

# **ACID-BASE Equilibria in SEAWATER**

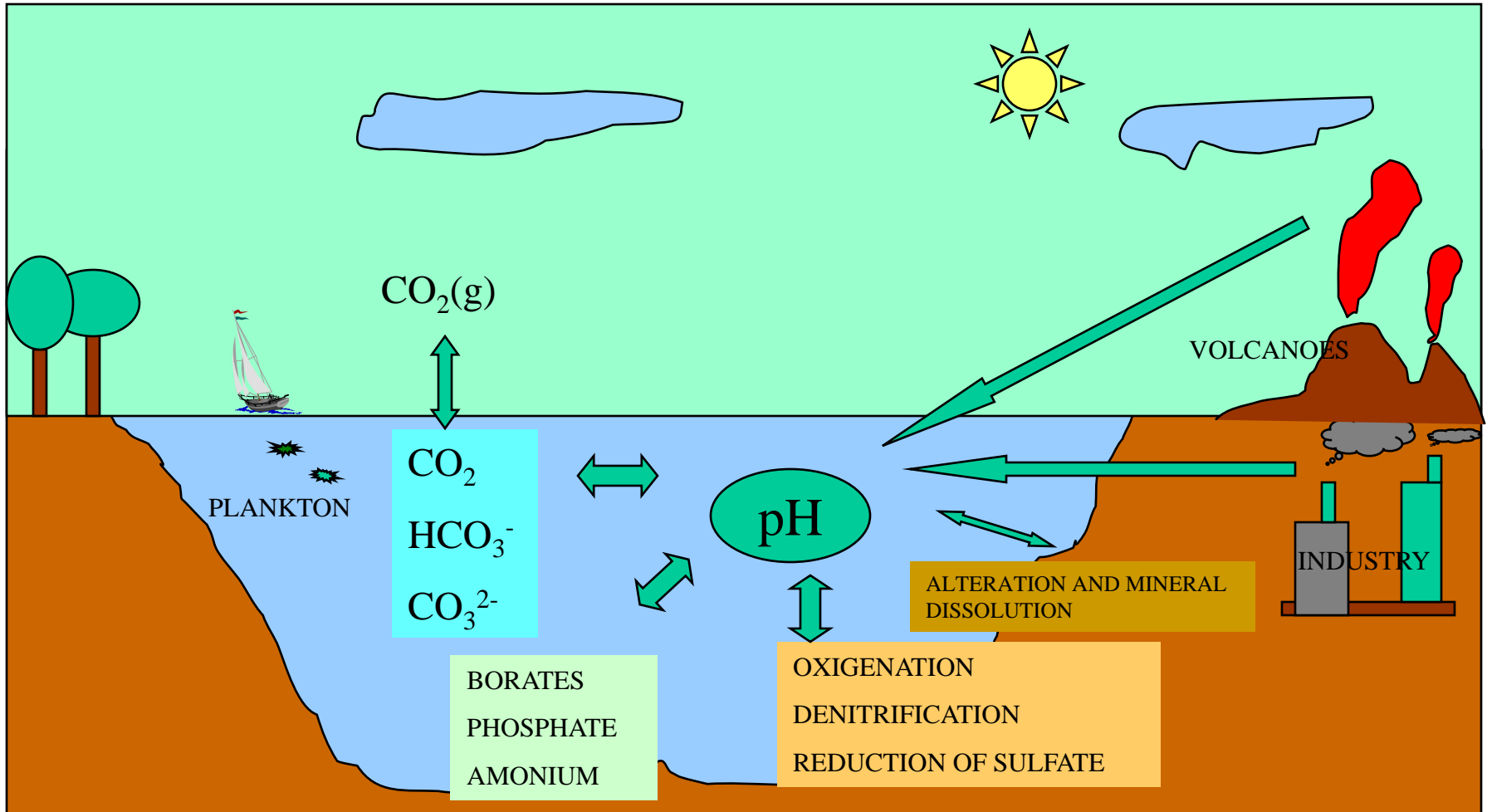
- Acid-base equilibria
- pH concept and scales
- pH measurements
- pH sensors, types
  - glass electrodes
  - Spectrophotometric sensors
  - Solid electrodes

## General considerations on Acid-Base equilibrium

**The physico-chemical composition of aqueous systems is controlled by:**



**Most of these processes are controlled by the acidic composition of the seawater solution. The title “master variable” has been given to the pH due to its importance in aquatic ecosystems. Determination of pH is critical in understanding the acid-base equilibria of aqueous species such as carbonate system variables and ammonium equilibria. Moreover, trace metal solubility and speciation, and consequently metal mobilization, are also highly pH dependent**



# acid-base systems in oceanic waters

## ACID-BASE REACTIONS



## COMPLEXATION REACTIONS



## ROLE OF $\text{H}^+$

## SOLUBILITY REACTION



## ADSORPTION REACTIONS



## OXIDATION-REDUCTION REACTIONS



# DISSOCIATION OF WATER



$$K_w = a_{\text{H}} a_{\text{OH}} / a_{\text{W}} = [\text{H}^+][\text{OH}^-] \gamma_{\text{H}} \gamma_{\text{OH}}$$

$$K_w^* = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

Pure water

$$\text{p}K_w = 14.00$$

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7}$$

$$\text{pH} = -\log [\text{H}^+] = 7.0 \quad \text{pOH} = 14 - \text{pH}$$

Seawater

$$\text{p}K_{\text{sw}} = 13.19$$

$$[\text{H}^+]_{\text{sw}} = [\text{H}^+]_{\text{F}} + [\text{HF}] + [\text{HSO}_4^-]$$

$$[\text{H}^+]_{\text{F}} = 85\% \quad \text{H}^+ + \text{SO}_4^{2-}$$



$$[\text{OH}^-]_{\text{F}} = 34\% \quad \text{OH}^- + \text{Mg}^{2+}$$

## pH scales

In seawater:  $[H^+] = [H^+]_F + [HSO_4^-] + [HF]$

### Free proton scale

$$pH_F = -\log[H^+]_F$$

### Total proton scale

$$[H^+]_T = [H^+]_F + [HSO_4^-]$$

$$pH_T = -\log[H^+]_T$$

$$[H^+]_T = [H^+]_F + [HSO_4^-] = [H^+] \left( 1 + \beta_{HSO_4} [SO_4^{2-}] \right)$$

$$pH_T = pH_F - \log(1 + \beta_{HSO_4} [SO_4^{2-}])$$

## pH scales

In seawater:  $[H^+] = [H^+]_F + [HSO_4^-] + [HF]$

### Seawater scale

$$[H^+]_{SWS} = [H^+]_F + [HSO_4^-] + [HF]$$

$$pH_{SW} = -\log[H^+]_{SW}$$

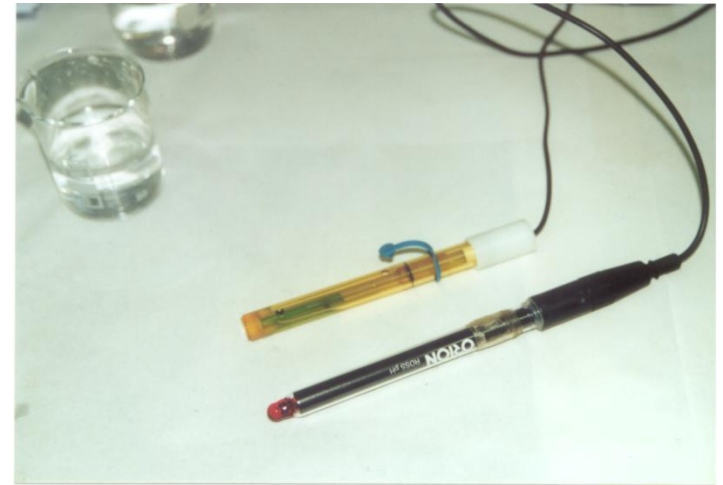
$$[H^+]_{SWS} = [H^+]_F + [HSO_4^-] + [HF] = [H^+]_F \left( 1 + \beta_{HSO_4} [SO_4^{2-}] + \beta_{SO_4} [F^-] \right)$$

$$pH_{SWS} = pH_F - \log(1 + \beta_{HSO_4} [SO_4^{2-}] + \beta_{HF} [F^-]) =$$
$$pH_T + \log((1 + \beta_{HSO_4} [SO_4^{2-}]) / (1 + \beta_{HSO_4} [SO_4^{2-}] + \beta_{HF} [F^-]))$$

pH measurement  $\begin{cases} \rightarrow \text{Potentiometric} \\ \rightarrow \text{Spectrophotometric} \end{cases}$

Potentiometric pH determination

pH(Glass electrode) | Solution (X) | KCl (aq) | Reference electrode





## Potentiometric determination

Although popular because of their simplicity and low cost, glass pH electrodes have several shortcomings for autonomous sensing in natural waters and seawater, especially low ionic strength and poorly buffered waters and non well defined junction potentials.

The primary problems arise from irreproducible junction potentials and junction potential drift encountered in both seawater and freshwater (two solutions of different concentrations are in contact with each other)

Even when calibrated frequently, large systematic errors can arise from differences between standard and sample junction potentials.

## **Potentiometric determination**

Electrode potentials take several minutes to stabilize after an electrode is placed in a new solution, and long-term pH electrode drift can be as much as  $0.01 \text{ pH h}^{-1}$

### **Remember:**

buffer solutions typically used in normal labs of 4, 7 and 9 are prepared in very low ionic strength solutions and the so called NBS/NIST pH calibrated electrodes are not valid in seawater solutions

## Potentiometric determination

The composition of the pH standards must closely match the experimental solution to avoid large changes in the liquid junction potential from calibration to measurement.

In seawater, this requires the use of synthetic seawater buffers (Dickson, 1993). However, even with careful calibration pH electrodes, with the exception of the hydrogen electrode, are not capable of achieving the needed accuracy (0.002 pH units) for inorganic carbon modeling.

Hydrogen electrodes have been used to estimate pH to within 0.002 pH units (DelValls and Dickson, 1998) but these measurements are difficult and not generally used in modern laboratories or for in situ pH studies.

How do we calibrate a pH glass electrode?

## Potentiometric determination

Using seawater buffers for calibration, we are able to obtain an accuracy of  $0.005 \pm 0.003$  pH units, but usually 0.01. However with great care, we can achieve 0.005 or 0.003 pH units.

Any residual liquid-junction error is minimized by matching the composition of the standard buffer to the sea water sample (buffer up in synthetic sea water)

The operational pH is defined (Nernst equation) by the expression

$$\mathbf{pH(X) = pH(S) + (E_S - E_x)/(RT \ln 10/F)}$$

We need values of pH(S) to various standard buffers in synthetic sea water (using cells without liquid junctions). Temperature should be known and controlled to within 0.1°C.

## Potentiometric determination

### *Synthetic sea water:*

We need reagent grade NaCl, Na<sub>2</sub>SO<sub>4</sub>, KCl dried in an oven at 110°C and calibrated MgCl<sub>2</sub> and CaCl<sub>2</sub> (the easiest way, by titrating with a calibrated silver nitrate solution using K<sub>2</sub>CrO<sub>4</sub> as indicator)

### *Buffer solutions*

- Calibrated HCl solution (e.g. titrated against a standard tris-NIST 723 base)
- 2-amino-2-hydroxymethyl-1,3-propanediol (tris) dried in a desiccator over phosphorus (V) oxide
- 2-aminopyridine dried in a desiccator over phosphorus (V) oxide

## Potentiometric determination

Composition of a buffer of salinity 35 (1000 g of H<sub>2</sub>O)

<u>Constituent</u>	<u>Moles</u>	<u>Weight (g)</u>
NaCl	0.38762	22.6446
KCl	0.01058	0.7884
MgCl <sub>2</sub>	0.05474	
CaCl <sub>2</sub>	0.01075	
Na <sub>2</sub> SO <sub>4</sub>	0.02927	4.1563
HCl	0.04000	
<i>One of:</i>		
TRIS	0.08000	9.6837
2 aminopyridine	0.08000	7.5231
<i>Total weight</i>		
TRIS		1044.09
2 aminopyridine		1041.93

## Potentiometric determination

**TRIS** on the total proton scale

$$\text{pH}(S) = (11997.0 + 3.7669 * S + 0.00178 * S^2) / T - 381.3088 + 0.011634 * S + 67.63163 * \ln(T) - 0.121538 * T - \log(1 - 0.00106 * S)$$

**2-Aminopyridine**

$$\text{pH}(S) = (111.35 + 5.44875 * S) / T + 41.6775 - 0.015683 * S - 6.20815 * \ln T - \log(1 - 0.00106 * S)$$

To be sure, the electrode is working properly, the response ( $s$ ) or slope of Nernst  $RT \ln 10 / F$  (0.05916 at 25°C,  $T = 298.15 \text{K}$ )

$$s = \frac{E_{AMP} - E_{TRIS}}{\text{pH}(S)_{TRIS} - \text{pH}(S)_{AMP}}$$

If the difference between  $s$  and ideal Nernst slope is more than 0.3%, clean, refill or replace the electrode.

# Potentiometric determination

## EXAMPLE

$$pH(X) = pH(S) + \frac{E_S - E_X}{RT \ln 10 / F}$$

pH(S) is the TRIS value on the total proton scale, in mol/Kg-soln)

Input data

$$t = 25^\circ\text{C} \quad (T = 298.15\text{K})$$

$$S = 35$$

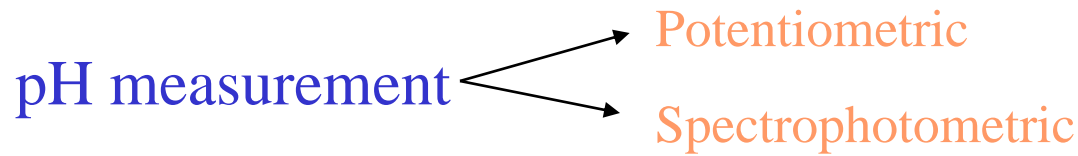
$$E_{\text{TRIS}} = -0.0720\text{V}$$

$$E_{\text{AMP}} = 0.0049\text{V}$$

$$E_X = -0.0670\text{V}$$

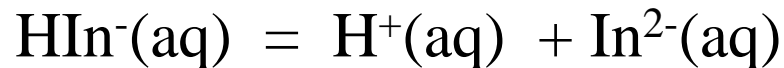
SEE EXCEL, [Potentiometric pH calculation sheet.](#)



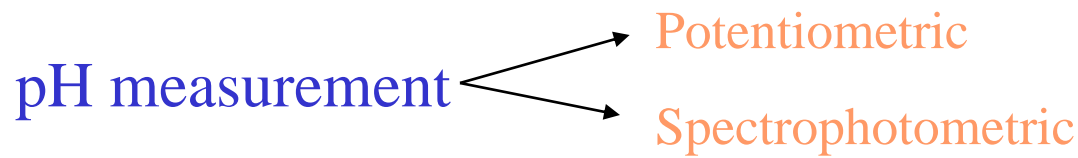


## **Spectrophotometric pH determination**

The pH of a seawater solution is determined by adding an indicator dye to sea water which has substantially different absorption spectra for the acid and basic forms of the dye



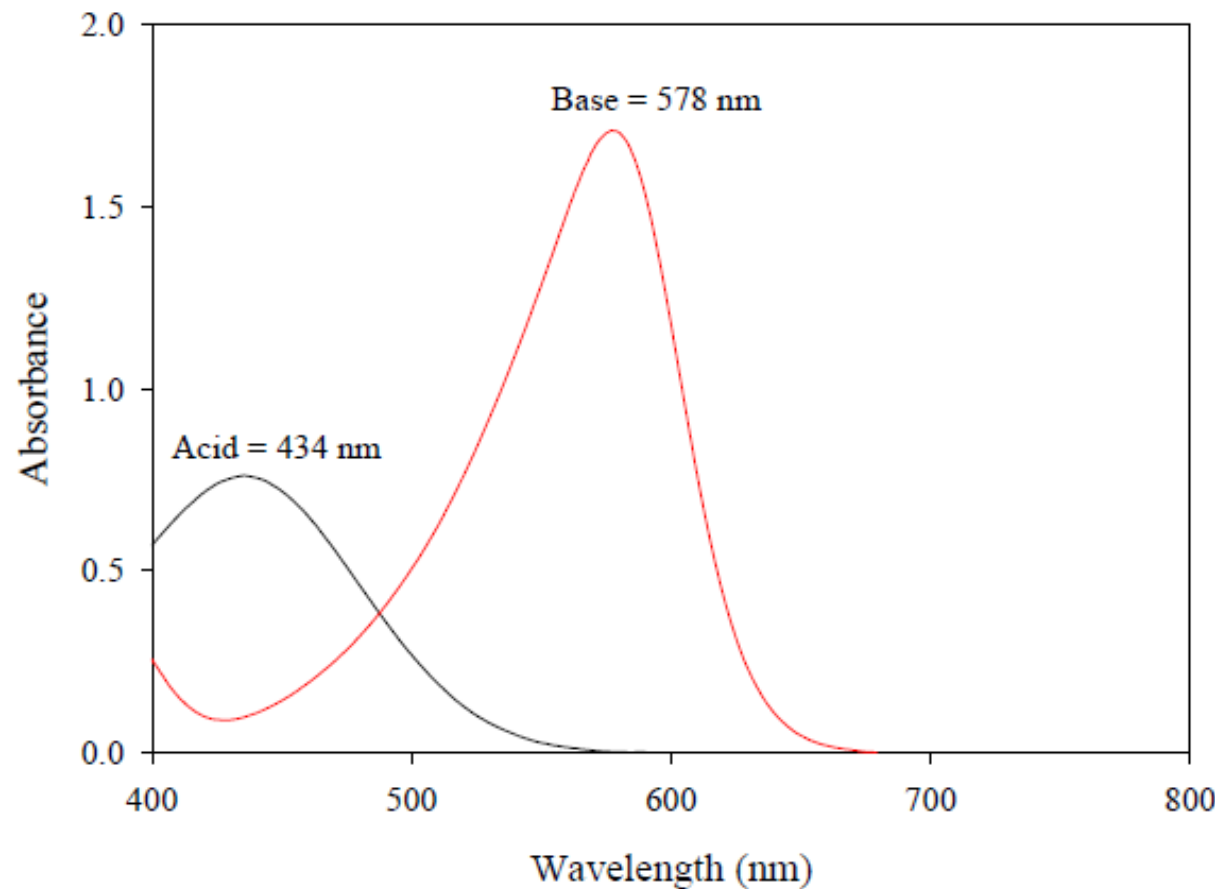
Since spectrophotometric pH measurements are made via absorbance ratios, spectrophotometric pH is directly related to indicator (sulfonephthalein) molecular properties, and measurements do not require the use of calibrating buffers

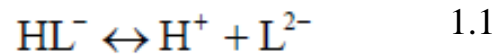


## Spectrophotometric pH determination

The most used indicator dyes are sulfonephthalein indicators such as m-cresol purple, because the dissociation constant for this equilibrium (the second one for the species) is inside the pH range of seawater solutions.

Bromocresol purple (BCP) and phenol red (PR) have also been used



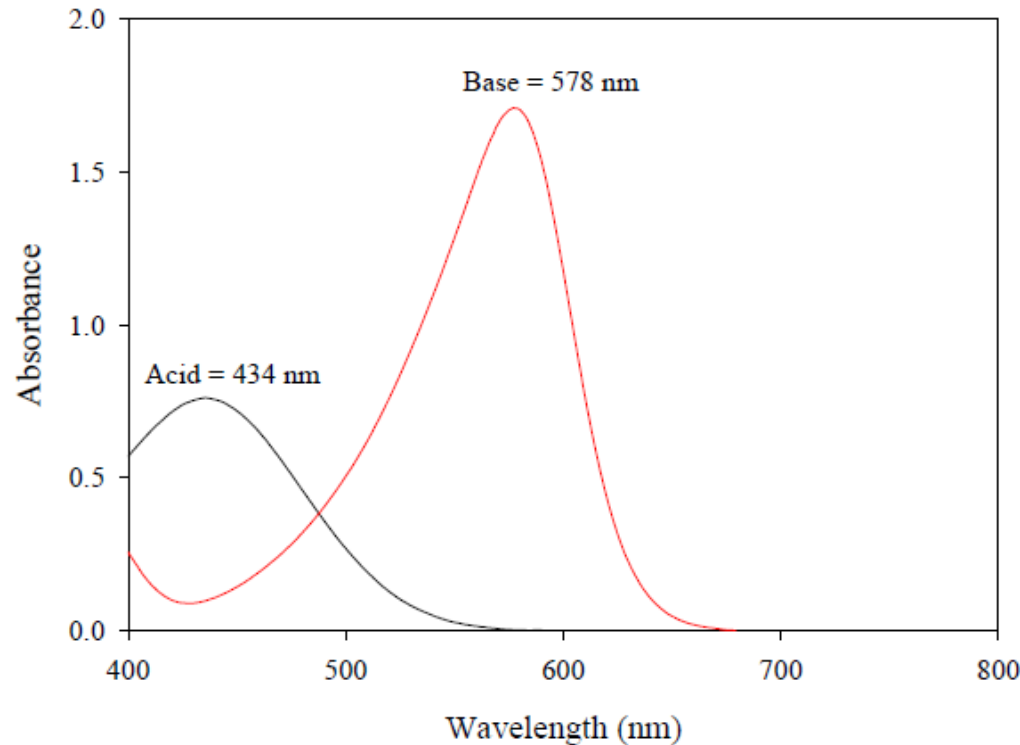


$$\text{pH} = \text{pK}_a' + \log \left( \frac{[\text{L}^{2-}]}{[\text{HL}^-]} \right) \quad 1.2$$

In Eq. 1.2, the  $\text{pK}_a'$  is the apparent dissociation constant for the dye and depends on the temperature and ionic strength. Remember,  $\text{pK}_a'$  does not need ion activity coefficients. For mCP the peak acid wavelength is 434 nm and the peak base wavelength is 578 nm.

Observe, absorbances for the acid and base forms overlap at the peak wavelengths and we should take into account the concentration of each indicator species present and its molar absorptivity

The Beer's law relationship is applied

$$A = \epsilon bc$$


$$A_1 = {}_{\text{HL}}\epsilon_{434}[\text{HL}^-]b + {}_{\text{L}^{2-}}\epsilon_{434}[\text{L}^{2-}]b \quad 1.3$$

$$A_2 = {}_{\text{HL}}\epsilon_{578}[\text{HL}^-]b + {}_{\text{L}^{2-}}\epsilon_{578}[\text{L}^{2-}]b \quad 1.4$$

$\epsilon$  is the molar absorptivity for each  $\text{HL}^-$  and  $\text{L}^{2-}$  forms of the indicator at each wavelengths and it is a physical property of the dye;  $b$  is the pathlength. In Eq 1.3 and 1.4 the terms  $B_\lambda$  and  $e$  should be added and account for background absorbance and error due to instrumental noise. When all these three equations 1.2 to 1.4 are combined, the pH of the seawater solutions containing a given concentration of dye will be

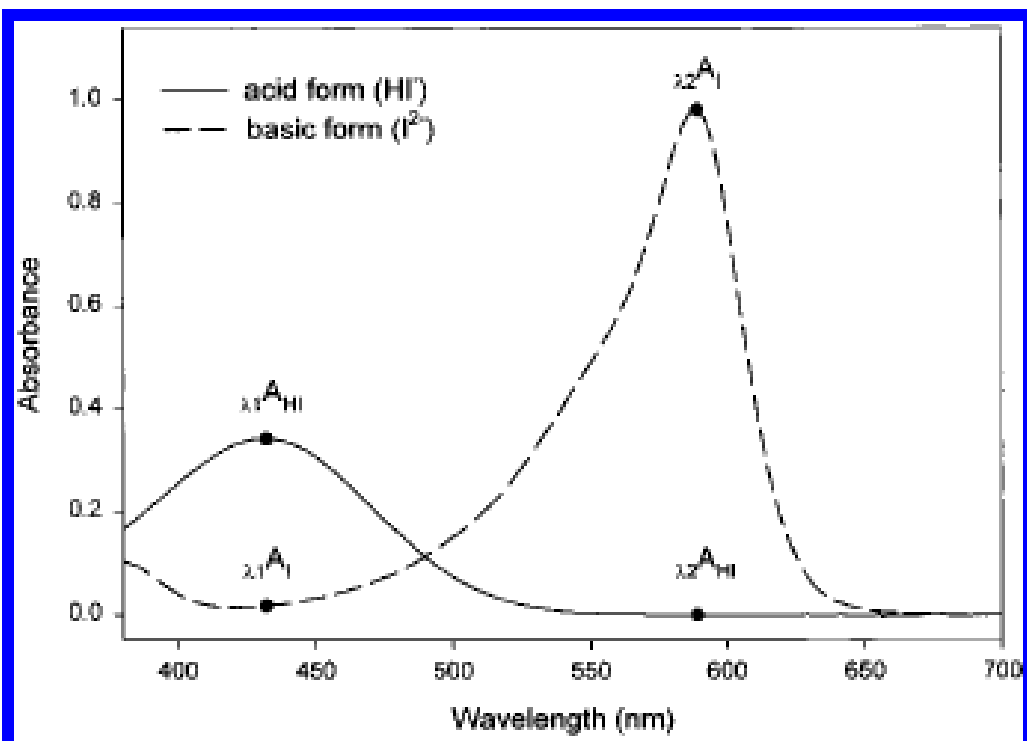
$$\text{pH} = \text{pK}'_a + \log\left(\frac{R - e_1}{e_2 - Re_3}\right) \quad 1.5$$

where  $R = A_{578}/A_{434}$

$$e_1 = \frac{\epsilon_{a578}}{\epsilon_{a434}} \quad e_2 = \frac{\epsilon_{b578}}{\epsilon_{a434}} \quad e_3 = \frac{\epsilon_{b434}}{\epsilon_{a434}} \quad 1.6$$

These parameters ( $\epsilon_i$ ) are obtained by examining the absorbance properties of indicators under sufficiently alkaline conditions that the total indicator concentration ( $I_T$ ) is equal to  $[I^{2-}]$  and at sufficiently acidic conditions that  $I_T = [HI^-]$ . Indicator molar absorption coefficients are expressed in terms of absorbances, indicator concentrations, and path length ( $l$ ) as follows

$$\lambda \epsilon_I = \lambda A_I / [I^{2-}] l \quad \lambda \epsilon_{HI} = \lambda A_{HI} / [HI^-] l$$



## We should know

- the value of  $pK_a'$  at the conditions we are measuring the pH
- The  $e_i$  ratios for the instrument used and for the dye batch used

## We need

- ❖ To mix the mCP indicator with the sea water sample
- ❖ To measure the absorbances at the peak wavelengths to calculate R.

## We should also consider:

- ✓ To correct for baseline drift
- ✓ The influence of the addition of indicator solution on the sample pH

Note: In lab, we use 10 cm pathlength cells with a small amount of indicator. We get high absorbances without perturbing the pH more than 0.001 units

➤ **The value of  $pK_a'$  at the conditions we are measuring the pH**

Clayton and Byrne, 1993 provided  $pK_a'$  values valid for the temperature range 20–30°C and salinity 30 to 37.

$$pK_{a,2} = 1245.69/(T)+3.8275+0.00211*(35-S) \quad 1.7$$

The  $pK_{a,2}$  can be extrapolated to other temperatures using the Van't Hoff equation (Seidel et al., 2008).

However, the extrapolation of Eq. (1.7) for temperatures until 10°C does not introduce a significant error as compared to that determined using the Van't Hoff equation.

$pK_a'$  values for other indicator dyes are also provided by Byrne's group.

➤ **The  $e_i$  ratios for the instrument used and for the dye batch used**

Clayton and Byrne, 1993 also provided  $e_i$  values for mCP and they have been used worldwide.

Extinction coefficient ratios for m-cresol purple

$$\lambda_1 = 578 \text{ nm}; \lambda_2 = 434 \text{ nm}$$

$$e_1 = \epsilon_{\text{HI}}^{578} / \epsilon_{\text{HI}}^{434} \quad 0.00691$$

$$e_2 = \epsilon_{\text{I}}^{578} / \epsilon_{\text{HI}}^{434} \quad 2.2220$$

$$e_3 = \epsilon_{\text{I}}^{434} / \epsilon_{\text{HI}}^{434} \quad 0.1331$$

However molar absorptivities are dependant on the bandpass of the instrument they are measured on (differences in the interference filters used to filter the white light source or among light sources; on the pathlength of the measurement cell; differences in impurities between indicator dye lots)



## Calculation of molar absorptivities $\epsilon$

The indicator solution used should be in the 2-6 mM in m-cresol purple, mCP, and 0.7 M NaCl solution.

The method employed is that described in Clayton and Byrne (1993). In brief, a pH value of 12 was used to calculate the  $\epsilon_i$  values for the basic  $L^{2-}$  form at 434 nm and 578 nm, by adding 5 different and known concentrations of the indicator dye into a NaOH 0.02 M and 0.68 M NaCl solution within the temperature range of 10-30°C.

In order to determine the corresponding  $\epsilon_i$  values for the  $HL^-$  at both wavelengths, a pH solution of 5.5 was used, consisting in 0.018 M sodium acetate, 0.67 M NaCl and an HCl 0.1 M solution added to reach the desired pH.

A pH of 5.5 was chosen in order to eliminate any presence of  $H_2L$  species at the sacrifice of increased  $L^{2-}$  concentrations.

## Calculation of molar absorptivities $\epsilon$

The  $L^{2-}$  was accounted for by calculating the concentrations of  $L^{2-}$  present at the measurement pH and **correcting** for its molar absorptivity contribution to the final absorbance value (Martz, 2005).

$$\epsilon_{HL}^{578} = \frac{{}_{578}A_1[I^{2-}]_2 - {}_{578}A_2[I^{2-}]_1}{[HI^-]_1[I^{2-}]_2 - [HI^-]_2[I^{2-}]_1}$$

$$\epsilon_L^{578} = \frac{{}_{578}A_2[HI^-]_1 - {}_{578}A_1[HI^-]_2}{[HI^-]_1[I^{2-}]_2 - [HI^-]_2[I^{2-}]_1}$$

$$\epsilon_{HL}^{434} = \frac{{}_{434}A_1[I^{2-}]_2 - {}_{434}A_2[I^{2-}]_1}{[HI^-]_1[I^{2-}]_2 - [HI^-]_2[I^{2-}]_1}$$

$$\epsilon_L^{434} = \frac{{}_{434}A_2[HI^-]_1 - {}_{434}A_1[HI^-]_2}{[HI^-]_1[I^{2-}]_2 - [HI^-]_2[I^{2-}]_1}.$$

The correction is around 53% for the initial value of  $\epsilon_{HL}^{578}$  due to an increase in the basic form of the indicator and the very small value of  $\epsilon_{HL}^{578}$ . For the other three molar absorptivities the corrections are less than 0.3% of the initial value.

See excel

## Calculation of molar absorptivities $\epsilon$

<b>Molar absorptivities</b>	$HL\epsilon^{434}$	$HL\epsilon^{578}$	$L\epsilon^{434}$	$L\epsilon^{578}$	$\epsilon_1$	$\epsilon_2$	$\epsilon_3$
<b>Temperature dependence</b>	17120 - 26*(t-25)	88 + (t-25)	2237 + 11.9*(t-25)	38018 - 71*(t-25)	0.0051 - 6.52e-5*(t-25)	2.2207 + 8e-4*(t-25)	0.1307 - 9e-4*(t-25)
<b>Precision</b>	43	8	31	94	0.001	0.0012	0.0023

Gonzalez-Dávila et al. 2015(submitted)

<b>Species</b>	<b>SAMI-47</b>	<b>SAMI-51</b>	<b>UV/Vis</b>
$HL\epsilon_{434}$	18808- 26(t-25)	18597 - 26(t-25)	17340 - 26(t-25)
$HL\epsilon_{578}$	94 + (t-25)	121 + (t-25)	79 + (t-25)
$L\epsilon_{434}$	2531 + 12(t-25)	2462 + 11.7(t-25)	2151 + 12(t-25)
$L\epsilon_{578}$	41848 - 71(t-25)	41225 - 71(t-25)	37973 - 71(t-25)

Seidel et al. (2008)

M González-Dávila Workshop, Trieste Sept 2015

## Calculation of molar absorptivities $\epsilon$

The values determined by González-Dávila et al., 2015 concord with those measured by Clayton and Byrne (1993) at 25°C.

In the range 20°C to 30°C, where a constant value for the ratios  $\epsilon_1 - \epsilon_3$  was assumed by C&B, the error in the pH estimation is  $\pm 0.003$ , increasing to an overestimate in the pH values of 0.008 pH units when the temperature is 10°C.

When the individual values are compared to those as determined by Seidel et al (2008), where Sigma-Aldrich dyes were also used, the differences in the determination of pH over the temperature range between 10° to 30°C was under 0.0014, and can be explained by the different indicator batch and optical configurations used.

Remember: detection systems with a larger bandpass (10 nm or more) should have smaller molar absorptivity values than instruments with a narrow band pass (1 or 2 nm)

## ✓ To correct for baseline drift

Changes in the spectrophotometric absorbance readings can also be due to changes in the stability of the system, instrumental shifts. It is needed to determine both a blank and the absorbance of at a non-absorbent wavelength for the seawater and dye as reference. A third wavelength with a value of 730-750 nm is used. This allows blank values to be collected for every pH measurement.

The typical standard deviation of 5-10 intensity values used for the blank determination is less than  $5.0 \times 10^{-4}$  absorbance units.

With blank determinations, the absorbance values are calculated using the detected intensity at each wavelength reading with respect to the intensity at the reference channel at 750 nm for both the seawater and the seawater+dye solutions

## ✓ To correct for baseline drift

At each of the three wavelengths (434, 578, 750 nm) we should subtract the absorbances for the background measurements (without dye) from that measured for the system containing dye.

$$A_{578} = A^{578,\text{dye}} - A^{578,\text{sw}}$$

$$A_{434} = A^{434,\text{dye}} - A^{434,\text{sw}}$$

$$A_{750} = A^{750,\text{dye}} - A^{750,\text{sw}}$$

It is then assumed that the magnitude of any observed shift in the equipment along a reading is identical across the visible spectrum. Observe, to do this, we subtract the measured shift from the background corrected absorbances at wavelength 434 and 578 in order to obtain the final corrected absorbance values at each wavelength and then we compute the ratio R

$$R = (A_{578} - A_{750}) / (A_{434} - A_{750})$$

## ✓ The influence of the addition of indicator solution on the sample pH

Spectrophotometric measurements of pH are actually measuring the pH of a solution that contains both sample and indicator. The addition of an indicator to seawater can change the pH of the sample and degrade accuracy. This pH perturbation is due to the weak acid properties of the indicator and dilution of the sample by the indicator solution.

The perturbation is dependent upon the concentration, dilution factor,  $pK_a'$ , and pH of the indicator solution added.

Different methods have been developed by researchers to deal with the pH perturbation due to indicator additions.

Most seawater pH methods use long path length cells (10 cm) to obtain sufficiently high absorbance readings with very small indicator additions (e.g. Clayton and Byrne, 1993).

## ✓ The influence of the addition of indicator solution on the sample pH

Typical indicator concentrations are around  $1 \times 10^{-6} \text{ mol kg}^{-1}$  for 10 cm cells. At this concentration, the magnitude of the perturbation is typically  $\sim 0.001$  pH units. Even so, various methods have been used to account for the pH perturbation due to indicator addition. In sensor equipment, the cell is 1 cm and important changes from  $\pm 0.012$  in the seawater pH can be produced when the indicator is added

**1.** A plot of R versus  $\Delta R$  for multiple additions of indicator to a sample can be linearly extrapolated to the y-axis to give an R value when the indicator concentration is zero (Zhang and Byrne, 1996). The pH perturbation determined from these tests were then used to correct pH measurements made using only one indicator addition, resulting in a constant pH perturbation offset being applied for pH measurements.



## ✓ The influence of the addition of indicator solution on the sample pH

In this method, we have to assure the dye is stable with time and there is not light and air contact with the solution, and for that reason, long deployments can produce drifts difficult to solve. Moreover, we should establish a new equation for each new prepared dye solution.

2. Another method uses the isosbestic absorbance, which is independent of the pH of the sample and dependent only on the total indicator concentration because the value for  $\epsilon$  is the same for the acid and base species at the isosbestic wavelength. The method can use several or only five indicator additions to a sample to create a plot of isosbestic absorbance versus R, or a plot of pH versus  $A_{\text{iso}}$  or  $[\text{Ind}]_{\text{Tot}}$  yielding an R or a pH value when no indicator is present by extrapolating

$$A_{\text{iso}} = \epsilon_{\text{iso}}^{\text{IH}} b[\text{IH}^-] + \epsilon_{\text{iso}}^{\text{I}} b[\text{I}^{2-}] = \epsilon_{\text{iso}} b ([\text{IH}^-] + [\text{I}^{2-}]) = \epsilon_{\text{iso}} b [\text{I}]_{\text{Tot}} \propto [\text{I}]_{\text{Tot}}$$

3.

$$A_1 = \epsilon_{434}^{\text{HL}} [\text{HL}^-] b + \epsilon_{434}^{\text{L}^{2-}} [\text{L}^{2-}] b$$

$$1 = 434$$

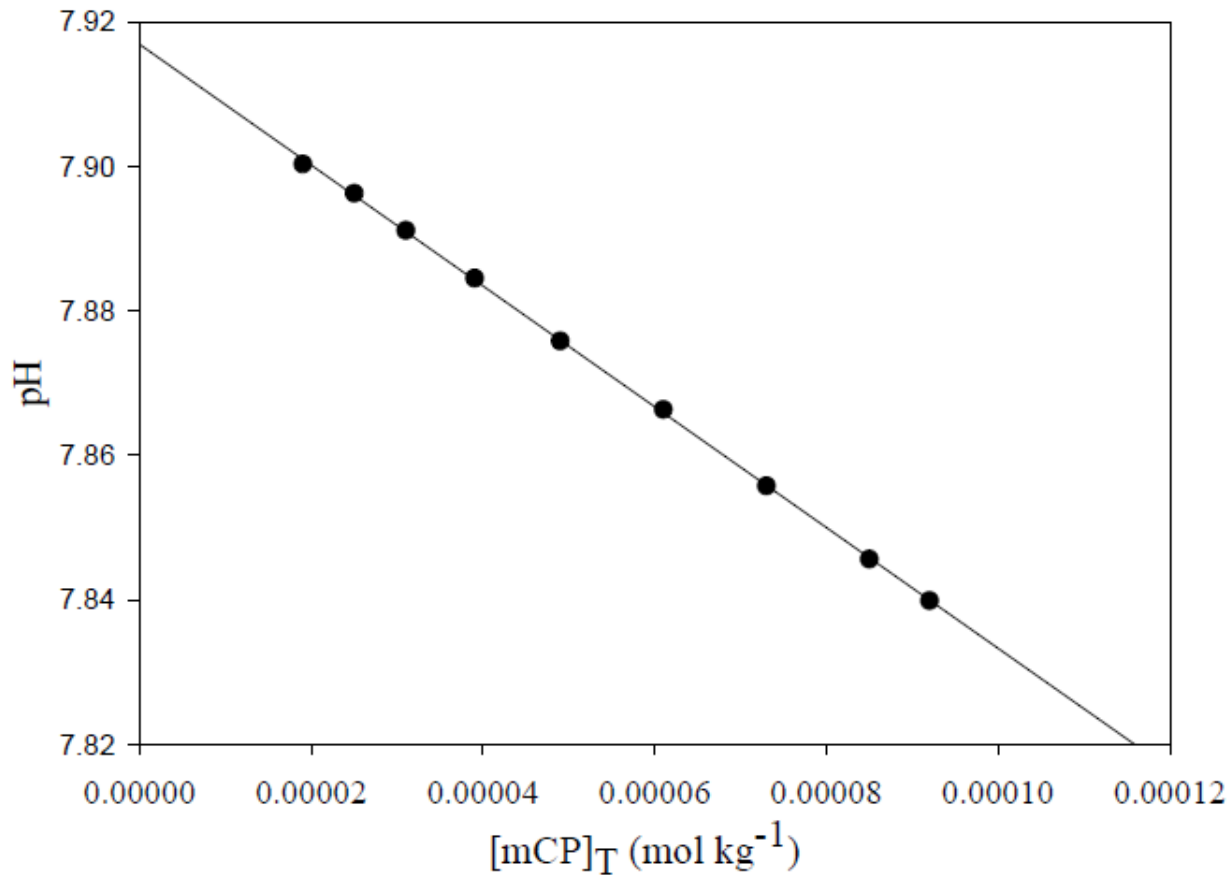
$$2 = 578$$

$$[\text{HL}^-] = \frac{A_{434} \epsilon_{578}^{\text{L}^{2-}} - A_{578} \epsilon_{434}^{\text{L}^{2-}}}{\epsilon_{434}^{\text{HL}} \epsilon_{578}^{\text{L}^{2-}} - \epsilon_{578}^{\text{HL}} \epsilon_{434}^{\text{L}^{2-}}}$$

$$A_2 = \epsilon_{578}^{\text{HL}} [\text{HL}^-] b + \epsilon_{578}^{\text{L}^{2-}} [\text{L}^{2-}] b$$

$$[\text{L}^{2-}] = \frac{A_{578} \epsilon_{434}^{\text{HL}} - A_{434} \epsilon_{578}^{\text{HL}}}{\epsilon_{434}^{\text{HL}} \epsilon_{578}^{\text{L}^{2-}} - \epsilon_{578}^{\text{HL}} \epsilon_{434}^{\text{L}^{2-}}}$$

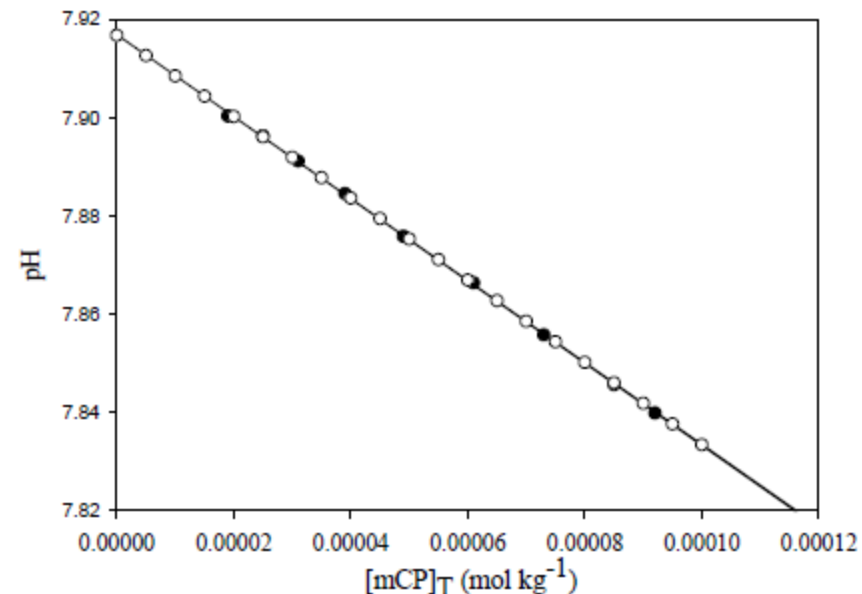
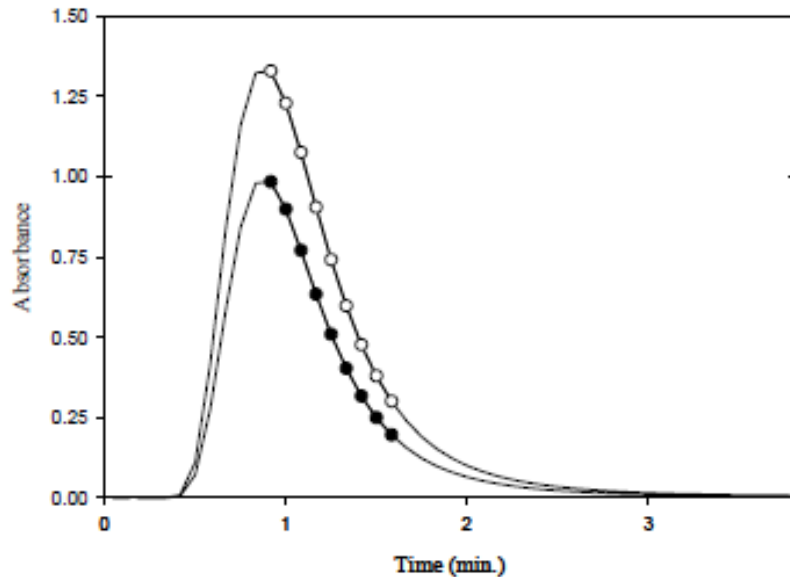
$$[\text{mCP}]_{\text{T}} = [\text{HL}^-] + [\text{L}^{2-}]$$



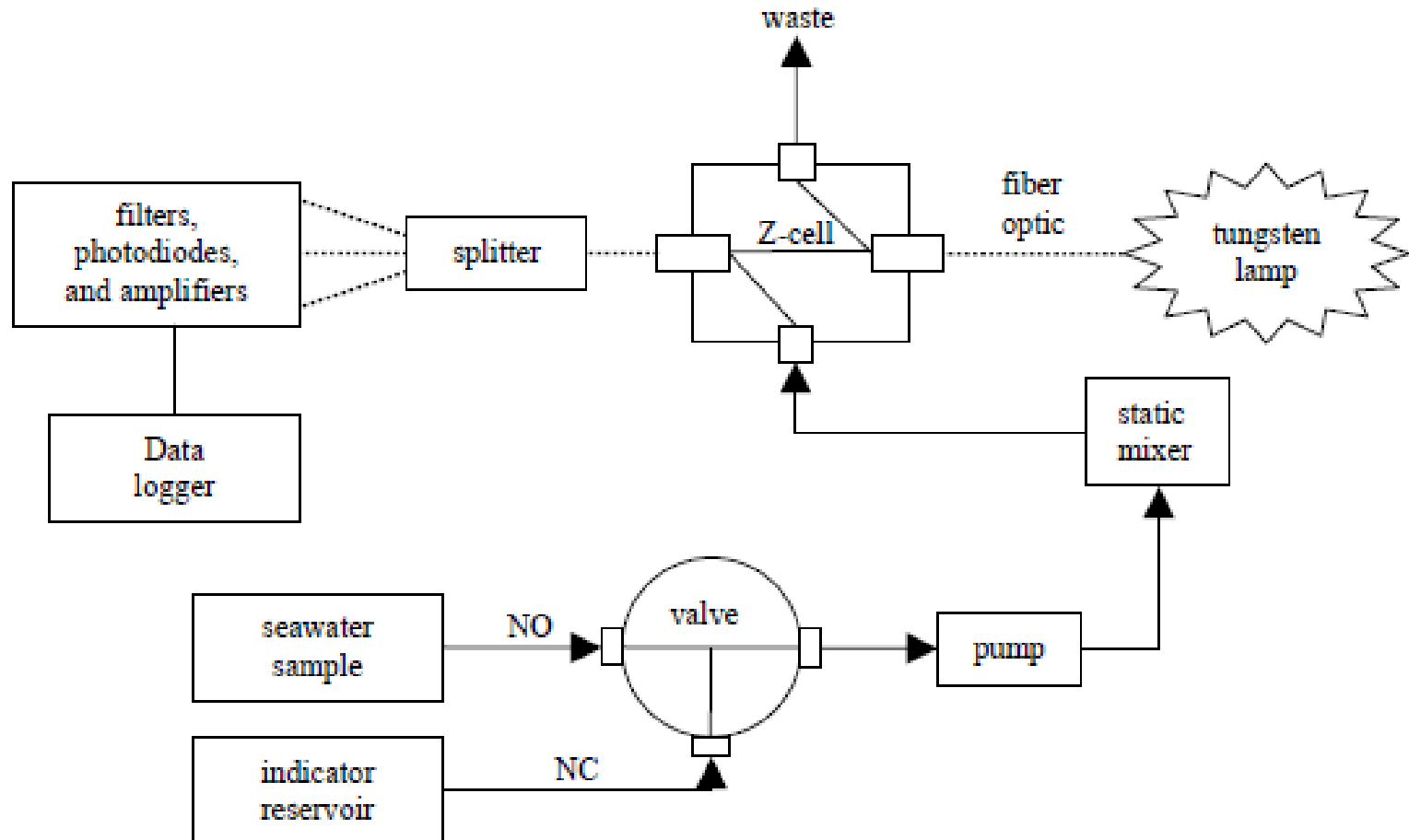
## How can we do it?

If we inject a small amount of dye in the seawater flow and they are allowed to mix in a coil or in a static mixer, as the sample and indicator are pushed toward the flow cell, mixing occurs at both the leading edge of the indicator slug and the tail end of the slug.

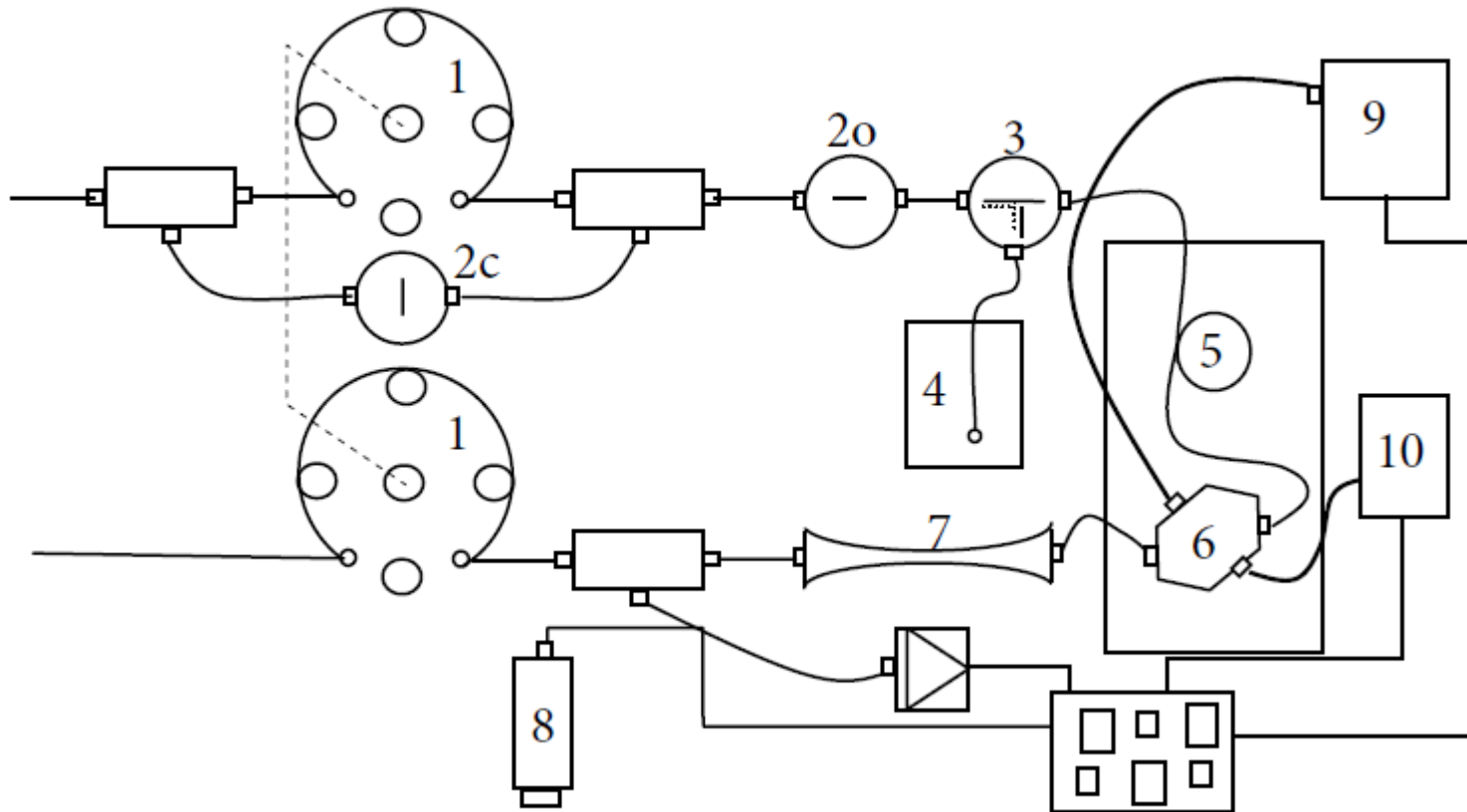
The tail end of the indicator peak, can provide many absorbance measurements at different dye concentrations that can be used to compute a pH at zero dye effects as indicated before



# SAMI pH SENSOR



# SENSORLAB pH SENSOR



1, two-channel peristaltic pump; 2, two-ways open (o) and close (c) electrovalves; 3, three ways electrovalve; 4, dye bag; 5, coiled PTFE tubing; 6, Z-type flow cell; 7, dumping tube; 8, pressure sensor; 9, Halogen lamp; 10, spectrophotometer.

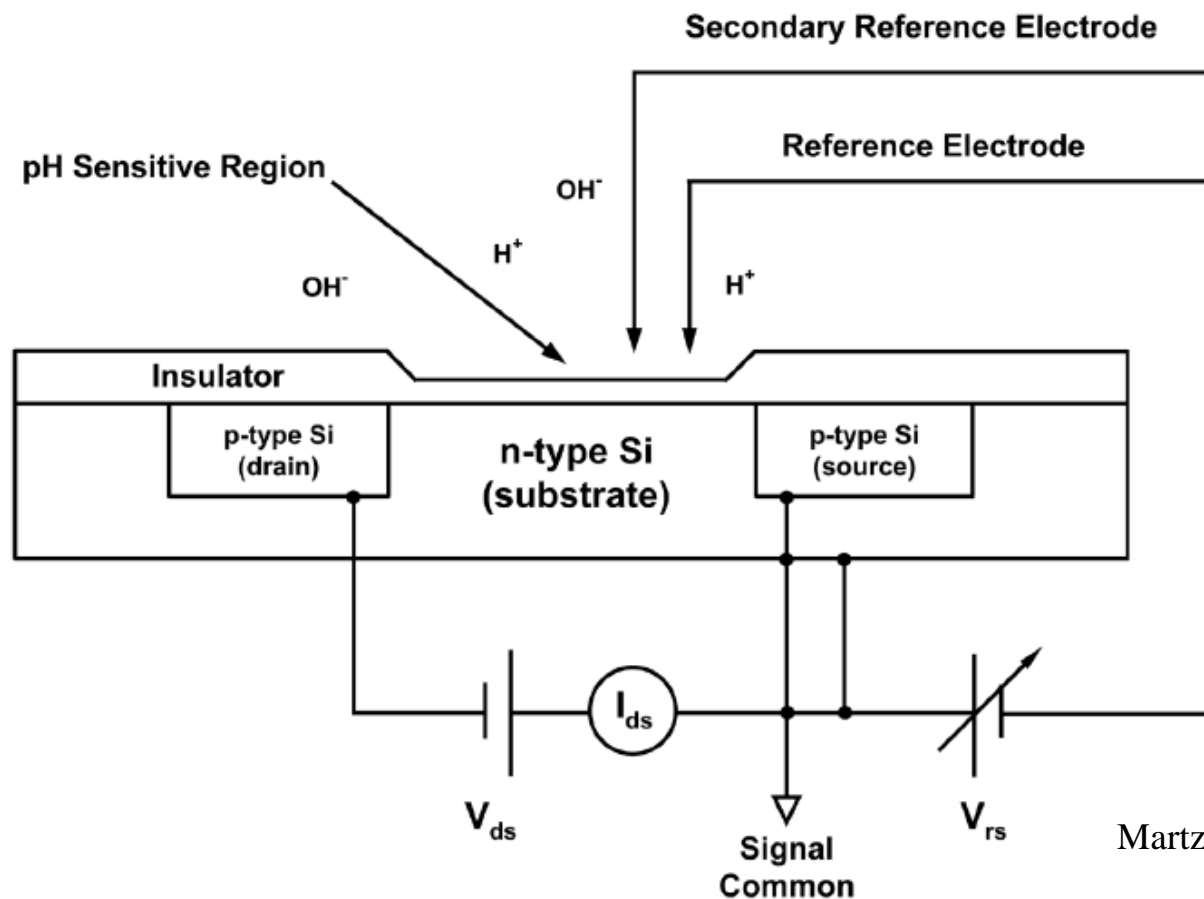
# THE ISFET TECHNOLOGY

A small number of research groups have measured seawater pH using Ion Sensitive Field Effect Transistor (ISFET) technology (Le Bris and Birot 1997; Shitashima et al. 2002; Bergveld (2003).

Briefly, an ISFET is a Metal Oxide Semiconductor Field Effect Transistor (MOSFET) without a metal gate electrode over the conduction channel. The conduction channel is covered by a thin insulating layer of amphoteric material such as silicon nitride ( $\text{Si}_3\text{N}_4$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ), yttrium oxide ( $\text{Y}_2\text{O}_3$ ), or tantalum pentoxide ( $\text{Ta}_2\text{O}_5$ ).

The pH of the solution at the insulator/solution interface controls the site-binding protonation/deprotonation state of the insulator material and, hence, the surface charge at the interface.

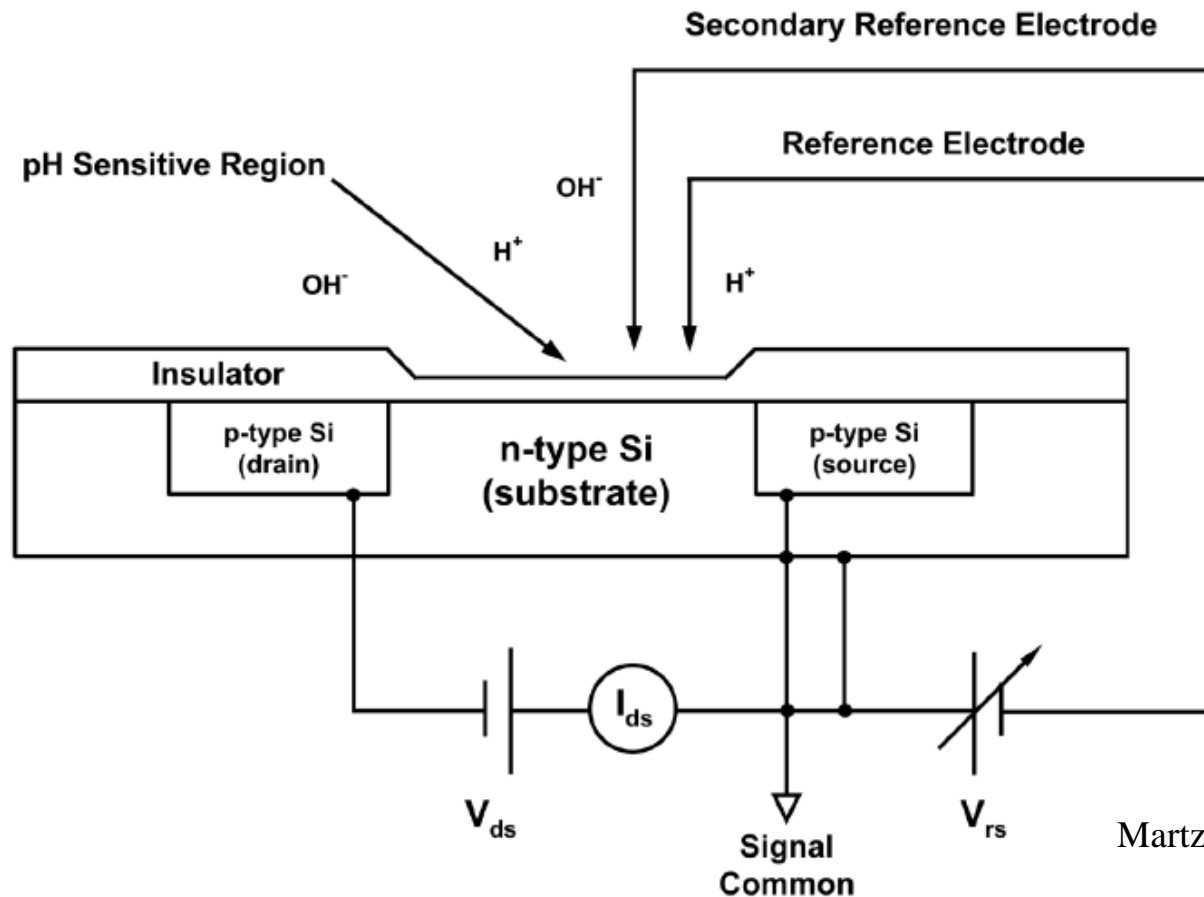
The interfacial charge determines the strength of the electric field in the conduction channel of the FET, located between the source and drain.



Martz et al., 2010 (L&O:M)

**Fig. 1.** Functional implementation of the ISFET operating principle. The Durafet is a p-channel enhancement mode ISFET, operated at a constant drain-source voltage and current. These conditions are obtained by adjusting an external reference electrode to source voltage ( $V_{rs}$ ) to maintain constant  $I_{ds}$ . The reference-source voltage ( $V_{rs}$ ) obeys a Nernstian response to protons in solution. The secondary reference EMF is also measured versus signal common.

ISFETs are commonly operated by applying a constant drain-source voltage and using a feedback circuit to hold the drain-source current constant. A conventional reference electrode is used in lieu of the now removed gate. The analytical pH signal is proportional to the reference electrode to source voltage



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The Durafet is a combination electrode with an internal reference formed by a Ag wire in a AgCl and KCl saturated gel in contact with the test solution through a liquid junction.

Honeywell's commercially available ISFET pH sensor, using the internal reference, appears to exhibit remarkable stability at 1 atm.

They have extensively tested the Durafet response in seawater using both the internal reference and a secondary Cl-ISE as a pseudo reference electrode.

A solid state chloride ion selective electrode (Cl-ISE), exposed to the seawater sample, suffers little pressure hysteresis, unlike a liquid-filled Ag/AgCl reference electrode with a liquid junction (Shitashima et al. (2002)

Both the Ag/AgCl internal reference electrode and the Cl-ISE exhibit a Nernstian response ( $S=RT\ln(10)/F$ ) to the free chloride ion.

The FET|EXT measures dissolved HCl directly in the sample while the FET|INT measures dissolved H<sup>+</sup> in the sample and dissolved Cl<sup>-</sup> in the reference gel. As the mean activity coefficient of HCl in seawater ( $\gamma_{(\text{HCl})}^{\pm 2} = \gamma_{\text{H}}\gamma_{\text{Cl}}$ ) is known through the oceans' range of temperature and salinity (Dickson 1990; Khoo et al. 1977), it is straightforward to calculate the concentration of free or total (free plus protons bound by sulfate ion) protons in seawater as the chloride ion concentration can always be obtained from salinity (Dickson et al. 2007).

We need salinity measurements at the same time pH is measured (similar to spectrophotometric pH sensors). However, the salinity dependence in the FET systems is over 1000 times that in the spec systems.

Retaining two reference electrodes thus provides a simple check during data QC: differences between pH<sup>INT</sup> and pH<sup>EXT</sup> serve as an indicator of sensor malfunction or fouling

## In the FET/INT system

$$E_{\text{INT}} = E_{\text{INT}}^* - S \times \log(m_{\text{H}});$$

$$E_{\text{INT}}^* = \left\{ E^*(\text{FET}|\text{INT}) - S \times \log[\gamma_{\text{H}}(\text{sw})] - S \times \log[a_{\text{Cl}}(\text{ref gel})] \right\};$$

$$\text{pH} = \frac{(E_{\text{INT}} - E_{\text{INT}}^*)}{S}.$$

## In the FET/EXT system

$$E_{\text{EXT}} = E^*(\text{FET}|\text{INT}) - S \times \log(\gamma_{\text{H}}\gamma_{\text{Cl}}) - S \times \log(m_{\text{Cl}}) - S \times \log(m_{\text{H}})$$

$$E_{\text{EXT}}^* = E^*(\text{FET}|\text{EXT});$$

$$\text{pH} = \frac{(E_{\text{EXT}} - E_{\text{EXT}}^*) + S \times \log(\gamma_{\text{H}}\gamma_{\text{Cl}}m_{\text{Cl}})}{S}.$$

Because the FET|EXT sensor is directly dependent on  $a_{\text{Cl}}$ , it is necessary to measure salinity along with FET|EXT voltage to calculate an accurate pH value.

Upon first contact with seawater, pH sensor voltages relative to both reference electrodes exhibit an asymptotic drift. This conditioning period arises from several sources: (1) achieving a stable flow of ions across the liquid junction of the internal reference electrode (nominally hours), (2) replacement of  $\text{Cl}^-$  with  $\text{Br}^-$  in the solid solution of  $\text{AgCl}$  of the  $\text{Cl}$ -ISE (nominally days), (3) an ISFET conditioning component, related to the initial power-up of the chip, the exact basis of which is not fully understood (nominally 1 day), and (4) a pressure effect on the ISFET and internal reference electrode through changes in the liquid junction potential that may become important if the sensor is deployed more than  $\sim 20$  m below the surface (nominally 1 h).

