MICA is an autonomous multi-parameter flow-through CO₂ system developed for simultaneous measurements of surface seawater pH, carbon dioxide partial pressure (pCO₂), total dissolved inorganic carbon (DIC) and total alkalinity (TA). All of the measurements are based on spectrophotometric determination of CO₂ 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 pCO₂ and DIC optical cells consist of Telfon AF 2400 (DuPont) capillary tubing sealed within a bore hole also machined from PEERK. The Telfon 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 pCO₂), seawater (providing seawater CO₂), or acidified seawater (providing DIC measurements). Both pCO₂ and DIC are then determined by measuring the pH of the internal solution.

The MICA system has been deployed previously to obtain high quality CO₂ 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 ±0.008 units for pH, ±0.9 µatm for pCO₂, and ±24 µmolkg⁻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 CO₂ measurements using MICA. Since the CO₂ 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⁻¹.

Measurements of four seawater inorganic carbon system parameters - pH, carbon dioxide fugacity (fCO₂) or partial pressure (pCO₂), 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 species 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 CO₂ system for simultaneous measurement of surface seawater CO₂, pH, DIC in the coastal environment.

**Measurement Principles**

All measurements of CO₂ parameters are based on spectrophotometric pH measurement. The solution pH can be measured based on the dissociation of sulfonephthalein indicators.

**Figure 1. Spectra of Thymol Blue dye**

**pH**

For surface seawater pH determinations, thymol blue λ = 435 nm and λ = 596 nm, is used for direct pH measurements. A third wavelength, λ = 730 nm, is used to correct for baseline shifts between blank and sample measurements.

**Figure 2. Optical cell for determination of pH**

**Figure 3. Schematic diagrams of pCO₂ and DIC optical cells.**

**Table 1. MICA Characteristics**

**Figure 4. MICA (B) System Schematics**

**Figure 5. Setup of MICA system.**

**Figure 6. Curves showing absorbance ratio (R) vs time for the LCW optical cell.**

**Table 2. Transect Data from Puget Sound**

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

**Conclusions**

The MICA system can simultaneously measure surface seawater CO₂, 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 CO₂ 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.