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Apr 2021

CALIBRATION SHEET (199) – SPECTRO Bio2

1 - SST CO2 calculation :

The temperature is computed from the thermistor (Th) and the 2 references measured by the spectro (Refh and Refb) :

When 4095 < Th, Refh, Refb < 8191, subtract 8192

$$T(°C) = \frac{1}{A + B\ln(R) + C*(\ln(R))^3} - 273.15$$

R = (R1*(RH/(RH+R1))+R1*(K*RL)/(RL+R1)-(R1*(K*RH)/(RH+R1)))/(1-(RH/(RH+R1))-((K*RL)/(RL+R1))+(K*RH)/(RH+R1))

K = (Th – Refh) / (Refb – Refh)

RL = 1959.2
RH = 7865.5 and
R0 = R1 = 21003

$A = 1.466296.10^{-3}$
$B = 2.38698.10^{-4}$
$C = 9.9959.10^{-8}$

2 - fCO2 calculation :

fCO2 (µatm) = a pCO2th + b (1)

The a, b,k and k' coefficients are given by the calibration of the spectrophotometer.

a = 0.9916
b = - 24.5
k = + 0.0024
k' = - 0.0400

$$pCO2th = \frac{K_i A_T}{\alpha K_1} X \left[\frac{1 - \frac{c}{A_T}\frac{1}{(1+X)}}{1 + \frac{2K_2}{K_i}\frac{1}{X}} \right] \quad (2)$$

and

$$X = \frac{Re_2 - e_3}{1 - Re_1}$$

with :

- $A_T = 2.04\ 10^{-3}$ mol/kg
- $c = 10^{-4}$ mol/kg
- $e1 = 0.0078$
- $e2 = 8.76277 - 0.04344T + 7.256.10^{-5}T^2$ (T en K)
- $e3 = -0.005765 + 5.8.10^{-4}T$ (T en K)
- solubility coefficient (Weiss, 1974)

$$\ln \alpha = -60.2409 + 93.4517(\frac{100}{T}) + 23.3585 \ln(\frac{T}{100}) + S\left[0.023517 - 0.023656(\frac{T}{100}) + 0.0047036(\frac{T}{100})^2\right]$$

- dissociation constants of carbonic acid in seawater (Lueker et al., 2000)

$$pK_1 = \frac{3633.86}{T} - 61.2172 + 9.67770 \ln T - 0.011555S + 0.0001152S^2$$

$$pK_2 = \frac{471.78}{T} + 25.9290 - 3.16967 \ln T - 0.01781S + 0.0001122S^2$$

- Thymol blue dissociation constant (Zhang and Byrne, 1996)

$$pK_i = 4.706\frac{S}{T} + 26.33 - 7.17218 \log(T) - 0.017316S$$

for pK_1, pK_2 et pK_i : $pK = -\log K$

for α, K_i, K_1 et K_2 : $S = 35$

- $R = \frac{A_{434}}{A_{596}}$

with : $A_{434} = k' + \log(\frac{810nm}{434nm})$ and $A_{596} = k + \log(\frac{810nm}{596nm})$

- Amax control

The stability of the dye can be checked with the calculation of Amax :

$$A\max = \frac{e_2}{e_2 - e_1 \times e_3}\{(e_2 - e_1) \times A(436) + (1 - e_3) \times A(596)\}$$

The quantity Amax varies with temperature. It decreases when the temperature increases. The slope of the relationship varies between –1.5 to –2.5 per mil per degree C.

3 - Control

3 parameters of the fCO2 sensor can be checked easily when testing the buoy:
810 nm, Ref H and Ref B

810 nm = 7363 (+/- 100)
Ref H = 3726 (+/- 2)
Ref B = 4578 (+/- 2)