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

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OBJECTIVES

This research, funded under 2007's NOPP Topic 3A, "Sensors for Measurement of Biological, Bio-Optical or Chemical Properties of the Ocean" uses the NOPP funding to achieve these objectives:

- implement design improvements established during redesign of the SAMI-CO_2including 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.

The proposed redesign will address current limitations while making the instrument less expensive and more versatile, and will include the ability to deploy on a wide range of fixed and mobile platforms.

PROGRESS

(*Note: Funding for this work was awarded in August 2008, so there are less than 4 months of work on this project to date.*)

The six specific goals outlined in our proposal are listed below with a short description of the problem to be solved followed by progress made.

1) Improve SAMI optical performance

We have observed inconsistent SAMI pH precision and accuracy. The precision differences arise from inconsistent light throughput and subsequent differences in amplification between instruments. We believe that increased light throughput using narrow-band, high output LEDs instead of the current tungsten light source should significantly improve the accuracy and precision. By increasing light throughput (signal) we will reduce noise and drift due to high gain amplification.

In early testing a cuvette based system was built to examine whether the use of modulated LEDs would create any unexpected problems . The system is built on a custom 3 inch square printed circuit board (PCB). The LEDs are modulated at 1 msec on-off and 180 degrees out of phase, so that each wavelength can be measured separately. The two signals are separated and rectified to a 0-5V output proportional to signal intensity (absorption). The 0-5 V out is currently measured using the prototype software, developed on LabView, and a USB Data Acquisition system (National Instruments DAQ-6009) which does the A/D conversion.

In this bench test we utilized two narrow-band LEDs with peak emissions at 435 nm and 620 nm, which are the wavelengths of interest for determining pH (6.4-8.4) using the indicator solution bromothymol blue (BTB).

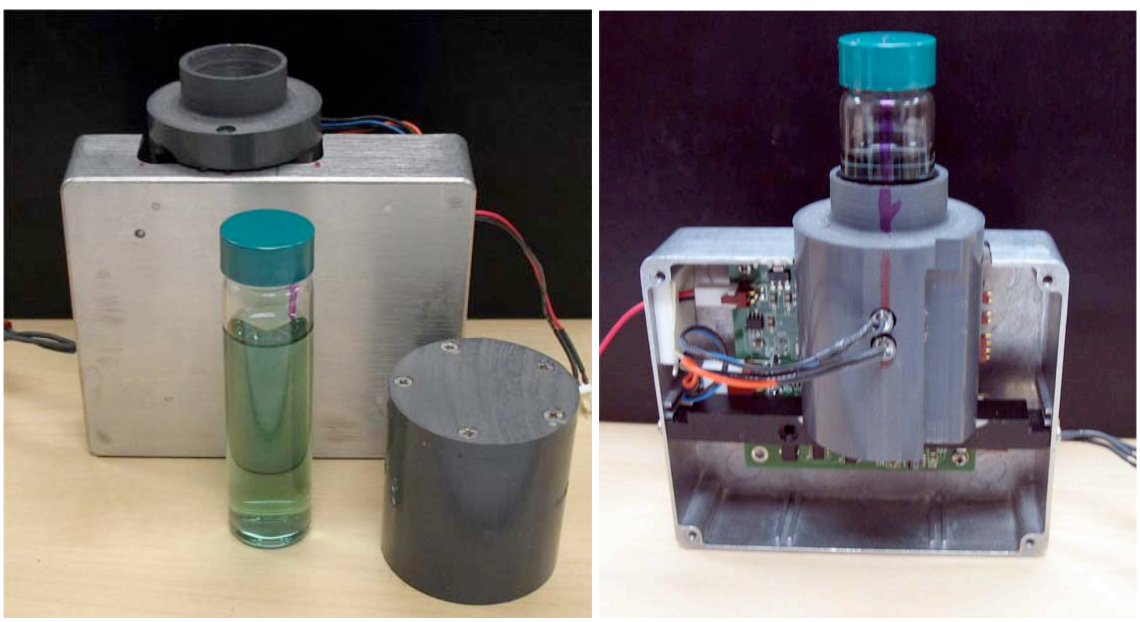

Figure 1: Cuvette system to test LED noise and accuracy of pH measurements

Noise Test

We targeted noise level of <±0.0005 absorbance units over the period of a measurement. To calculate the noise for each of the wavelength channels, a blank solution was used to record the intensity over a time (t) interval of one minute. Absorbance for the 620 nm channel is $A_{620}=\log(I_{620}/I_{0620})$ and for the 434nm channel $A_{434}=\log(I_{434}/I_{0434})$ where I_0 is the intensity at t=0. We performed tests using a LabView program that performed a 5-point and a 10-point averaging of signals. The following graphs show the results of 5 and 10-point averaging. The targeted noise level was achieved using 5-point averaging, with noise reduced further by a 10 point average as shown in Figure 2.

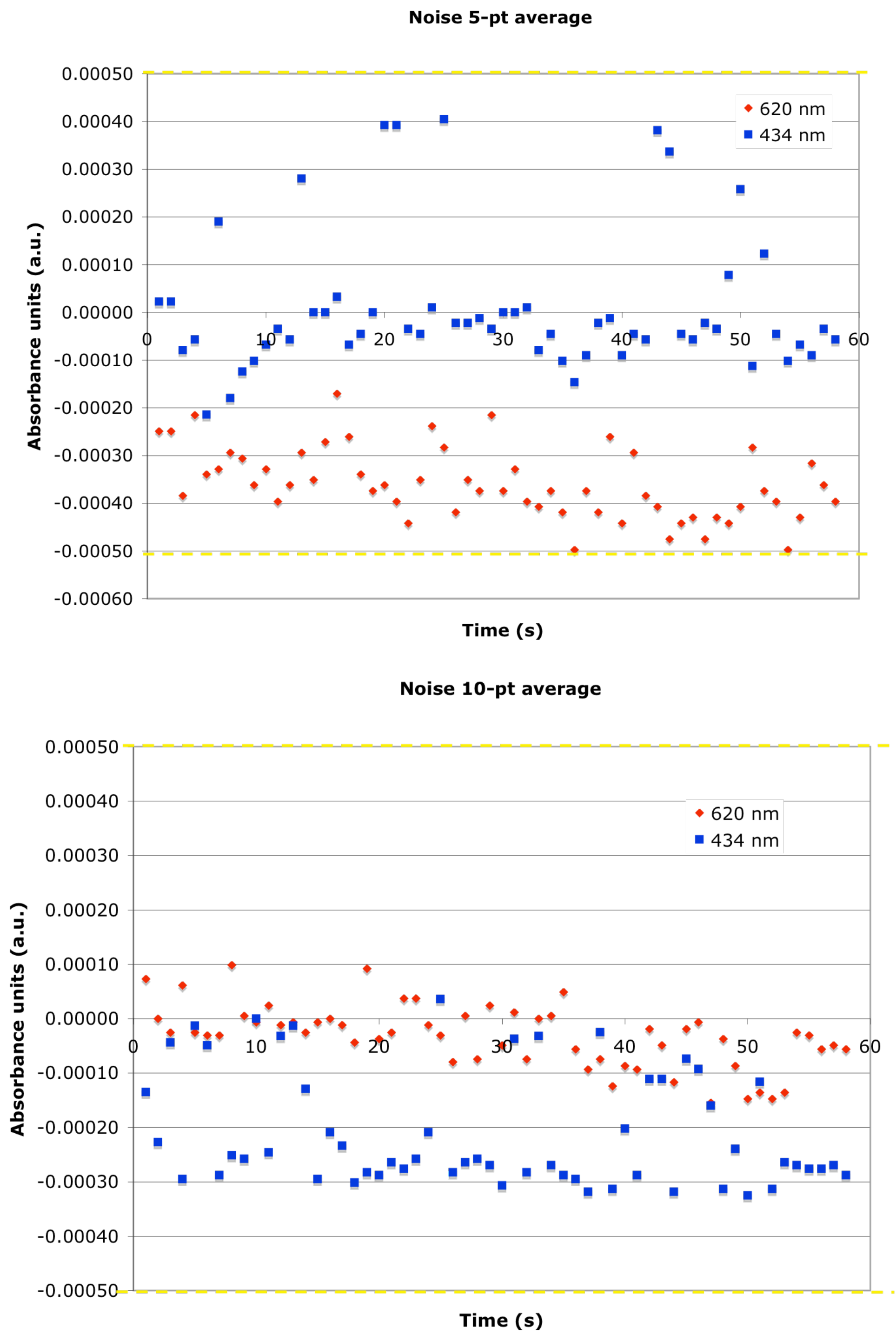

Figure 2: Noise measurements for cuvette system using 5 and 10 point averaging.

Conclusions and Next steps

These tests results were adequate to give us confidence that we can use a modulated LED based system to measure pH. We are currently building a LED bench top system with pump and flow-cell to test a benchtop version of the SAMI-pH . In this system we will use m-cresol-purple (mCP) as is currently used in the SAMI-pH and switch to a 578 nm LED instead of 620 nm. Rather than an analog board, we will use a micro-processor driven board based on a similar design developed for the SAMI-CO_2.

2) Minimize pH perturbation

We have found that the performance is sensitive to the extent of mixing between the indicator and sample. For reasons not yet fully understood, if the dilution curve is not sufficiently broad, the calculated pH can be systematically low by 0.005 to 0.01 pH units. Because the perturbation is linear over the measurement range, it should not depend on which section of data is used. The offsets are observed, however, if insufficient data are obtained at the low indicator concentration range.

The two proposed solutions are 1) adjusting the indicator pH to be as close to the expected sample pH range as possible and/or 2) increasing the optical path length. Parts have been ordered to test these solutions but testing of the two proposed solutions has not yet begun and there are no results to report.

3) Minimize analysis time

The 4 minute analysis time, although adequate temporal resolution for mooring deployments, requires significant power and is not optimal for some types of deployments such as profiling floats. Ideally the analysis time would be <20 seconds which is comparable to the Aanderaa O_2 optode that has been widely deployed on profiling floats. While this might not be feasible because of power constraints, we will reduce the response time as much as possible. At present, the response time is limited by the pumping rate of the small volume solenoid pump and the need for a broad indicator/sample dilution curve for the perturbation correction.

To reduce the analysis time we will be testing a dual pump system where the seawater sample is driven by a 350 ml solenoid pump, while the current 50 ml injects reagent by a 'tee'. Parts have been ordered for this testing and it should commence in the next month. Testing is already underway of the feasibility of using downstream pumping (pump located downstream of mixer and flow cell) to determine whether this is viable for the SAMI-pH. Testing of downstream pumping on the SAMI-CO_2 has shown downstream pumping to be better in terms of minimizing bubble formation. The SAMI-pH, however, may not perform as well due to changes in mixing.

4) Improve ease of assembly, operation and troubleshooting

The current SAMI design suffers from many of the design and software limitations of the SAMI-CO_2 and therefore, the improvements in the SAMI-CO_2 have already and will continue to benefit the SAMI-pH. In the current design all of the sensor components and additional cabling are limited to the area of one end-cap The fiber optic feed-throughs greatly restrict the freedom in positioning other components, particularly the optical flow cell. Consequently, operation, maintenance and troubleshooting are difficult because of the confined space and exposed fiber optics.

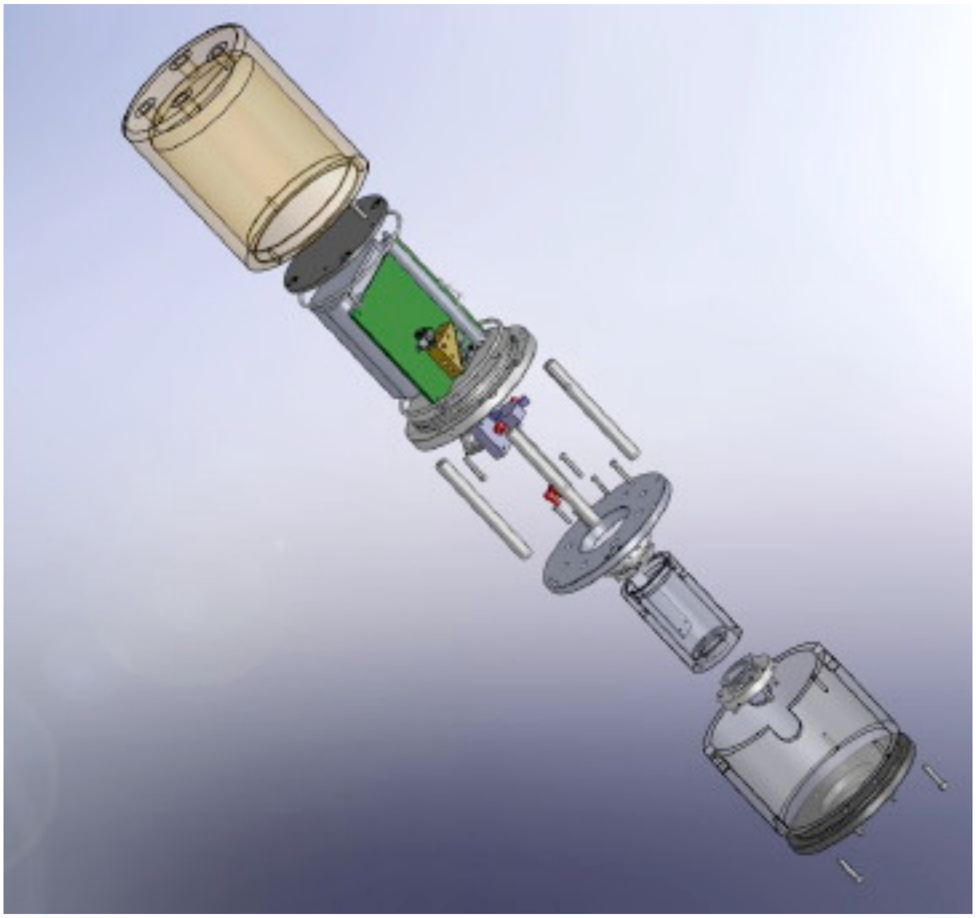

Figure 3: Exploded view of the new SAMI-CO_2

A redesign of the SAMI-CO_2 has just been completed under separate funding (Figure 3). Many of the ideas and innovations of this design will be carried over to the SAMI-pH. We expect to use a very similar circuit board, using surface mount components and a beam-splitter. The electronics housing will be very similar and be rated to 500 m. There will be changes to the center section to accommodate the mixer and the flow-cell. If dual pumps are used, there will be a significant change to the pump-valve housing as well.

5) Reduce power consumption

Because of the pumping and necessity to have the light source on during the pump cycle, the power requirements allow only 3000 measurements with the 18 D-cell battery pack. This is compared to ~9000 measurements for SAMI-CO_2 using the same battery pack. Two to three times more measurements with a smaller batter pack would allow for high frequency measurements on autonomous profilers or year long deployments on moorings.

The new LED based SAMI-CO_2 has a much higher efficiency than its predecessor with a projected life of at least 4x longer. On the SAMI-pH, more of the total power is consumed by pump cycles. Early analyses indicate that a dual pump system may increase efficiency. The LEDs which are only turned on for a few msec per measurement (vs minutes for the tungsten light source) will also use much less power. As the design comes into focus we will have a better idea of the expected life.

6) Implement in situ quality control

While the spectrophotometric measurement is very reproducible on good quality spectrophotometers, custom instrumentation deployed for long periods need occasional checks on performance.

This goal will be undertaken in the latter part of the work on this proposal.

IMPACT AND APPLICATIONS

Economic Development

This research and development will help make the SAMI-pH a robust, less-expensive means of measuring seawater pH. The high cost and complexity of the current design is a disincentive to sales, and widespread adoption within the oceanographic research community.