Overview of instrumentation for Carbonate- system measurements:

Techniques & Sensors for Studies of Ocean Acidification

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USGS
science for a changing world

Outline

- Introduction
- Sensors/Techniques for carbonate parameters
  - 1. pH
  - 2. DIC
  - 3. pCO_2
  - 4. Alkalinity- TA
  - 5. CO_3^{-2}
- Resources
- Parameters and sensors that are right for your application- discussion

Disclaimer:

We make no endorsements implicit or explicit in describing equipment and chemicals

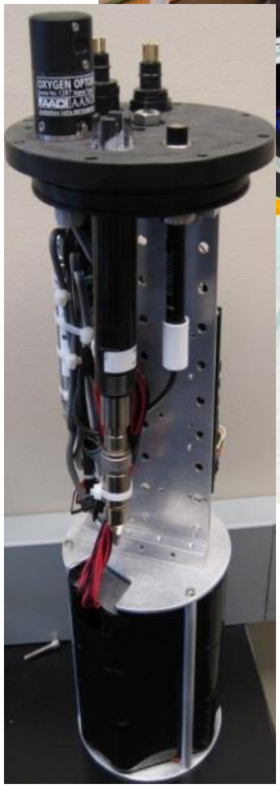
INSTRUMENTATION

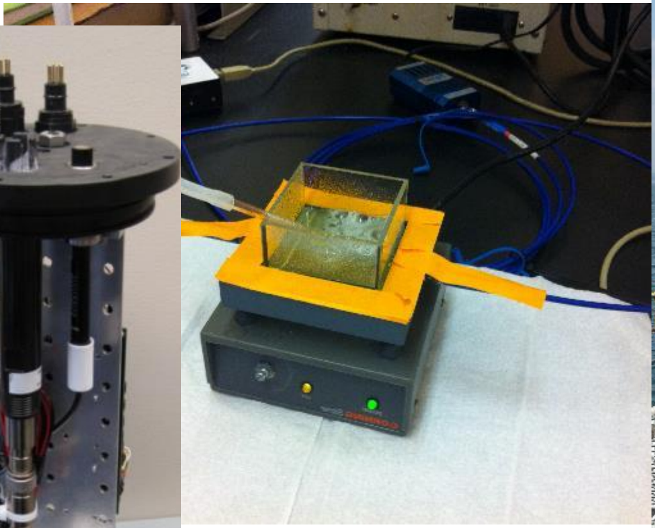
Challenges in instruments and sensors

- Accuracy/precision
- Routines for quality assessment/quality control
- Long term drift
- Size/weight
- Power requirements and consumption
- Compatibility with other equipment
- Costs for installation and maintenance
- Ease of use and maintenance
- Sensitivity to biofouling
- Frequency of measurements
- Ruggedness
- Response time

Summary of Techniques & Sensors

INSTRUMENTATION





pH Sensors

Commercially available pH systems

	Benchtop - discrete samples	Underway	Autonomous
pH	• Poteniometric: Orion, Metrohm • Spectrophotometers, ie., Agilent,	AFT-pH *Sunburst* SP200-SM *SensorLab*	SAMI-pH *Sunburst* SeaFET *Satlantic* SP101-LB *Sensorlab*

Modified From: Martz et al 2015, Oceanography

Benchtop pH Sensors

INSTRUMENTATION

- **Potentiometric determination with Certified Tris or seawater Buffers**

Difference of electrical potential across glass membrane- usually use a glass electrode/ reference electrode pair

- **Spectrophotometric using indicators (eg., m-Cresol Purple or thymol blue)**

pH sensitive indicator dye is added to seawater sample then a multi-wavelength absorbance is measured on a spectrophotometer

INSTRUMENTATION

pH Measurements

- **Potentiometric pH of seawater using glass reference electrode**
  - Available for less than $1,000USD (~6300 RMB)
  - Must minimize gas exchange when handling samples
  - Temperature control of solutions
  - Electrodes have varying degrees of reliability
  - Must use Certified Tris or seawater buffers to calibrate
  - Calibration time can be lengthy
  - Need to frequently calibrate- drift of system
  - Precision of ~0.02- 0.002 pH units

pH Measurements

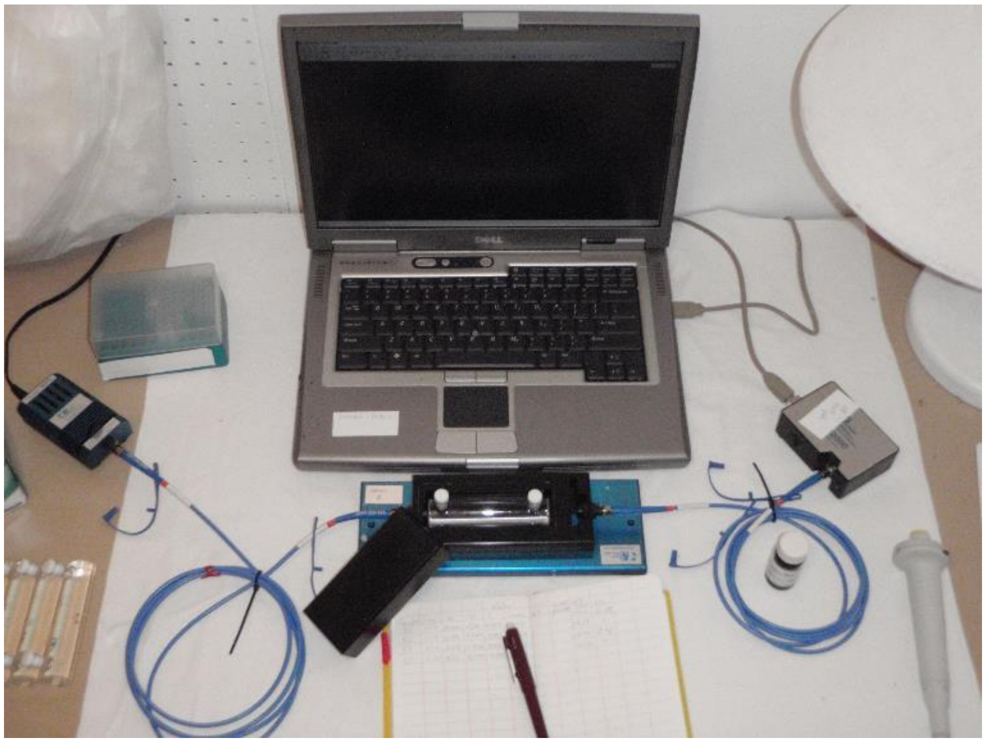
- **Spectrophotometric pH**
  - Can be automated
  - Some set ups allow continuous measurement
  - Must minimize gas exchange when handling samples
  - Temperature must be controlled for solutions and cells
  - Dyes have specific pH range- need to also run perturbation test- need to ~ know the pH of water ahead of time to use the right indicator dye
  - mCP impurity (Yao & Byrne, 2007) will cause the measurement uncertainty (about 10 times its reproducibility)
  - Run time less than 20min (sample to data)
  - Limited amounts of pH reference materials available

INSTRUMENTATION

pH Measurements

	Spectrophotometric pH	Potentiometric pH
Advantages	Calibration is straightforward; Procedure can be somewhat automated; hi precision	Electrodes are cheaper than spec Run Time is short -once electrode calibrated- Convenient
Disadvantages	More expensive Indicator impurity; Need time to warm up spec for stability Dyes have narrow pH range; need to perform perturbation test Cells are expensive; T= ~ 3-20 min	Drift of calibration- need to recalibrate; Sensitive to ionic strength; Less precise (< 0.001); Electrodes must be chosen judiciously (eg., Ross Orion)
Hardware/Chemical/ Stds	Spectrophotometer (3K/7.5-12.5K(spec ~>7.5-12.5K+)(48000RMB- 80,000+), temp control (2-4K), cell holder (400); glass/optical cells(200 ea) ; indicator, software (1K); std??	pH electrode, mV meter, temp control device, buffer standards
Precision/ Accuracy	< 0.003-.0008 / ±0.002	0.001/ ±0.002 pH units
When to use	Discrete and semi-discrete flow-through samples; High accuracy and precision for monitoring in situ and laboratory carbon system changes; flow thru good for monitoring rapid changes spatially	Monitoring- for tank experiments and pH stat, for smaller samples, where precision isn't necessary; suited for monitoring rapid pH changes*

DIY: Components of one of the cheapest ~~pH~~ Spec pH



- Spec (Ocean optics)
- Light source
- Fiber optics
- Computer/software
- Cell
- Cell holder
- Indicator dye
- Water bath/cell jacket
- ~ $4,500 USD (~28.5K RMB)

Talk to me if you want more information about this

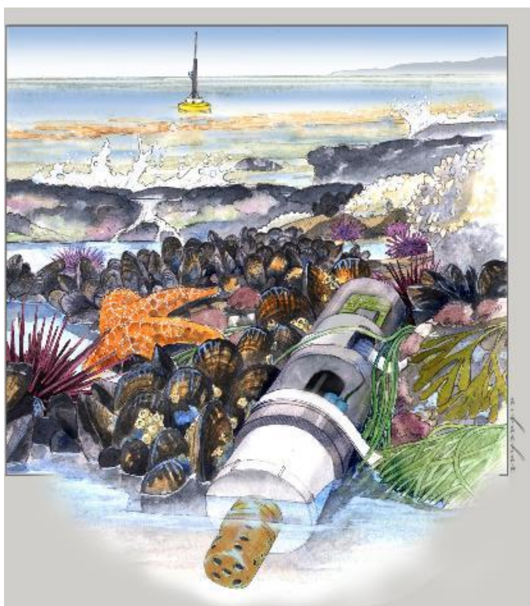
INSTRUMENTATION

Popular Commercially available pH Sensors

INSTRUMENTATION

Honeywell DuraFET® is being used as autonomous systems operating in the
- upper 100m of the ocean (Martz)
- intertidal applications (F Chavez MBARI)
- Deep water (Ken Johnson)
- estuary in McMurdo Sound (Gretchen Hofmann)

SeaFET- can be used autonomous or flow thru- precision .001



SeaFET Ocean pH sensor

Measurement Range: 2-12 pH
Initial Accuracy: 0.01 (estimated)
Typical Stability: 0.005/ month (estimated)
Precision: better than 0.0011 Calibration: spectrophotometric determination of pH referenced to certified TRIS buffer

2. Dissolved inorganic carbon

- Coulometric
- Infrared Gas Analyzer

Popular Total Carbon Analyzers

- BENCHTOP DIC ANALYZERS
- Marianda Co
  - VINDTA 3C: discrete sampling
  - VINDTA 3D: discrete and underway
  - Airica: discrete sampling
- Apollo Scitech DIC Analyzer AS-C3
- NIHON Ans Co

2. Dissolved inorganic carbon

INSTRUMENTATION

	Benchtop	Underway	Autonomous
DIC	VINDTA 3D/3C *Marianda* AIRICA *Marianda* AS-C3 *APOLLO SCITECH*	VINDTA 3D (discrete and underway) *Marianda*	

Principles of Operation

- **Total Inorganic Carbon (DIC)**

Sample delivered into the sample flask

System is purged with a CO_2- free carrier gas to eliminate atmospheric carbon dioxide.

Aliquot of acid added thru the acid dispenser into the sample flask, causing inorganic carbon to be evolved.

Built-in heater and magnetic stirrer facilitates the fast expulsion inorganic carbon

CO_2-free carrier gas transports the reaction products through a post-scrubber (to remove potential interferences)

Resulting CO_2 is measured using absolute coulometric titration, potentiometry, or infrared spectroscopy

SENSORS

DIC Measurements

	Coulometric DIC	NDIR DIC	Spec DIC
Advantages	Small samples (5 ml); proven long term stability; good precision	Faster per sample than Coulom (6-10/hour); Less hazardous waste; Good sensitivity on small samples (0.75mls)	Could be cheaper than other techniques (~20K) if set up yourself
Disadvantages	Not as precise as NDIR Expensive > 50K May be "over kill" for the biologist; Cost: ~50K; 4 samples/hour	Calibration issue (shape of calibration curve, temp dependent); calibrate often; must protect from gas exchange; Cost: ~ 50K;	Uses spec- needs time to achieve stability Optical cell used
Hardware/Chemical /Std	Coulometer, chemicals, carrier gas, extraction chamber, gas loops/carbonate/ CRM	IR Analyzer, carrier gas, extraction chamber, CRM	Custom
Precision/ Accuracy	± 0.05%/ 1um/kg	0.1% (±2 μmol/kg)	
When to use	Discrete; less sensitive to sample matrix; indep of T and P	Discrete, Semi-discrete; less sensitive to sample matrix; indep of T and P	Discrete and semi-discrete flow through
Commercially available	UIC, Marianda, VINDTA 3D (SOMMA),	Apollo SciTech, moored DIC, Airica	MICA, SEAS- (not commercially avail.)

INSTRUMENTATION

UIC Coulometer

Apollo Scitech

3. $p\mathrm{CO}_2$ sensors & equilibration

INSTRUMENTATION

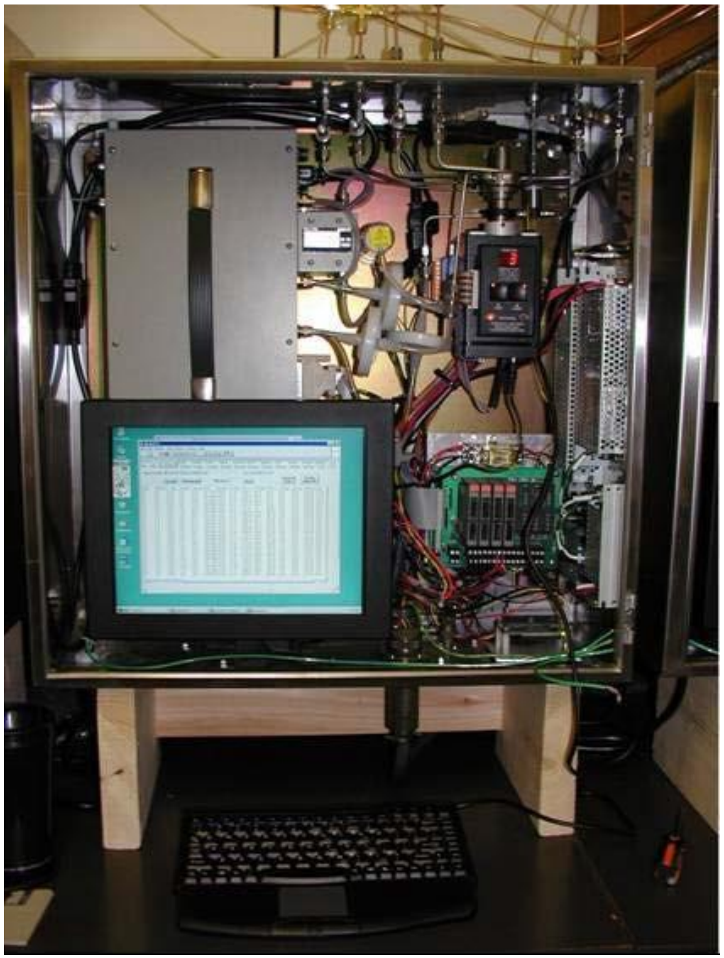
1. *Discrete- calculated*

- CO2 measurements without "flow thru" system involves taking water samples and measuring pH, AT or DIC

2. *Autonomous*

- Or autonomous buoy with pCO2 sensor

3. Flow through- underway systems



General Oceanics Inc

Lamont- built pCO2 Analyzer aboard the Coast Guard Cutter Healy

pCO_2 Sensors

INSTRUMENTATION

p(CO2):

Equipment for this measurement is ~ $10,000-50,000USD. It usually requires a flowing stream of seawater and is calibrated using tanks of air with known CO_2 levels.

Disadvantage: Set up may take some time, but can be relatively straightforward to use once running.

Advantage: these systems are designed to run autonomously.

There are multiple ways of extracting CO2 from seawater:

Non-dispersive infra-red (NDIR) analyzer e.g. LiCOR CO2/H2O analyzer CO2 gas measurements and Spectrophotometric measurements

- Air-water CO2 equilibration mechanism (flowing SW equilibrates with gas/air)

Rain-type: showerhead + headspace air

Bubbler type: (bubble seawater with carrier gas)

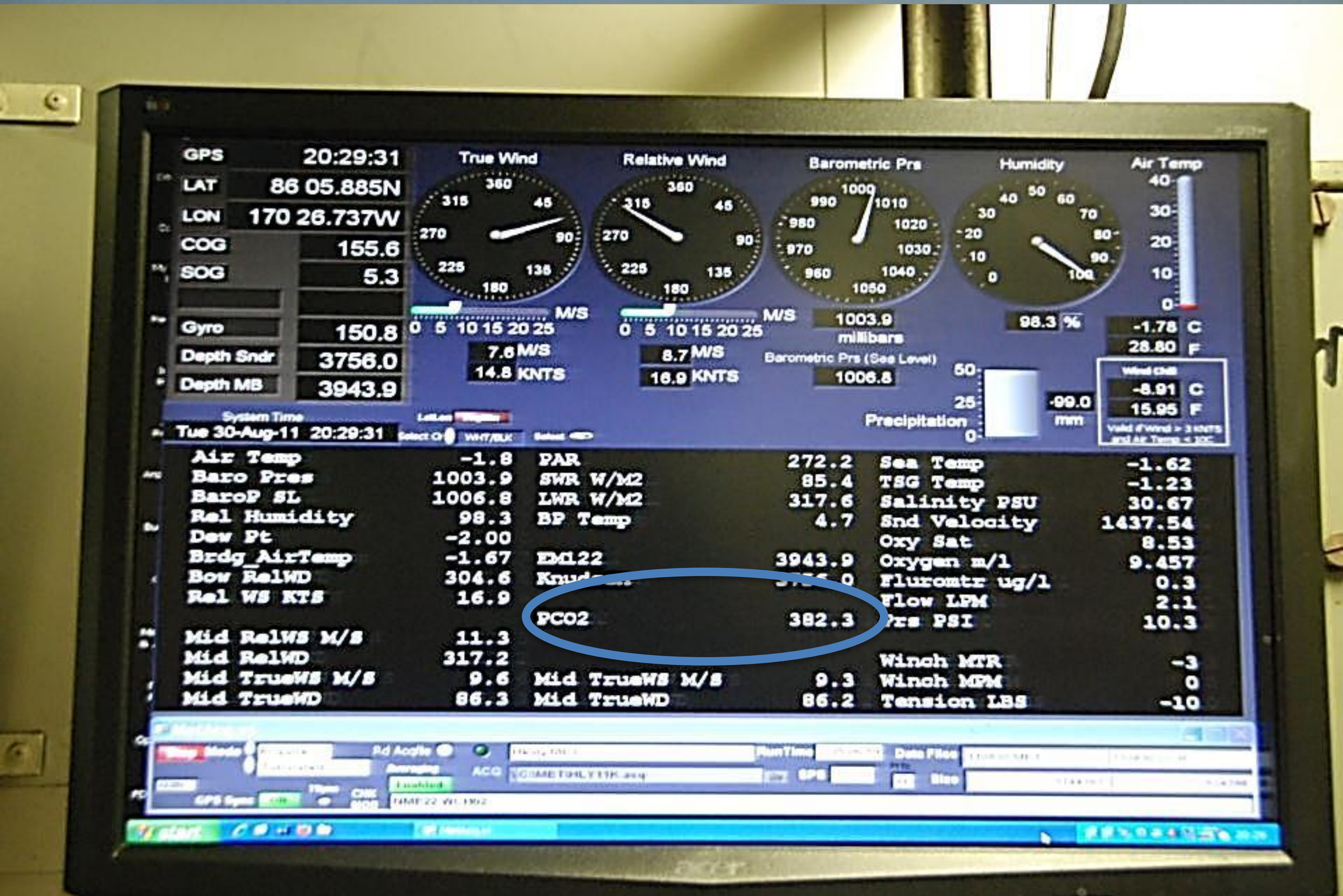
Thin film: (CO2 gas permeable membrane)

- Calibration against standard CO2 gases
- Automation (engineering)

$p\mathrm{CO_2}/f(\mathrm{CO_2})$ Measurements

INSTRUMENTATION

	NDIR-based (flow thru and in situ systems)	Spectrophotometric $p\mathrm{CO_2}$ (flow thru and in situ)
Advantages	No Chemicals required	Does not require calibrations during measurements
Disadvantages	Needs regular calibration	Must prepare and calibrate alkalinity of dye solution, May be more susceptible to biofouling
Hardware/Chemical/ Std	NDIR, equilibrator, standard gases	Spec, indicator dye solution, equilibration membrane
Precision/accuracy	.01ppm/1ppm	± 2-3 uatm
When to use	In situ monitoring	In situ monitoring
Commercially available	Batelle Seaology, Pro-Oceanus, General Oceanics, Kimoto air-marine CO2, Sundans (Marianda)	Sunburst (AFT), Picarro,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LON 170 26.737W
COG 155.6
SOG 5.3
Gyro 150.8
Depth Sndr 3756.0
Depth MB 3943.9
True Wind
Relative Wind
Barometric Prs
Humidity
Air Temp
7.6 M/S
14.8 KNTS
8.7 M/S
16.9 KNTS
1003.9
millibars
Barometric Prs (Sea Level)
1006.8
98.3 %
-1.78 C
28.80 F
-8.91 C
15.95 F
Precipitation
-99.0
mm
System Time
Tue 30-Aug-11 20:29:31
Air Temp -1.8
Baro Pres 1003.9
BaroP SL 1006.8
Rel Humidity 98.3
Dew Pt -2.00
Brdg_AirTemp -1.67
Bow RelWD 304.6
Rel WS KTS 16.9
Mid RelWS M/S 11.3
Mid RelWD 317.2
Mid TrueWS M/S 9.6
Mid TrueWD 86.3
PAR 272.2
SWR W/M2 85.4
LWR W/M2 317.6
BP Temp 4.7
EM122 3943.9
PCO2 382.3
Mid TrueWS M/S 9.3
Mid TrueWD 86.2
Sea Temp -1.62
TSG Temp -1.23
Salinity PSU 30.67
Snd Velocity 1437.54
Oxy Sat 8.53
Oxygen m/l 9.457
Fluromtr ug/l 0.3
Flow LPM 2.1
Prs PSI 10.3
Winch MTR -3
Winch MPM 0
Tension LBS -10

INSTRUMENTATION

pCO2 Instrumentation

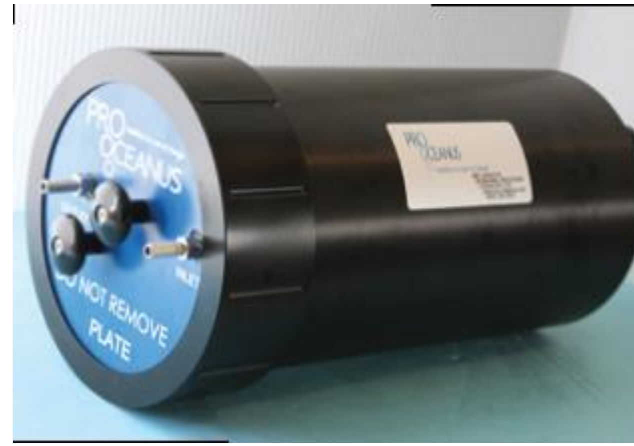
	Benchtop	Underway	Autonomous
pCO2		GO 8050 Gen oceanics MOG 701 Kimoto SuperCO2 *Sunburst* OceanPack *SubCTech* AFT-pCO2 *Sunburst* AS-P2 *APOLLO SCITECH* SUNDANS *Marianda*	Seaology *Batelle* SAMI-CO2 *Sunburst* HydroC *Contros* CO2-PRO *Pro-Oceanus* OceanPack *SubCTech* C-Sense *Turner Design*

Some pCO_2 Sensors $

- Battelle Seaology: 31-42K
- Pro-Oceanus Systems CO2-Pro
  - CO2-Pro CV : 18.4K
  - Mini Pro *CO2: 15.4K*
- Sunburst Sensors
  - SAMI-CO2 -14K
  - SUPERCO2 system
  - AFT-CO2 :

Pro-Oceanus Systems Inc. CO2-PRO™

INSTRUMENTATION

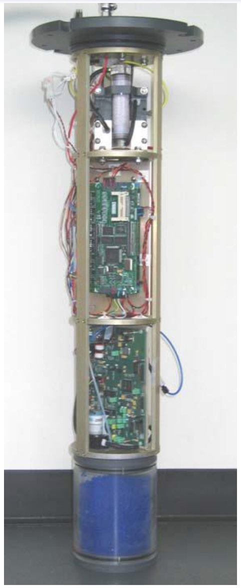


The PSI CO2-Pro™ is fitted with an IR detector and interface to provide an equilibrated gas stream to the detector. The PSI CO2-Pro™ is factory calibrated from 0–600 ppm*

Accuracy:
CO2 concentration ± ~1 ppm
Gas stream humidity ±1 mb
Gas stream pressure ±2 mb
Precision:
CO2 concentration 0.01 ppm
Gas stream humidity 1 mb
Gas stream pressure 1 mb
Calibration range 0–600 ppm (alternate ranges available by special order)
Temperature range -2 to 35˚C

Autonomous pCO_2 Sensors

INSTRUMENTATION



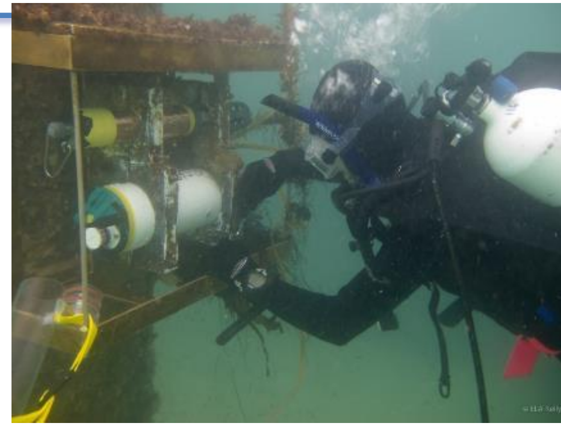
MAPCO

SAMI-CO2

Pro Oceanus

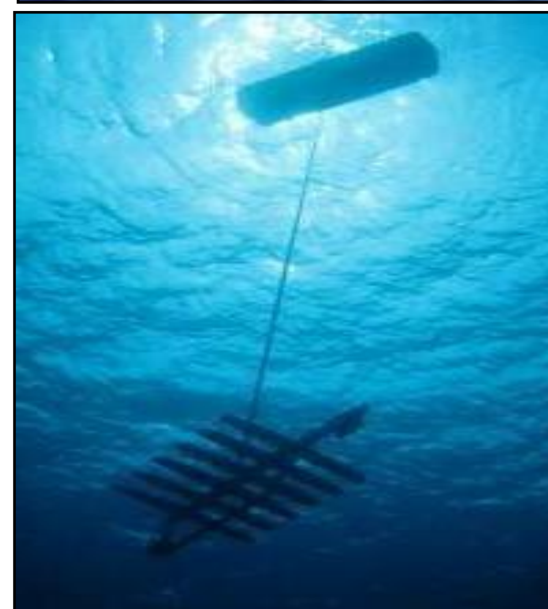
Autonomous pCO_2 Sensor Platforms

INSTRUMENTATION



Scripps Ocean Acidification Real-time (SOAR) Monitoring Program

THE CORAL REEF OCEAN ACIDIFICATION MONITORING PORTFOLIO (CROAMP)

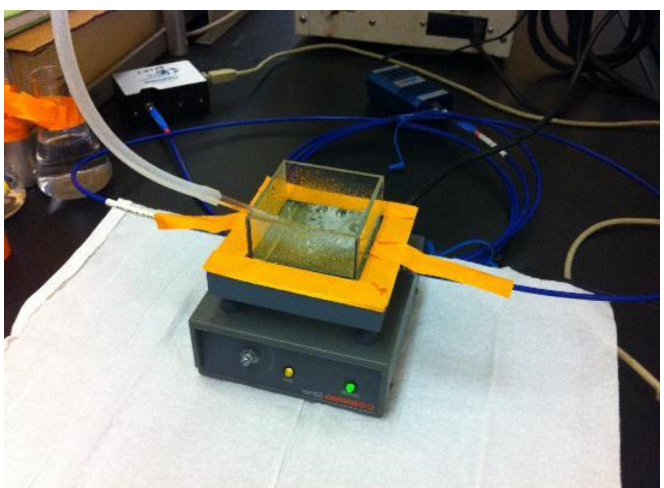


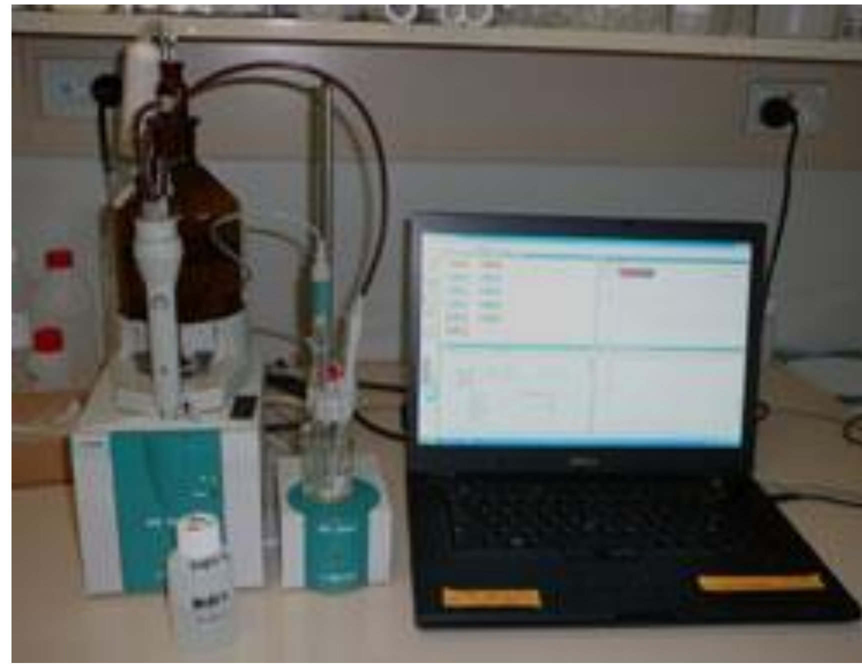
INSTRUMENTATION

4. Total Alkalinity

Determined by adding acid to seawater sample and analyze the change in electromagnetic field of a pH electrode

- Potentiometric titration: Open & closed cell titrimeter
- Spectrophotometric





INSTRUMENTATION

	Closed-cell titration	Open-cell titration/ potentiometric	Spectrophotometric TA
Advantages	Can give DIC at same time;	Run time includes stabilization of the potential so run time 10-12 min; Easy to set up; Can be automated;	Shortest run time: ~7- 8 min; can measure pH w same spec; 1 uM prec; 2uM acc Uses 20-100 ml sample; Calibrate with CRM
Disadvantages	Very bubble sensitive, Piston sticks, cannot weigh sample, complex apparatus	needs good electrode	Indicator, one point titration (acid dispensing should be v. accurate); sensitive bubbles;
Hardware/Chem/ Standard	Simple set up: Titration cell, electrode, pH meter, acid, sample & acid dispenser; CRM	Electrode, pH meter, acid, sample ,and acid dispenser, CRM	Spec titration cell, spectrophotometer, dye, acid, sample and acid dispenser, CRM
Precision/accuracy	+- 5 umol/kg precision +- 1 umol/kg accuracy	+-0.1% (prec: lab 0.7 uM; 1.5 uM prec at sea); precision goes up with more than one point titration	~1umol precision ~2umol accuracy
When to Use	Open ocean carb characterization; avoid nutrients and org acids	Open ocean; calcification studies (avoid hi nuts and organic acids)	Calcification studies (avoid hi nutrients and organic acids)
Available instruments	Marianda (mostly cell)	Kimoto Apollo Sci Tech Marianda VINDTA 3S Dickson Metrohm	

Total Alkalinity Systems

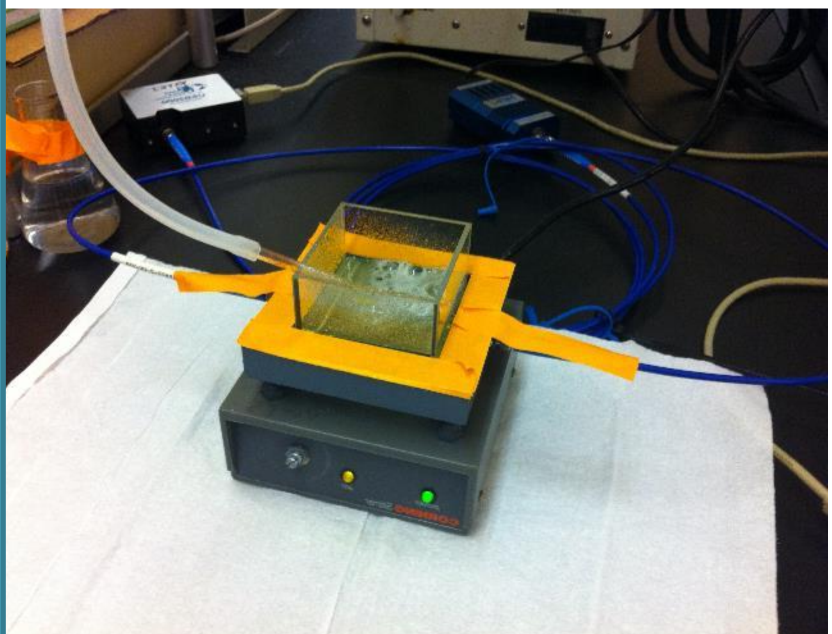
	Benchtop	Underway	Autonomous
TA	VINDTA 3S/3C AS-ALK2 *Marianda* *APOLLO SCITECH* *Scripps Total AT* *Kimoto Total AT*	HydroFIA *Contros*	

- Sample volume ~125 mL
- Repeatability ~0.5 µmol/kg
- Combined std uncertainty ~1.5 µmol/kg

VINDTA 3S in the lab (VINDTA # 005)

INSTRUMENTATION

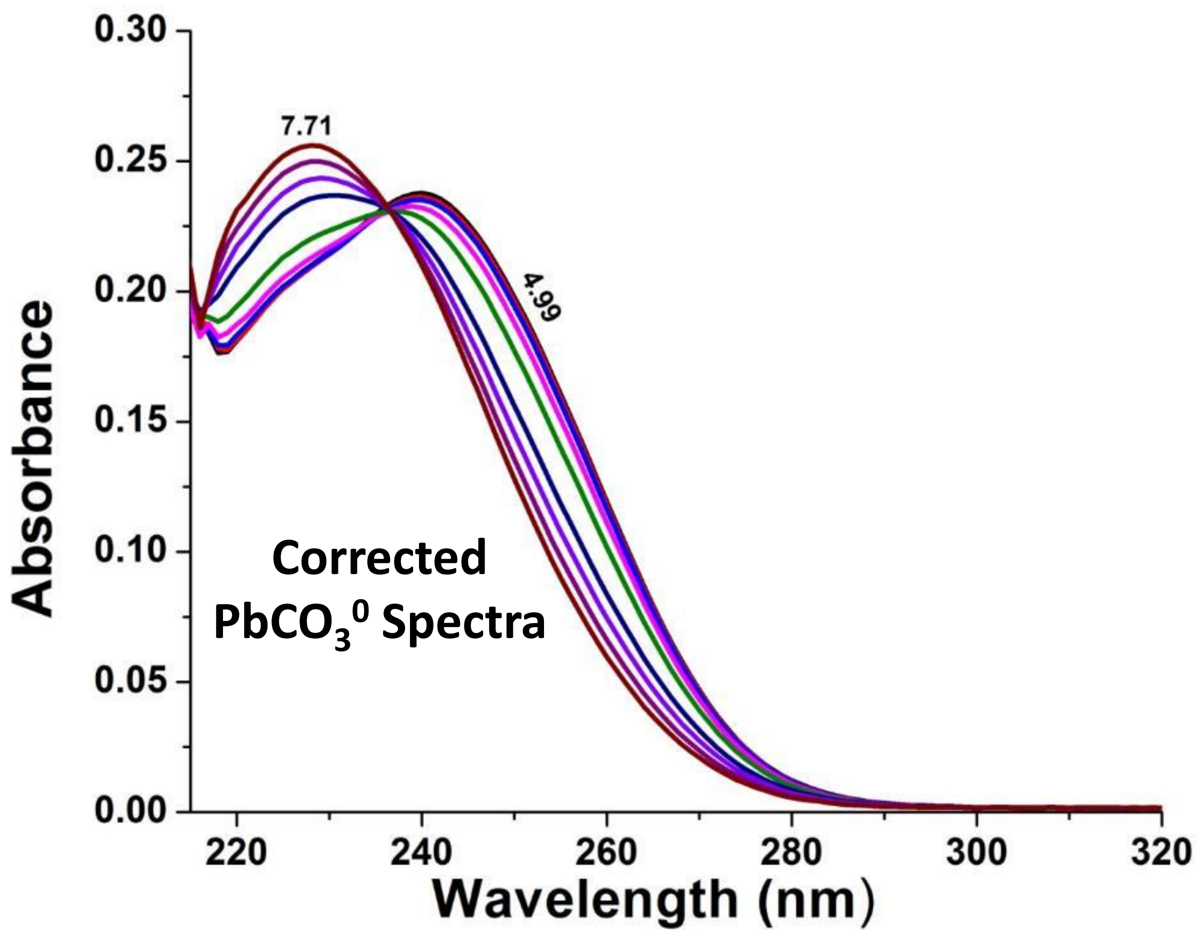
DIY Alkalinity Set up



- Spec (Ocean optics)
- Light source
- Fiber optics
- Computer/software
- Square cell- Helma Glass
- Cell holder
- Indicator dye-GCB
- Stir plate
- Nitrogen gas

5. Measuring Carbonate Ion

Carbonate ion system using spectrophotometric techniques



INSTRUMENTATION

Parameter now being used

FACILTIES

	Spec CO_3^{-2}	
Advantages	Direct measurement of carbonate ion	
Disadvantages	New; some of the carbon programs (CO2sys, CO2calc, etc) don't include for calculation of carbon parameters	
Hardware/ Chemical/ Standard	Spectrophotometer, temp controlled, optical cells, indicator pb-carbonate	
When to use	Calculating saturation state	

	Benchtop	Underway	Autonomous
DIC	VINDTA 3D/3C *Marianda* AIRICA *Marianda* AS-C3 *APOLLO SCITECH*		
TA	VINDTA 3S/3C *Marianda* AS-ALK2 *APOLLO SCITECH*	HydroFIA *Contros*	
pH		AFT-pH *Sunburst* SP200-SM *SensorLab*	SAMI-pH *Sunburst* SeaFET *Satlantic* SP101-LB *Sensorlab*
pCO2		GO 8050 Gen oceanics MOG 701 Kimoto SuperCO2 *Sunburst* OceanPack *SubCTech* AFT-pCO2 *Sunburst* AS-P2 *APOLLO SCITECH* SUNDANS *Marianda*	Seaology *Batelle* SAMI-CO2 *Sunburst* HydroC *Contros* CO2-PRO *Pro-Oceanus* OceanPack *SubCTech* C-Sense *Turner Des*

Parameters and Sensors that are right for your application

SENSORS

	Open Ocean	Estuary/ Coastal	Lab Exp
pH			
TA			
DIC			
pCO2			

Do you have at least two parameters?

How did you choose the parameters?

What equipment do you have? Do you need spatial and temporal resolution of the data?

Will you co-locate instruments to capture the variability of physical, chemical, and biological process? What kind of precision do you need?

So what parameters should you measure?

SENSORS

- First parameter : DIC is good and has advantages
  - Independent of matrix, temperature, pressure, and cell density
  - Second parameter: depends on your situation what is appropriate or not:
    - Calcification or deep waters- TA good parameter (but not in the case of high nutrients or organic acids)
    - If you are monitoring pCO2 then that's the best variable to measure- except when volume is limited such as lab experiments
    - Spec pH is good variable to measure: but need to choose right indicator dye; and not a good pair with pCO2

Finally, don't forget the Certified Reference Material (CRM)!

SENSORS

Alkalinity Titration System

The Scripps total alkalinity titration system has been designed and optimized for accurate measurement of the total alkalinity of discrete seawater samples. It is essentially identical to the system currently used in the Scripps CO_2 Reference Material Program to assign total alkalinity values to our CO_2 in seawater reference materials. The same design of system is also used for at-sea measurements of total alkalinity made during the US Repeat Hydrography Program.

Approach

This titration system implements a modified version of a published potentiometric titration method that has been detailed in SOP 3b of the *Guide to Best Practices for Ocean CO_2 Measurements*. A known amount of sample is acidified to a pH of ~3.6, the evolved CO_2 is removed, and the titration continued to a pH of ~3. The equivalence point corresponding to the total alkalinity is evaluated from titration points in the pH region 3.0 – 3.5 using a non-linear least-squares procedure that corrects for the reactions with sulfate and fluoride ions that are present in the seawater.

Specifications

The titration system is based around a Metrohm 876 Dosimat Plus (with a calibrated 5 mL exchange unit) and an Agilent 34970A Data Acquisition / Data Logger Switch Unit with a custom-made unity gain amplifier for the glass pH electrode cell.

The standard system includes a low profile desktop computer with a serial (RS-232) card adapter. The control software, written in LabVIEW 2013, is provided as an executable.

The recommended titration temperature is 20 °C, and requires a refrigerated temperature control bath that is capable of maintaining 20.00 ± 0.05 °C, and of pumping water externally through a closed loop (>10 L min^{-1}). *The bath is not included in the system.*

The recommended pH electrode is the Metrohm Ecotrode Plus; the system is supplied with one such electrode that has been tested to ensure it is operating appropriately.

Sample volume	~125 mL
Repeatability (1 std. dev.)	~0.5 µmol kg^{-1}
Combined standard uncertainty*	~1.5 µmol kg^{-1}
Initial start-up (from cold)	< 1 hour
Measurement throughput:	4–6 per hour
Titration temperature probe	±0.05 °C
Burette temperature probe	±0.1 °C
Air temperature probe	±0.1 °C
Power supply:	120 V
Power line frequency	60 Hz
Power cord/plugs	NEMA 5-15
Power outlets required	5
(Other power options are available)	

* Achieving this uncertainty (specified at a salinity of ~33) requires use of an acid titrant, whose density is known as a function of temperature, and that has been calibrated with a relative uncertainty of ~0.02%; as well as careful adherence to a suitable QA/QC program.

Optional Accessories/Services

- Metrohm Ecotrode Plus pH electrode, tested to demonstrate suitability for performing accurate total alkalinity titrations of seawater (with certificate).
- Second cell and stirrer; required to enable highest sample throughput.
- Extended support (provided by email and/or telephone).
- Alkalinity reference materials, and calibrated titration acid (available from co2crms@ucsd.edu).

Contact for further information

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SENSORS

Read More

- Martz et al. 2015 Technology for Ocean Acidification Research- Needs and Availability, Emerging Themes in Ocean Acidification Science, *Oceanography*, vol 28, n2, 40-47.
- Alliance for Coastal Technologies (ACT, http://www.act-us.info
- International Ocean Carbon Coordination Project (IOCCP http://www.ioccp.org)
- Byrne, RH, 2014, Measuring ocean acidification: New technology for a new era of ocean chemistry. Environmental Science and Technology 48:5,352-5,360

http://dx.doi.org/10.1021/es405819p.