PTB
Physikalisch-Technische Bundesanstalt
National Metrology Institute

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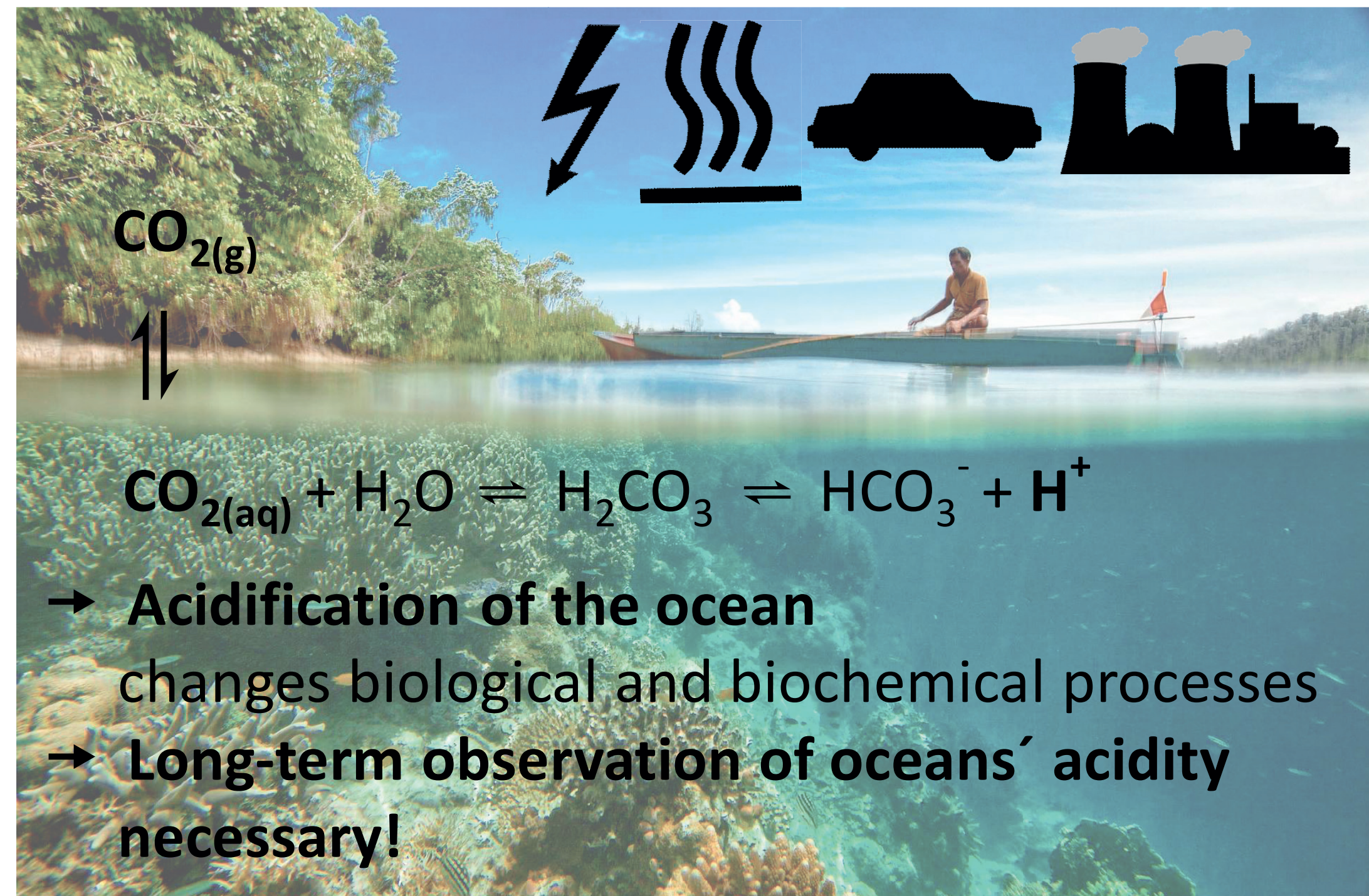Steffen Seitz, Gregor Rehder

Electrochemical pH_T measurements of TRIS buffered artificial seawater samples in the salinity range 5-20

Motivation and Background

Anthropogenic **CO_2** emission:

$CO_{2(g)}$

$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + \mathbf{H^+}$

➜ **Acidification of the ocean**
changes biological and biochemical processes
➜ **Long-term observation of oceans´ acidity necessary!**

Acidity is expressed by the „**pH**" of an aqueous solution:
$$pH = -lg(a(H^+))$$ internationally accepted, IUPAC definition, activity $a(H^+)$ measured potentiometrically, valid only for dilute solutions of ionic strength ≤ 0.1 mol·kg⁻¹ (salinity 5) ➜ this pH value is not yet measurable in seawater media
➜ Instead: $\mathbf{pH_T = -lg(c(H^+) + c(HSO_4^-))}$, commonly measured in oceanography.
pH_T scale is based on the total H^+ concentration including HSO_4^- also contributing to H^+
pH_T is frequently determined spectrophotometrically e.g. on ships using an indicator dye like m-cresol purple
➜ traceability of pH_T measurement results to an internationally agreed standard or to the SI is not established in the middle salinity range (5-20) up to now
➜ no comparability of pH_T measurement results

Objective

Determination of pH_T values of equimolal TRIS/TRIS·H⁺ buffered artificial seawater solutions enabling traceability of spectrophotometrically measured pH_T values to a primary (Harned cell) pH_T measurement procedure

Interlaboratory collaboration between PTB and IOW

1. Potentiometric measurement of pH_T of equimolal TRIS/TRIS·H⁺ buffered artificial seawater solutions of salinity 5-20 at three different total TRIS molalities (0.02, 0.05 and 0.08 mol·kg⁻¹) using Harned cells at **PTB** (completion of the works of Bates & Hetzer 1961 at salinity ≤ 5 and DelValls & Dickson 1998 at salinity 20-40)

Measurement equation (equivalent to the above mentioned pH_T- definition according to DelValls & Dickson, 1998):
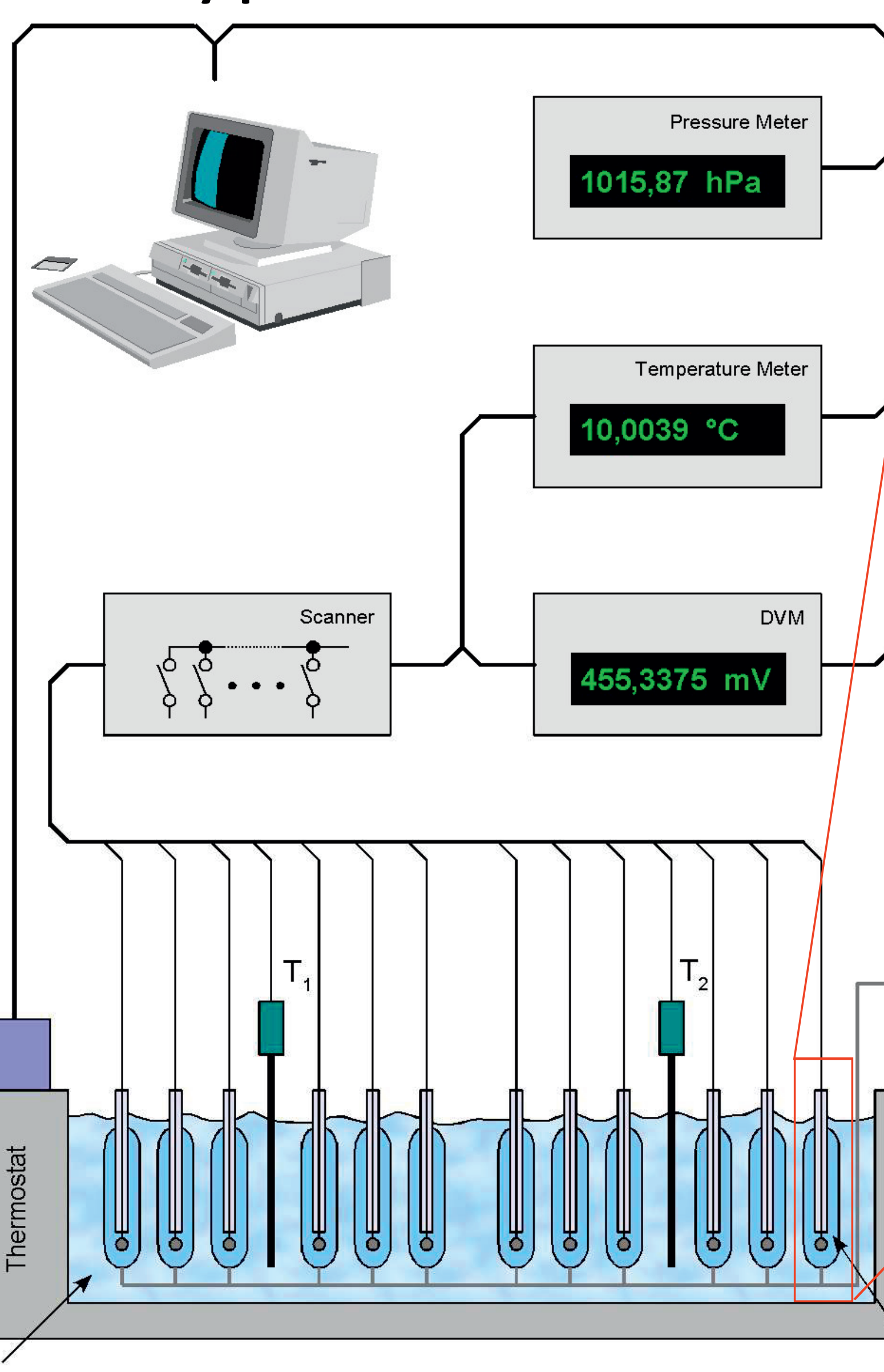
$$pH_T = \frac{(E - E^{0*})F}{RT\ln 10} + lg(b_{Cl^-}) - lg(\omega_{H_2O})$$

E: Electric potential of the Harned cell filled with artificial seawater
E^{0*}: Standard potential of the Ag/AgCl electrode in artificial seawater (to be determined in an extra experiment)
b_{Cl^-}: Molality of chloride of the artificial seawater
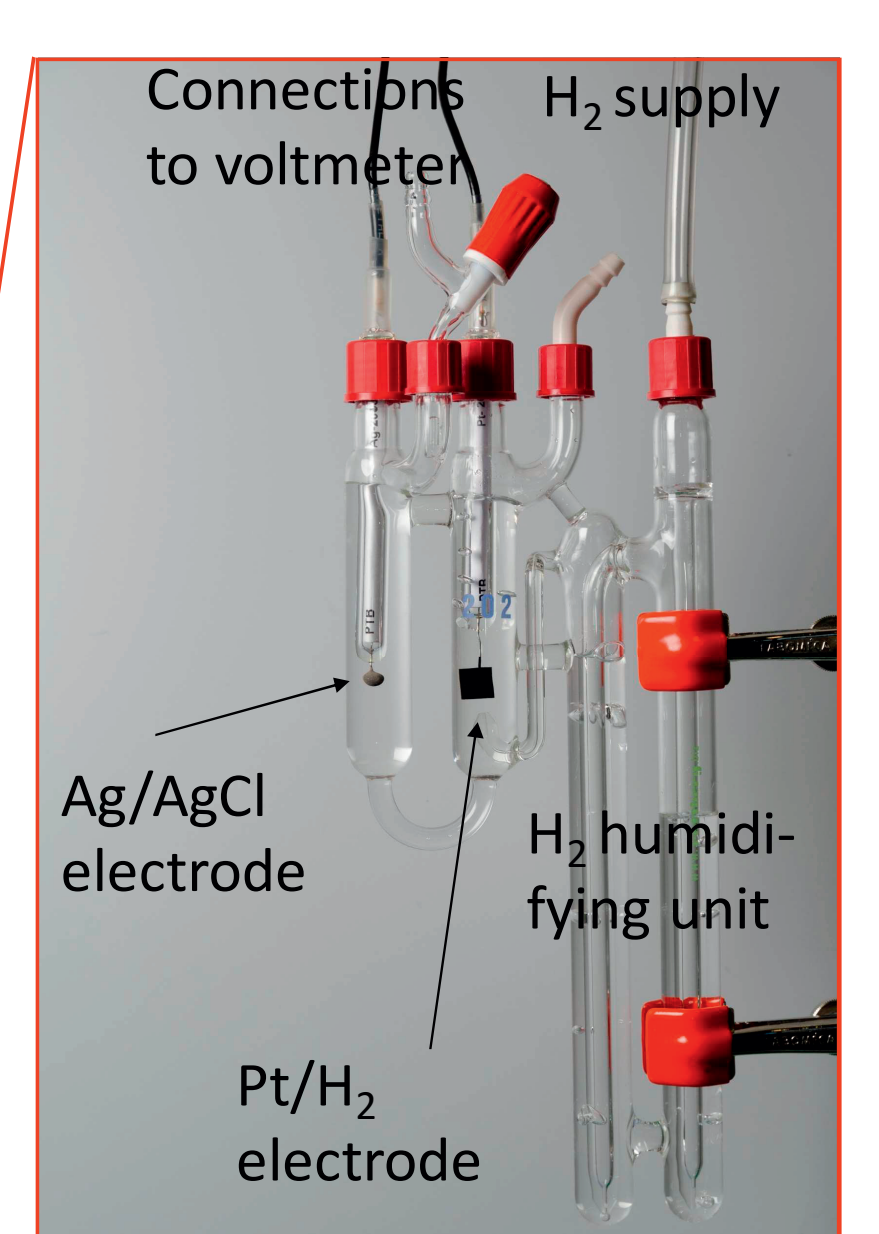ω_{H_2O}: Water content of the artificial seawater

2. Determination of the dissociation constant of spectrophotometric dye m-cresol purple at **IOW** in the framework of the Innovation Project BONUS PINBAL using the same buffered artificial seawater solutions characterised at PTB. See poster of Müller $et\ al$ (P228) and talk by Rehder $et\ al$)
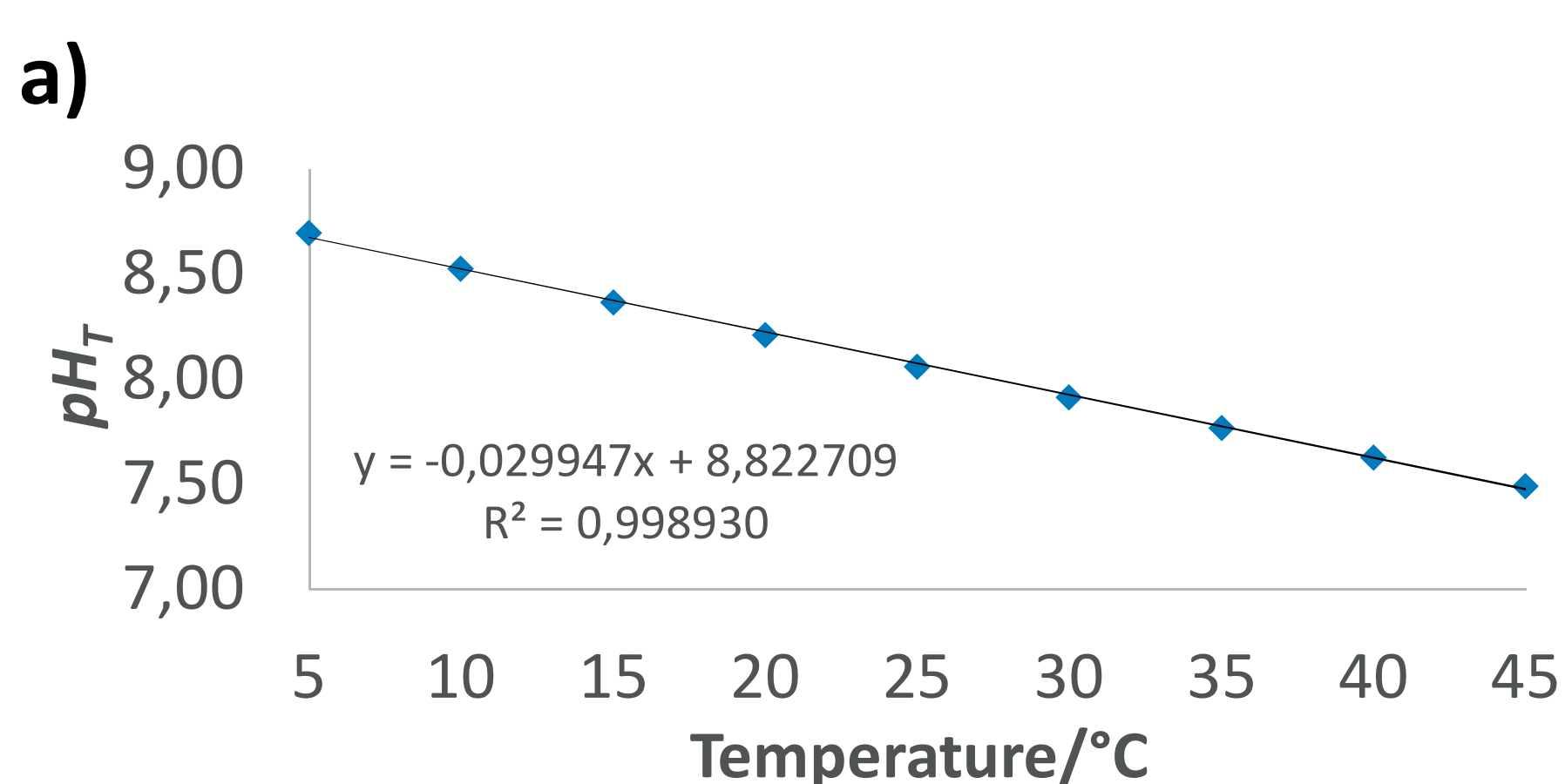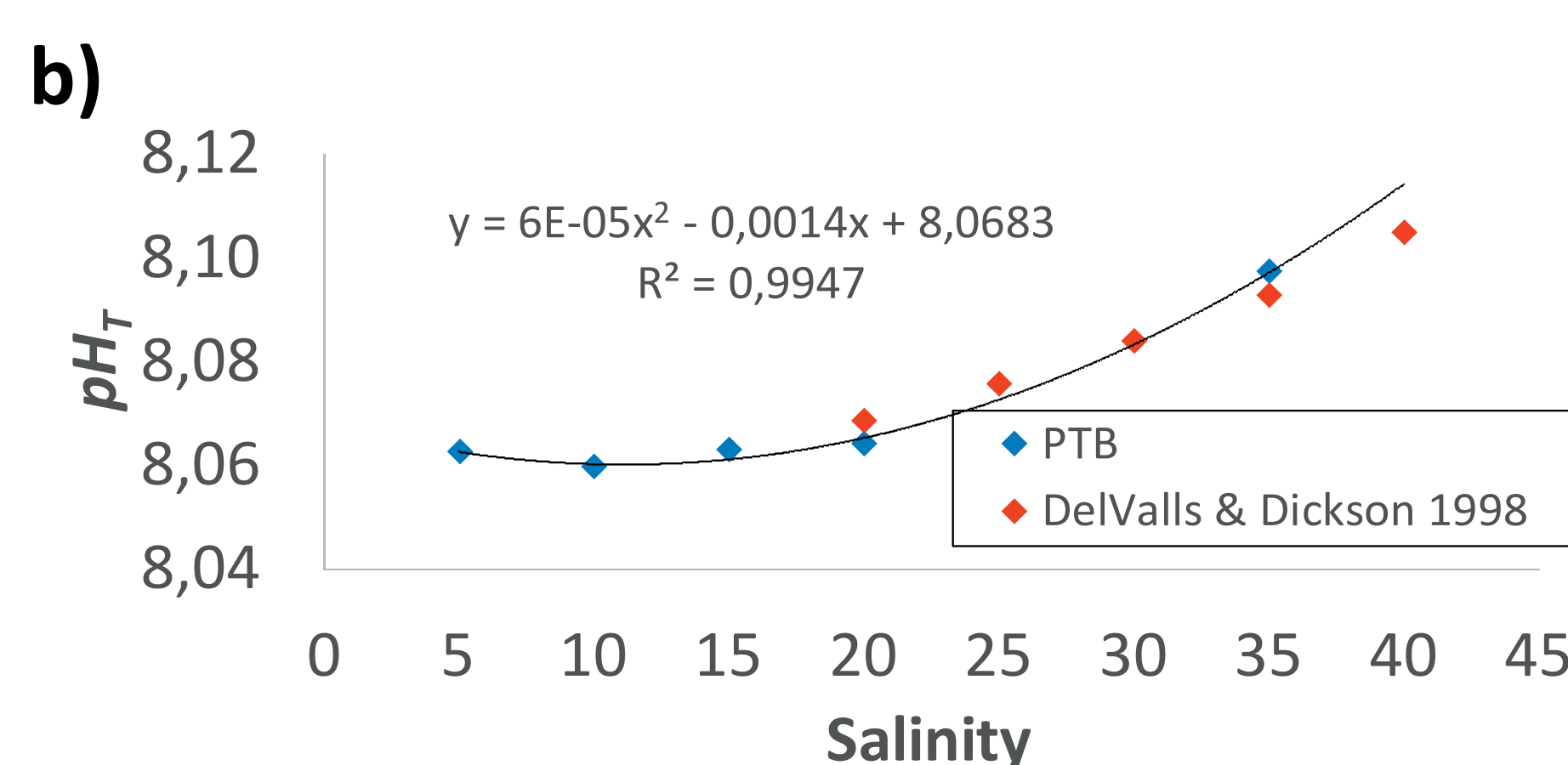
Leibniz-Institut für Ostseeforschung Warnemünde

Primary pH standard at PTB

Harned Cell

Results

a)

$y = -0,029947x + 8,822709$
$R^2 = 0,998930$

Temperature dependence of pH_T values at salinity 10 and 0.08 mol·kg⁻¹ total TRIS molality

b)

$y = 6E-05x^2 - 0,0014x + 8,0683$
$R^2 = 0,9947$

PTB
DelValls & Dickson 1998

Salinity dependence of pH_T values at 25 °C and 0.08 mol·kg⁻¹ total TRIS molality measured at PTB (blue) and by DelValls & Dickson 1998 (red)

c)

$y = -0,3527x^2 + 0,1709x + 8,0483$
$R^2 = 1$
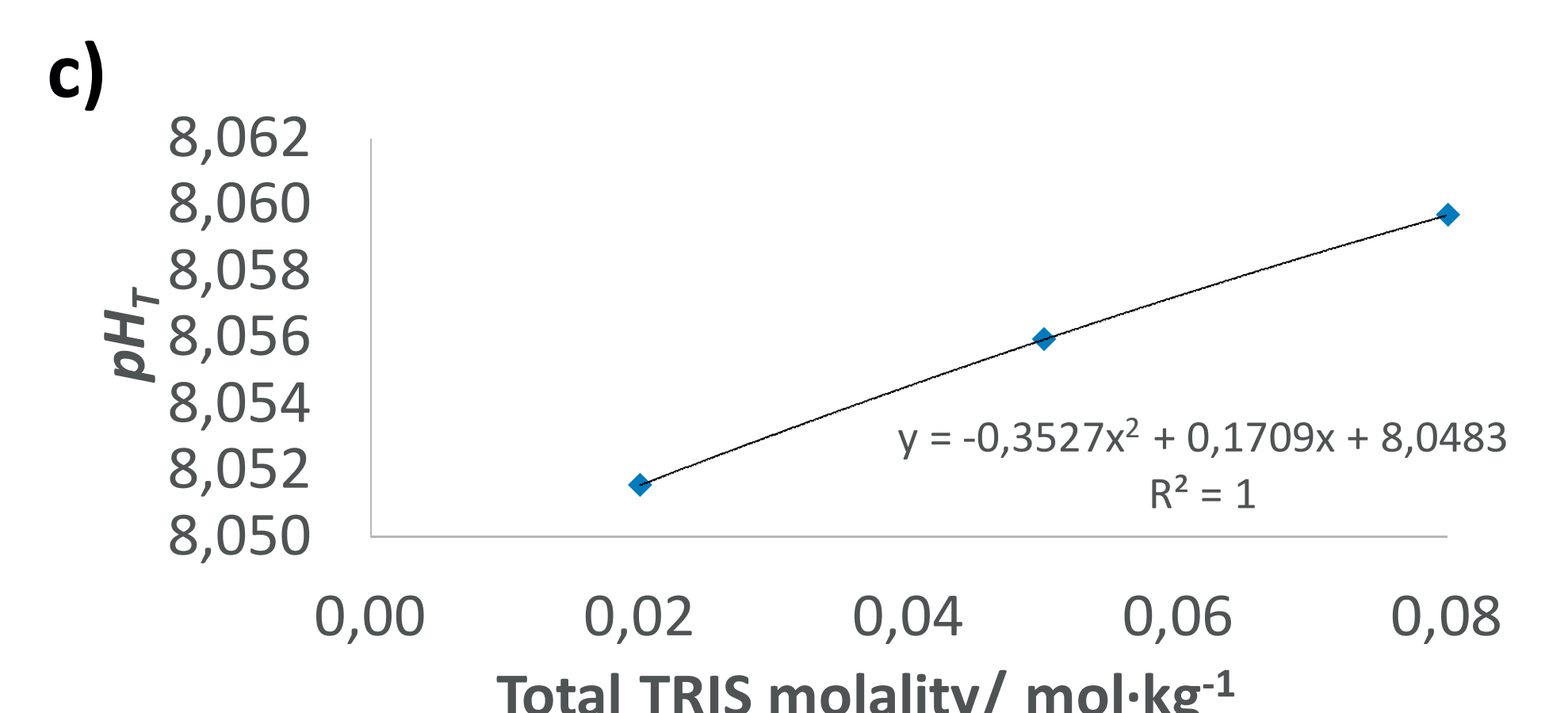
TRIS dependence of pH_T values at salinity 10 and 25 °C

Acknowledgements

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