An autonomous indicator-based pH sensor for oceanographic research and monitoring

PI: Micheal D. DeGrandpre, PhD
Dept. of Chemistry, University of Montana, Missoula, MT 59812
Phone: (406) 243-4118 FAX: (406) 243-4227 E-mail: mailto:michael.degrandpre@umontana.edu

Co-PI: Jim Beck, MSME
Sunburst Sensors, LLC, 1226 W. Broadway, Missoula, MT 59802
Phone: (406) 532-3246 FAX: (406) 532-3247 E-mail: jim@sunburstsensors.com

Co-PI: Andrew Dickson, PhD
Scripps Institution of Oceanography, The University of California-San Diego
9500 Gilman Drive, La Jolla, CA 92093
Phone: (858) 822-2990 FAX: (858) 822-2919 E-mail: adickson@ucsd.edu

Award Number: *(Grant or Contract or Document Number)*
NSF – OCE0836807

LONG-TERM GOALS

This project, funded under NOPP Topic 3A *Sensors for Measurement of Biological, Bio-Optical or Chemical Properties of the Ocean* uses NOPP funding to improve an autonomous, in situ indicator-based pH sensor that was developed in the PI's lab, and to commercialize the redesigned system through Sunburst Sensors, LLC. Studies conducted using the original design have found excellent precision, accuracy, and long-term stability (Seidel et al. 2007). However, the original design was complex and power limited. The goal of this project is to improve upon the strengths of the existing sensor, while reducing complexity and power consumption.

OBJECTIVES

The specific objectives of this project, as originally stated in the funding proposal are to:

- Implement design improvements established during redesign of the SAMI- CO_2 including the optical detection system, control and data acquisition electronics, fluidics, and user software.
- Redesign the features that are specific to the SAMI-pH, focusing on optimizing the mixing protocol, power consumption, ease of troubleshooting, and expanding deployment versatility.
- Establish rigorous manufacturing quality control criteria to verify absorbance and pH precision and accuracy prior to shipment.
- Implement in situ data validation using pH certified reference materials (CRMs) made by Andrew Dickson's laboratory as part of this proposal.
- Commercialize the sensor through Sunburst Sensors, LLC.

APPROACH AND WORK PLAN

To accomplish our proposed goals the redesigned SAMI2-CO_2 instrument was modified and optimized for pH measurements. The changes from the SAMI2- CO_2 instrument include optimization of the electronics and optics for use on the redesigned pH instrument (SAMI2-pH), changes to the fluidics to accommodate those used by the SAMI2-pH (including an additional valve for an internal standard), and software updates. Additionally, a second system using the same components was designed to function as a benchtop flow-thru system, which can be used for continuous shipboard or laboratory measurements. Data processing on the original pH system was slow and time consuming. This process has been updated and automated, and is now done using custom Matlab scripts. Once the new system was operational it was tested and optimized.

Modification of the SAMI2- CO_2 electronics, fluidics, and software took place at Sunburst Sensors, LLC, and were performed by Jim Beck and Jenny Newton. Matlab code for data processing was written by Jenny Newton, and tested by her and Tommy Moore, a post-doc in the PI's lab funded on this project. Testing and optimization of the redesigned system was conducted by Jenny Newton and Tommy Moore.

Future work will include further testing and optimization of the instrument, refinement of the data processing software, and field testing of the instrument. Mixing coils and other mixing devices will be tested to see if the fluidics of the instrument can be refined, which would lower the power consumption. Multiple instruments will also be tested against each other to determine if the instruments are similar enough to use the same calibration values, thus making the instrument standardization process easier and more efficient. Field testing will take place on the NH-10 mooring off of the Oregon coast (http://agate.coas.oregonstate.edu/data/nh10.html) and off of the the Scripp's pier as has been done previously (Seidel et al. 2007).

WORK COMPLETED

To date a number of our proposed goals have been accomplished. The electronics and software from the SAMI2- CO_2 instrument have been modified and optimized for use on the SAMI2-pH instrument, and at present a working version of the instrument is available. Testing has found that data collected by the SAMI2-pH has an accuracy and precision comparable to the old instrument (SAMI-pH), and will likely improve with further testing and optimization. Power consumption by the instrument has been reduced by more than half, enabling longer deployments. The system has been to designed to allow for the measurement of an in situ standard, which will ensure higher quality data from field deployments. Commercialization of the new instrument has already begun, and at present 5 instruments have been manufactured, with 2 being tested in the PIs lab and 3 shipped to customers.

RESULTS

The new SAMI2-pH instrument was redesigned based upon the new SAMI2- CO_2 system (Figure 1). The tungsten light source and associated optics were replaced with two LEDs and beam splitter (Figure 2). These changes reduce instrument operation time, as the tungsten lamp used in the SAMI-pH instrument required 30 seconds to warm up, and the LEDs have a higher light throughput, which reduces the need for amplification, thus decreasing signal noise. The data logger used in the original SAMI-pH has been discontinued, so we have begun using a custom data-logger, which has reduced the board size by 75% and increased the available memory from 1MB to 8MB. This change in hardware resulted in a need to change software as well, which is more user friendly and stable.

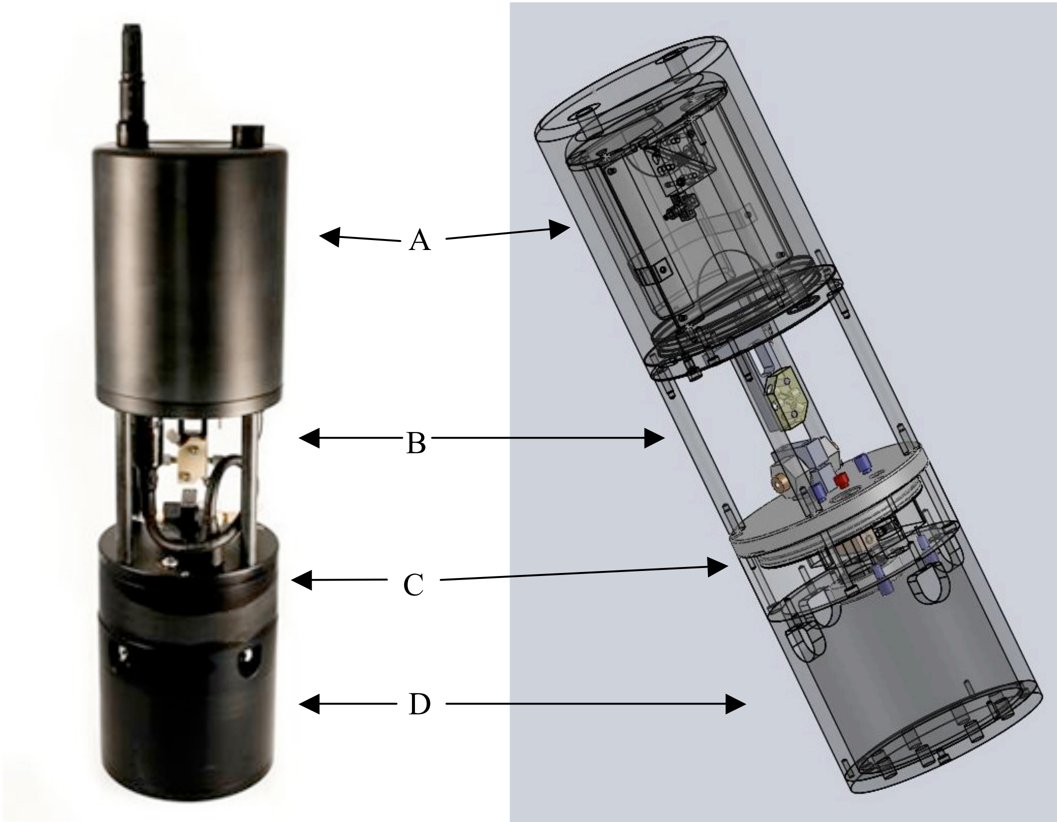

Figure 1: The redesigned SAMI-pH instrument. Picture of the instrument on the left, schematic of the instrument on the right. A.) Electronics and battery housing. B.) Sample inlet and Z-cell. C.) Pump and valve housing. D.) Reagent bag housing.

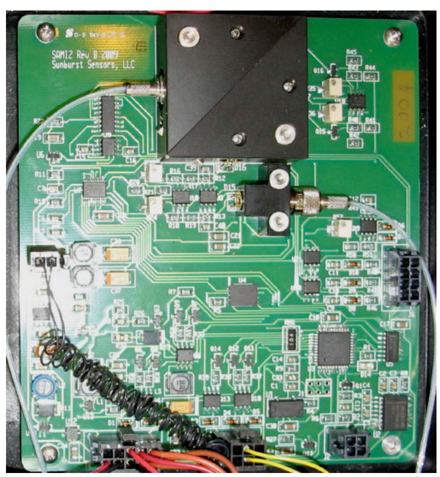

Figure 2: Custom data-logger board and optics. The black box at the top houses the LEDs and beam splitter. Dimensions are ~10x10 cm.

Once a working version of the new SAMI2-pH instrument was available it was further modified to operate as a benchtop flow-thru system (Figure 3). This system uses the same components and software as the SAMI2-pH system, but has been built into a box for ease of use in a benchtop environment, such as continuous monitoring of pH in a laboratory or continuous sampling from a ship-board water supply. This system has the same accuracy and precision as the SAMI2-pH, but is not intended for in site applications.

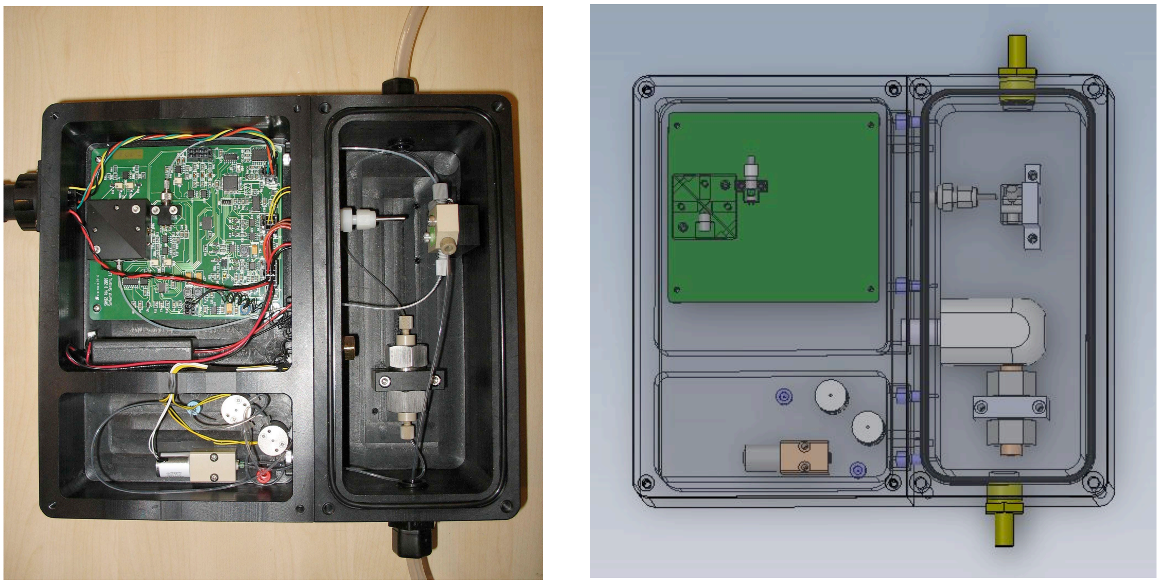

Figure 3: Benchtop flow-thru pH instrument.

Testing of the redesigned instrument has shown that is has met and/or exceeded our expectations. Power consumption by the instrument is down by more than 50% (Table 1), which is important, as the original instrument was power limited. Signal noise on a blank solution run over night was +/- 0.00019 absorbance units (n=93), which is comparable to that obtained by the SAMI-pH instrument. Accuracy tests of a pH standard (Tris) had an accuracy and precision of 0.0004 +/- 0.0006 pH units, which is an improvement on the original instrument (0.0017 +/- 0.0007 pH units). Overnight tests on a seawater sample also had excellent precision (+/- 0.0007, Figure 4). Overall these tests show that the SAMI2-pH instrument is as good as or better than its predecessor.

Table1: Daily current draw for the old (SAMI-pH) and redesigned (SAMI2-pH) instrument.

	SAMI-pH	**SAMI2-pH**
Measurement Interval (min)	**Current draw per day (mAhr)**	
15	799	330
30	399	165
60	199	82.5
120	99.9	41.3
180	50.0	20.6

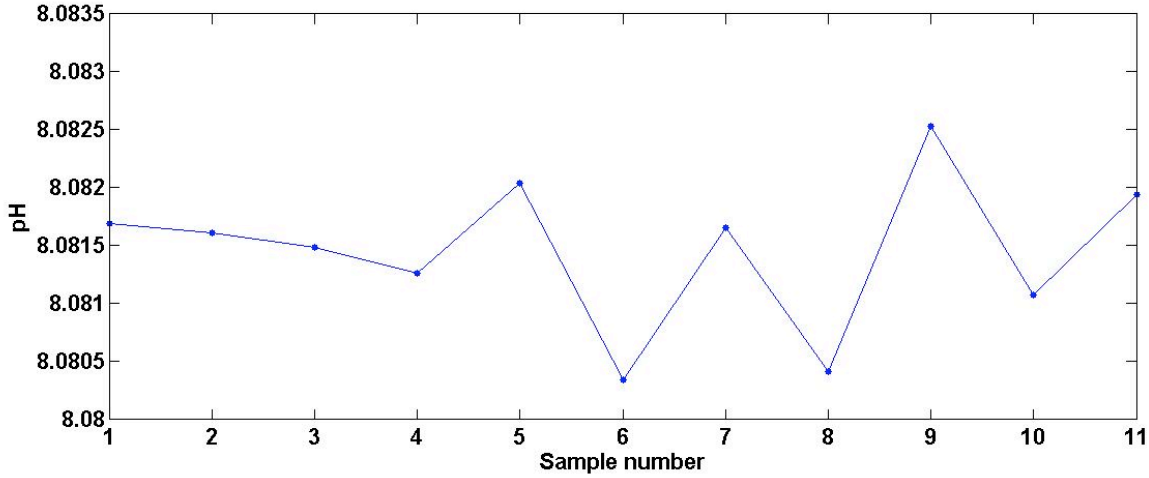

Figure 4: pH of a seawater sample run in the laboratory at 20 °C.

The software used to operate the SAMI2-pH has also been updated. It now operates via a graphical user interface, and exports the data as a text file, making processing easier. All aspects of the instrument can be easily controlled through the new interface, allowing for easy changes in experimental parameters, sampling frequency, and the monitoring of auxiliary channels if additional (up to 4) sensors are attached. Data processing has been simplified through the writing of custom Matlab scripts, which will automatically calculate pH from the SAMI2-pH data, and allows for straight forward quality control.

IMPACT AND APPLICATIONS

Economic Development

Initial testing of this instrument has shown it to highly accurate with low power consumption, making it ideal for long-term deployments. Continuous in situ measurements of pH are essential for monitoring ocean acidification, making this a highly applicable and marketable instrument.

Quality of Life

Ocean acidification has the potential to affect marine ecosystems at all levels. Continuous in situ observations of the pH of the oceans will provide a comprehensive understanding of the changes caused by ocean acidification, which can then be used to inform policy makers and the public about the state of our oceans.

Science Education and Communication

As this project is a joint effort between academia and industry it has served as a tool to educate graduate students and post doctoral researchers in the PI's lab and other researchers using the instrument about instrument design, testing, and applications. Additionally, pH data collected by the instrument can be used with other parameters to look at carbon dynamics in the oceans, which is a useful educational tool.

TRANSITIONS

Economic Development

The accuracy and energy efficiency of the SAMI2-pH make it ideal for long in situ deployments, which is essential for ocean observing projects. At present a SAMI2-pH instrument has been deployed as part of the the NH-10 buoy observatory (http://agate.coas.oregonstate.edu/data/nh10.html), and we are planning on deploying another instrument there this winter.

Quality of Life

The SAMI2-pH instrument could readily be incorporated into ocean observing projects, directly monitoring ocean acidification. Doing so would contribute to our understanding of these processes and would serve as a source of information for policy makers and the public.

Science Education and Communication

Testing and optimization of the SAMI2-pH instrument is a useful educational tool, teaching researchers about instrument design. Applications of the instrument can be used with other data to examine the carbon cycle in seawater, which is a great educational tool in oceanography and environmental chemistry.

RELATED PROJECTS

Commercialization of autonomous sensor systems for quantifying pCO2 and total inorganic carbon. NOPP Award Number: OCE-052955. http://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.,* 18-28.