Dissolved oxygen sensors

Calibration needs, current practices and alternatives

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O2 Meeting – Paris/LOCEAN, 09/28/15

1 – Current status: needs, practices and lacks

2 – Up to date recommendations

3 – Performance testing

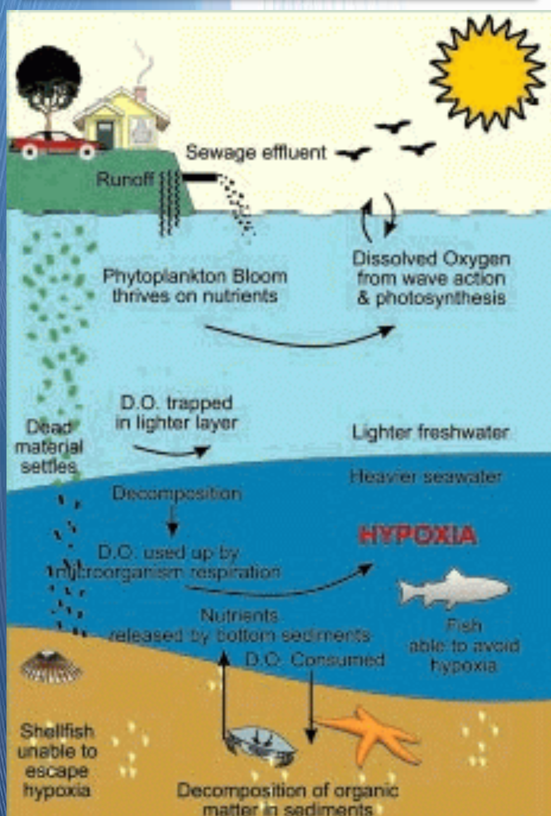
4 – Alternatives

Scientific needs

Coastal waters

- Water quality index
- Biomass indicator

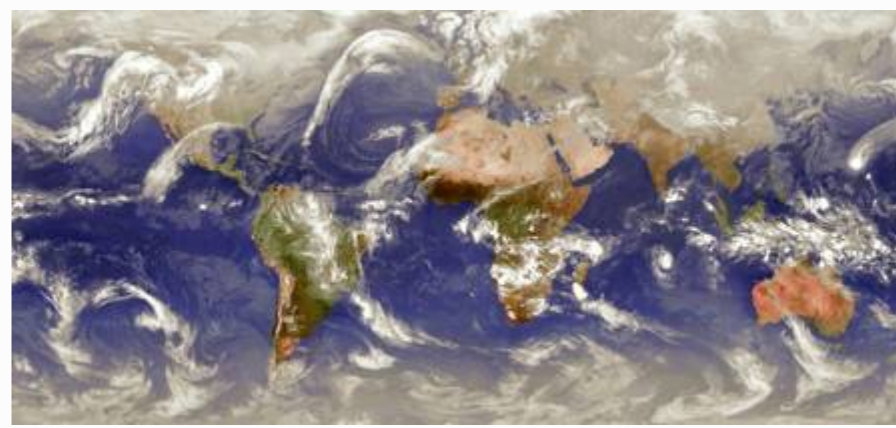
≈ 5 to 6 µmol/l



Open ocean

- Climatology
- Water masses
- Mixing processes
- Biogeochemical processes

≈ 1 µmol/l



Situation (practices and lacks)

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

Situation (practices and lacks)

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, … ?)

1 – Current status: needs, practices and lacks

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Up to date recommendations (optical sensors)

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)"

$$[O_2] = P_0 / P_c - 1 / K_{sv} \quad \text{with } K_{sv} = c_0 + c_1 t + c_2 t^2$$

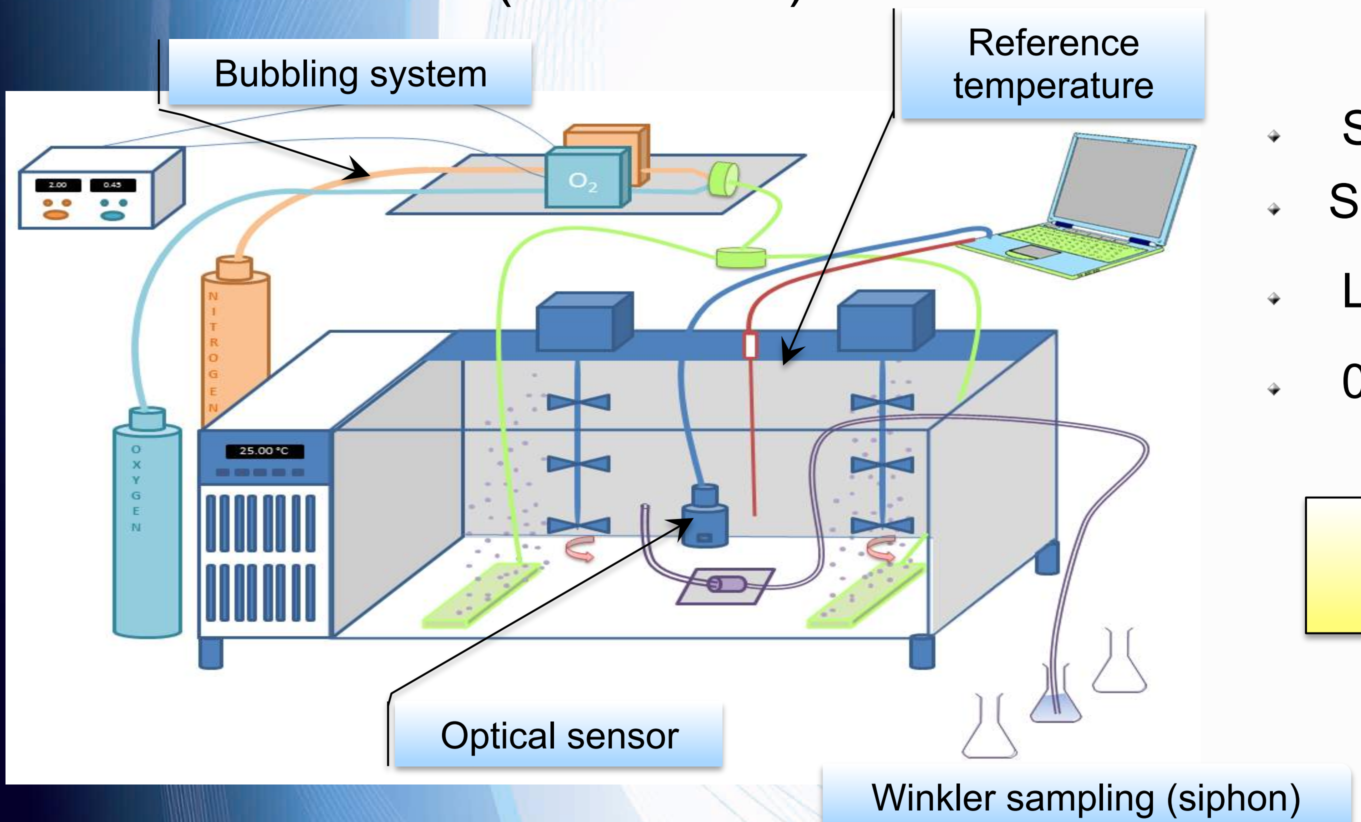
$$P_0 = c_3 + c_4 t \qquad P_c = c_5 + c_6 P_r$$

Up to date recommendations (optical sensors)

Existing multipoints calibration facilities for oceano:

- Bubbling systems:

- Ifremer (F. Salvetat)



- Stability < 0.5 µmol/l
- Several hours stability
- Lowest level: nearly 0%
- 0_2 homogeneity < 2µmol/l

Fulfill requirement: a few µmol/l

Existing multipoints calibration facilities for oceano:

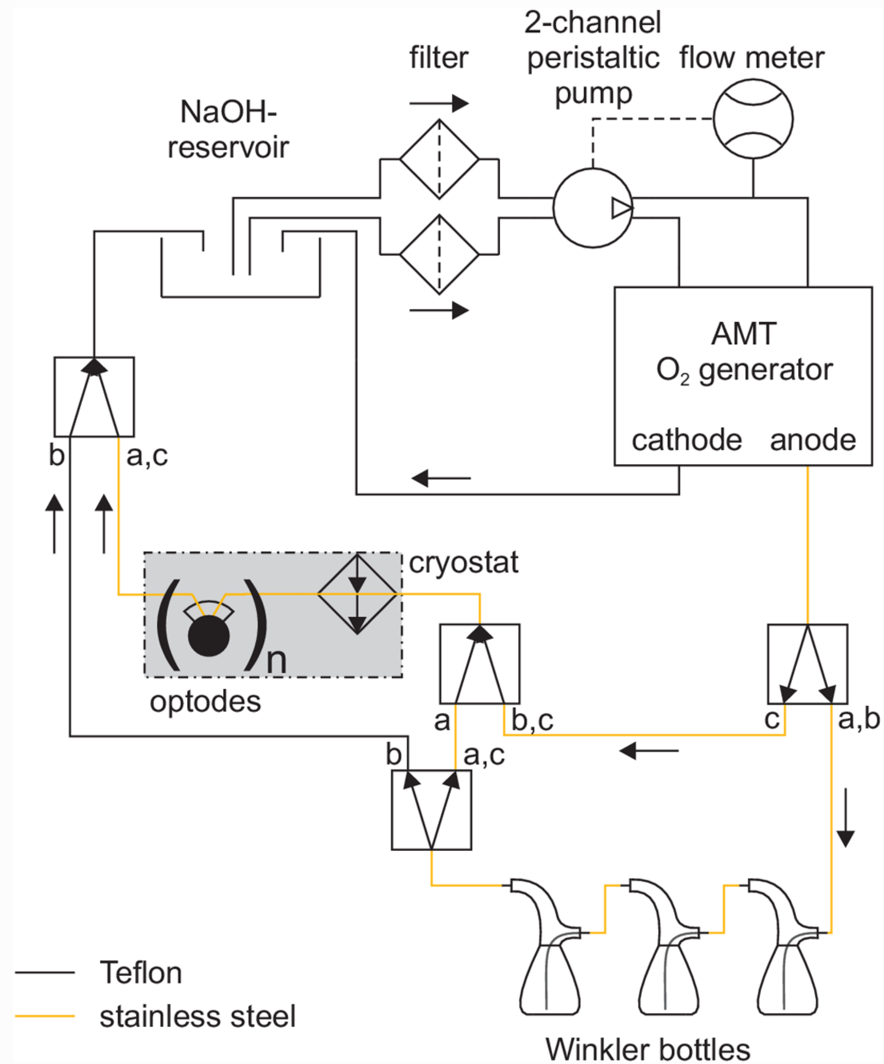
- Electrochemical systems:

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)



Up to date recommendations (optical sensors)

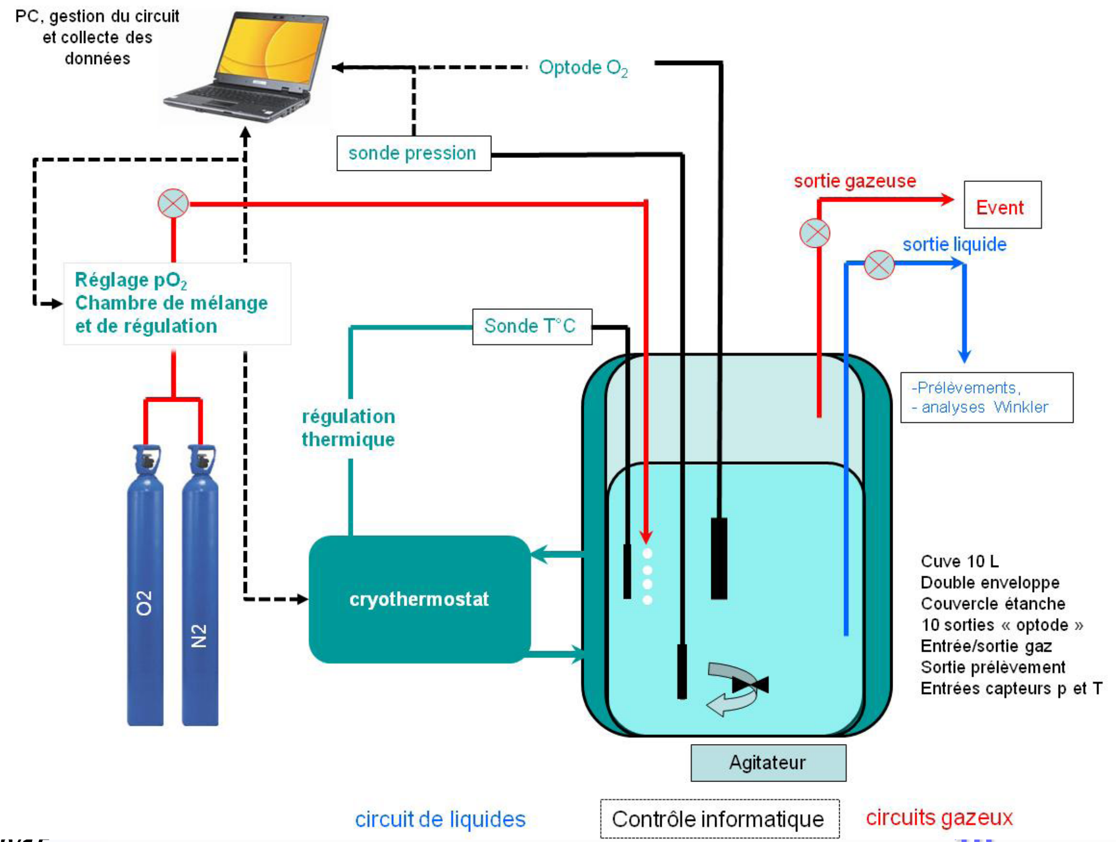
Existing multipoints calibration facilities for oceano:

- Bubbling systems:

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

  Specific bench designed for optodes

- MIO (D. Lefèvre)



Up to date recommendations (optical sensors)

Existing multipoints calibration facilities for oceano:

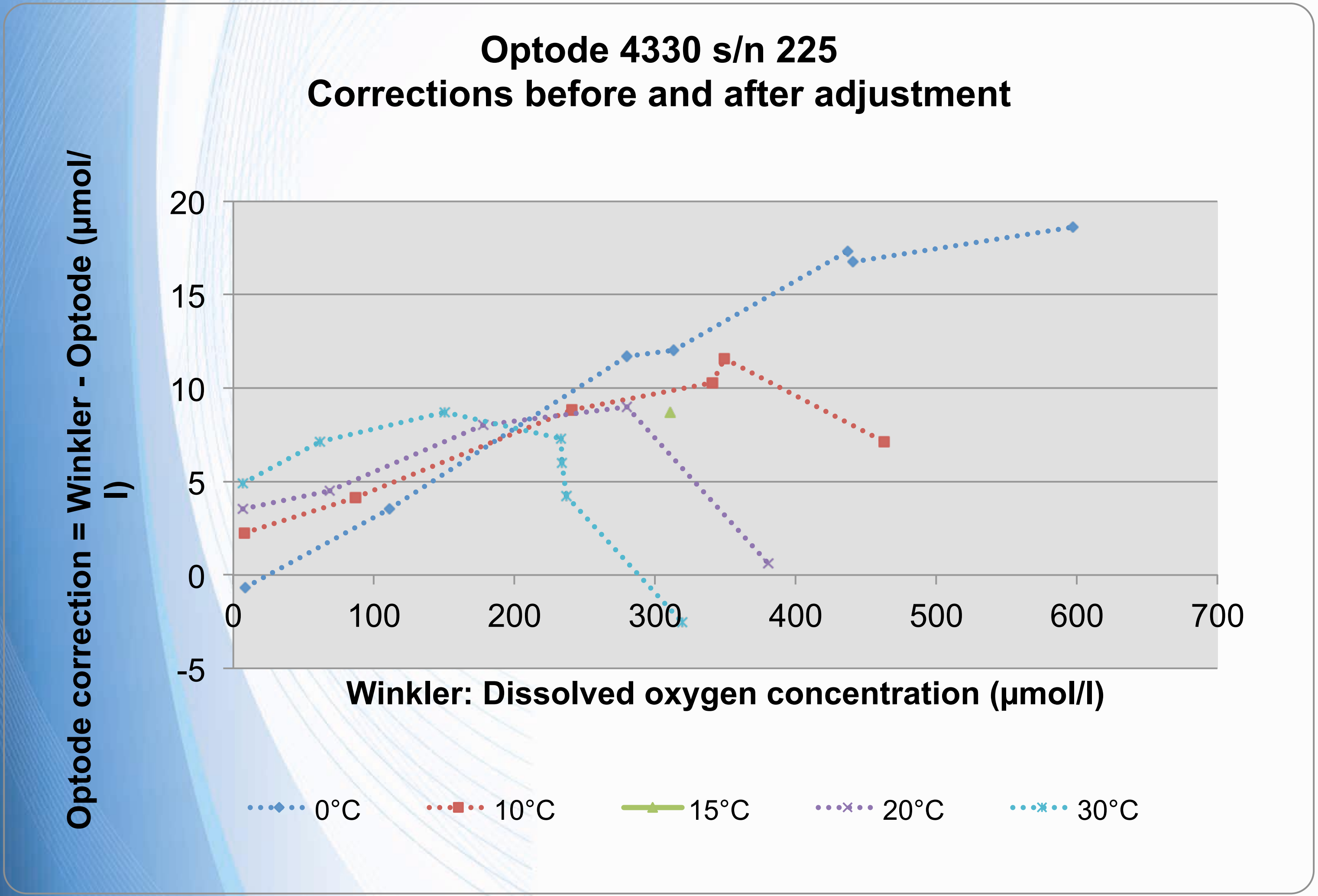
- Bubbling systems:

- MPI (F. Janssen)

- JAMSTEC (H. Uchida)

Up to date recommendations (optical sensors)

Results of a multipoints calibration (Ifremer)

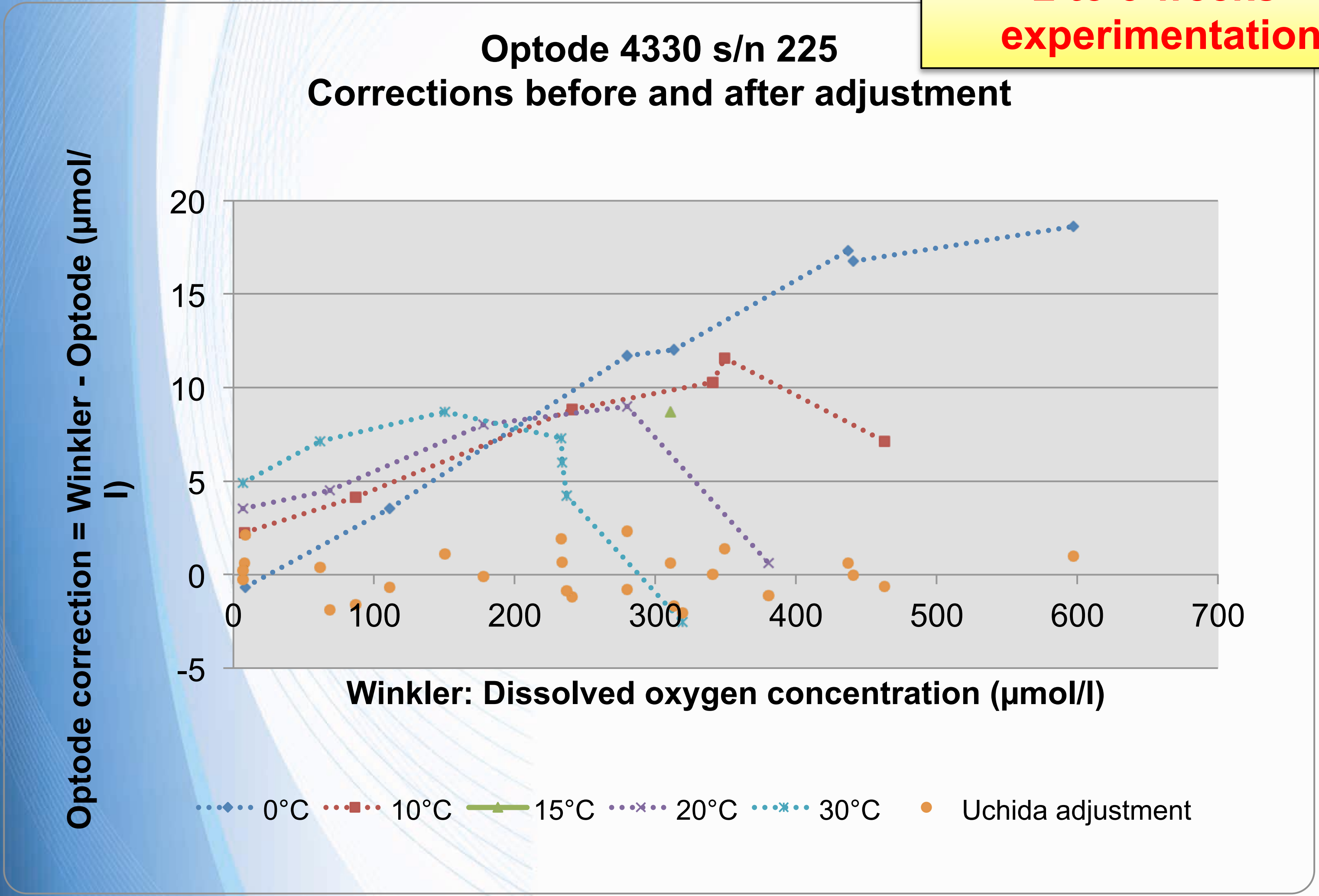


Up to date recommendations (optical sensors)

Ifremer

Results of a multipoints calibration (Ifremer)

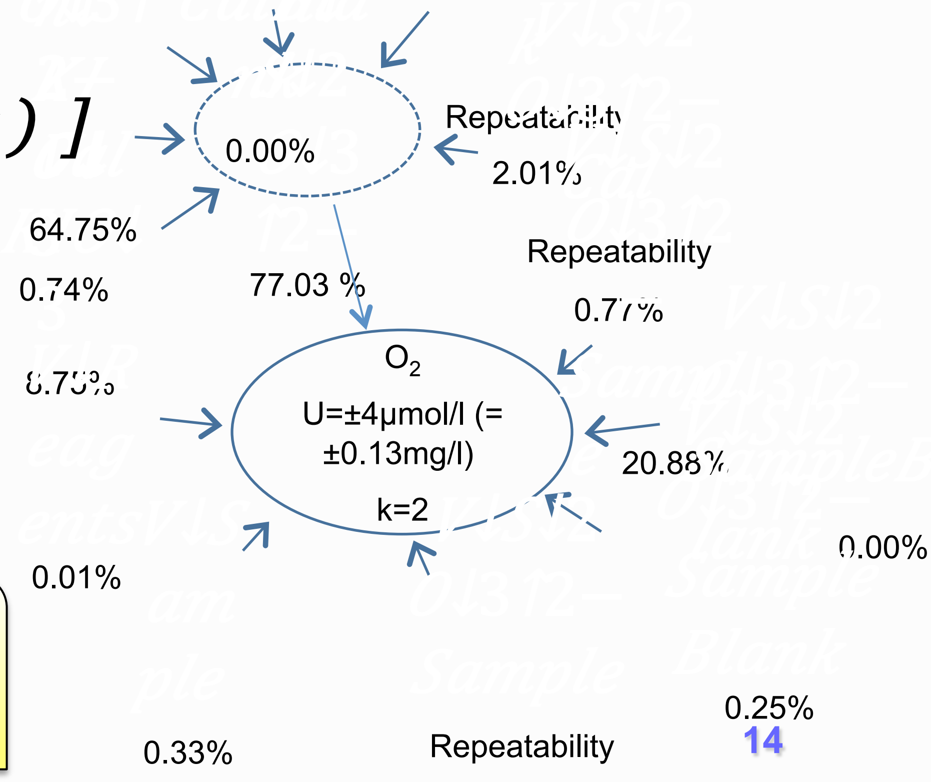
2 to 3 weeks experimentation



Results of a multipoint calibration (Ifremer)

- Uncertainty calibration budget: U ≈ ± 7 µmol/l (at 440 µmol/l) with U (Winkler) = 4 µmol/l

[O↓2] µmol/l=[■n↓KIO↓3 V↓KIO↓3 /
(V↓S↓2 O↓3↑2− Cal −V↓S↓2 O↓3↑2−
CalBlank)×(V↓S↓2 O↓3↑2− Sample −
V↓S↓2 O↓3↑2− SampleBlank)/4 ×
1000000/(V↓S... ↓Reagents)]
−38×V↓Rea... ...mple

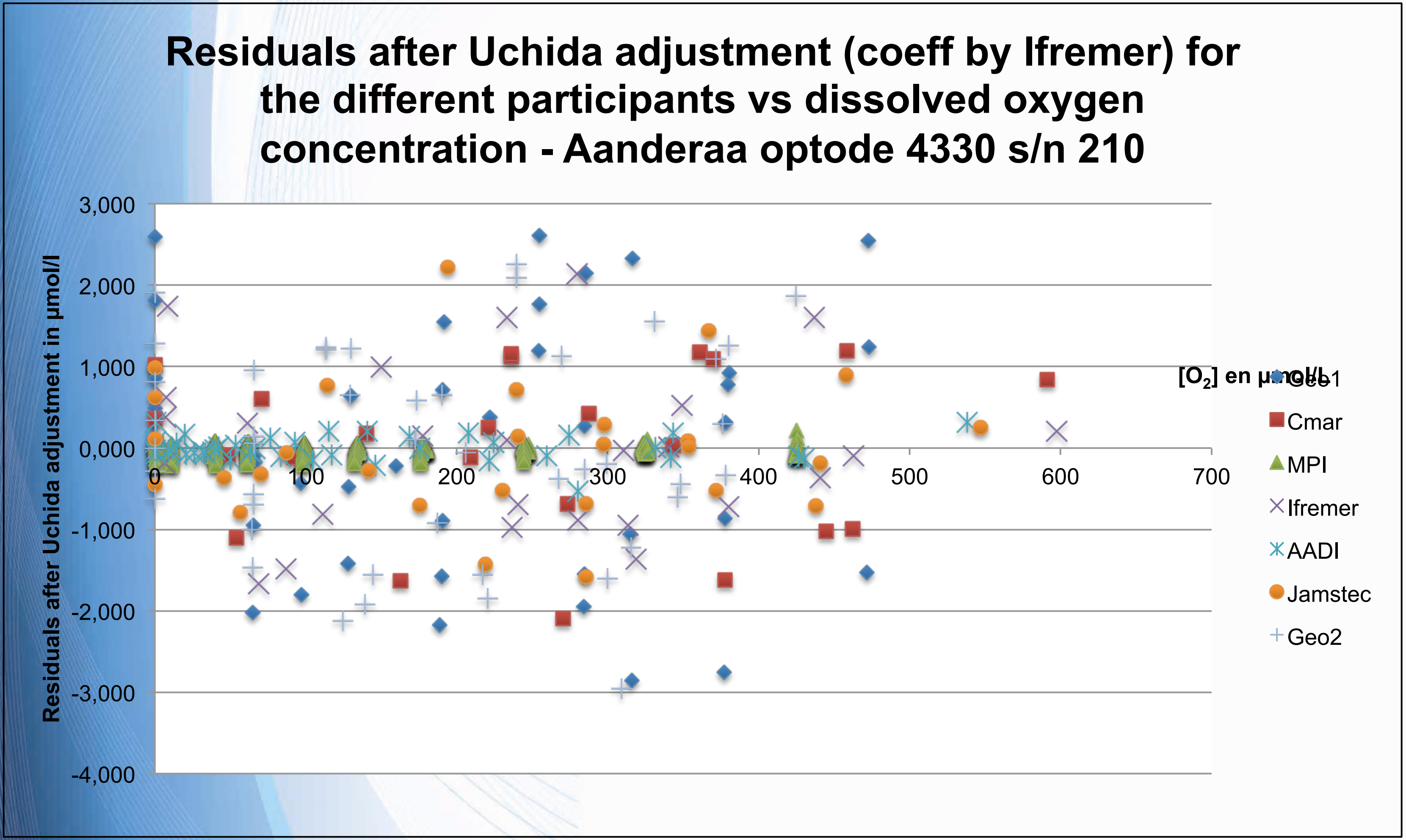


Gravimetric Winkler: U/2
I.Helm, L.Jalukse, I. Leito, Anal. Chim. Acta. 741 (2012) 21-31.

Up to date recommendations (optical sensors)

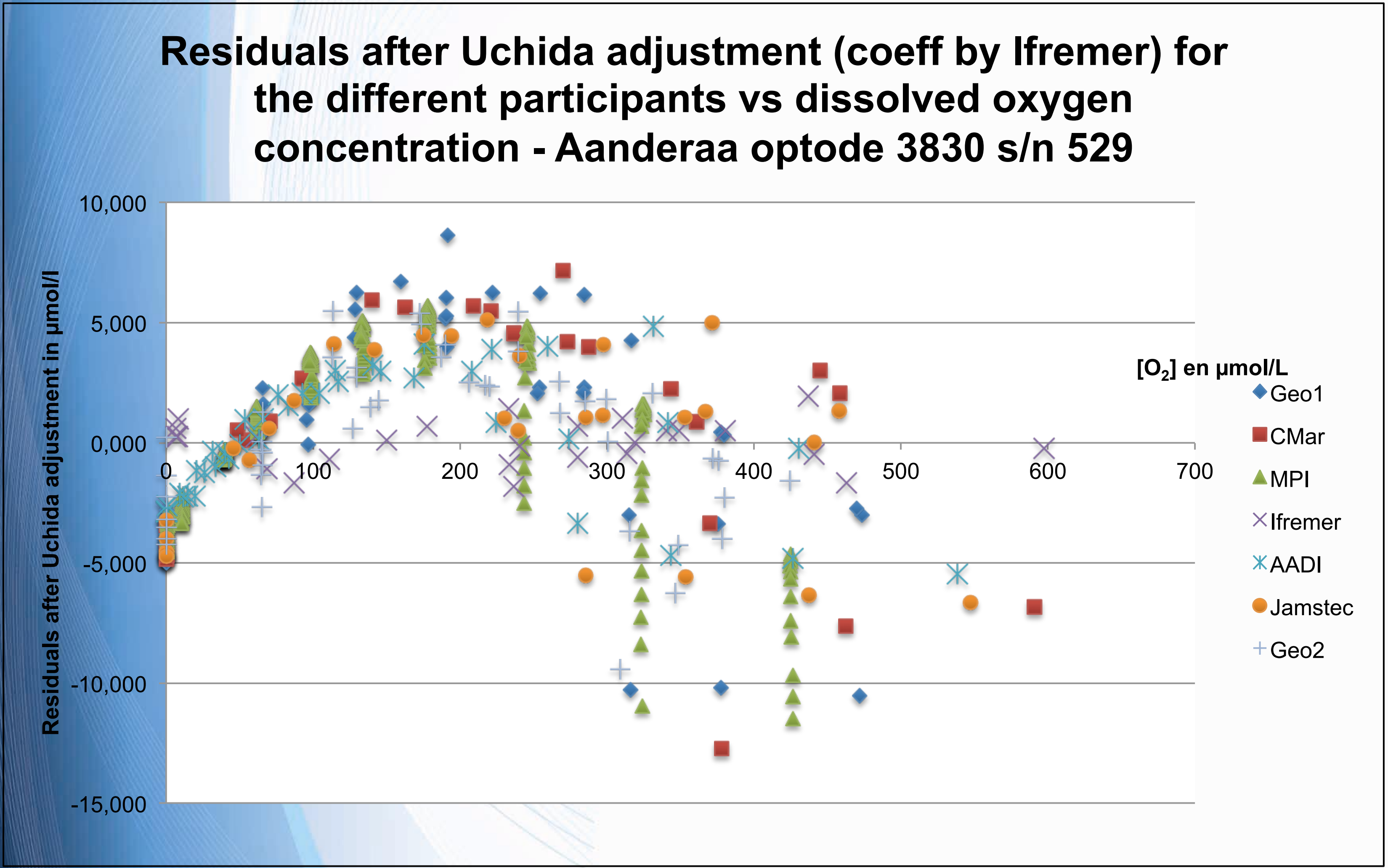
Ifremer

Few results of the Argo multipoint calibration intercomparison



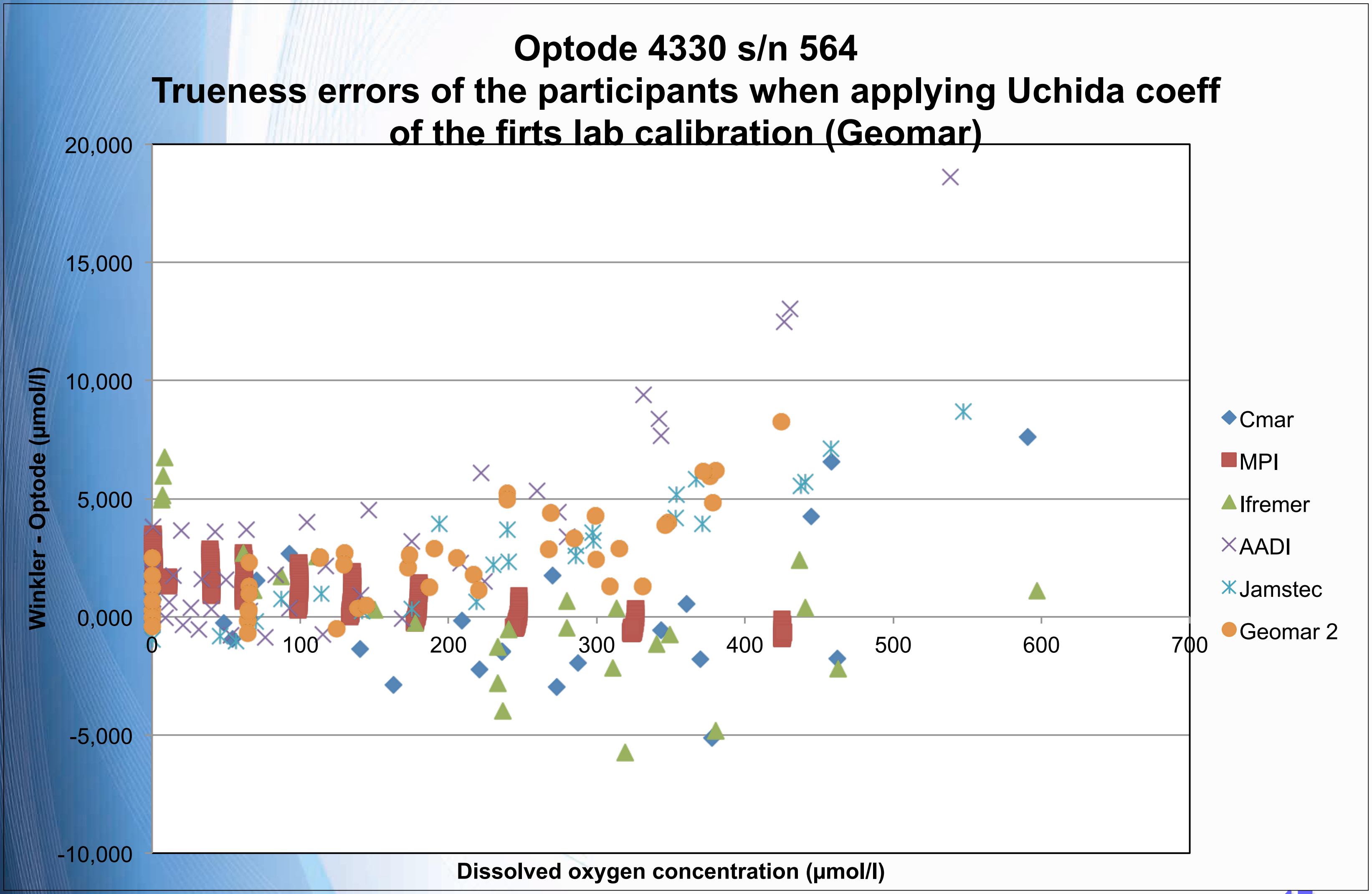
Up to date recommendations (optical sensors)

Few results of the Argo multipoint calibration intercomparison



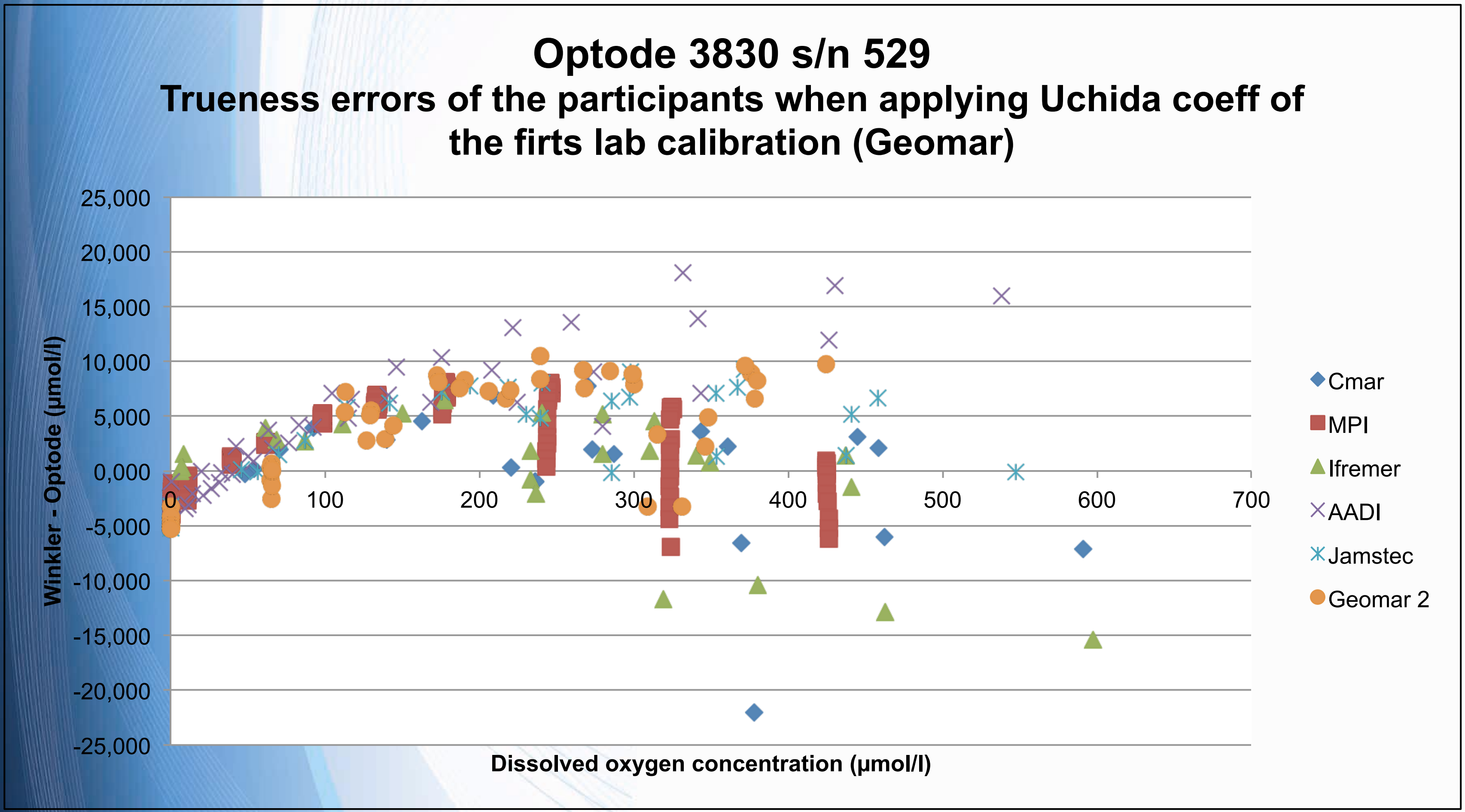
Up to date recommendations (optical sensors)

Few results of the Argo multipoint calibration intercomparison



Up to date recommendations (optical sensors)

Few results of the Argo multipoint calibration intercomparison



1 – Current status: needs, practices and lacks

2 – Up to date practices

3 – Performance testing

4 – Alternatives

prEN 16479-2 group CEN/TC 230 WG4

Performance testing

	Capteurs de conductivité	Capteurs d'oxygène dissous
Justesse, linéarité et répétabilité	P1	P1
Effet de matrice de l'échantillon	P1	P1
Température d'échantillon	P1	P1
Temps de réponse	P2	P2
Test de lumière incidente	P3	P3
Dérive	P3	P3
Impédance de sortie	-	-
Tension d'alimentation	-	-
Température et humidité relative ambiantes	Sans objet	Sans objet
Perte d'alimentation électrique	-	-
Débit d'échantillon	Sans objet	Sans objet
Pression d'échantillon	-	-

Response time

			0% en bisulfite		0% en azote	
			0% -> 100%	100% -> 0%	0% -> 100%	100% -> 0%
Aanderaa 3835	N°1199	Essai 1	1min14s	13 s	1min41s	impossible de maintenir un 0% stable avec introduction du capteur
		Essai 2	1min15s	44s	1min40s	
		Essai 3	1min18s	39 s	1min32s	
		Essai 4	-	25s	-	
		Essai 5	-	49s	-	
	N°1161	Essai 1	-	-	1min48s	
		Essai 2	-	-	-	
		Essai 3	-	-	-	
Aanderaa 4330	N°184	Essai 1	6min06s	15s	1min18s	
		Essai 2	4min39s	38s	1min34s	
		Essai 3	4min55s	49s	1min24s	
		Essai 4	-	-	1min24s	
		Essai 5	-	21s	-	
		Essai 6	-	48s	-	
OTT MS5	-	Essai 1	14s	33s	-	
		Essai 2	15s	32s	-	
		Essai 3	13s	26s	-	

Trueness

Aanderaa 3835

Définition de l'essai			Optode Aanderaa 3835 n°1199					
Salinité	Température °C	Oxygène %	Correction de justesse (performance attendue < 5% en valeur absolue ou 0.2mg/l)) mg/l					%
			Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	Moyenne	Moyenne
S = 0	20	0% bullage --> 14%	0.19	0.17	0.16	-	0.17	12.96
		35% bullage	0.40	0.36	0.34	-	0.37	10.49
		70% bullage	0.30	0.30	0.28	0.27	0.29	4.67
		105% bullage	-0.08	-0.18	-0.14	-0.23	-0.16	-1.64
		140% bullage	-0.64	-0.71	-0.70	-0.76	-0.70	-5.27

Aanderaa 4330

Définition de l'essai			Optode Aanderaa 4330 n°184					
Salinité	Température °C	Oxygène %	Correction de justesse (performance attendue < 5% en valeur absolue ou 0.2mg/l)) mg/l					%
			Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	Moyenne	Moyenne
S = 0	20	0% bullage --> 14%	0.24	0.21	0.20	-	0.22	16.56
		35% bullage	0.30	0.28	0.28	-	0.29	8.10
		70% bullage	0.23	0.25	0.23	0.22	0.23	3.68
		105% bullage	-0.07	-0.08	-0.09	-0.11	-0.09	-0.90
		140% bullage	-0.49	-0.56	-0.53	-0.55	-0.53	-4.04

Définition de l'essai			Optode Aanderaa 4330 n°325					
Salinité	Température °C	Oxygène %	Correction de justesse (performance attendue < 5% en valeur absolue ou 0.2mg/l)) mg/l					%
			Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	Moyenne	Moyenne
S = 0	20	0% bullage --> 14%	0.29	0.27	0.24	-	0.27	21.23
		35% bullage	0.40	0.39	0.39	-	0.39	11.37
		70% bullage	0.33	0.36	0.35	0.34	0.34	5.62
		105% bullage	-0.11	-0.07	-0.08	-0.11	-0.09	-0.95
		140% bullage	-0.69	-0.76	-0.74	-0.75	-0.74	-5.51

Trueness

OTT DS5X

Définition de l'essai			OTT DS5X					
Salinité	Température	Oxygène	Correction de justesse (performance attendue < 5% en valeur absolue ou 0.2mg/l))					
			mg/l					%
	°C	%	Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	Moyenne	Moyenne
S = 0	20	0% bullage --> 14%	0.16	0.13	0.13	-	0.14	10.12
		35% bullage	0.07	0.10	0.11	-	0.09	2.53
		70% bullage	0.03	0.07	0.06	0.05	0.05	0.82
		105% bullage	-0.04	0.01	0.03	-	0.00	0.00
		140% bullage	0.02	-0.01	0.02	-	0.01	0.08

OTT MS5

Définition de l'essai			OTT MS5					
Salinité	Température	Oxygène	Correction de justesse (performance attendue < 5% en valeur absolue ou 0.2mg/l))					
			mg/l					%
	°C	%	Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	Moyenne	Moyenne
S = 0	20	0% bullage --> 14%	0.15	0.12	0.13	-	0.13	9.63
		35% bullage	0.05	0.08	0.09	-	0.07	1.99
		70% bullage	0.01	0.05	0.03	0.03	0.03	0.47
		105% bullage	-0.05	0.00	0.01	-0.01	-0.01	-0.13
		140% bullage	-0.02	-0.05	-0.02	-	-0.03	-0.24

Repeatability and Drift

Aanderaa 3835

'essai — Optode Aanderaa 3835 n°1199

Oxygène %	Correction de justesse mg/l Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	Répétabilité (performance attendue < 2.5% ou 0.1 mg/l) mg/l	%	Dérive (performance attendue < 2.5%) mg/l	%
0% bullage --> 14%	0.19	0.17	0.16	-	0.02	1.25	0.03	2.18
35% bullage	0.40	0.36	0.34	-	0.03	0.84	0.06	1.53
70% bullage	0.30	0.30	0.28	0.27	0.01	0.21	0.03	0.44
105% bullage	-0.08	-0.18	-0.14	-0.23	0.06	0.67	0.15	**1.59**
140% bullage	-0.64	-0.71	-0.70	-0.76	0.05	0.38	0.12	0.93

Aanderaa 4330

essai — Optode Aanderaa 4330 n°325

Oxygène %	Correction de justesse (performance attendue < 0.2mg/l en valeur absolue) mg/l Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	Répétabilité (performance attendue < 2.5% ou 0.1 mg/l) mg/l	%	Dérive (performance attendue < 2.5%) mg/l	%
0% bullage --> 14%	0.29	0.27	0.24	-	0.02	1.91	0.05	3.56
35% bullage	0.40	0.39	0.39	-	0.01	0.24	0.02	0.42
70% bullage	0.33	0.36	0.35	0.34	0.02	0.27	0.04	0.60
105% bullage	-0.11	-0.07	-0.08	-0.11	0.02	0.21	0.04	**0.45**
140% bullage	-0.69	-0.76	-0.74	-0.75	0.03	0.23	0.07	0.53

l'essai — Optode Aanderaa 4330 n°184

Oxygène %	Correction de justesse (performance attendue < 0.2mg/l en valeur absolue) mg/l Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	Répétabilité (performance attendue < 2.5% ou 0.1 mg/l) mg/l	%	Dérive (performance attendue < 2.5%) mg/l	%
0% bullage --> 14%	0.24	0.21	0.20	-	0.02	1.63	0.04	3.04
35% bullage	0.30	0.28	0.28	-	0.01	0.24	0.02	0.40
70% bullage	0.23	0.25	0.23	0.22	0.01	0.19	0.03	0.43
105% bullage	-0.07	-0.08	-0.09	-0.11	0.01	0.14	0.03	**0.33**
140% bullage	-0.49	-0.56	-0.53	-0.55	0.03	0.23	0.07	0.55

Repeatability and Drift

OTT DS5X

l'essai	OTT DS5X							
Oxygène	Correction de justesse (performance attendue < 0.2mg/l en valeur absolue) mg/l				Répétabilité (performance attendue < 2.5% ou 0.1 mg/l)		Dérive (performance attendue < 2.5%)	
%	Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	mg/l	%	mg/l	%
0% bullage --> 14%	0.16	0.13	0.13	-	0.02	1.16	0.03	2.01
35% bullage	0.07	0.10	0.11	-	0.02	0.51	0.04	0.98
70% bullage	0.03	0.07	0.06	0.05	0.02	0.26	0.04	0.60
105% bullage	-0.04	0.01	0.03	-	0.04	0.38	0.07	**0.74**
140% bullage	0.02	-0.01	0.02	-	0.02	0.14	0.03	0.24

OTT MS5

l'essai	OTT MS5							
Oxygène	Correction de justesse (performance attendue < 0.2mg/l en valeur absolue) mg/l				Répétabilité (performance attendue < 2.5% ou 0.1 mg/l)		Dérive (performance attendue < 2.5%)	
%	Essai 1 : Sem 48 et 49	Essai 2 : Sem 50	Essai 3 : Sem 50 et 51	Essai 4 : Sem 51	mg/l	%	mg/l	%
0% bullage --> 14%	0.15	0.12	0.13	-	0.02	1.02	0.03	2.00
35% bullage	0.05	0.08	0.09	-	0.02	0.51	0.04	0.97
70% bullage	0.01	0.05	0.03	0.03	0.02	0.24	0.04	0.60
105% bullage	-0.05	0.00	0.01	-0.01	0.03	0.28	0.06	**0.63**
140% bullage	-0.02	-0.05	-0.02	-	0.02	0.14	0.03	0.24

Linearity

Aanderaa 3835

Définition de l'essai			Optode Aanderaa 3835 n°1199			
Salinité	Température °C	Oxygène %	Winkler mg/l Moyenne	Données optodes mg/l Moyenne	Linéarité (performance attendue < 2.5% ou 0.1 mg/l) mg/l	%
S = 0	20	0% bullage --> 14%	1.54	1.36	0.27	19.58
		35% bullage	3.85	3.49	-0.12	-3.48
		70% bullage	6.49	6.20	-0.27	-4.34
		105% bullage	9.56	9.72	-0.08	-0.82
		140% bullage	12.64	13.34	0.20	1.51

Aanderaa 4330

Définition de l'essai			Optode Aanderaa 4330 n°184			
Salinité	Température °C	Oxygène %	Winkler mg/l Moyenne	Données optodes mg/l Moyenne	Linéarité (performance attendue < 2.5% ou 0.1 mg/l) mg/l	%
S = 0	20	0% bullage --> 14%	1.54	1.32	0.17	13.01
		35% bullage	3.85	3.57	-0.06	-1.67
		70% bullage	6.49	6.26	-0.18	-2.94
		105% bullage	9.56	9.65	-0.08	-0.82
		140% bullage	12.64	13.17	0.15	1.16

Définition de l'essai			Optode Aanderaa 4330 n°325			
Salinité	Température °C	Oxygène %	Winkler mg/l Moyenne	Données optodes mg/l Moyenne	Linéarité (performance attendue < 2.5% ou 0.1 mg/l) mg/l	%
S = 0	20	0% bullage --> 14%	1.54	1.27	0.26	20.16
		35% bullage	3.85	3.46	-0.08	-2.40
		70% bullage	6.49	6.15	-0.28	-4.55
		105% bullage	9.56	9.65	-0.13	-1.31
		140% bullage	12.64	13.37	0.23	1.75

Linearity

OTT DS5X

Définition de l'essai			OTT DS5X			
Salinité	Température °C	Oxygène %	Winkler mg/l Moyenne	Données optodes mg/l Moyenne	Linéarité (performance attendue < 2.5% ou 0.1 mg/l) mg/l	%
S = 0	20	0% bullage --> 14%	1.54	1.40	-0.02	-1.09
		35% bullage	3.84	3.75	0.00	0.07
		70% bullage	6.47	6.42	0.01	0.17
		105% bullage	9.58	9.58	0.02	0.25
		140% bullage	12.63	12.62	-0.02	-0.19

OTT MS5

Définition de l'essai			OTT MS5			
Salinité	Température °C	Oxygène %	Winkler mg/l Moyenne	Données optodes mg/l Moyenne	Linéarité (performance attendue < 2.5% ou 0.1 mg/l) mg/l	%
S = 0	20	0% bullage --> 14%	1.54	1.40	-0.02	-1.26
		35% bullage	3.84	3.77	0.01	0.23
		70% bullage	6.47	6.44	0.01	0.21
		105% bullage	9.53	9.55	0.01	0.12
		140% bullage	12.63	12.66	-0.02	-0.13

Sample temperature

Aanderaa 3835

Définition de l'essai			Optode Aanderaa 3835 n°1199				
Salinité	Température °C	Oxygène %	Winkler µmol/l	Données optode µmol/l	Correction µmol/l	Effet température (performance attendue < 2.5%) µmol/l	%
S = 0	0	68.4% bullage	335.81	309.56	26.25	37.77	12.20
	6	80.32% bullage	324.57	310.75	13.82		
	12	100% sans bullage	328.18	323.74	4.44		
	18	105.6% bullage	308.01	308.23	-0.22		
	25	121.07% bullage	311.26	322.78	-11.52		

Aanderaa 4330

Définition de l'essai			Optode Aanderaa 4330 n°184				
Salinité	Température °C	Oxygène %	Winkler µmol/l	Données optode µmol/l	Correction µmol/l	Effet température (performance attendue < 2.5%) µmol/l	%
S = 0	0	68.4% bullage	316.534	335.81	19.276	25.496	7.59
	6	80.32% bullage	312.165	324.57	12.405		
	12	100% sans bullage	323.566	328.18	4.614		
	18	105.6% bullage	308.12	308.01	-0.11		
	25	121.07% bullage	317.48	311.26	-6.22		

Définition de l'essai			Optode Aanderaa 4330 n°325				
Salinité	Température °C	Oxygène %	Winkler µmol/l	Données optode µmol/l	Correction µmol/l	Effet température (performance attendue < 2.5%) µmol/l	%
S = 0	0	68.4% bullage	335.81	308.606	27.204	39.884	12.92
	6	80.32% bullage	324.57	304.482	20.088		
	12	100% sans bullage	328.18	318.914	9.27		
	18	105.6% bullage	308.01	308.279	-0.269		
	25	121.07% bullage	311.26	323.94	-12.68		

Sample temperature

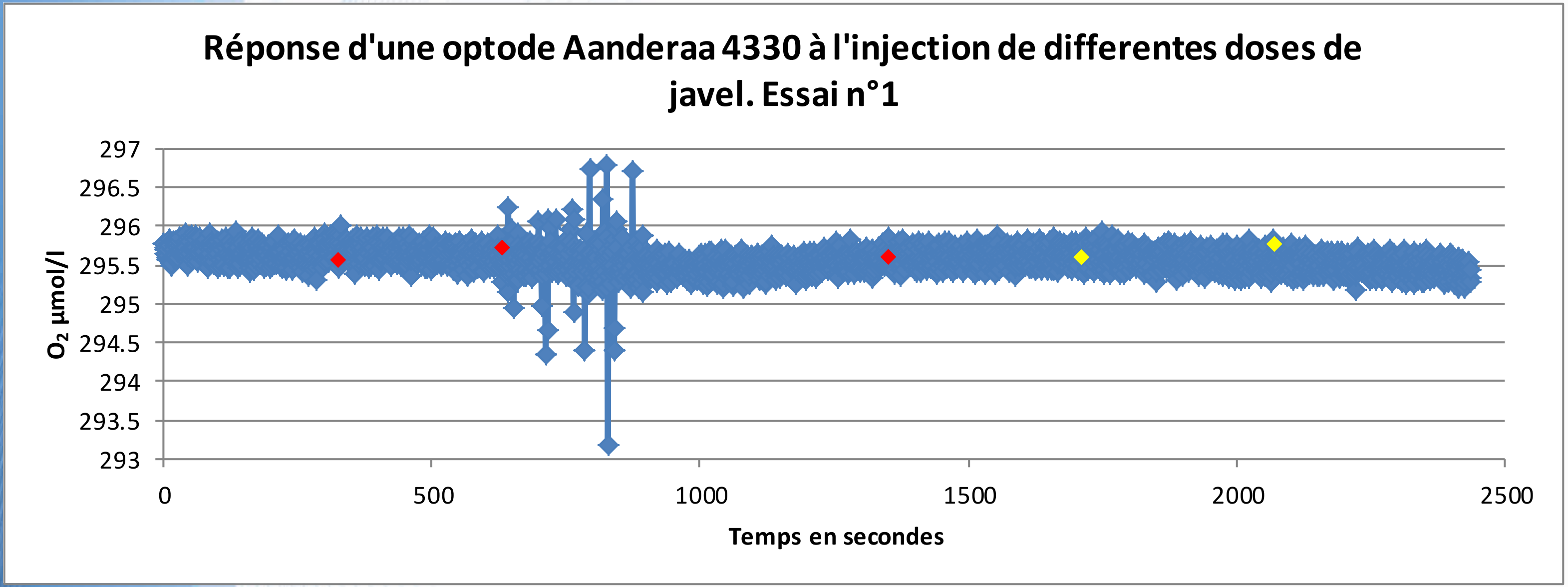
OTT DS5X

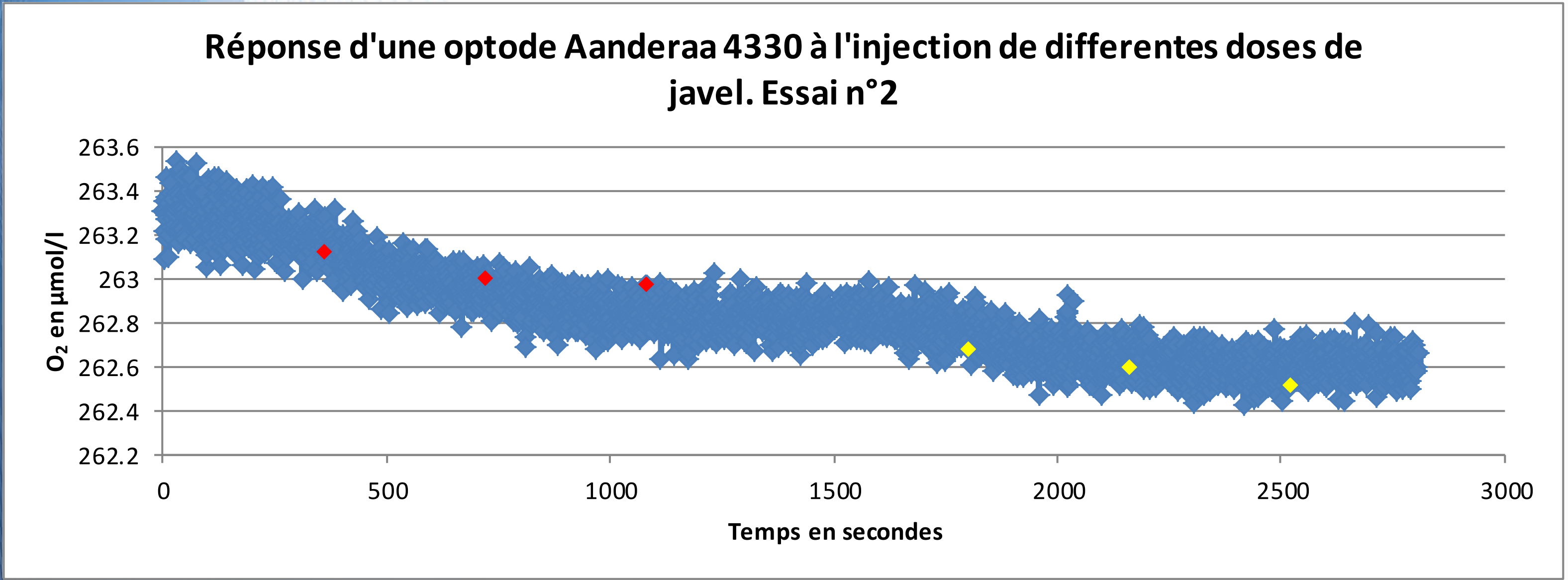
Définition de l'essai			OTT DS5X				
Salinité	Température °C	Oxygène %	Winkler mg/l	Données optode mg/l	Correction mg/l	Effet température (performance attendue < 2.5%) mg/l	%
S = 0	0	68.4% bullage	10.26	10.62	0.36	0.37	3.48
	6	80.32% bullage	10.06	10.27	0.21		
	12	100% sans bullage	10.27	10.35	0.08		
	18	105.6% bullage	9.69	9.74	0.05		
	25	121.07% bullage	9.86	9.85	-0.01		

OTT MS5

Définition de l'essai			OTT MS5				
Salinité	Température °C	Oxygène %	Winkler mg/l	Données optode mg/l	Correction mg/l	Effet température (performance attendue < 2.5%) mg/l	%
S = 0	0	68.4% bullage	10.42	10.62	0.2	0.21	1.98
	6	80.32% bullage	10.17	10.27	0.1		
	12	100% sans bullage	10.33	10.35	0.02		
	18	105.6% bullage	9.75	9.74	-0.01		
	25	121.07% bullage	9.86	9.85	-0.01		

Sample matrix effects: chlorine

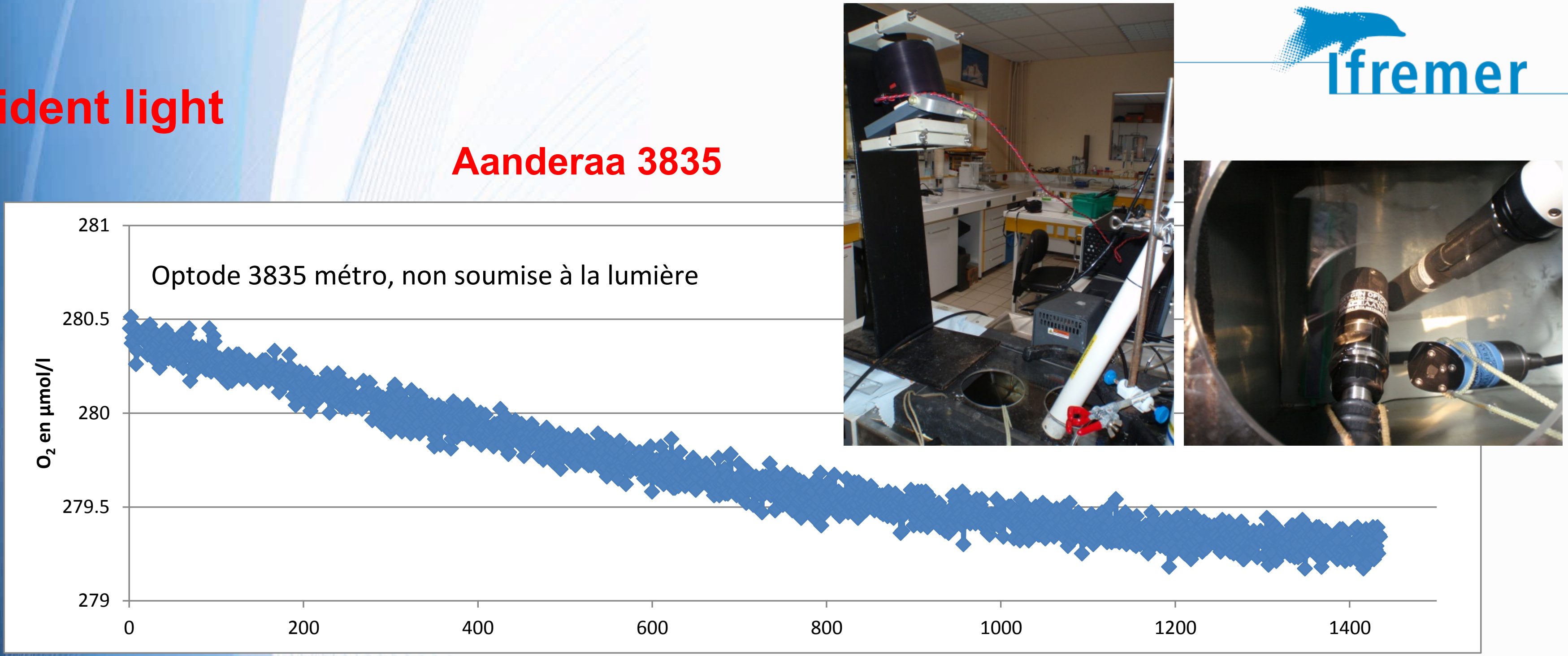


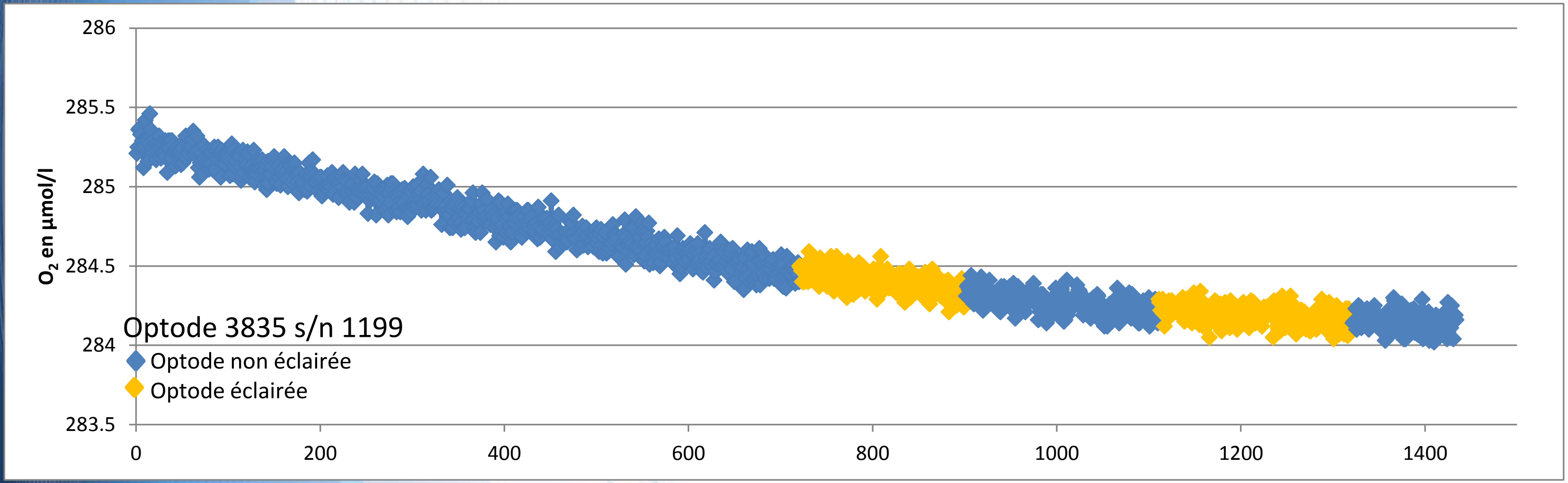


◆ Injection de 226µL d'eau de javel à 9,6% de chlore actif
◆ Injection de 1mL d'eau de javel à 9,6% de chlore actif

Incident light

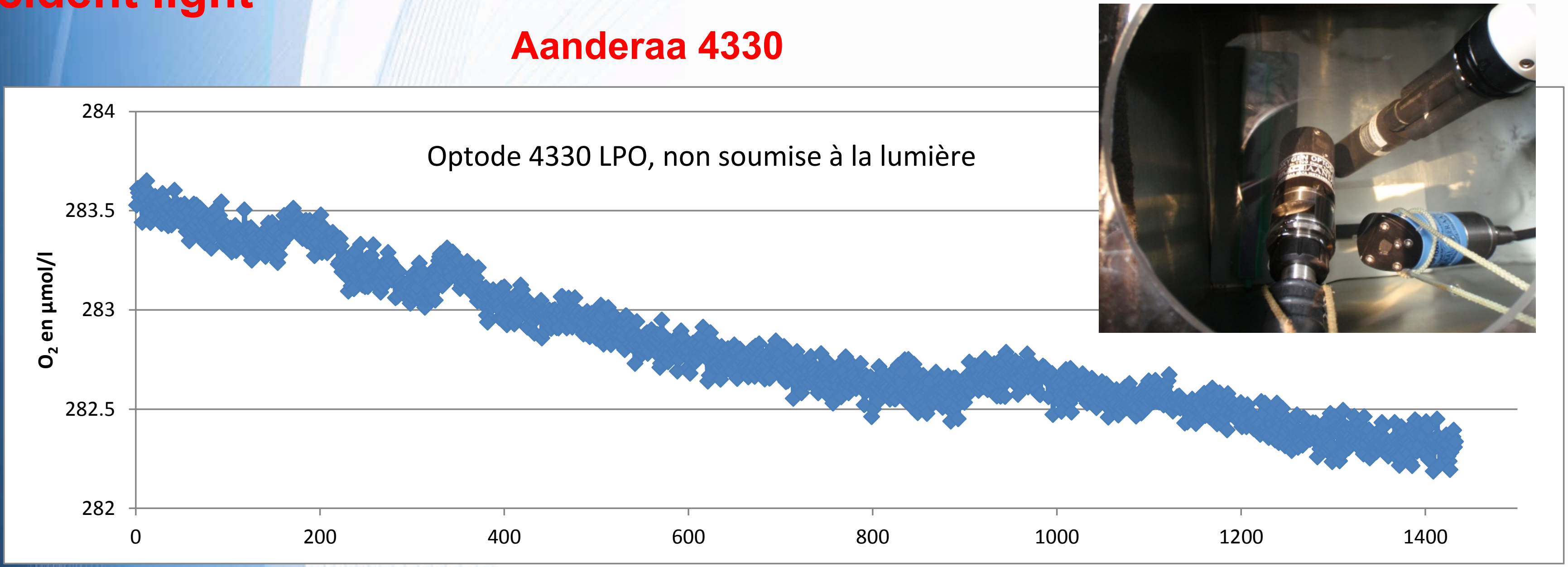
Aanderaa 3835

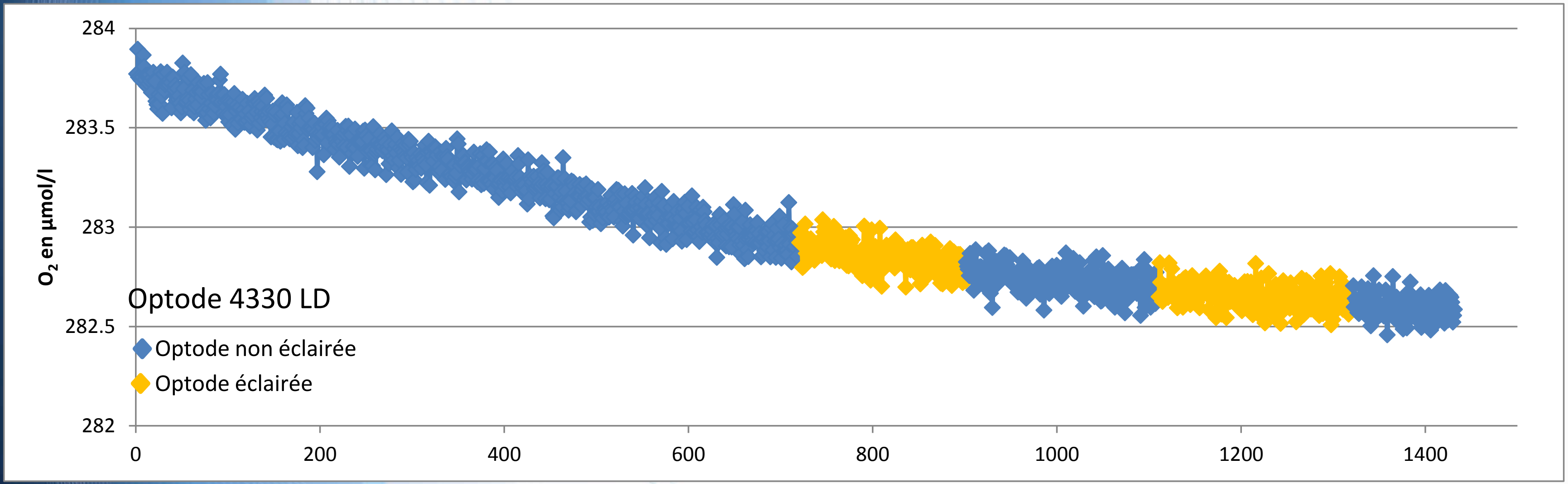




Incident light

Aanderaa 4330





What for ?

- Have common practices to quantify the performances of a sensor
- Calculate uncertainties in a different way than the classic method proposed in the GUM:

$$U = \pm 2 \times \sqrt{\left(\%Trueness/\sqrt{3}\right)^2 + \left(\%Linearity/\sqrt{3}\right)^2 + \ldots}$$

$$U \leq \text{tolerance \% (proposed in prEN 16479-2)}$$

- prEN 16479-2 indicates also field test procedures and field test tolerances

1 – Current status: needs, practices and lacks

2 – Up to date practices

3 – Performance testing

4 – Alternatives

Alternatives…

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