Use of the MICA System for Coastal CO_2 Research

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MICA is an autonomous multi-parameter flow-through CO_2 system developed for simultaneous measurements of surface seawater pH, carbon dioxide partial pressure (fCO_2), total dissolved inorganic carbon (DIC) and total alkalinity (TA). All of the measurements are based on spectrophotometric determinations of solution pH at multiple wavelengths using sulfonephthalein indicators. The pH and TA optical cells are machined from a PEEK polymer rod, and have a 15-cm optical pathlength. The fCO_2 and DIC optical cells consist of Teflon AF 2400 (DuPont) capillary tubing sealed within a bore hole also machined from PEEK. The Teflon AF tubing, filled with a standard indicator solution that has a fixed total alkalinity, forms a liquid core waveguide (LCW). The LCW functions as both a long pathlength (15 cm) optical cell and a membrane that equilibrates the internal standard solution with either external air (providing air pCO_2), seawater (providing seawater fCO_2), or acidified seawater (providing DIC measurements). Both pCO_2 and DIC are then determined by measuring the pH of the internal solution.

The MICA system has been deployed previously to obtain high quality CO_2 system datasets across ocean basins. The system makes repetitive observations with measurement frequencies on the order of seven samples per hour. Measurement precisions in the field have been evaluated as ± 0.0008 units for pH, ± 0.9 µatm for pCO_2, and ± 2.4 µmol kg^{-1} for DIC. These precisions are close to those obtained with conventional methods in the laboratory.

We herein present a new procedure for obtaining coastal CO_2 measurements using MICA. Since the CO_2 chemistry of the coastal ocean is exceedingly dynamic relative to the open ocean, much faster sampling rates are required. The new procedure designed to address this challenge provides sample acquisition rates of approximately 25/hr.

Introduction

Measurements of four seawater inorganic carbon system parameters – pH, carbon dioxide fugacity (fCO_2) or partial pressure (pCO_2), total dissolved inorganic carbon (DIC), and total alkalinity (TA) – are essential for carbon cycle investigations on both global and local scales. Both observational and modeling efforts rely on high-quality inorganic carbon data from field measurements. Extensive efforts have been devoted to improving methodologies and instruments for determination of carbon parameters in seawater.

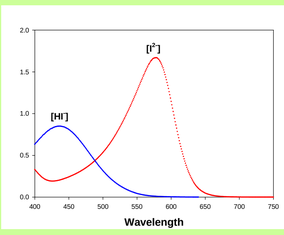
In conventional methodologies, the four core parameters of the seawater inorganic carbon system are measured using diverse instrumentation (e.g., potentiometry, spectrophotometry, gas chromatography, non-dispersive infrared analysis, and coulometry). It is highly desirable that all four parameters are measured simultaneously and continuously with high temporal resolution and with high precision and accuracy.

Among all available methodologies for measurements of inorganic carbon species in seawater, spectrophotometric methods are especially promising because they can be used to unify measurements of different parameters and achieve simultaneous multi-parameter measurements at relatively low cost. Moreover, spectrophotometric methods have many advantages for measuring inorganic carbon species in seawater: high sensitivity, good stability and selectivity, simplicity, and low rates of sample and reagent consumption.

The available spectrophotometric methodologies developed over years for measurements of inorganic carbon parameters were engineered into a single system that is primarily intended for high-resolution underway monitoring onboard research vessels. We describe herein application of an autonomous multi-parameter flow-through CO_2 system for simultaneous measurement of surface seawater Ct, pH, fCO_2 in the coastal environment.

Measurement Principles

All measurements of CO_2 parameters are based on spectrophotometric pH measurement. The solution pH can be measured based on the dissociation of sulfonephthalein indicators



$$HI^- \xleftrightarrow{K_1} H^+ + I^{2-}$$

$$pH = pK_I + \log \frac{R - e_1}{e_2 - Re_3}$$

Figure 1. Spectra of Thymol Blue dye

pH

For surface seawater pH_T determinations, thymol blue: λ_1 = 435 nm and λ_2 = 596 nm, is used for direct pH measurements. A third wavelength, λ_{ref} = 730 nm, is used to correct for baseline shifts between blank and sample measurements.

Phenol red is the indicator of choice for low-ionic-strength applications (e.g. river water).

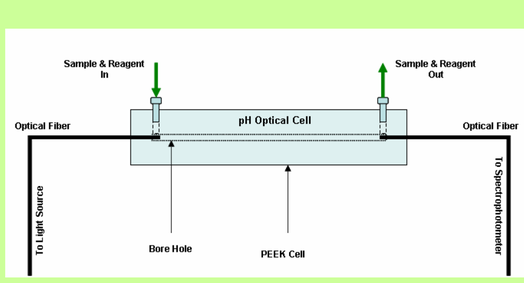


Figure 2. Optical cell for determination of pH

fCO_2, air pCO_2, and DIC

Measurements are based on CO_2 gas equilibration between sample and reagent: the Teflon LCW cell acts as both a spectrophotometer cell and a gas-permeable membrane. For DIC analyses, the sample is acidified to pH 3.

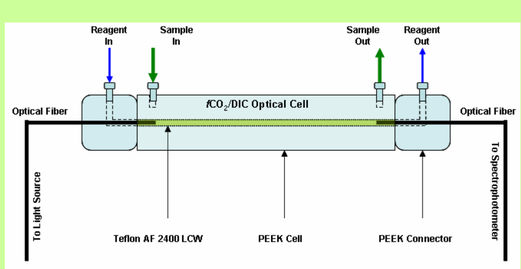


Figure 3. Schematic diagrams of pCO_2 and DIC optical cells.

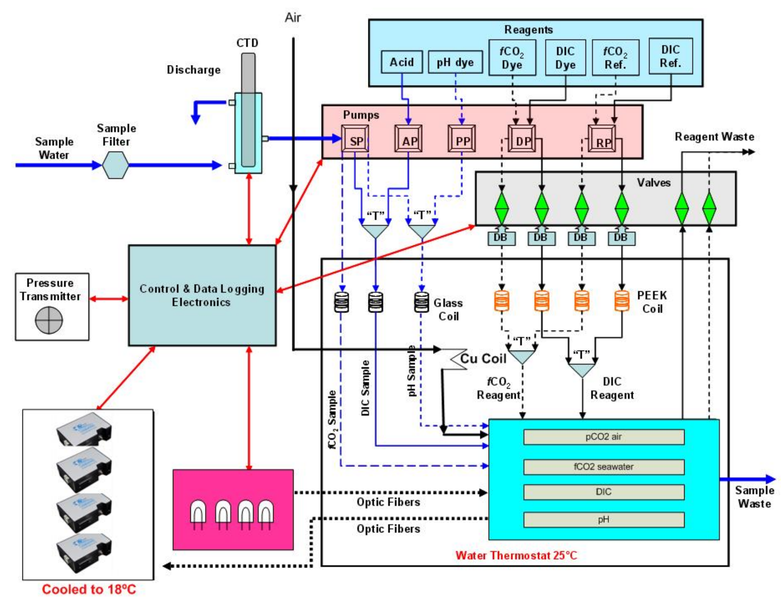


Figure 4. MICA (I) System Schematics

Table 1. MICA Characteristics

	fCO_2 Channel	DIC Channel	pH Channel
Optical cell	Teflon AF 2400 LCW sealed in a PEEK cell	Teflon AF 2400 LCW sealed in a PEEK cell	PEEK rod with bore-hole
Indicator	Phenol red	Bromocresol purple	Thymol blue
Reagent consumption	13 ml/hr for old procedure, 2 ml/hr for new procedure	13 ml/hr for old procedure, 2 ml/hr for new procedure	10 µL min^{-1} indicator
Calibration	Against standard CO_2 gases;	Against certified reference material (CRM)	Established previously; no field calibration is required
Equilibration time	6 min -first sample 2 min –subsequent sample	6 min -first sample 2 min –subsequent sample	Instant
Sampling frequency	7 readings/hr– old 25 readings/hr—new	7 readings/hr –old 25 readings/hr—new	7 readings/hr –old 25 readings/hr –new
Field precision	±0.9 µatm	±2.4 µmol kg^{-1}	±0.0008 pH units

A New Procedure for Coastal CO_2 Research

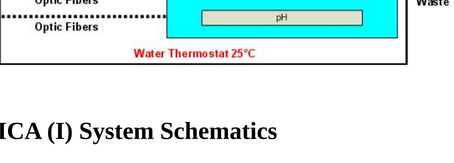
In the past few years we have used the MICA system extensively on major open ocean cruises. Figure 5 shows the MICA system on board the R/V Ronald H. Brown and on a ship of opportunity. Figure 7 shows excellent agreement between pH, Ct and pCO_2 data obtained using the automated MICA instrument and obtained using conventional methodologies to analyze discrete samples. In the original MICA measurement procedure, a new dye solution was introduced to the LCW after each reading and each new sample was fully equilibrated (Figure 6 and Figure 8a). In general, all data acquisition, including Ct, pCO_2 and pH, required about 8 minutes (7 measurements per hour).

Coastal waters, including embayments, are highly dynamic systems. Chemical characteristics can change dramatically on scales of a few hundred meters. For an eight-minute analysis time at normal cruise speeds, measurements can represent averages over of a distance of two or more miles. Consequently, due to differences in the time required for measurements of pH and other CO_2 parameters, calculations that relate various CO_2-system parameters may not exhibit thermodynamic consistency. This adds uncertainty to assessments of data quality.

A new procedure (Figure 8b) has been developed for use of MICA in coastal CO_2 research. The procedure is, of course, also applicable to research in the open ocean. Sample throughput is greatly increased by reducing the frequency of replenishment of the MICA internal standard solutions. Each equilibration is begun with the conditions developed in the previous sample equilibration. As such, each equilibration is begun close to equilibrium and full equilibrium is achieved much more quickly. This procedure increases sample measurement frequency to about 25 samples per hour, and reagent consumption is reduced to approximately 2 ml per hour.

Table 2. Transect Data from Puget Sound

Date	S	T	Ct	pCO2 (25)	pH
8/15/2008 7:32	30.66	12.23	2081.7	1463.1	7.5356
8/15/2008 7:34	30.65	12.47	2091.1	1470.7	7.5188
8/15/2008 7:37	30.64	12.45	2089.5	1469.9	7.5139
8/15/2008 7:39	30.76	12.24	2089.3	1491.1	7.5125
8/15/2008 7:41	30.76	12.17	2094.7	1520.3	7.5242
8/15/2008 7:44	30.66	12.28	2095.2	1502.7	7.5102
8/15/2008 7:46	30.65	12.27	2093.2	1481.2	7.5215
8/15/2008 7:49	30.66	12.27	2092.0	1472.3	7.5105
8/15/2008 7:51	30.64	12.32	2091.6	1480.6	7.5217
8/15/2008 7:53	30.80	12.04	2091.1	1517.7	7.5097
8/15/2008 7:56	30.68	12.19	2097.6	1540.3	7.4978
8/15/2008 7:58	30.74	12.12	2096.5	1527.4	7.5139
8/15/2008 8:00	30.74	12.10	2098.5	1534.7	7.4970
8/15/2008 8:03	30.74	12.12	2100.3	1539.8	7.5091
8/15/2008 8:05	30.78	12.06	2097.7	1539.8	7.5127
8/15/2008 8:07	30.84	11.94	2097.7	1559.3	7.4925
8/15/2008 8:10	30.89	11.75	2105.6	1597.1	7.5046
8/15/2008 8:12	30.94	11.62	2112.5	1626.9	7.4959
8/15/2008 8:14	31.03	11.51	2113.6	1639.7	7.4784
8/15/2008 8:17	31.08	11.39	2119.1	1688.9	7.4833
8/15/2008 8:19	30.92	11.56	2119.3	1679.5	7.4632
8/15/2008 8:21	30.89	11.64	2110.1	1603.7	7.4787
8/15/2008 8:24	30.81	11.78	2109.4	1577.4	7.4950
8/15/2008 8:26	30.69	11.96	2099.6	1523.6	7.4997
8/15/2008 8:28	30.63	12.03	2092.3	1495.9	7.5124
8/15/2008 8:31	30.60	11.97	2087.0	1484.1	7.5146



(a) (b)

Figure 8. Comparison of original (a) and new (b) procedures of MICA.

A transient signal can be measured with the new procedure on MICA

Acknowledgement

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On Ship of Opportunity

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Figure 5. Setup of MICA system. The instrument occupies about 40"x20" of desk space.

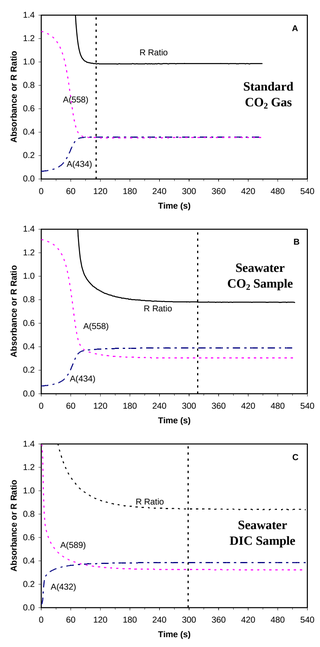


Figure 6. Curves showing absorbance ratio (R) versus equilibration time for the LCW optical cells

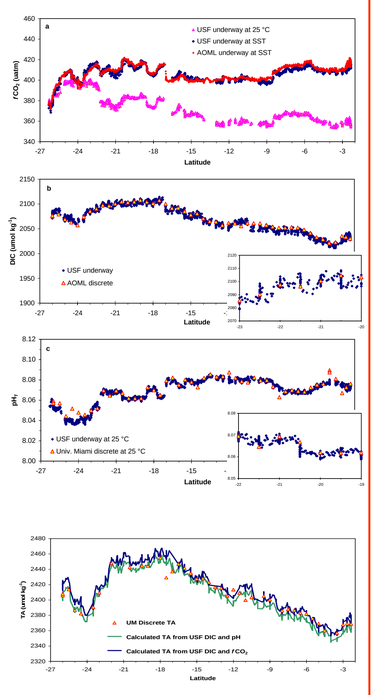


Figure 7. Comparisons of MICA measurements with measurements obtained using established standard methods

Conclusions

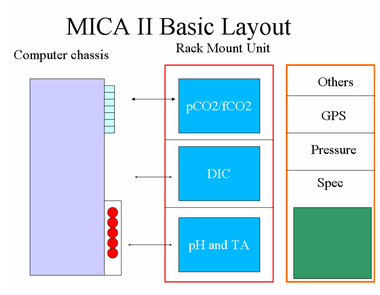
The MICA system can simultaneously measure surface seawater fCO_2, DIC, and pH with sensitivities and accuracies consistent with those of state-of-the-art discrete measurements.

The system can be repackaged for deployments on moorings and other platforms. Reconfiguration is required to withstand harsh environments and extend system endurance.

The current system makes underway measurements at a constant temperature using a large thermostated water bath. Mooring operations would require use of small thermostating devices or, alternatively, thermostating could be eliminated and system calibrations could allow all measurements to be performed at in situ temperatures.

Given the cost and complexity of current conventional analytical methods, wherein each CO_2-system measurement requires approximately two shipboard personnel, automated systems such as those described in this study are likely to be increasingly utilized in coastal, open ocean, and riverine systems.

Current Development



Currently, the MICA system is being repackaged to eliminate the need for a large thermostating water bath. An alkalinity channel will also be added so all CO2 parameters can be characterized directly on single instrument. Like pH, TA is measured by simple mixing of acid/indicator dye with the sample in a continuous flowing mode.