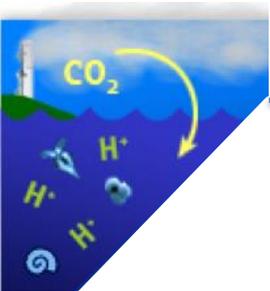


TRAINING COURSE ON BEST PRACTICES OA RESEARCH

Overview of instrumentation for Carbonate- system measurements: Techniques & Sensors for Studies of Ocean Acidification

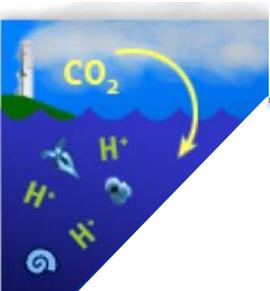
Lisa Robbins

Cape Town, South Africa



Outline

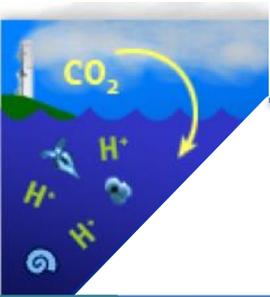
- Introduction
- Sensors/Techniques for carbonate parameters
 - 1. pH
 - 2. DIC
 - 3. $p\text{CO}_2$
 - 4. Alkalinity- TA
 - 5. CO_3^{-2}
- Resources
- Parameters and sensors that are right for your application- discussion



Disclaimer:

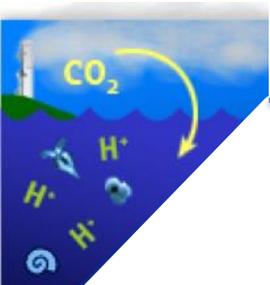


We make no endorsements implicit or explicit in describing equipment and chemicals



Some References

- International Ocean Carbon Coordination Project (IOCCP) <http://www.ioccp.org>
- 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>)
- 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>.



<http://www.ioccp.org>

SENSORS

http://www.ioccp.org/

HOME

> Home

The IOCCP promotes the development of a global network of ocean carbon observations for research through technical coordination and communication services, international agreements on standards and methods, and advocacy and links to the global observing systems. The IOCCP is co-sponsored by the Scientific Committee on Oceanic Research and the Intergovernmental Oceanographic Commission of UNESCO. Read more...



SOCAT version 3 released! Data submission deadline for SOCAT v4 on 31 December 2015

SOCAT V3 brings together 14.5 million quality controlled CO2 measurements from 3630 data sets collected between 1957 >>

- > Underway CO₂ Observations
- > Ocean Interior Observations
- > Time Series Efforts
- > Synthesis Activities
- > Ocean Acidification
- > Nutrients
- > Framework for Ocean Observing
- > Data and Information Management
- > Instruments and Sensors
- > Sensors Summer Course 2015
- > Related Projects

Calendar

IOCCP meetings, IOCCP-related meetings as well as events related to a wider scene in marine

News

Interwined Ocean and Climate - a policy brief by the Oceans 2015 Initiative + more news
Thursday, 24 09 2015

The Oceans 2015 Initiative has produced a Policy Brief to try raising the profile of the ocean at 21st session of the Conference of the Parties to the UNFCCC (COP21) and beyond. The English version is available now while the French, Spanish and Chinese versions will be available in the next few weeks from the website below. Do not hesitate to disseminate.

<http://www.iddri.org/Publications/Interwined-ocean-and-climate-implications-for-international-climate-negotiations>

A plea to ocean acidification scientists
Thursday, 27 06 2015

http://www.ioccp.org/instruments-and-sensors

HOME

International Ocean Carbon Coordination Project
Towards a sustained global observation network for marine biogeochemistry

ABOUT US CONTACTS IOCCP CONVEYOR DOCUMENTS JOBS

> Home > Instruments and Sensors

> Underway CO₂ Observations

> Ocean Interior Observations

> Time Series Efforts

> Synthesis Activities

> Ocean Acidification

> Nutrients

> Framework for Ocean Observing

> Data and Information Management

> Instruments and Sensors

> Sensors Summer Course 2015

> Related Projects

Instruments and Sensors Directory

This directory provides information about sensors and instruments developed and used by the ocean carbon research community. We try to list hardware that is available "off the shelf". Occasionally we decide to list instruments / sensors that are not yet commercially available but underwent substantial tests and can be obtained from developers. Information provided by developers and commercial partners might sporadically become out-dated. Please contact us with suggestions for updates. IOCCP does not, in any way, "endorse" hardware listed below. To add a sensor or instrument to this directory, please contact Maciej Telszewski at m.telszewski@ioccp.org.



Todd Martz
Responsible
SSG Member



Dissolved Inorganic Carbon | Alkalinity | pCO₂ | pH | Particulate Carbon

DISSOLVED INORGANIC CARBON INSTRUMENTS

Calendar

IOCCP meetings, IOCCP-related meetings as well as events related to a wider scope in marine biogeochemistry.





wider scope in marine biogeochemistry.

[VIEW](#)

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DISSOLVED INORGANIC CARBON INSTRUMENTS

MARIANDA COMPANY VINDTA 3C SYSTEM

Brief Description: The Versatile INstrument for the Determination of Total inorganic carbon and titration Alkalinity (VINDTA) combines the alkalinity titration concept with a simplified extraction unit for coulometric DIC measurements; 3 samples / hour.

Platforms: discrete sampling

More information and contact [VINDTA 3C](#); Dr. Ludger Mintrop (info@marianda.com)

References:

MARIANDA COMPANY VINDTA 3D SYSTEM

Brief Description In principle the VINDTA 3D is a DIC part of the VINDTA 3C. DIC by coulometric titration; 4 samples / hour. Precision typically +/- 1 $\mu\text{mol kg}^{-1}$ in open ocean water.

Platforms: discrete sampling, underway systems

More information and contact [VINDTA 3D](#); Dr. Ludger Mintrop (info@marianda.com)

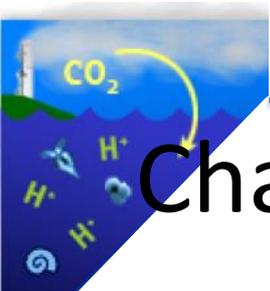
References:

MARIANDA COMPANY AIRICA SYSTEM

Brief Description: The Automated Infra Red Inorganic Carbon Analyzer (AIRICA) is based on the IR-detection of CO₂ purged from acidified sample ; 6-10 samples/hour, sample volume < 10 ml.

Platforms: discrete sampling

More information and contact



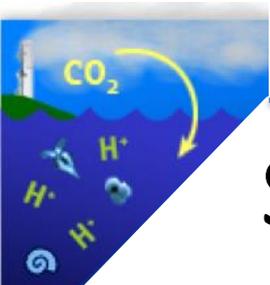
Challenges in instruments and sensors

Discrete Sampling

- Accuracy/precision
- Routines for quality assessment/quality control
- Ease of use and maintenance
- Response time
- Compatibility with other equipment

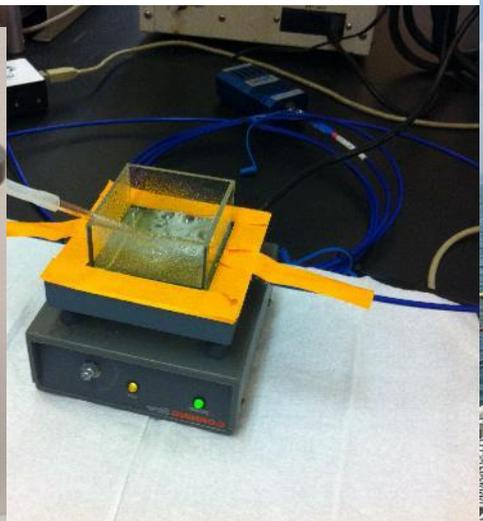
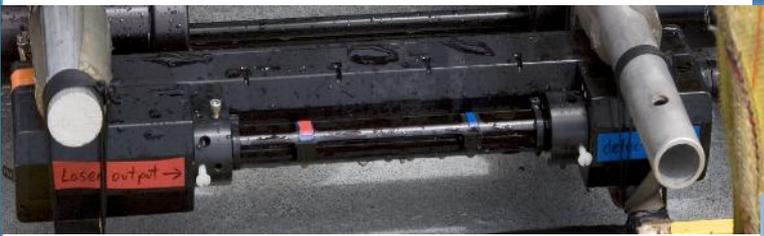
Autonomous

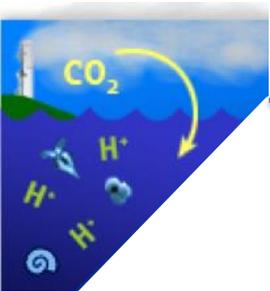
- Accuracy/precision
- Routines for quality assessment/quality control
- Costs for installation and maintenance
- Long term drift
- Size/weight
- Ease of use and maintenance
- Sensitivity to biofouling
- Frequency of measurements
- Power requirements and consumption
- Ruggedness
- Response time
- Compatibility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



Summary of Techniques & Sensors

INSTRUMENTATION





Benchtop pH Sensors

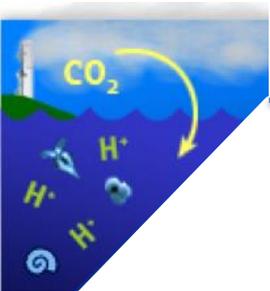
- **Potentiometric determination with Certified Tris or seawater Buffers**

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)**

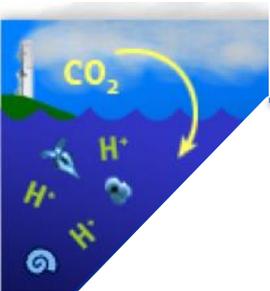
pH sensitive indicator dye is added to seawater sample then a multi-wavelength absorbance is measured on a spectrophotometer





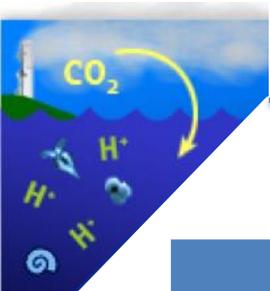
pH Measurements

- **Potentiometric pH of seawater using glass reference electrode**
 - Available for less than \$1,000USD
 - 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



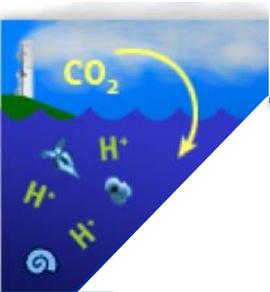
pH Measurements

- **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



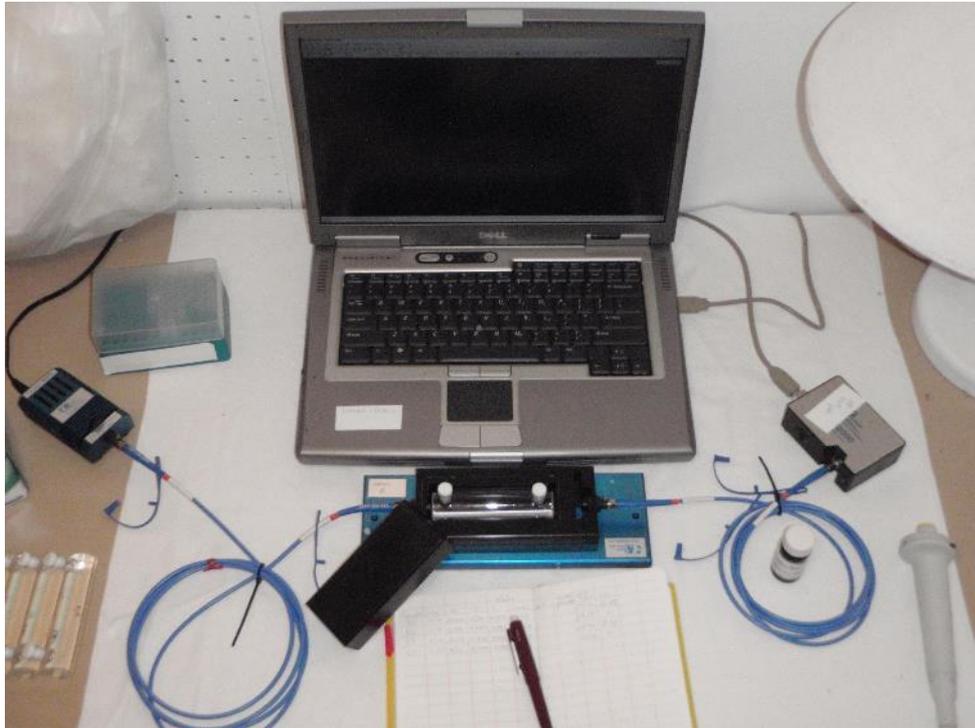
pH Measurements

	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+), 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*



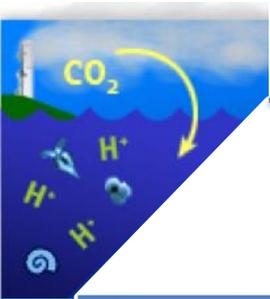
DIY: Components of one of the cheapest ^{Spec} pH

INSTRUMENTATION



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

Will see in lab this afternoon

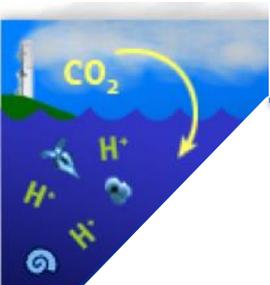


pH Sensors

Commercially available pH systems

	Benchtop - discrete samples	Underway		Autonomous	
pH	<ul style="list-style-type: none"> Potentiometric: Orion, Metrohm Spectrophotometers, ie., Agilent, 	AFT-pH <i>Sunburst</i>	SP200-SM <i>SensorLab</i>	SAMI-pH <i>Sunburst</i>	SeaFET <i>Satlantic</i>
		SeaFET <i>Satlantic</i>		SP101-LB <i>Sensorlab</i>	

Modified From: Martz et al
2015, Oceanography



pH: COMMERCIAL SENSORS

SUNBURST SAMI-pH SENSOR

Brief Description Autonomous indicator-based sensors for measurement of seawater pH. pH range 7.5-8.5; Accuracy 0.002; precision <0.001. Accommodates up to 3 additional sensors such as PAR, O2 optodes, beam-c transmissometers, and chl-a fluorometers. Underway and in situ configurations available.

Platforms: underway systems, moorings, drifters

More information and contact <http://www.sunburstsensors.com/>; Jim Beck (jim@sunburstsensors.com)

References: Seidel, M.P., DeGrandpre, M.D. and A.G. Dickson. (2008). A sensor for in situ indicator-based measurements of seawater pH, *Mar. Chem.*, 109, 18–28. Martz, T.R., Carr, J.J., French, C.R. and M.D. DeGrandpre. (2003). A submersible autonomous sensor for spectrophotometric pH measurements of natural waters. *Anal. Chem.*, 75,1844-1850.

SATLANTIC SEAFET pH SENSOR

Brief Description The SeaFET™ Ocean pH sensor is an ion selective field effect transistor (ISFET) type sensor for accurate long-term pH measurements in salt water. Measurement range 6.5-9.0 pH; Initial accuracy 0.05 (estimated); Typical stability 0.005/month (estimated).

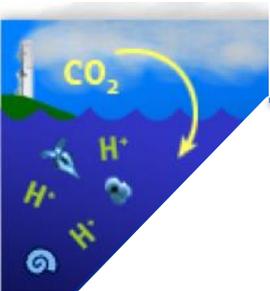
Platforms: underway systems, moorings, drifters

More information and contact <http://satlantic.com/seafet>

References: Martz, T, Connery J.G., Johnson, K.S (2010) Testing the Honeywell Durafet® for seawater pH applications *Limnol. Oceanogr* 172-184 doi:10.4319/lom.2010.8.172.

RETURN

PARTICULATE CARBON SENSORS

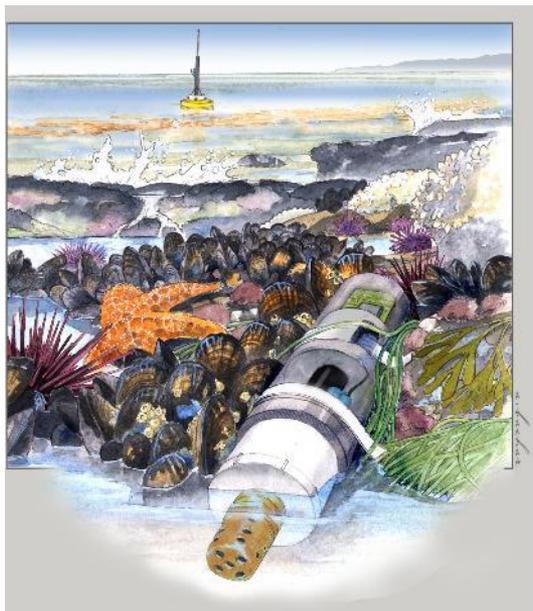


Popular Commercially autonomous pH Sensors

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

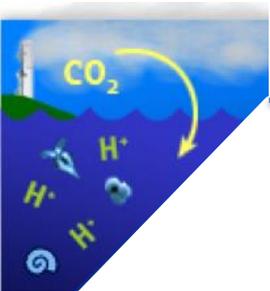
INSTRUMENTATION

SeaFET Ocean pH sensor



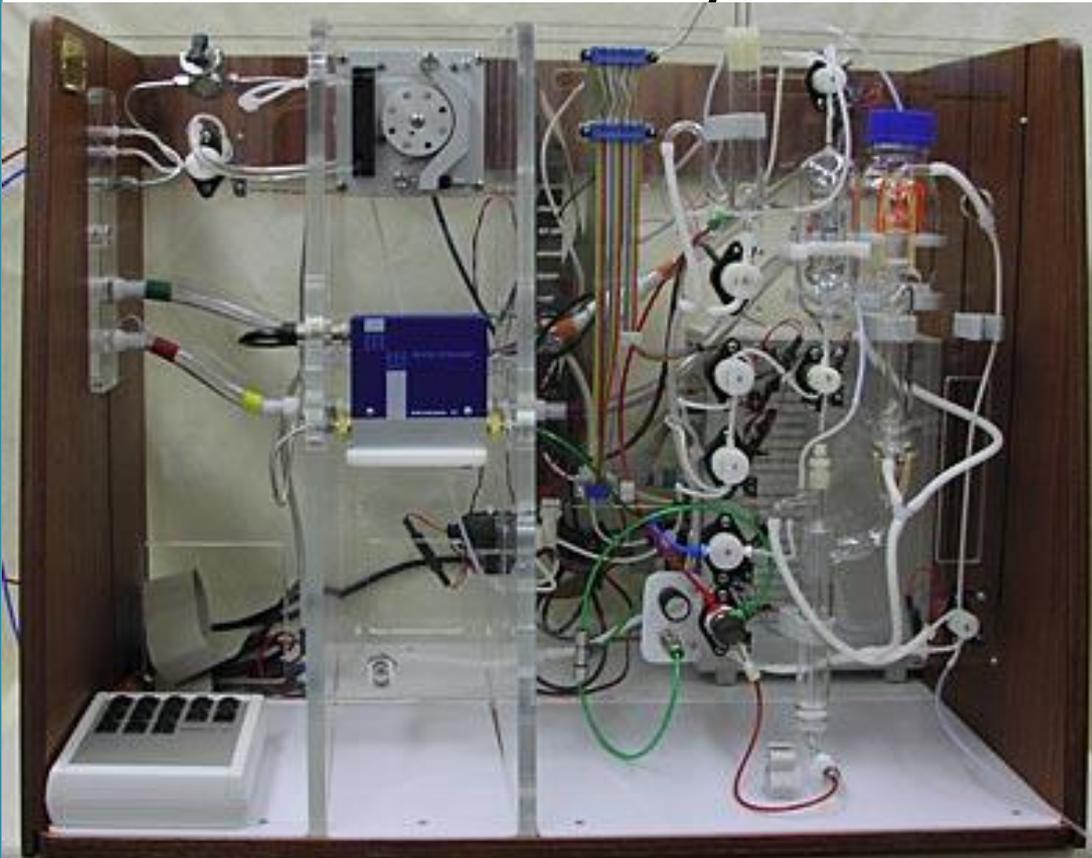
Measurement Range: 2-9 pH
Initial Accuracy: 0.05 (estimated)
Typical Stability: 0.005/ month (estimated)
Precision: better than 0.0011 Calibration: spectrophotometric determination of pH referenced to certified TRIS buffer

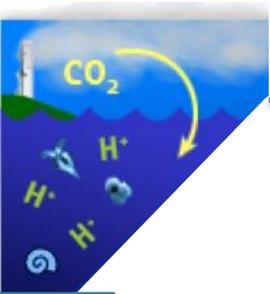




2. Dissolved inorganic carbon

- Coulometric
- Infrared Gas Analyzer

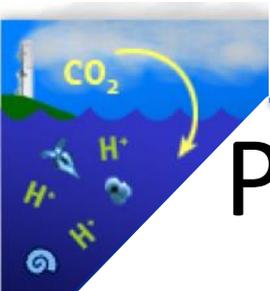




2. *Dissolved inorganic carbon*

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

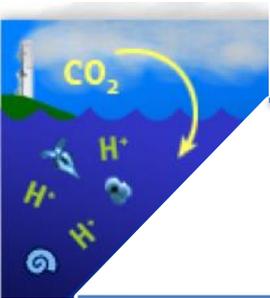
INSTRUMENTATION



Popular Total Carbon Analyzers

BENCHTOP DIC ANALYZERS

- Marianda Co
 - VINDTA (Versatile Instrument for the determination of Total inorganic carbon and titration Alkalinity) 3C: discrete sampling
 - VINDTA 3D: discrete and underway
 - Airica: discrete sampling
- Apollo Scitech DIC Analyzer AS-C3
- NIHON Ans Co

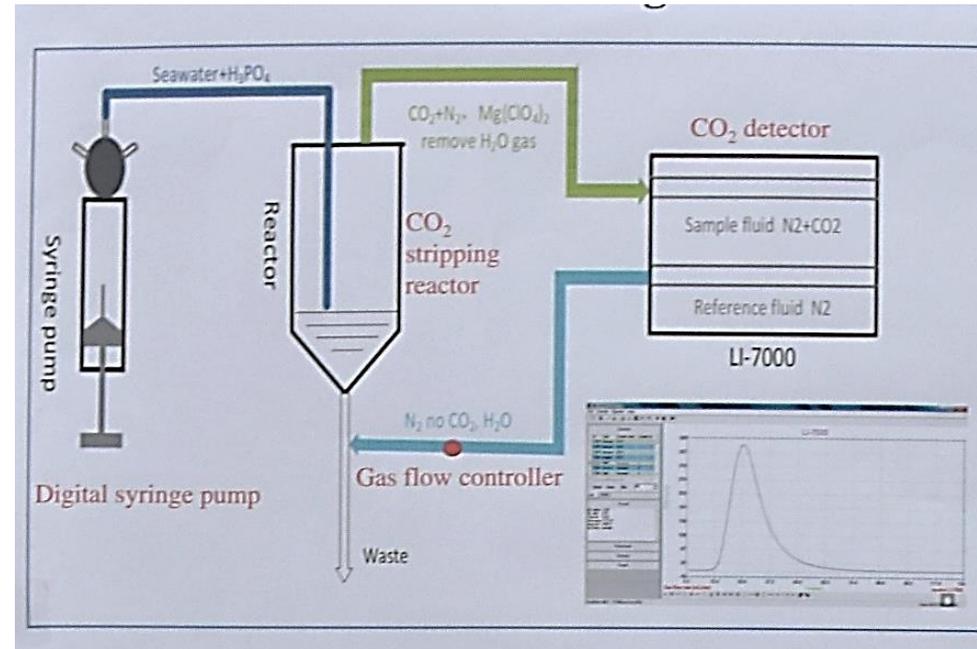


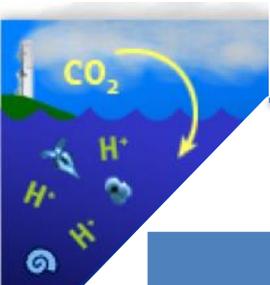
Principles of Operation

DIC

INSTRUMENTATION

- Sample delivered into the sample flask
- System is purged with a CO₂- 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
- CO₂-free carrier gas transports the reaction products through a post-scrubber (to remove potential interferences)
- Resulting CO₂ is measured using absolute coulometric titration, potentiometry, or infrared spectroscopy





DIC Measurements

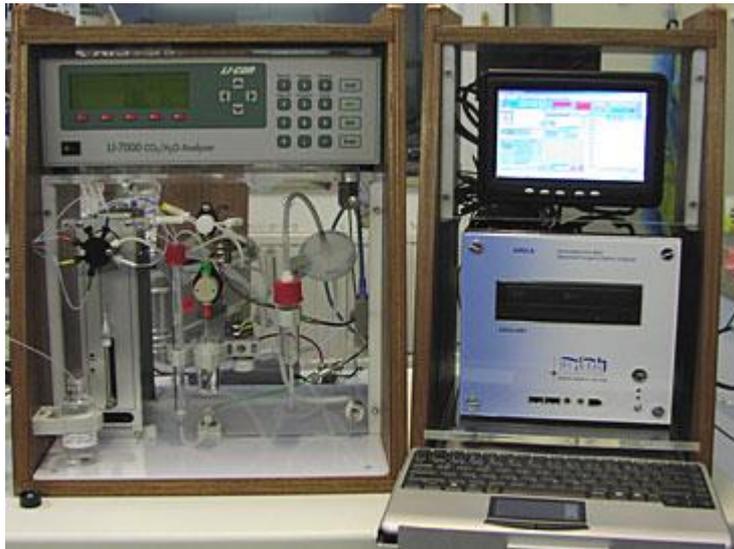
SENSORS

	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.)

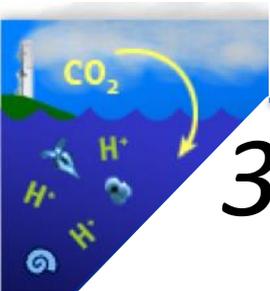
UIC Coulometer



Apollo Scitech



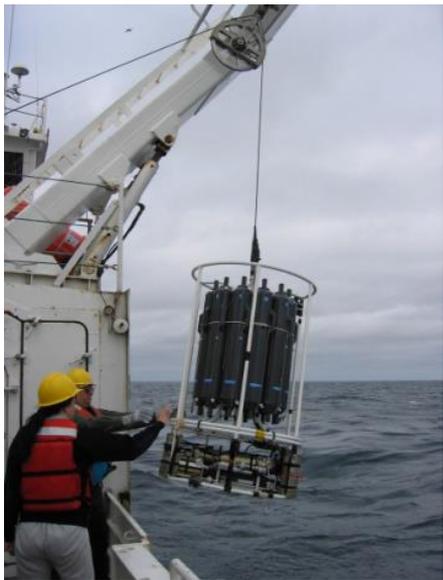
Airica (Automated Infra Red Inorganic Carbon Analyzer) with LI-COR 7000



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

1. *Discrete- calculated*

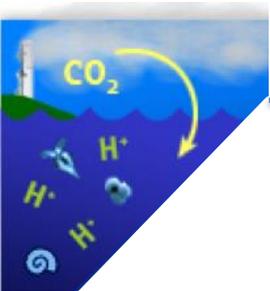
- CO_2 measurements without “flow thru” system involves taking water samples and measuring pH, AT or DIC



2. *Autonomous*

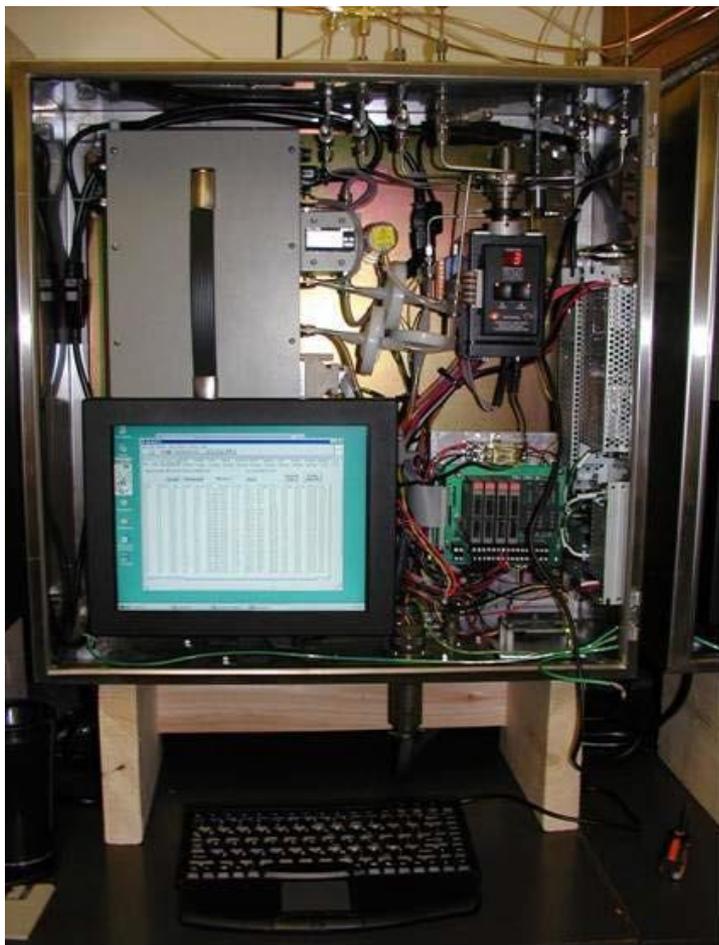
- On autonomous buoy or glider with $p\text{CO}_2$ sensor





3. Flow through- underway systems

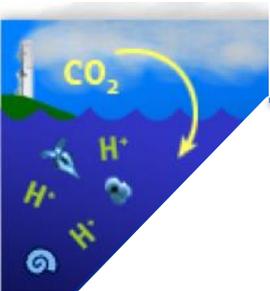
INSTRUMENTATION



General Oceanics Inc



Lamont- built pCO2 Analyzer aboard the Coast Guard Cutter Healy



pCO₂ Sensors

***p*(CO₂):**

Equipment for this measurement is ~ \$10,000-50,000+USD. It usually requires a flowing stream of seawater and is calibrated using tanks of air with known CO₂ 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.

Multiple ways of analyzing CO₂ from seawater:

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

Spectrophotometric measurements

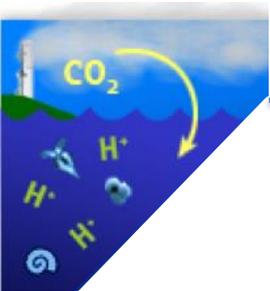
- Air-water CO₂ equilibration mechanism (flowing SW equilibrates with gas/air)

Rain-type: showerhead + headspace air

Bubbler type: (bubble seawater with carrier gas)

Thin film: (CO₂ gas permeable membrane)

- Calibration against standard CO₂ gases

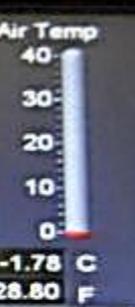


$p\text{CO}_2/f(\text{CO}_2)$ Measurements

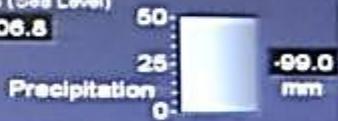
INSTRUMENTATION

	NDIR-based (flow thru and in situ systems)	Spectrophotometric $p\text{CO}_2$ (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	$\pm 2-3$ 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 (ring-down cavity)

GPS 20:29:31
 LAT 86 05.885N
 LON 170 26.737W
 COG 155.6
 SOG 5.3
 Gyro 150.8
 Depth Sndr 3756.0
 Depth MB 3943.9



System Time Tue 30-Aug-11 20:29:31

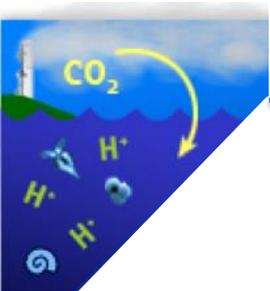


Wind Chill
 -8.91 C
 15.95 F
Valid if wind > 3 knots and Air Temp > 32C

Air Temp	-1.8	PAR	272.2	Sea Temp	-1.62
Baro Pres	1003.9	SWR W/M2	85.4	TSG Temp	-1.23
BaroP SL	1006.8	LWR W/M2	317.6	Salinity PSU	30.67
Rel Humidity	98.3	BP Temp	4.7	Snd Velocity	1437.54
Dew Pt	-2.00	EM12	3943.9	Oxy Sat	8.53
Brdg AirTemp	-1.67	Knud	3756.0	Oxygen m/l	9.457
Bow RelWD	304.6	PCO2	382.3	Fluorotr ug/l	0.3
Rel WS KTS	16.9	Prs PSI	10.3	Flow LPM	2.1
Mid RelWS M/S	11.3	Winch MTR	-3	Winch MPM	0
Mid RelWD	317.2	Winch LBS	-10		
Mid TrueWS M/S	9.6				
Mid TrueWD	86.3				

Way Mode: [] Rd Acq/ls: [] Averaging: ACC RunTime: [] Data Files: []

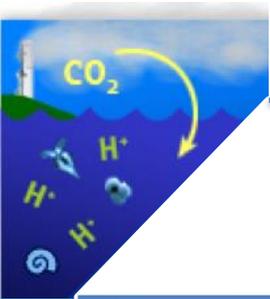
GPS Syste: [] TIME 22 01 1902



PCO2 sensors- lots of options

Bench top -Underway

- SUNDANS (Surface Underway carbon dioxide partial pressure Analyser)
- Picarro G1200 CO2/H2O (wavelength scanned cavity ring down spectrometer- uses near IR laser to measure spectral signal of CO2 molec)
- SubCTech Ocean Pack
- Contros Hydroc CO2 flow through
- Kimoto portable CO2 analyzer and Air-Marine CO2 autonomous monitoring system
- Sunburst: AFT-CO2 and SAMI CO2; Super CO2
- Apollo Sci Tech
- General Oceanics
- Pro Oceanus: CO2-Pro CV, Mini Pro, CO2 Pro
- Batelle



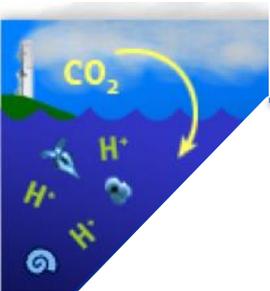
pCO₂ sensors more limited if you want immersible

Immersible

- Contros Hydroc CO₂ flow thru- to 6000m
- Pro Oceanus: CO₂ Pro CV (to 600m)
- Pro Oceanus: CO₂ Pro (to 110m)
- Pro Oceanus: Mini ProCO₂ (to 300m)
- Batelle
- Turner Designs- C-Sense (to 600m)

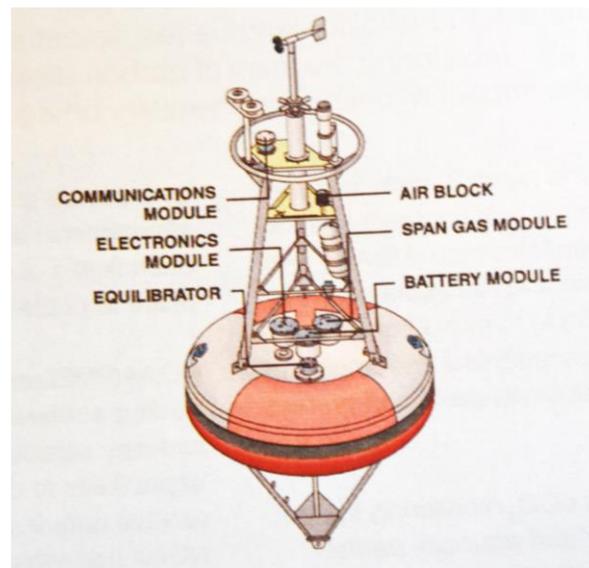
Moorings/Gliders / AUVs

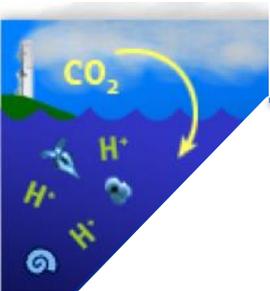
- Picarro- surface
- Sunburst SAMI- CO₂



Some pCO₂ Sensors \$

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





Pro-Oceanus Systems Inc. CO2-PRO™

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*

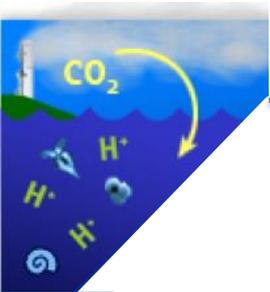
Accuracy:

CO2 concentration $\pm \sim 1$ ppm
Gas stream humidity ± 1 mb
Gas stream pressure ± 2 mb

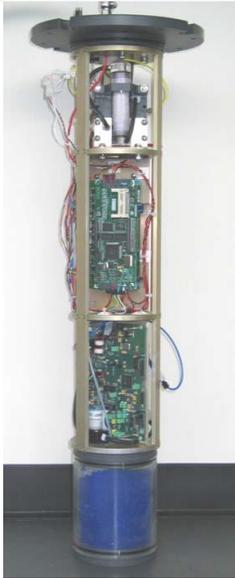
Precision:

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 pCO₂ Sensors



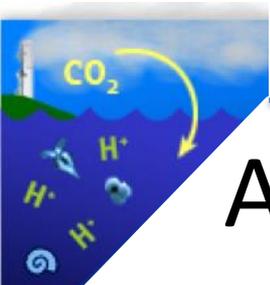
MAPCO



SAMI-CO2

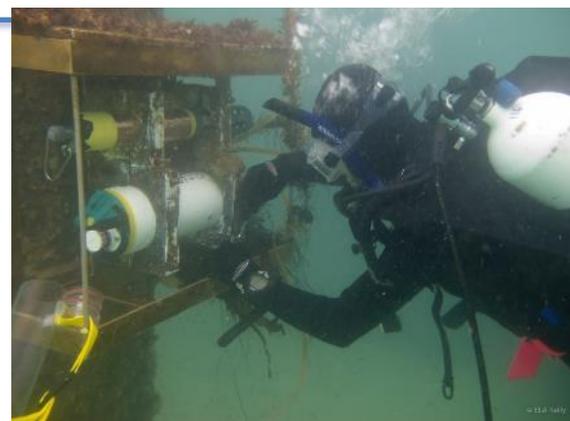


Pro Oceanus



Autonomous pCO₂ Sensor Platforms

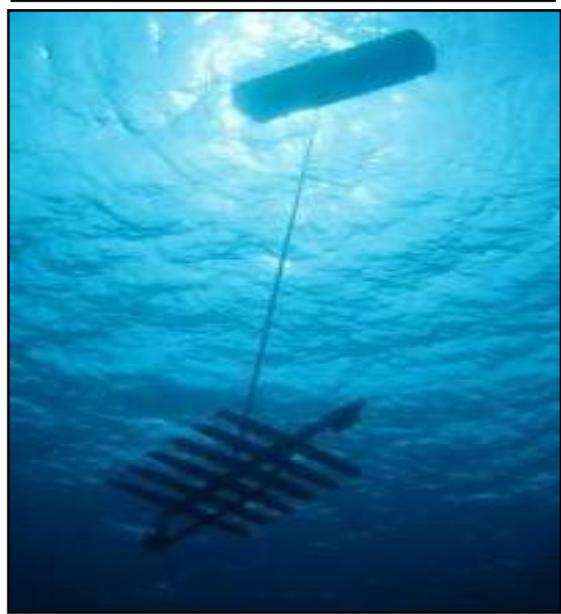
INSTRUMENTATION

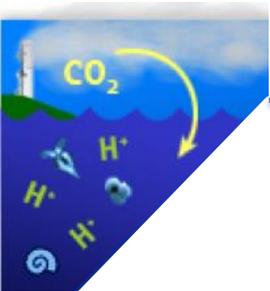


Scripps Ocean Acidification Real-time (SOAR) Monitoring Program



THE CORAL REEF OCEAN ACIDIFICATION MONITORING PORTFOLIO (CROAMP)

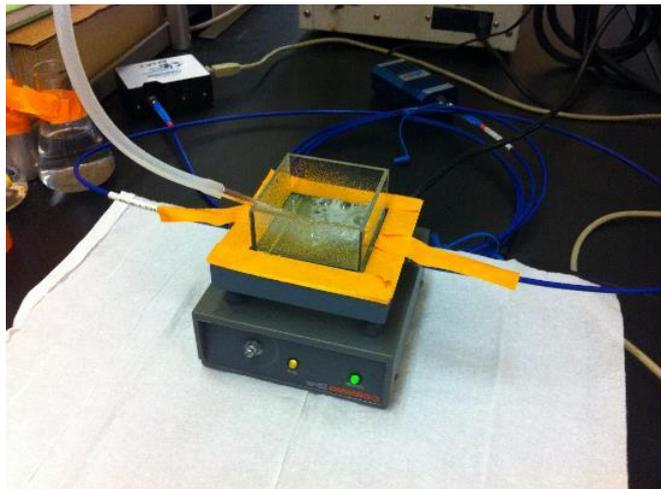


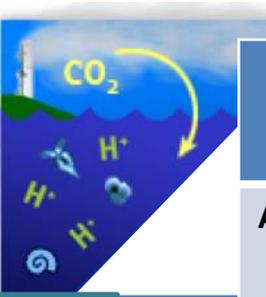


4. Total Alkalinity

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

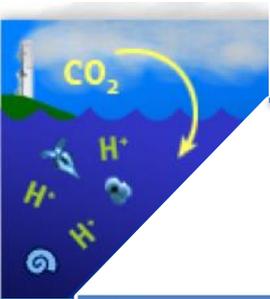
- Potentiometric titration: Open & closed cell titrimeter
- Spectrophotometric





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

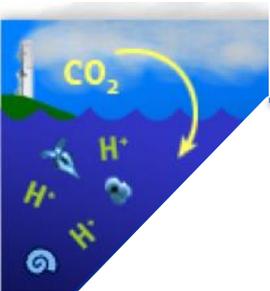
	Benchtop	Underway	Autonomous
TA	VINDTA 3S/3C AS-ALK2 Marianda APOLLO SCITECH Scripps Total AT Kimoto Total AT	HydroFIA Contros	



- Sample volume ~125 mL
- Repeatability ~0.5 $\mu\text{mol/kg}$
- Combined std uncertainty ~1.5 $\mu\text{mol/kg}$

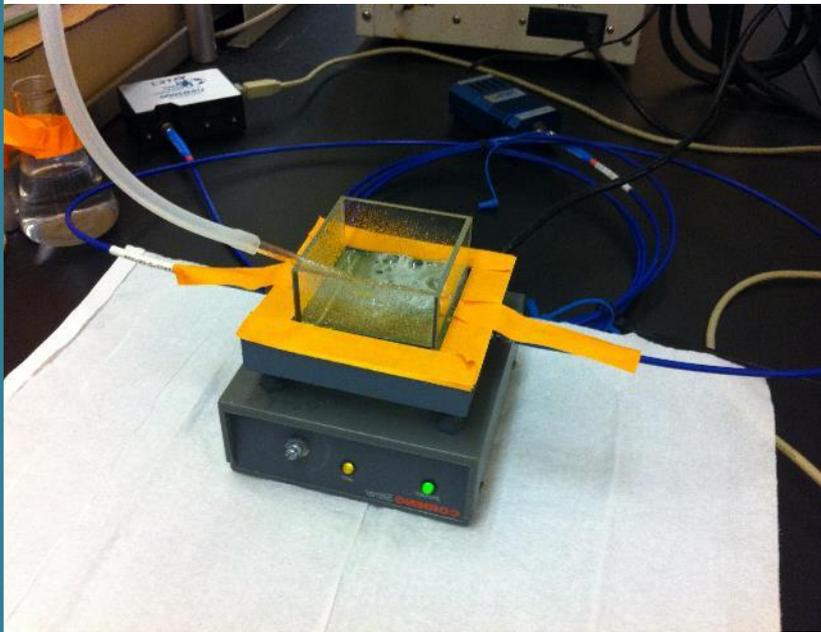


VINDTA 3S in the lab (VINDTA # 005)

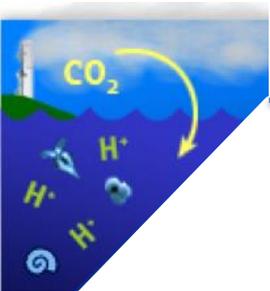


DIY Alkalinity Set up

INSTRUMENTATION

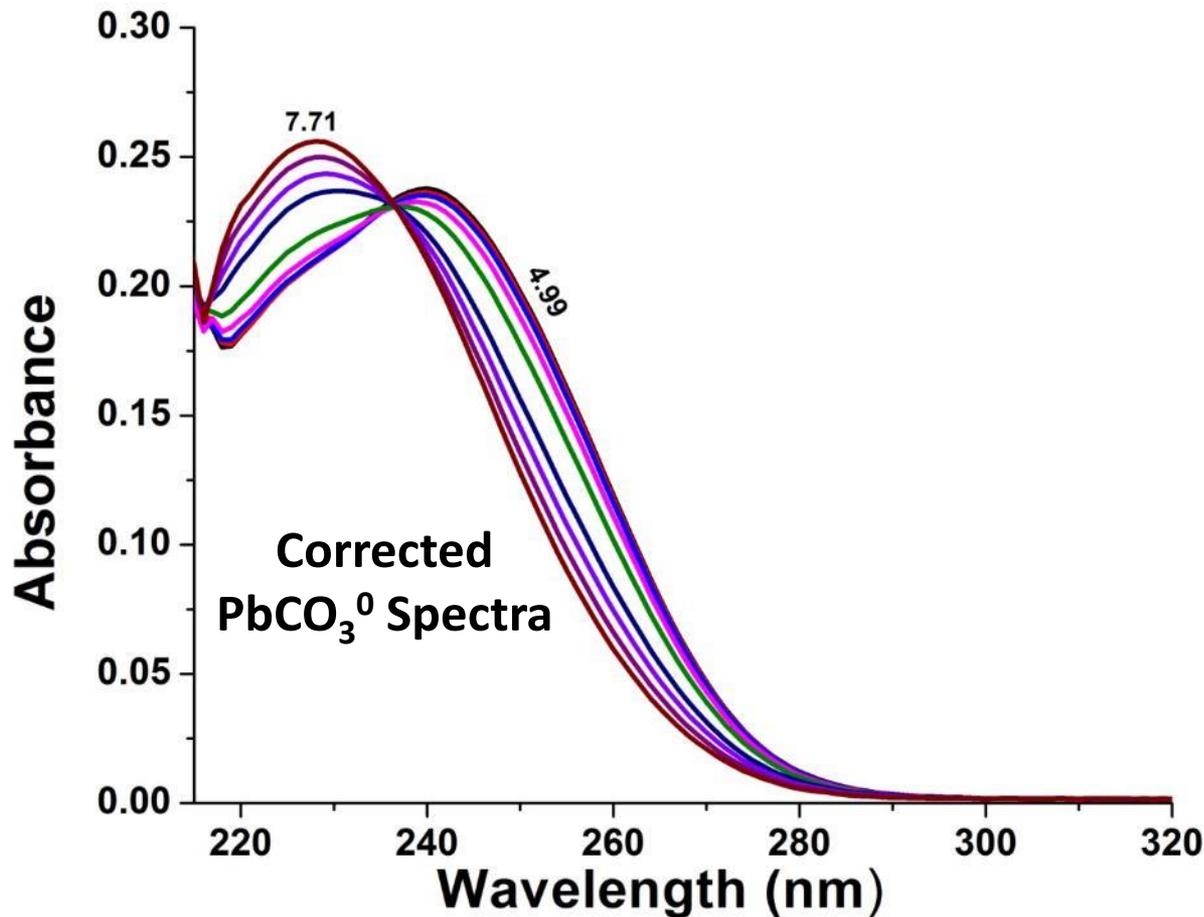


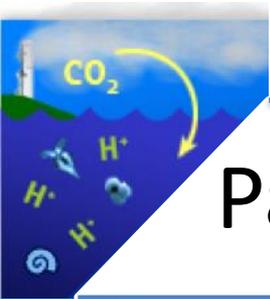
- Spec (Ocean optics)
- Light source
- Fiber optics
- Computer/software
- Square cell- Helma Glass
- Cell holder
- Indicator dye-GCB
- Stir plate
- Nitrogen gas



5. Measuring Carbonate Ion

Carbonate ion system using spectrophotometric techniques

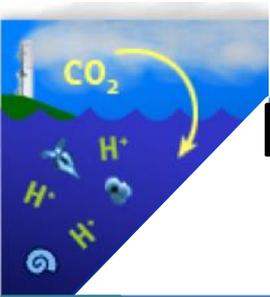




Parameter now being used

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



Parameters and Sensors that are right for your application

	Open Ocean	Estuary/ Coastal	Lab Exp
pH			
TA			
DIC			
pCO ₂			

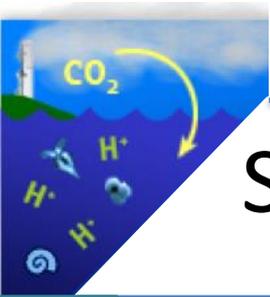
SENSORS

Do you have at least two parameters?

How did you choose the parameters?

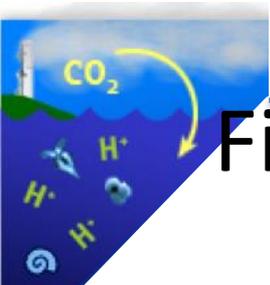
What equipment do you have? Do you need spatial and temporal resolution of the data?

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



So what parameters should you measure?

- 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 CO₂ Reference Material Program to assign total alkalinity values to our CO₂ 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 CO₂ Measurements*. A known amount of sample is acidified to a pH of ~3.6, the evolved CO₂ 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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