**Supplementry Discussion Topic:**

# Advantages and disadvantages of current analytical approaches and the best carbon pair for you

## pH Measurements

| | Spectrophotometric pH (Recommended for OA ) | Potentiometric pH (discouraged for most applications) |
|---|---|---|
| Advantages | "Calibration free" during actual measurements.<br>Very precise | Convenient<br>Less expensive |
| Disadvantages | Indicator impurity issue<br>pH perturbation due to addition of indicator | Frequent calibration<br>Less precise<br>Sensitive to changes in ionic strength |
| Hardware/Chemical /Standard | Spectrophotometer, temp-control device, optical cells<br>Indicator, no standard | pH electrode, mV meter, temp-control device, buffer standards |
| When to use | Monitoring in situ and laboratory carbon system changes | May be needed for pH-stat<br>May be better for monitoring very rapid pH changes |

## $C_T$ Measurements

| | NDIR-Based | Coulometer-based |
|---|---|---|
| Advantages | Faster measurements, reasonable sensitivity on small sample size, Fewer hazardous chemicals | Better precision, Proven long term accuracy |
| Disadvantages | Cost ~$50K<br>Calibration issue (shape of the calibration curve, temp dependent) | Cost ~$50K<br>Long set up time, chemicals, limited life of cell |
| Hardware/Chemical /Standard | IR analyzer, carrier gas, extraction chamber, CRM | Coulometer, chemicals, carrier gas, extraction chamber, gas loops/carbonate/CRM |
| When to use | Recommended as primary parameter for OA studies, less sensitive to sample matrix than other parameters, independent of T and P | Recommended as primary parameter for OA studies, good for open ocean, less sensitive to sample matrix than other parameters, independent of T and P |

## $A_T$ Measurements

| | Closed-cell titration (older technology) | Open-cell titration | Spectrophotometric TA (developing technology) |
|---|---|---|---|
| Advantages | Can give you DIC at the same time (often not v. accurate DIC estimate) | 10-12 mins<br>Easy to set it up<br>Precision 0.7-1.5 umol/kg | Short running time (7 mins), can measure pH with the same spec, 1 umol/kg precision |
| Disadvantages | Bubble sensitive, sticking Piston, cannot weigh sample, complex apparatus | Needs good electrode | Indicator, one point titration (Acid dispensing must be v. accurate), sensitive to bubbles |
| Hardware/Chemical/ Standard | Titration cell, electrode, pH meter, acid, sample & acid dispenser, CRM | electrode, pH meter, acid, sample & acid dispenser, CRM | Spec titration cell, spec., dye, acid, sample & acid dispenser, CRM |
| When to use | Open ocean carbon characterization, calcification studies (avoid hi nuts and organic acids) | Open ocean carbon characterization, calcification studies (avoid hi nuts and organic acids) | calcification studies (avoid hi nuts and organic acids) |

## *P*($CO_2$)/*f*($CO_2$) Measurements

| | NDIR-based (flow through and in situ systems) | Spectrophotometric *p*($CO_2$) (flow through and in situ systems) |
|---|---|---|
| Advantages | No chemicals required | Does not require calibrations during measurement period |
| Disadvantages | Needs regular calibration, must ensure no contamination from outside air while maintaining system at ambient pressure | Must make up and calibrate alkalinity of dye solution, generally more susceptible to biofouling |
| Hardware/Chemical /Standard | NDIR, equilibrator, standard gases | Spectrophotometer, dye solution with known alkalinity, equilibration membrane |
| When to use | In situ monitoring | In situ monitoring |

# So, what should I measure?

## Just tell me already…

Recommendation: $C_T$ is a good primary variable with many advantages: it is clear what you are measuring; it is generally independent of matrix, temperature, pressure; measurement is not strongly affected by high cell density…

The real decision should be what is the best second (or third) variable…

Each of the three other parameters have situations that make them appropriate or not:

- If you are interested in calcification or measurements below mixed layer, then $A_T$ is a good parameter…but not if you have very high organic acids or nutrients.
- If you are trying to control or monitor $p(CO_2)$, then you should measure $p(CO_2)$…but not practical with some low volume applications.
- Spectrophotometric pH is generally a good parameter to measure…dye response not fully characterized in low salinity estuaries, not a good pair with $p(CO_2)$.