:

- **Range: from 0µmol/l to over-saturation**
- **Current Procedure:**
  - **calibration at 0% (sodium sulphite) and 100% (stirred water)**
  - **Winkler titration as standard method**

Issues:

- **Linearity control: 1 or 2 calibration / adjustment points are not enough**

Main issues

Dissolved oxygen calibration:

Issues:

- **Substance matrix: seawater**

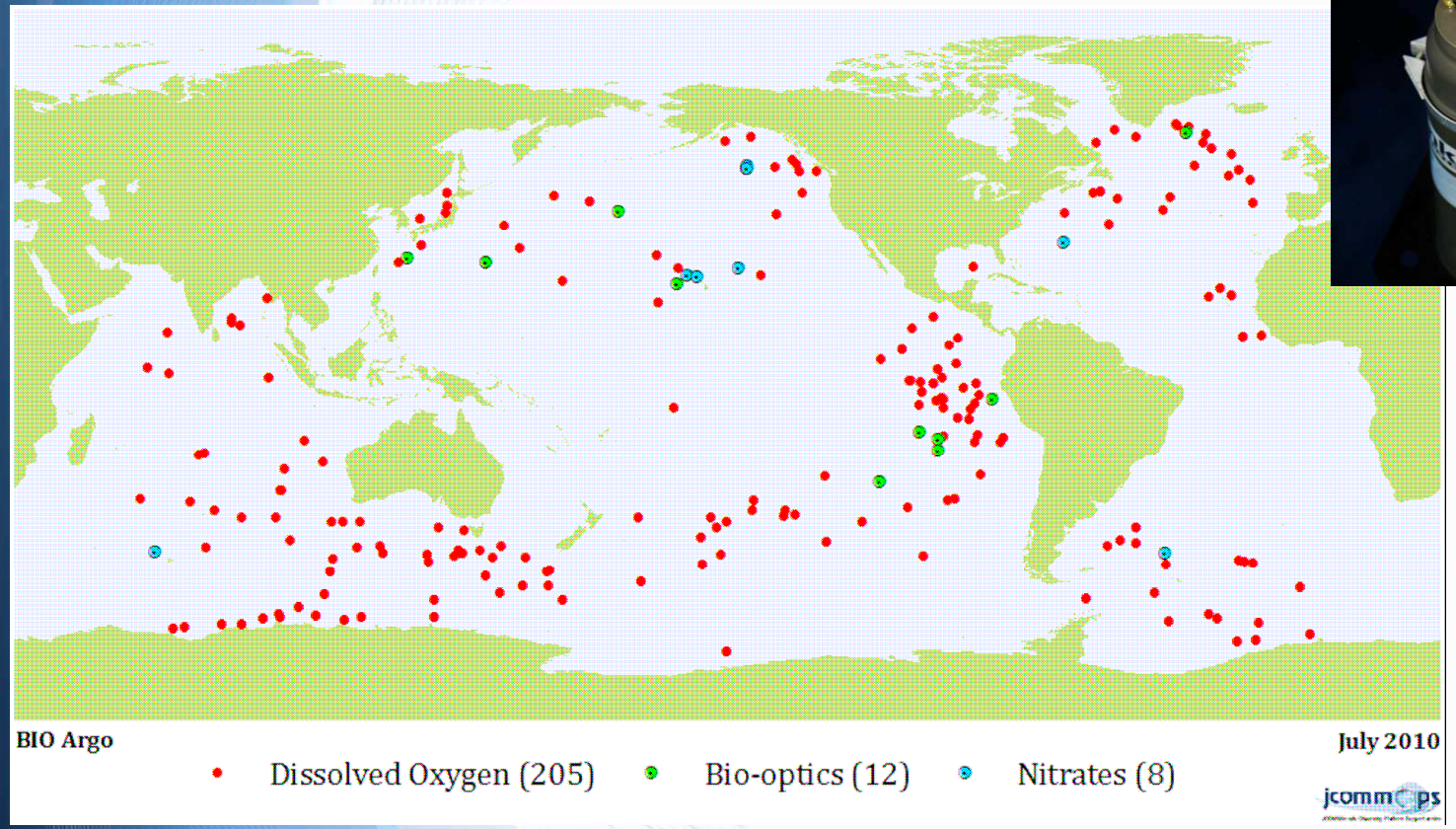
(Winkler's method overestimates dissolved oxygen in seawater: Iodate interference and its oceanographic implication. *George T.F. Wong and Kuo-Yuan Li, Marine Chemistry, 2009, vol.115, n°1-2, pp.86,91)*

- **Lack of understanding of optical sensors (optodes) behaviour (interferences, corrosion issues, interactions with some materials, …)**

Main issues

Dissolved oxygen calibration:

Argo project

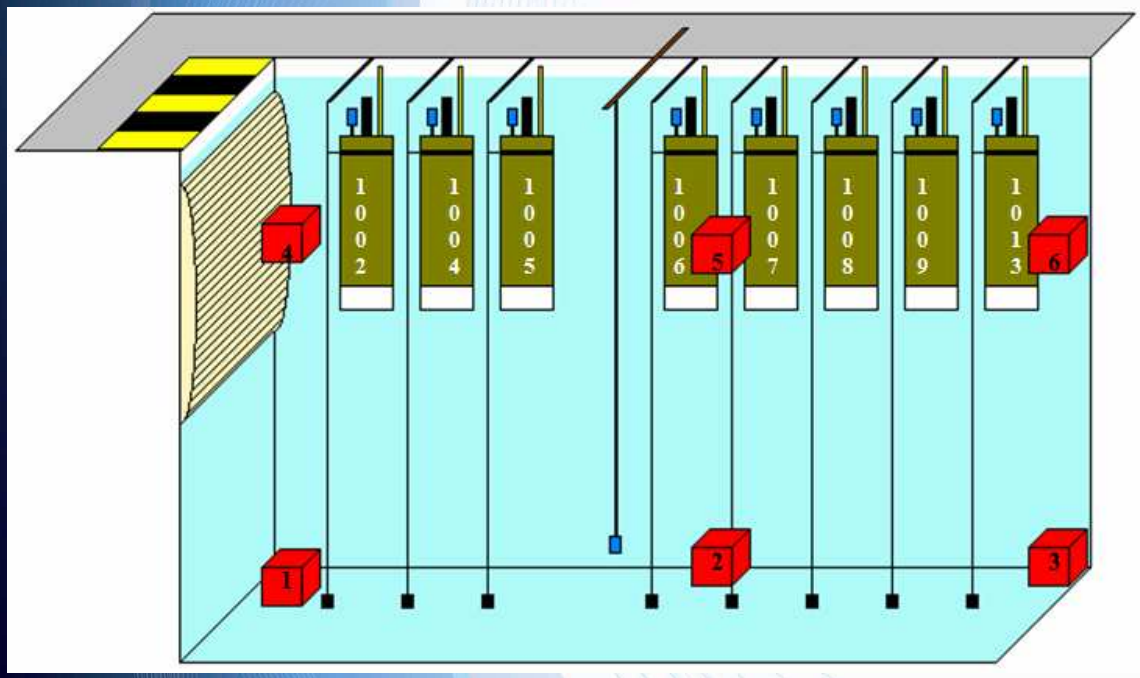


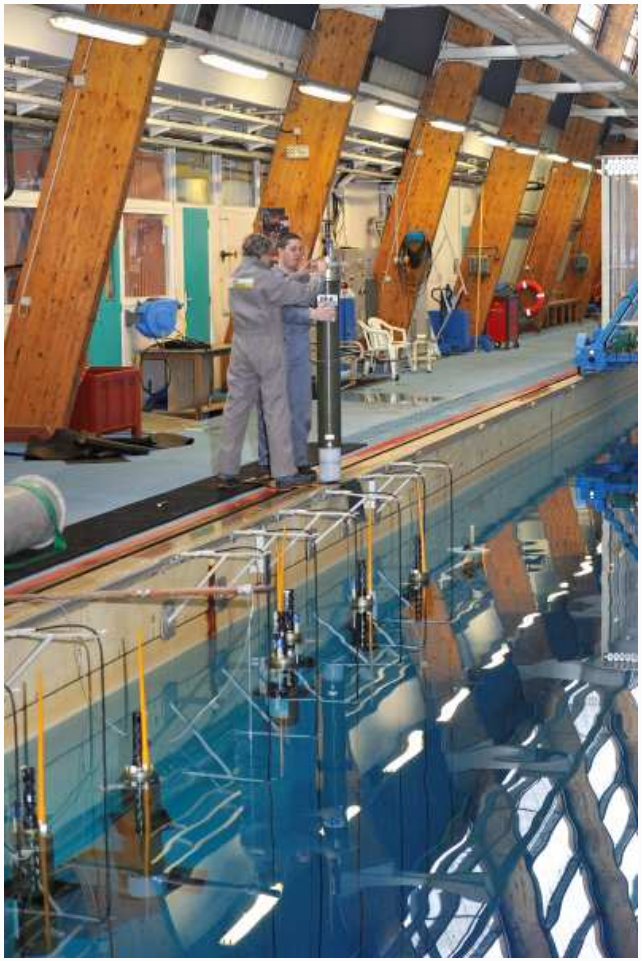
Ifremer - Argo oxygen meeting - May 2011 - V. Thierry et al.

Main issues

Dissolved oxygen calibration:

Argo project

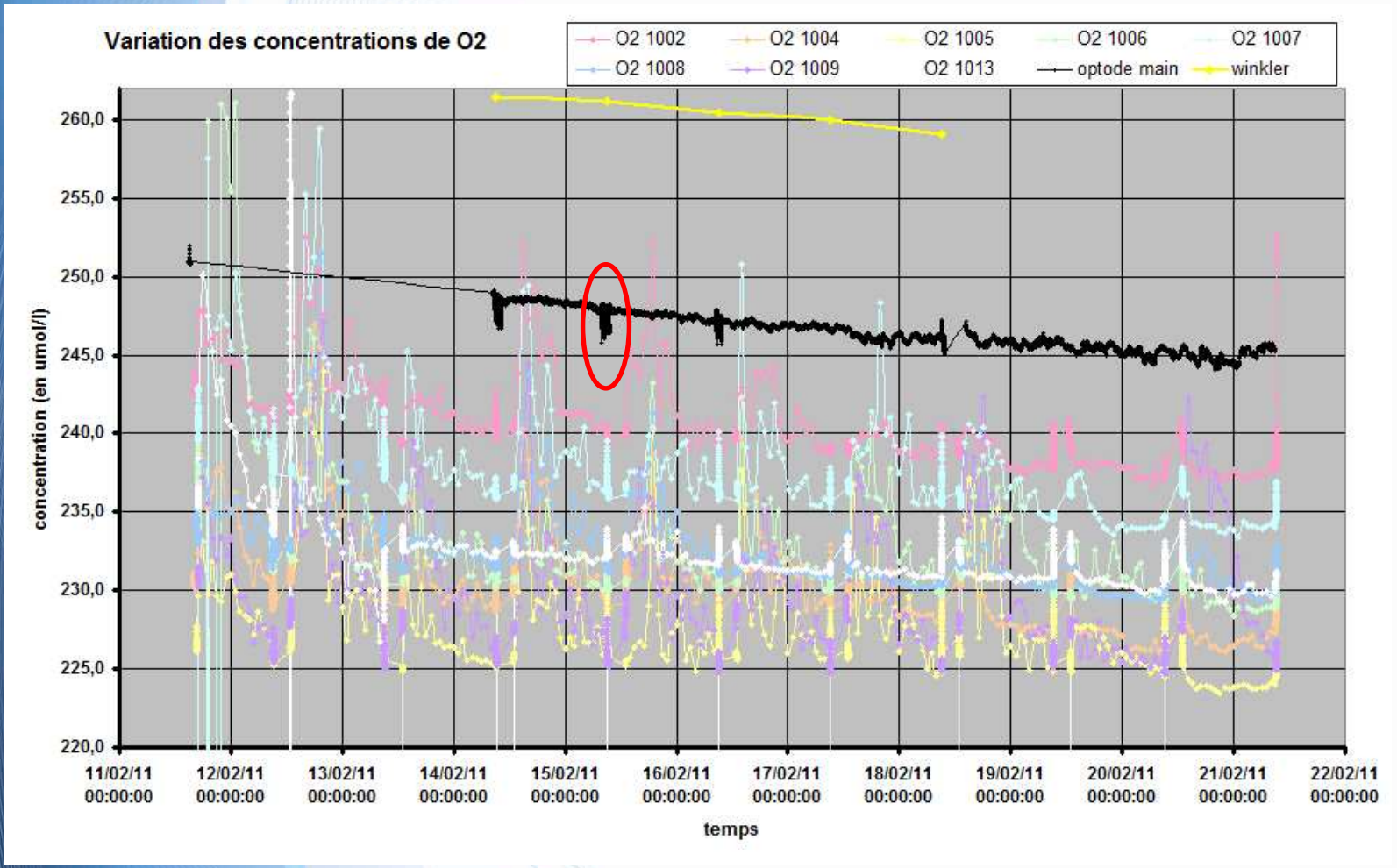




Ifremer - Argo oxygen meeting - May 2011 - V. Thierry et al.

Main issues

Dissolved oxygen calibration: Argo project



Main issues

Salinity calibration:

- **Range: from 2 to 42**
- **Current Procedure:**

  calibration in temperature regulated bath for different stages of temperature and salinity (natural seawater diluted with fresh water)

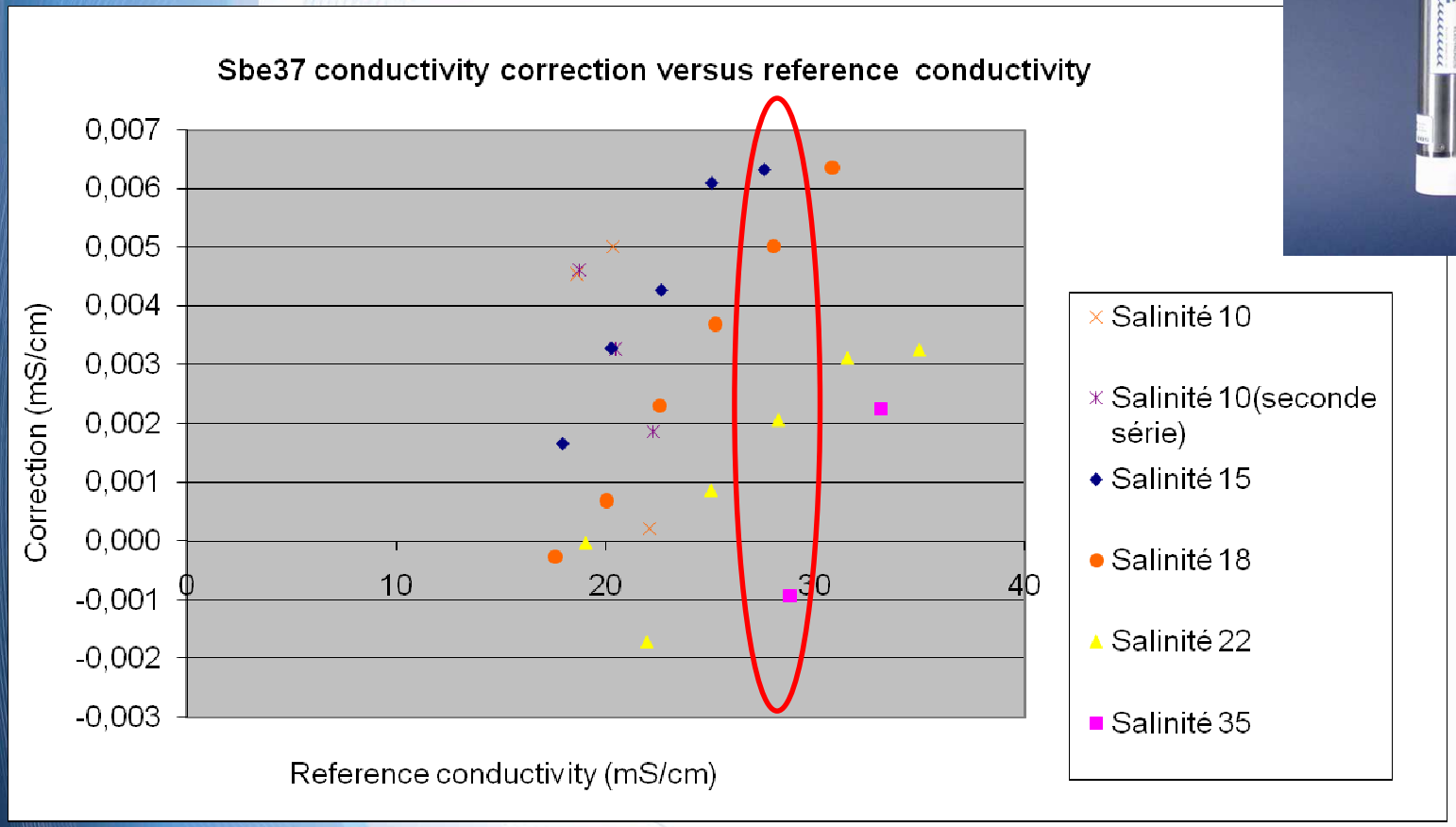
Issues:

- **No Certified Reference Material (no traceability)**

Main issues

Issues:

- **Conductivity sensor response dependent on salinity**



Main issues

pH calibration:

- **Range: from 0 to 14**
- **Current Procedure:**

  calibration with standard pH solutions

Issues:

- **Standard matrix: no seawater → no Certified Reference Material (no traceability)**

Main issues

Turbidity calibration:

- **Range: from 0 to 1000 FNU**
- **Current Procedure:**

  calibration with formazin solutions

Issues:

- **Not the measurand to achieve (suspended matter)**
- **No CRM (no traceability)**
- **Lack of understanding of optodes behaviour (signal drift, noise, … interactions with parameters to be found)**

Main issues

Fluorescence calibration:

Context: chlorophyll *a* calibration with pigment extraction:

- **Time consuming**
- **Dependent on algae species**
- **Dependent on algae physiology**

Ifremer's choice:

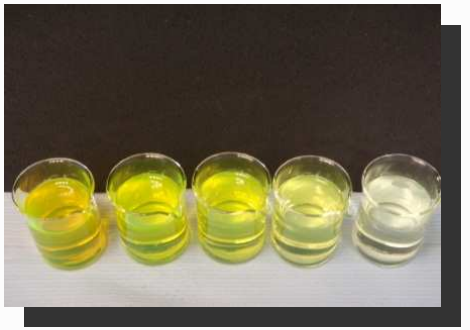
Perform calibration in fluorescence rather than in chlorophyll *a* concentration

Main issues

Fluorescence calibration:

- **Range: depending on sensor / fluorophore**
- **Current Procedure:**

  calibration with fluorescein solutions



Fluorescein

Issues:

- **Controls only the drift and the stability of measurement**
- **Not the measurand to achieve**

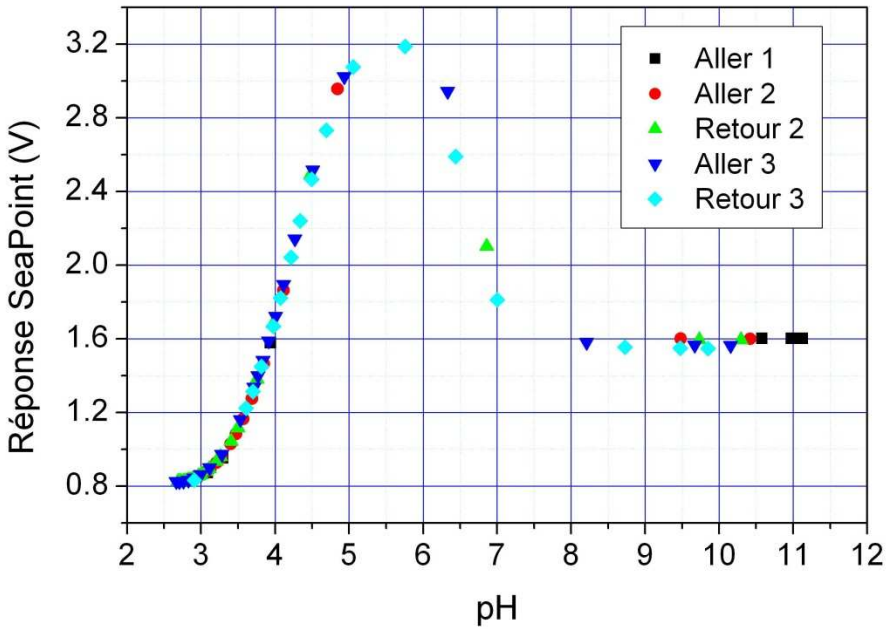
  (µg/l vs chlorophyll *a* or algae estimation)
- **No Certified Reference Material (no traceability)**

Main issues

Fluorescence calibration:

Issues:

- **pH influence on fluorescein**

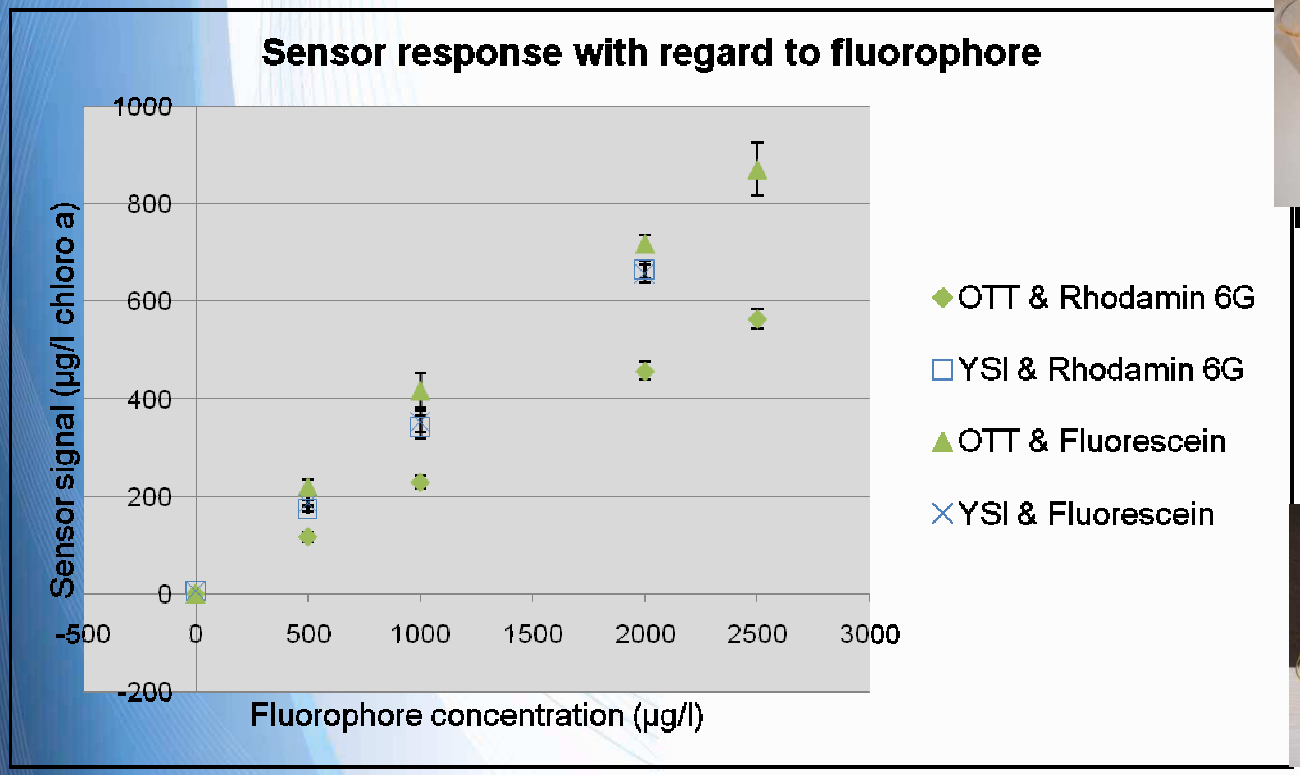


Main issues

Fluorescence calibration:

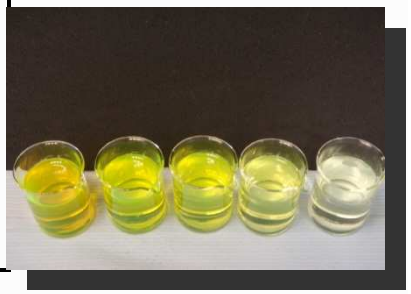
Issues:

- **Sensor comparison impossible: sensor response dependent on technology**



Rhodamin 6G

Fluorescein



Main issues

Fluorescence calibration:

Issues:

- **Lack of understanding of optode response (signal drift, noise, … interactions with parameters to be found)**

Main issues

Traceability ?

Parameters							
Temperature	**Pressure**	**Current**	**O_2**	**pH**	**Salinity**	**Turbidity**	**Fluorescence**
YES	YES	YES / NO (sensor technology)	YES -> NO	YES -> NO	NO	NO	NO
Regulated bath + Pt25 reference thermometer	Relative pressure balance	Towing canal	Regulated bath + Winkler titration	Standard pH solution	Salinometer calibrated by IAPSO standard	Formazin solutions	Fluorophore solutions

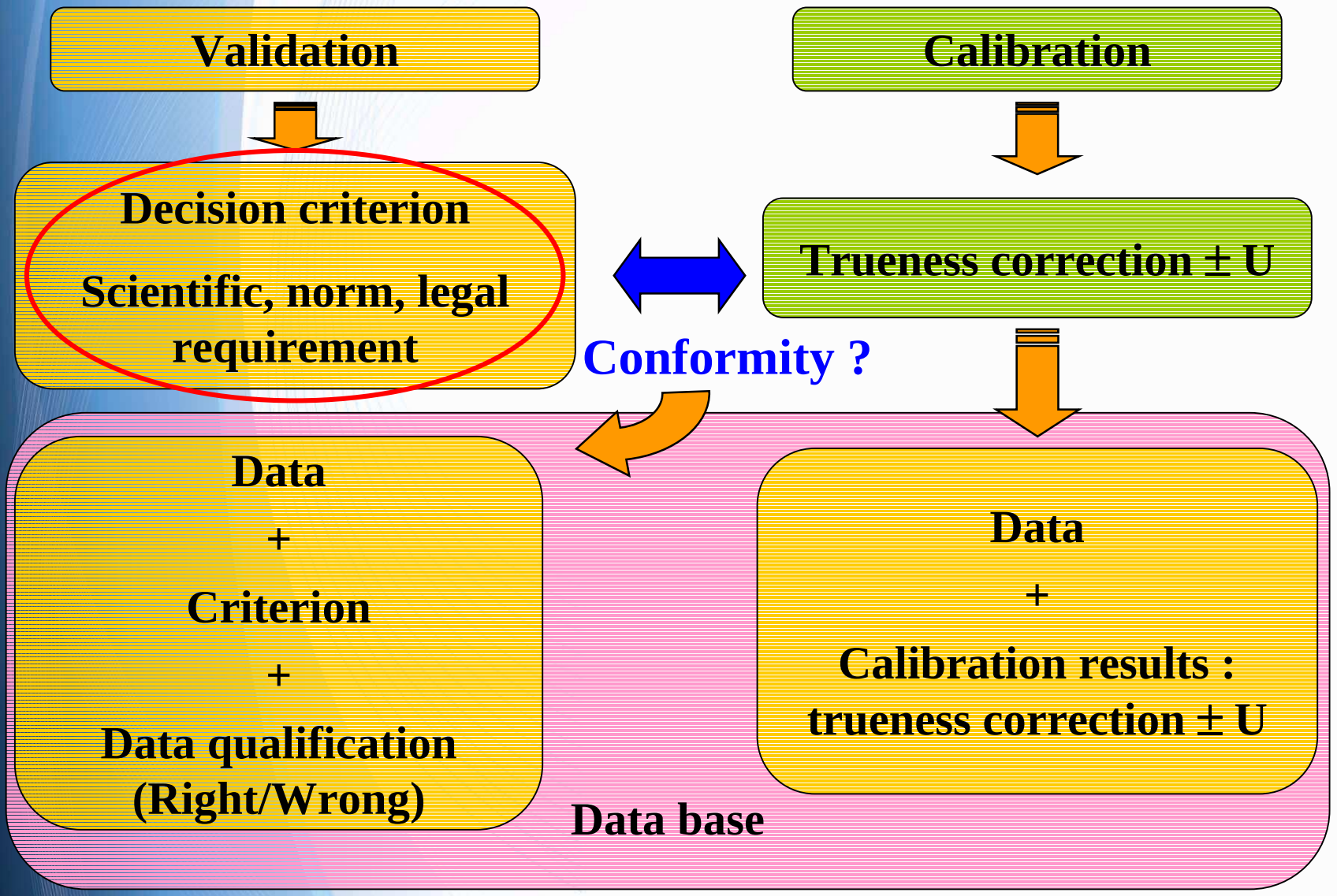
No norm in technology

- **No representativeness (substance matrix, …)**
- **No relation to SI units**
- **Not universal in regard to the different technologies**

No reference material or No reference method

Main issues

Consequences: Validation issues



1 – Context

2 – Main issues

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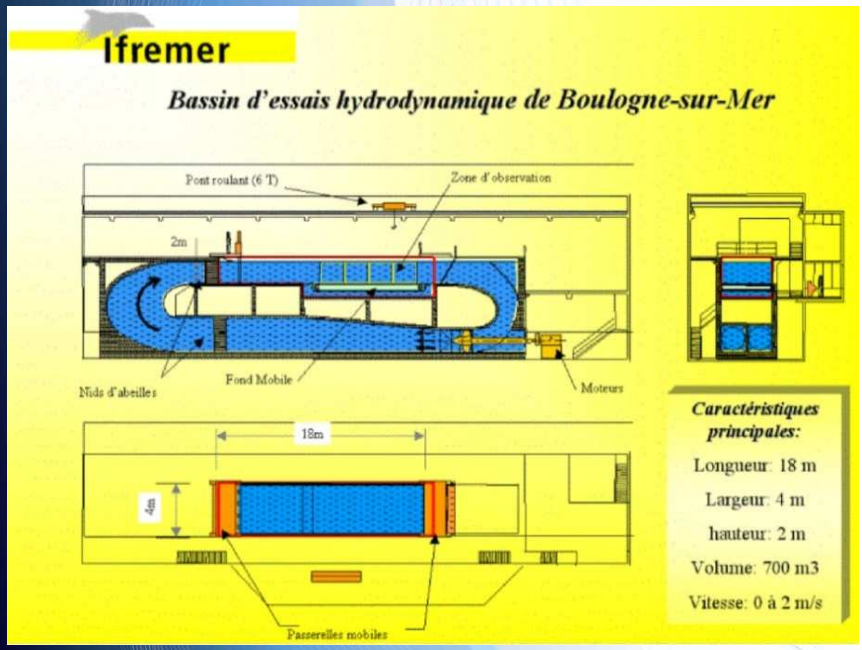
On going studies

Current calibration:

- Contact with accreditated laboratories for acoustic Doppler current meter (Metas)

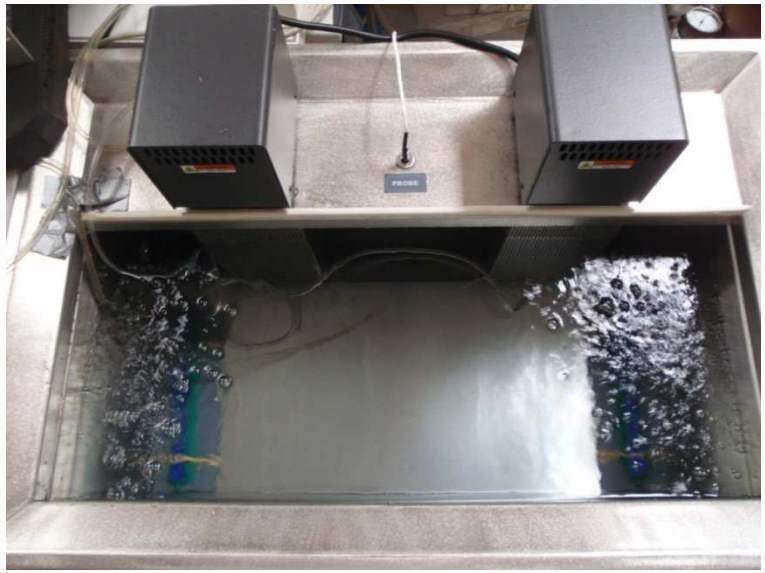
- Evaluate the calibration feasibility in the towing canal at Brest and in the water vein at Boulogne



On going studies

Oxygen calibration:

- **Characterization of an oxygen multi-level bench**



- ✓ **Stability:**
  - **< 0.5 µM within 1 hour**
  - **long stability levels (several hours)**
- ✓ **Lowest level: nearly 0%**
- ✓ **0_2 homogeneity: < 2µM (! first results)**

On going studies

Oxygen calibration:

- **Hypox, Argo projects:**

  Inter-laboratory comparison (Australia, USA, Germany (2), manufacturers):

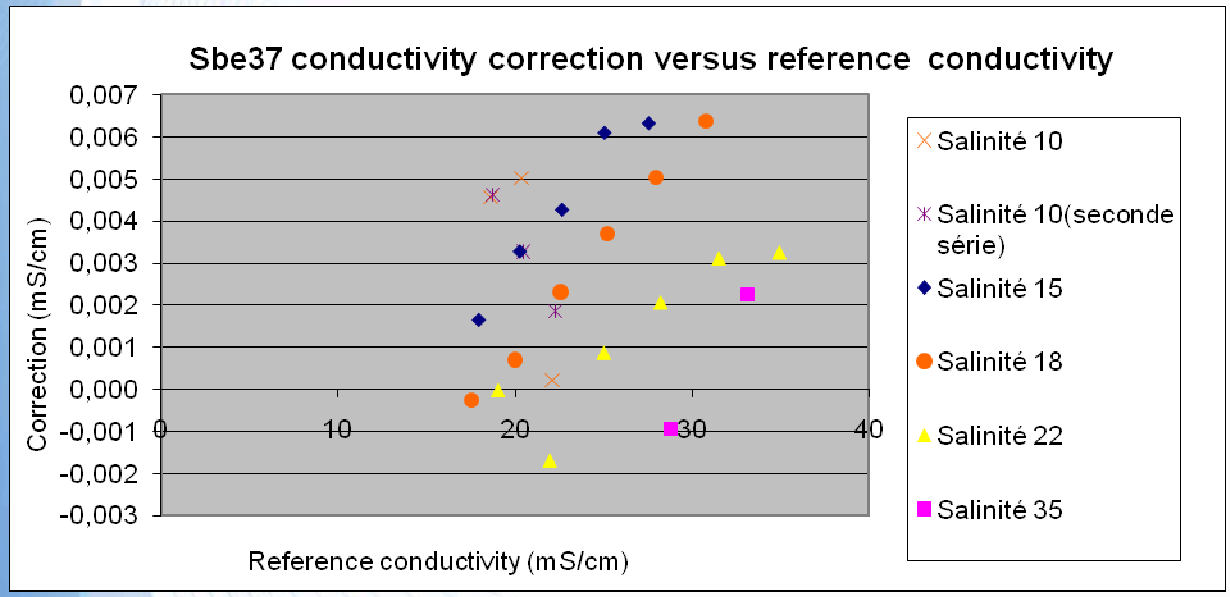
  - ✓ **Chemical systems**
  - ✓ **Bubbling systems**
  - ✓ **mixed waters saturated with gas**
  - ✓ **…**

- **Jerico: calibration CIL ? (sea tech week)**

On going studies

Salinity calibration:

- **Carry on the investigation on salinity effect**



- **Uncertainty budget (CIL ?)**
- **ENV05 Ocean project (European Metrology Research Programme) : reference methods and standards**

On going studies

Turbidity calibration:

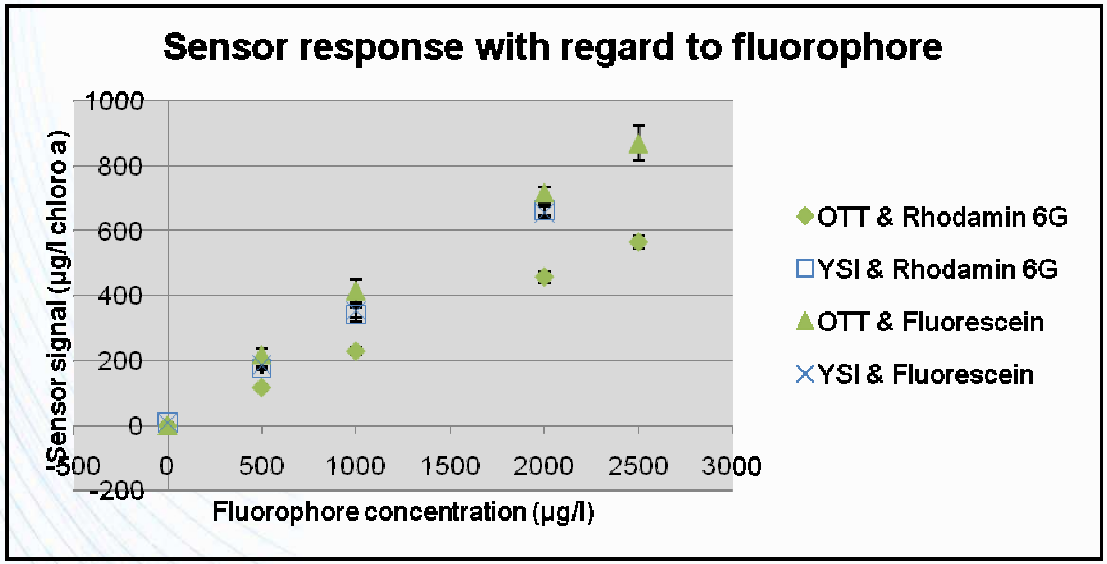
- **Calibration protocols improvements on multi-parameter probes (YSI, OTT, NKE):**

  - ✓ **Temperature influence**
  - ✓ **Stirring effect**

On going studies

Fluorescence calibration:

- **Calibration protocol studies on multi-parameter probes (YSI, OTT, NKE, Seapoint, Seatech): fluorophore effect**



- ***In situ* campaign studies (YSI, OTT, NKE, Seapoint, Seatech) with chlorophyll a extraction.**

On going studies

Parameters							
Temperature	**Pressure**	**Current**	**O_2**	**pH**	**Salinity**	**Turbidity**	**Fluorescence**
YES	YES	YES / NO (sensor technology)	YES -> NO	YES -> NO	NO	NO	NO
Regulated bath + Pt25 reference thermometer	Relative pressure balance	Towing canal	Regulated bath + Winkler titration	Standard pH solution	Salinometer calibrated by IAPSO standard	Formazin solutions	Fluorophore solutions

Protocol evaluation

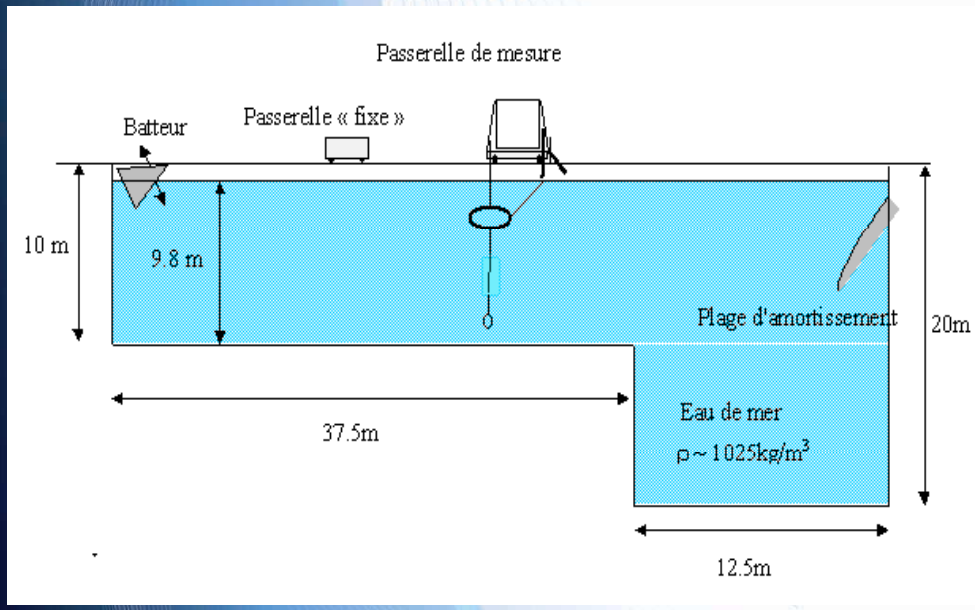
New calibration bench (temperature and O_2 regulated/salinity levels) + Uncertainty estimate + Accreditation

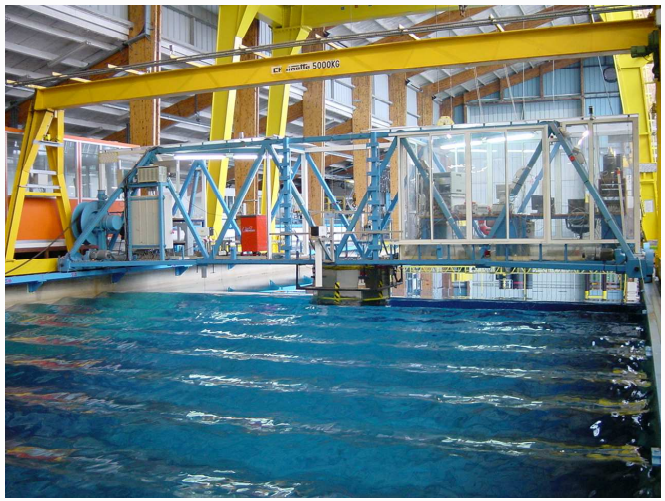
Uncertainty estimate Salinity influence

Calibration Protocols improvements

National or international inter-laboratory comparisons projects
Metrology laboratory collaboration (eg. Aquaref)

THANKS FOR YOUR ATTENTION.



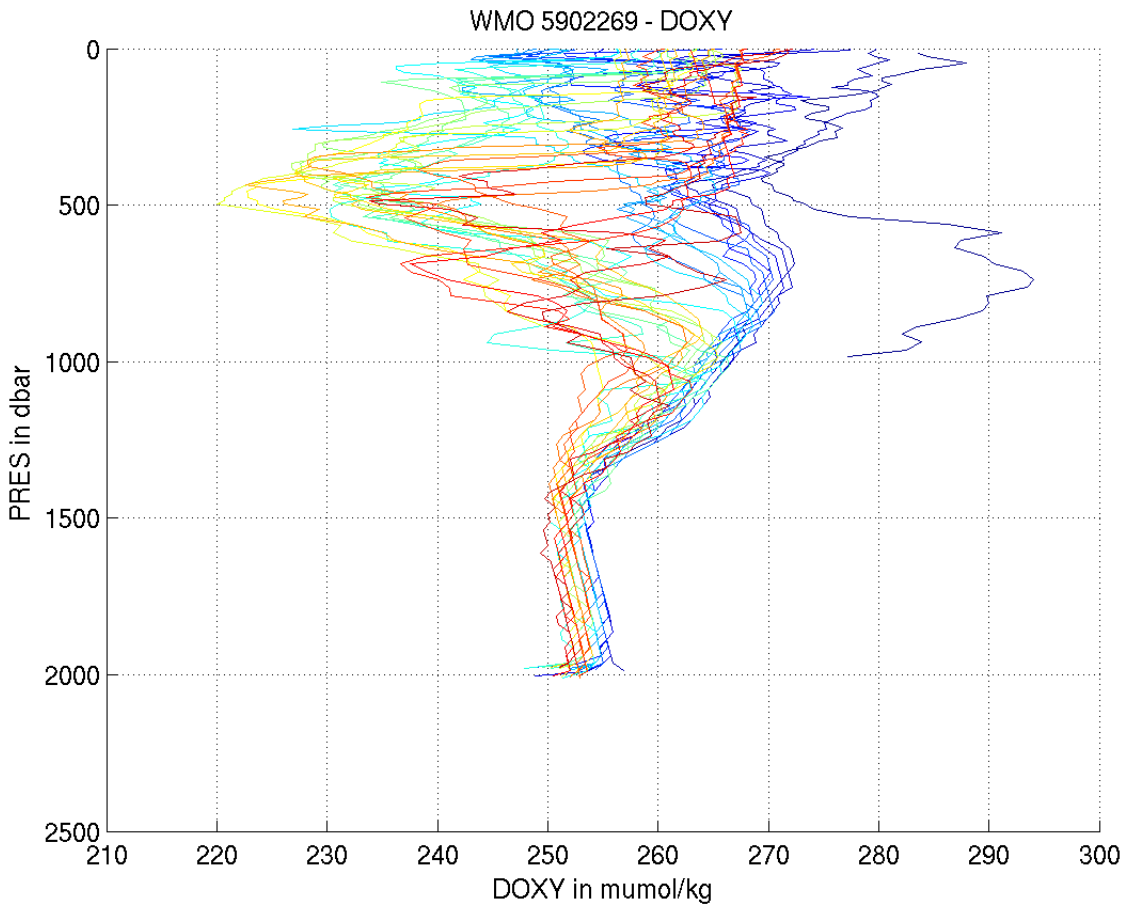


Main issues

Dissolved oxygen calibration:

Argo project

Dryness

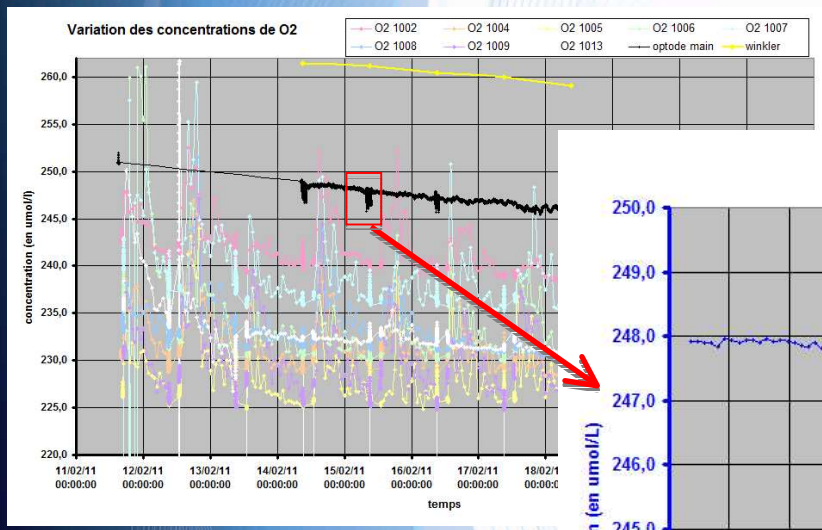


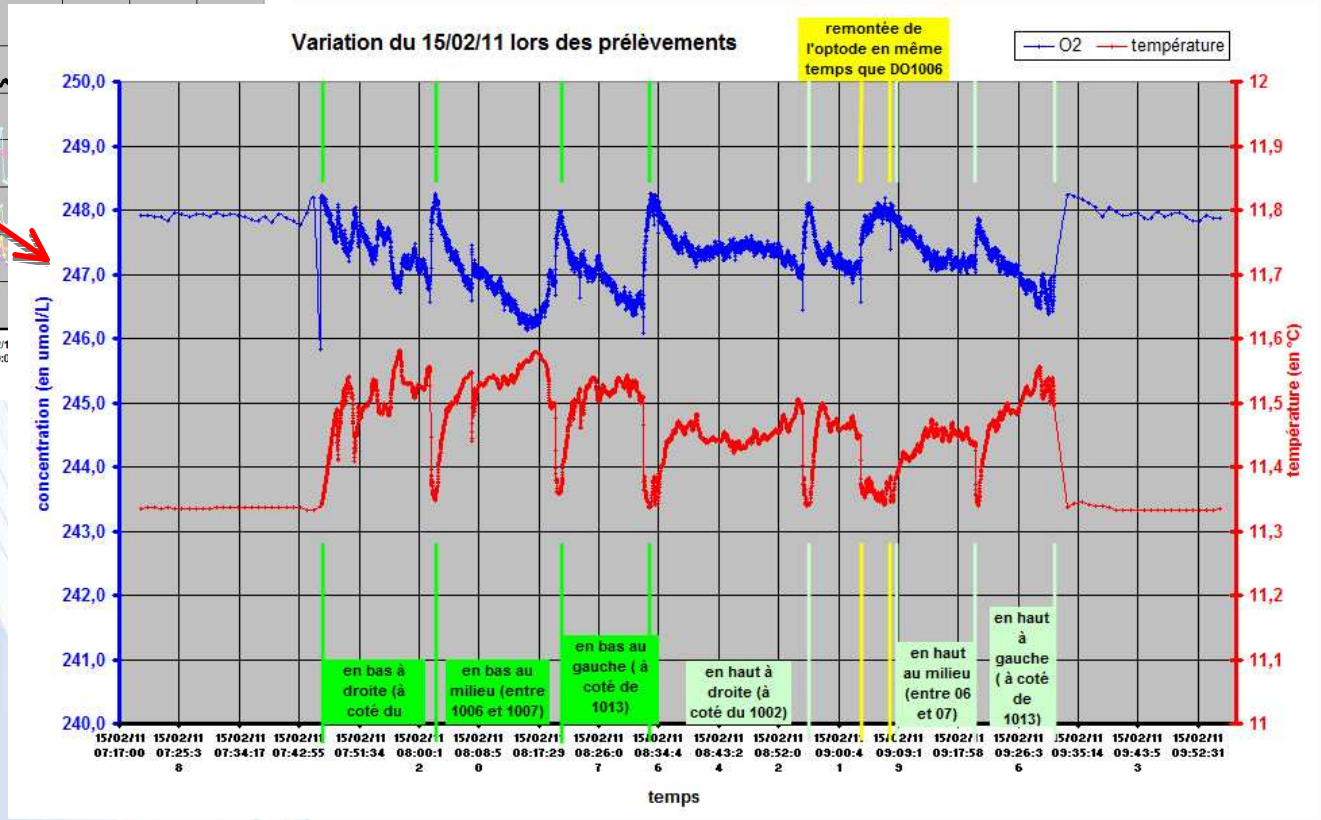
Main issues

Traceability to SI units ?

Dissolved oxygen calibration:

Argo project





Self heating depending on sampling

Ifremer - Argo oxygen meeting - May 2011 - V. Thierry et al.

Main issues

Some ideas :

- **For "New" sensors development: Involve metrology in the first steps of development**
  - **Technical choices**
  - **Ensure method validation**

- **For unknown parameters metrology:**
  - **increase collaborations between metrology laboratory concerned (Aquaref)**
  - **organise / participate Inter Laboratory Comparisons**
  - **operate a number of sensor in parallel to increase results reliability**

Main issues

Some ideas :

- **Recondition sensors *in situ* (standard signal or reagent)**

  To follow some sensor specifications (qualification of the drift, measurement trueness and repeatability)

  ! : stability of reagent/standard need to be evaluate (degradation and biodegradation, drift, …)