Spectrophotometric pH and alkalinity determination for use in underway measuring systems

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FerryBox Workshop 2011

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Centre for Materials and Coastal Research

CO_2 concentration

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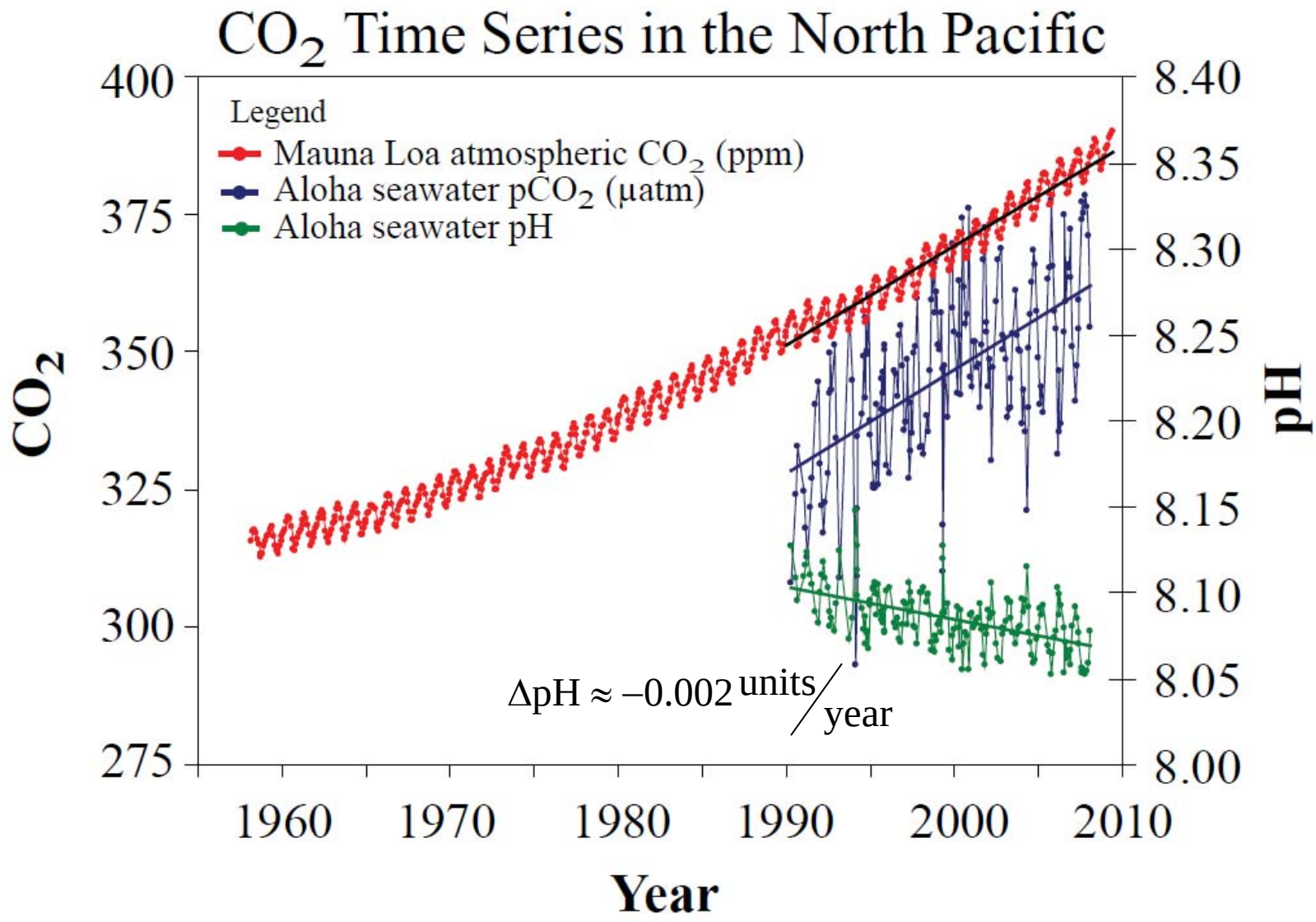
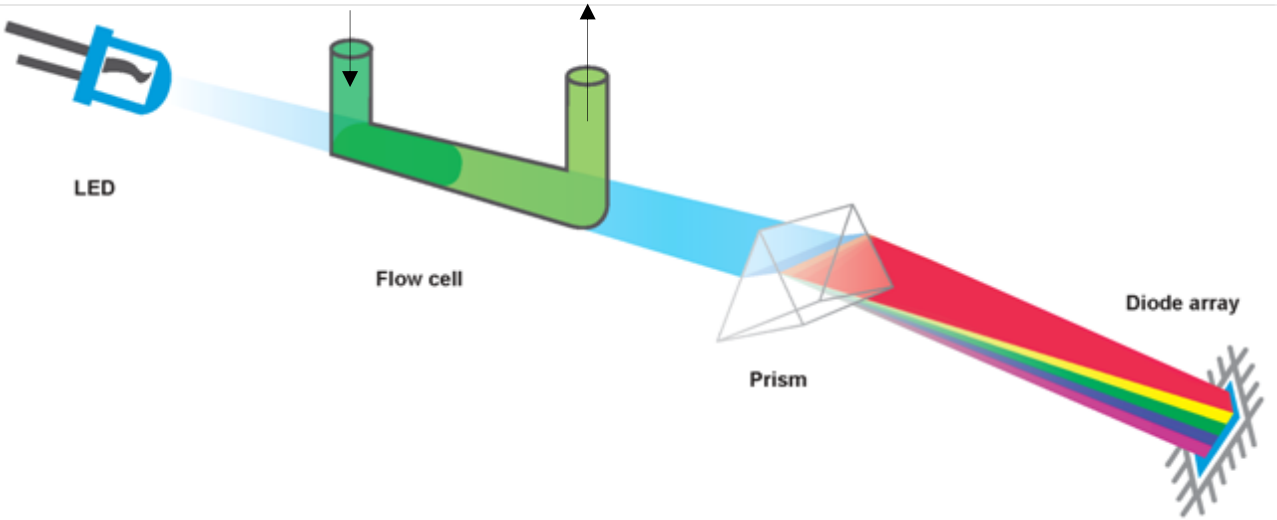
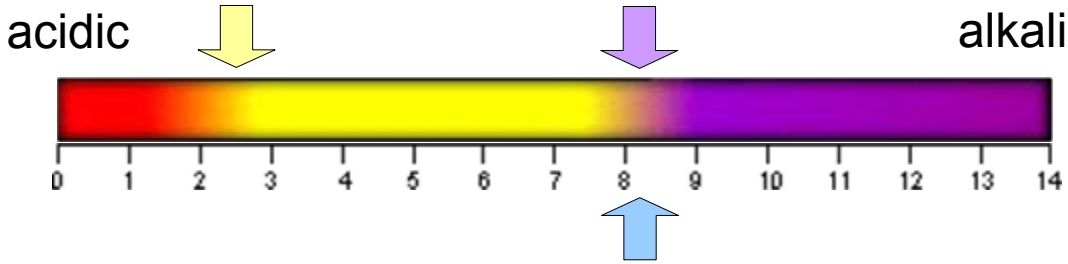


[NOAA Ocean and Great Lakes Acidification Research Plan, 2010]

Measurement principle for pH



Indicator ranges of *m*-Cresol Purple



$$\mathrm{pH} = -\log_{10}\left[\mathrm{H}^{+}\right]$$

$$\mathrm{HI}^{-} \leftrightarrow \mathrm{H}^{+} + \mathrm{I}^{2-}$$

$$K_{\mathrm{a}} = \frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{I}^{2-}\right]}{\left[\mathrm{HI}^{-}\right]}$$

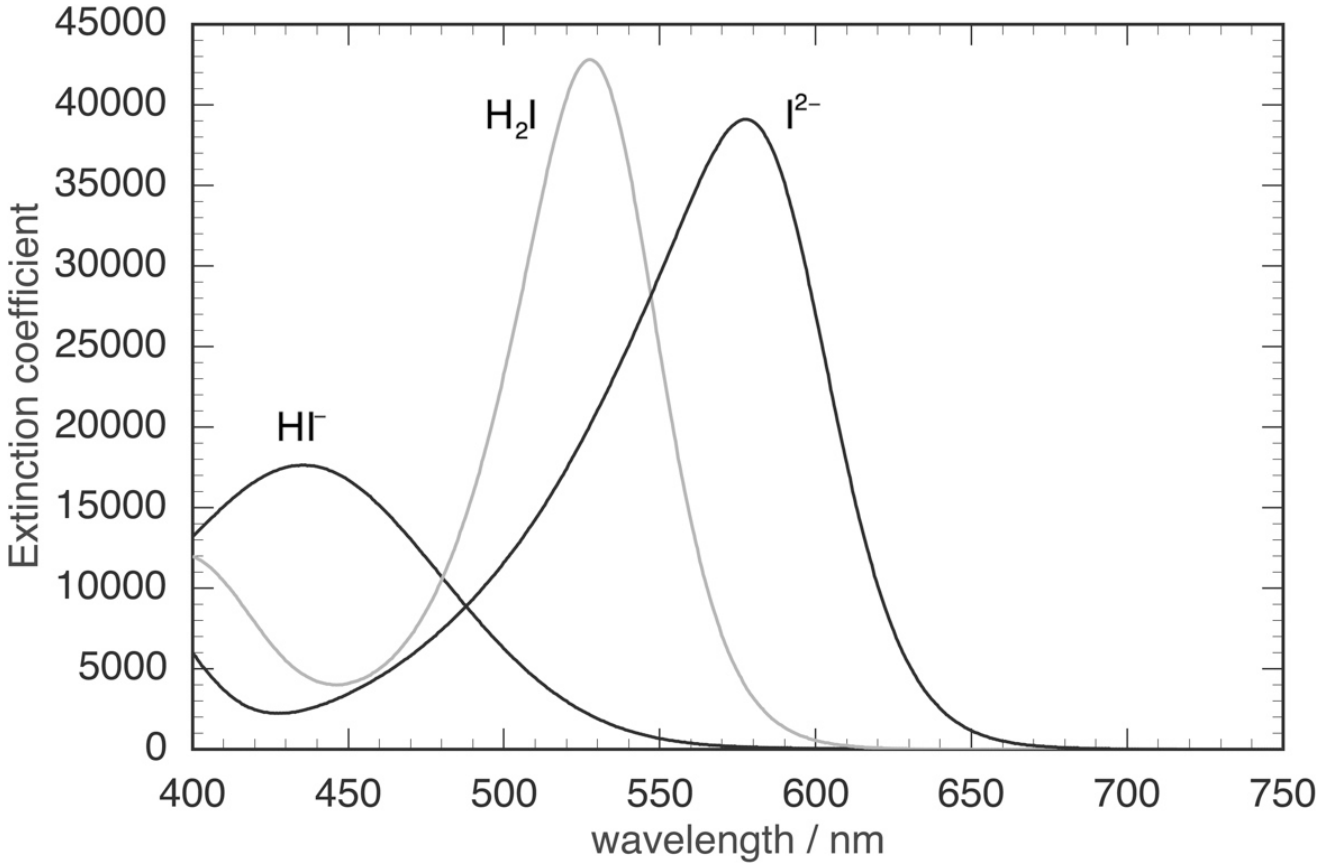
$$\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \lg\frac{\left[\mathrm{I}^{2-}\right]}{\left[\mathrm{HI}^{-}\right]}$$

Total scale

$$\mathrm{pH} = -\log_{10}\left[\mathrm{H}^{+} + \mathrm{HSO}_{4}^{-}\right]$$

pH calculation

$$\mathrm{pH} = \mathrm{p}K_a + \lg \frac{[\mathrm{I}^{2-}]}{[\mathrm{HI}^-]} \quad \longrightarrow \quad \mathrm{pH}_T = \mathrm{p}K_a + \lg\left(\frac{R - e_1}{e_2 - R \cdot e_3}\right)$$



$$R = \frac{A^{\max}_{Ind-}}{A^{\max}_{HInd}} = \frac{A^{578}}{A^{434}}$$

$$e_1, e_2, e_3 = const.$$

Ratios / Constants
No absolute values!

Perturbation due to indicator addition

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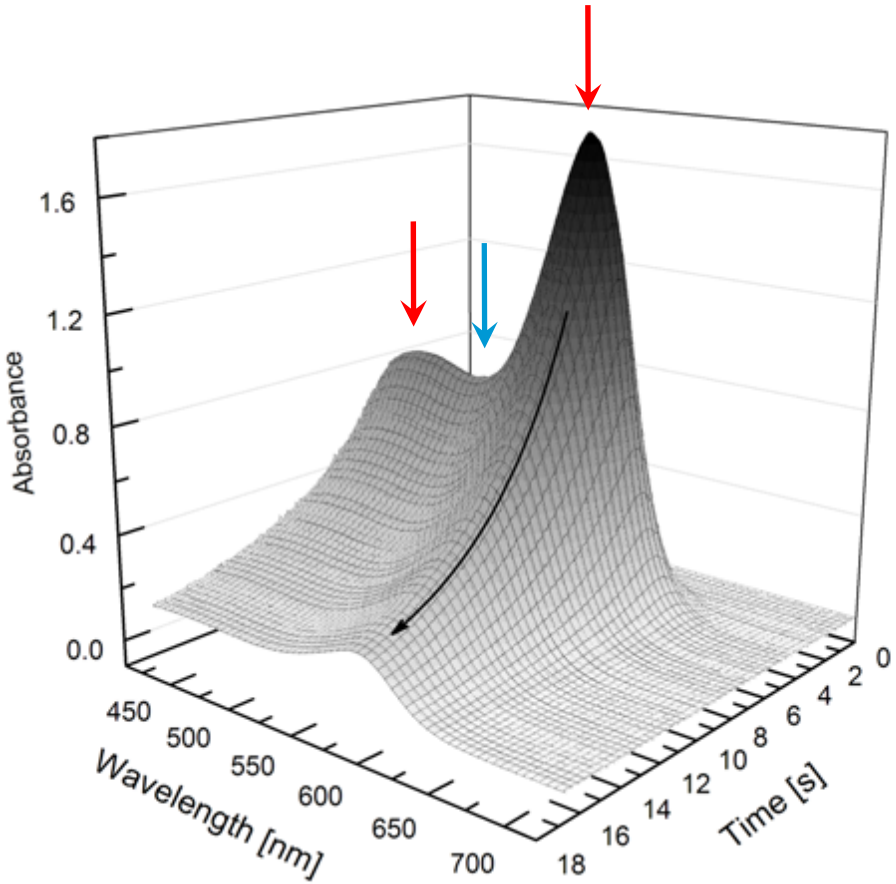
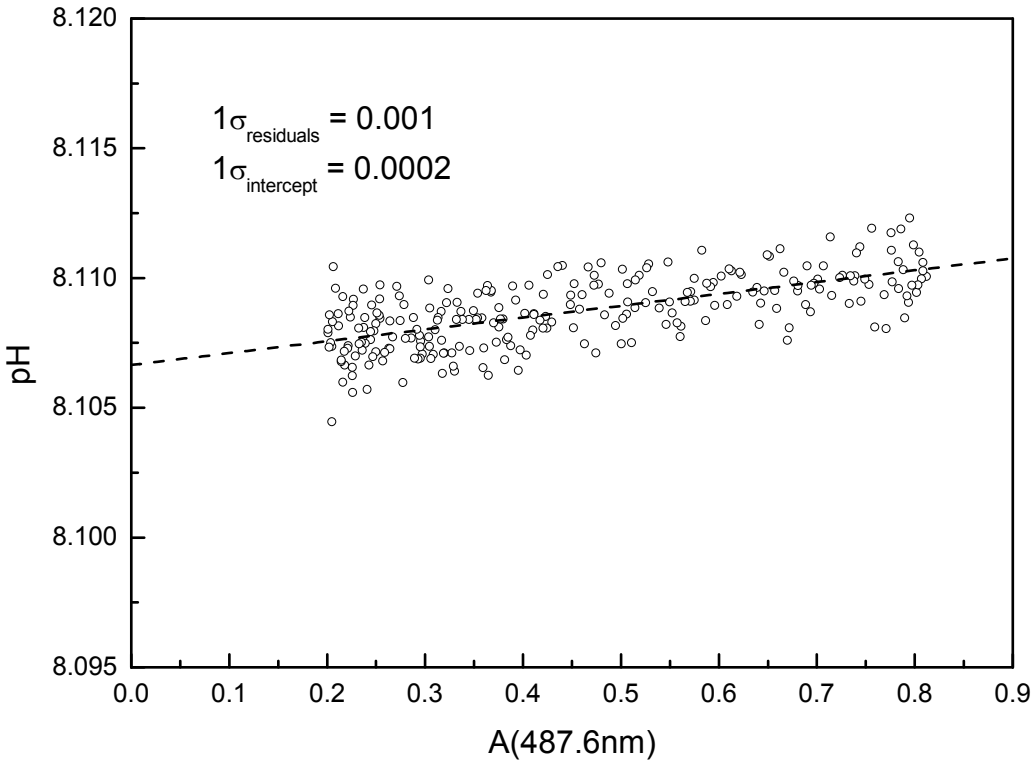
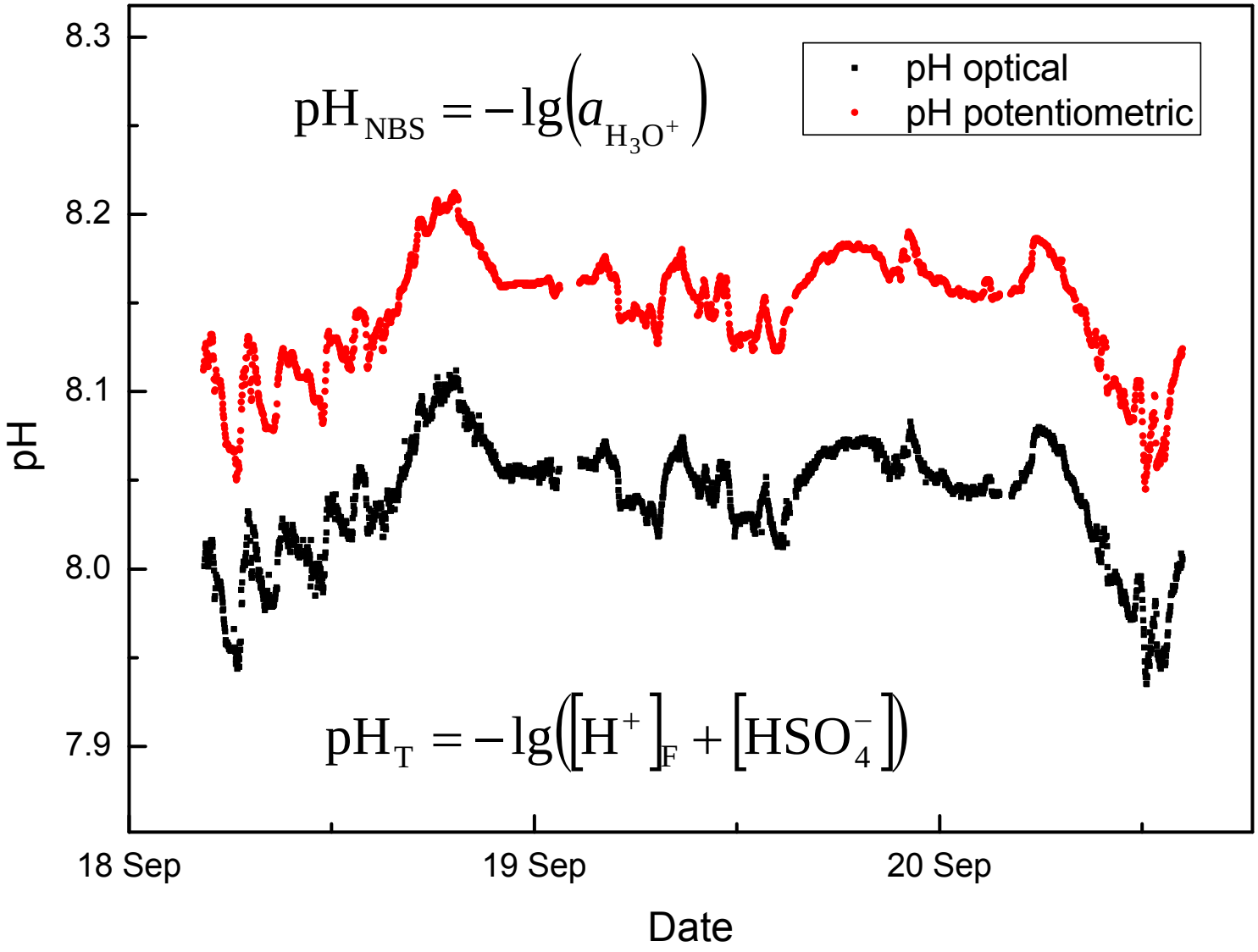




Some data: North Sea in Sep. 2010



Summary – pH

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For use in Seawater

Salinity = 20 … 40
Temperature = 5 … 35 °C
pH = 7 … 9

Measurement frequency: **1 min^{-1}**

Precision: **±0.0007**

Offset: **0.0005**

Compared to Bench-top spectrometer

Accuracy: **0.008***

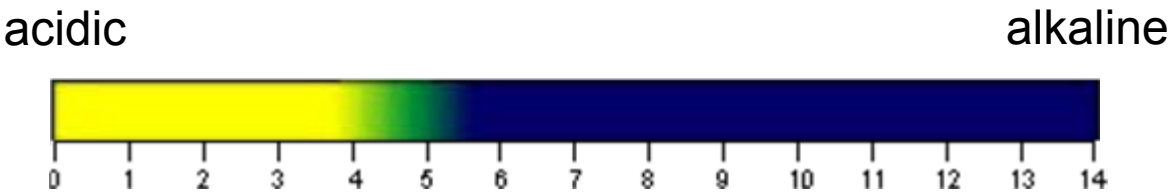
Compared to CRM
*can be traced back to impurities of the indicator dye

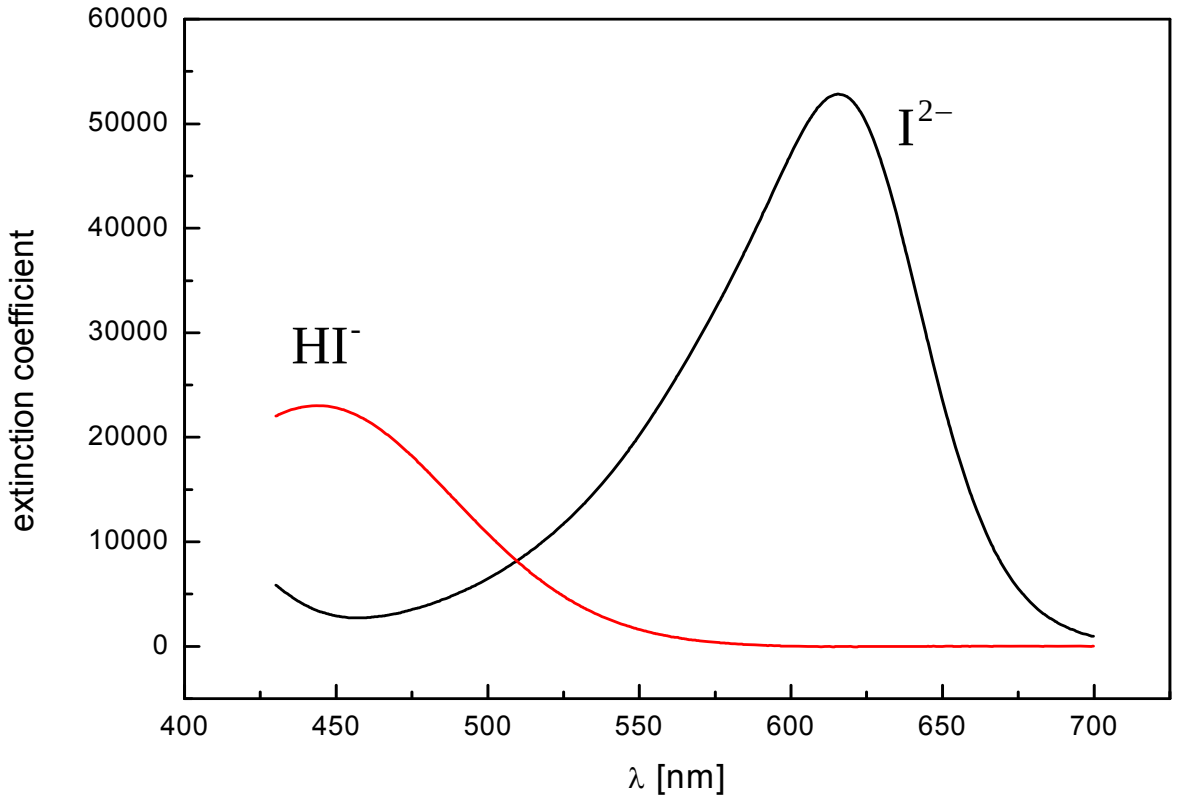
Approach

- → One-point open cell titration
- → Combining a seawater sample with an acid / indicator solution in a constant ratio → pH ≈ 4
- → Removing the dissolved gasses (CO_2) through an online degasser
- → Optical determination of the pH value using an acid-base indicator dye (bromocresol green)

pH calculation for A_T

Bromocresol green





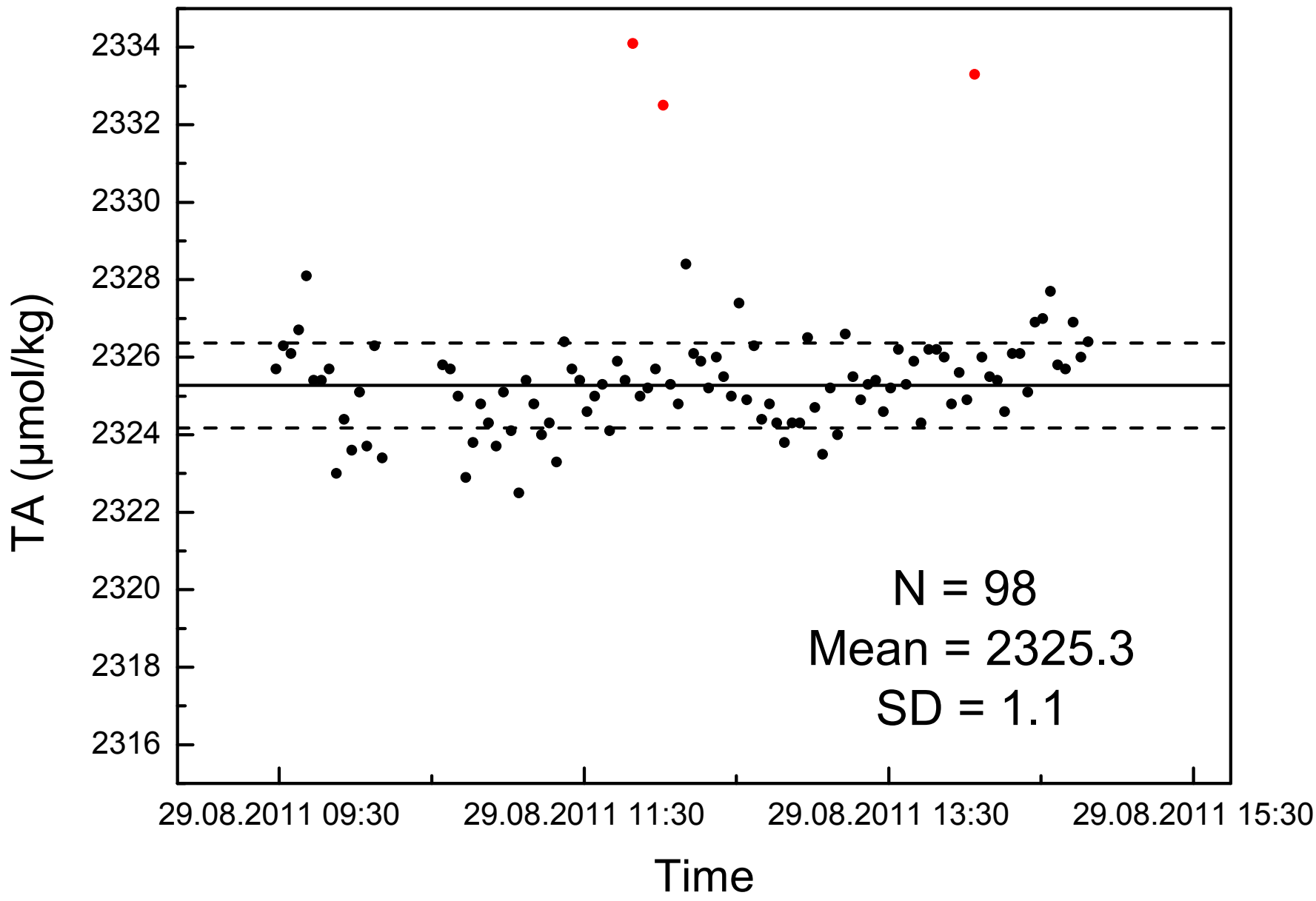
$$\mathrm{pH} = \mathrm{p}K_a + \lg \frac{[\mathrm{I}^{2-}]}{[\mathrm{HI}^-]}$$

$$\mathrm{pH}_T = \mathrm{p}K_a + \lg\left(\frac{R - e_1}{e_2 - R \cdot e_3}\right)$$

Calculation of the A_T

$$A_T M_{SW} = N_A M_A - [\mathrm{H}^+]_{ASW} M_{ASW}$$

Precision


TA (µmol/kg)
2334
2332
2330
2328
2326
2324
2322
2320
2318
2316
N = 98
Mean = 2325.3
SD = 1.1
29.08.2011 09:30
29.08.2011 11:30
29.08.2011 13:30
29.08.2011 15:30
Time

Summary – A_T

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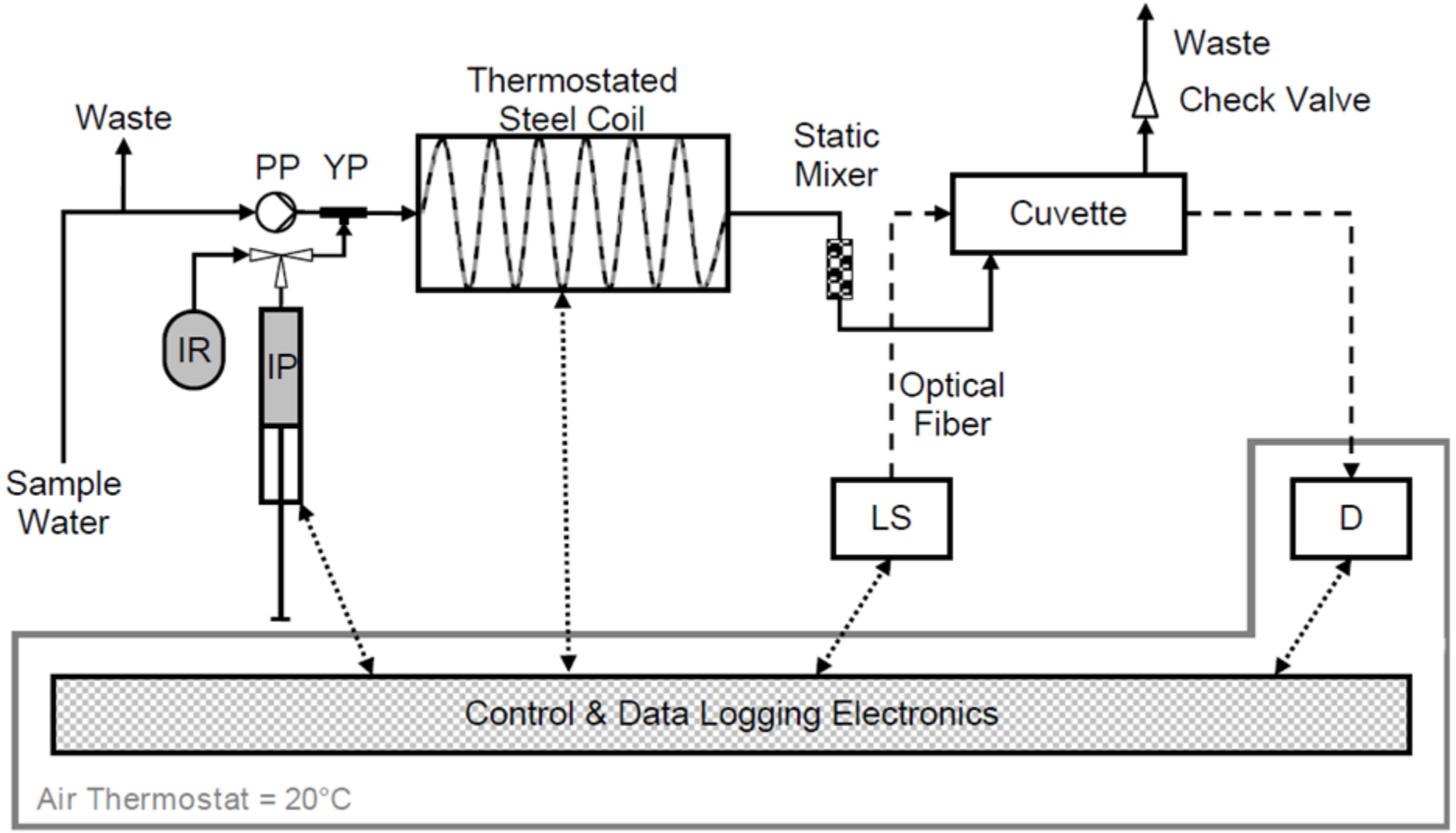
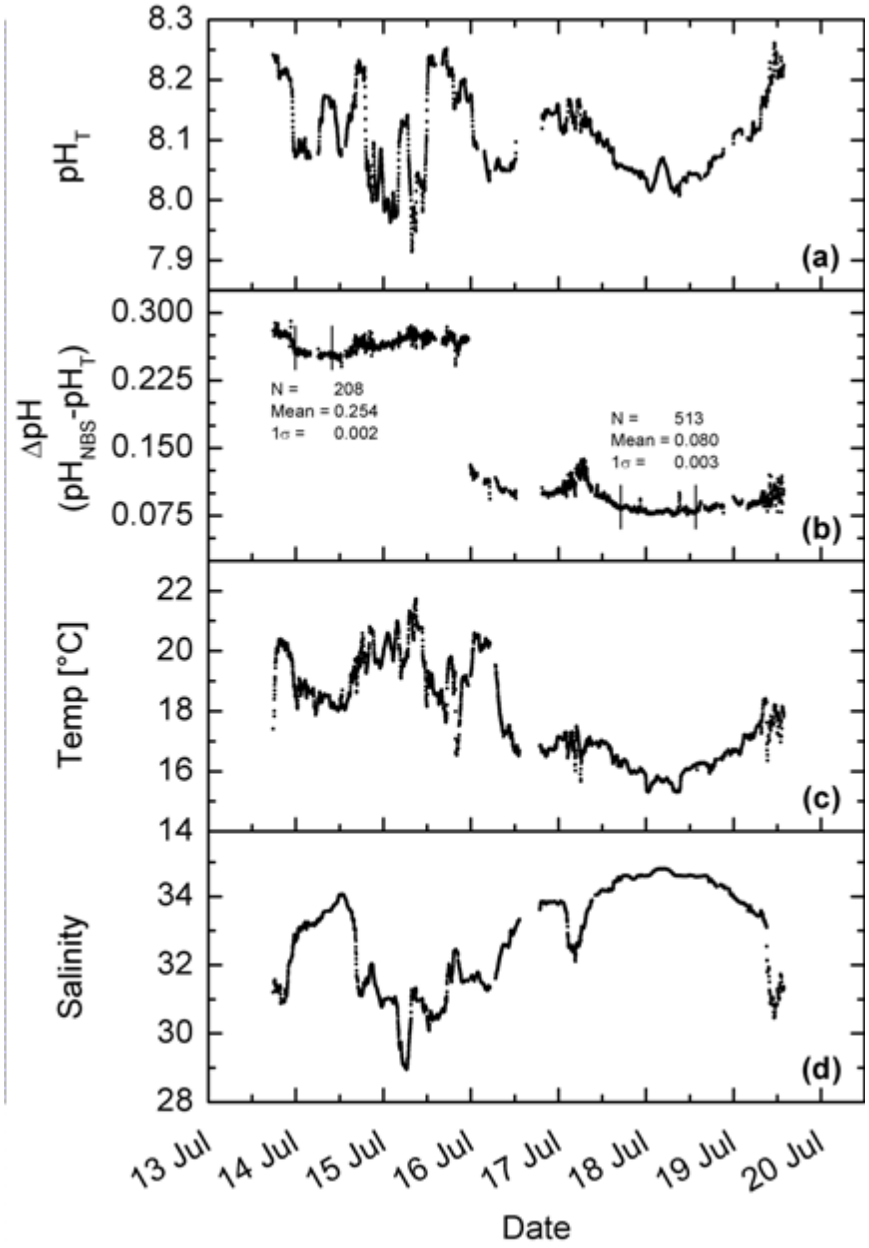
For use in Seawater	Salinity = 29 … 37 Temperature = 13 … 32 °C
Measurement cycle:	**< 5 min^{-1}**
Precision:	**< ±1.5 µmol/kg**
Accuracy:	**not determined yet**

Thank you

Setup


Waste
PP
YP
Thermostated Steel Coil
Static Mixer
Waste
Check Valve
Cuvette
IR
IP
Optical Fiber
Sample Water
LS
D
Control & Data Logging Electronics
Air Thermostat = 20°C

Aßmann et al., 2011



Broad data acquisition

Characterization of the CO_2 system

(DIC, pCO_2, A_T, pH, CO_3^{2-}, HCO_3^-, etc.)

Understanding the marine carbon cylcle

Anthropogenic CO_2 input

Modeling

A_T Model

$$A_T = \sum Bases - \sum Acids$$

Practical Alkelinity:

$$A_T = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] + \left[OH^-\right] - \left[H^+\right]_F - \left[HSO_4^-\right]$$

pH ≈ 4 and degassing of CO_2:

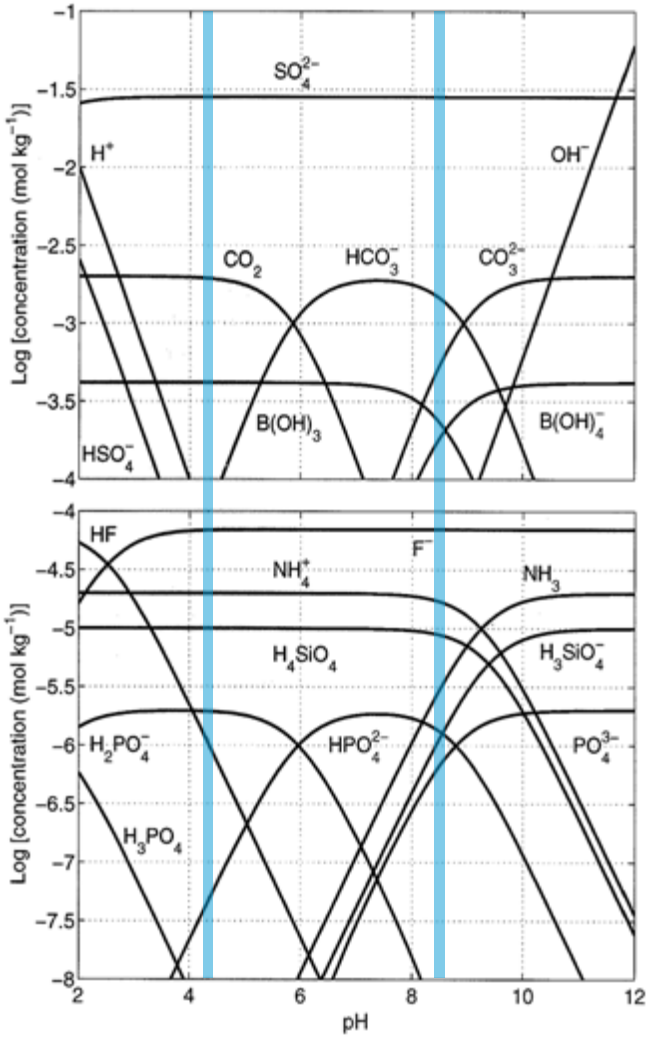
$$A_T = -\left[H^+\right]_F - \left[HSO_4^-\right]$$

Total scale:

$$\left[H^+\right]_T = \left[H^+\right]_F + \left[HSO_4^-\right]$$

Calculation of the A_T

$$A_T M_{SW} = N_A M_A - \left[H^+\right]_{ASW} M_{ASW}$$



Comparison

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Optical

Pro

Drift free

Calibration free in the field

High precision

Con

Error in pK_a	0,005
Perturbation from Indicator	0,005
Impurities of the Indicator	0,01

Uncertainty: 0,01

Potentiometric

Pro

Low cost

Small in size

Con

Non-ideal behavior	0,02
Error in buffers	0,005
Salinity (S < 5)	0,01
NBS scale (IUPAC)	0,05

High calibration rate

0,05