Commercialization of autonomous sensor systems for quantifying pCO_2 and total inorganic carbon

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OBJECTIVES

This research, funded under 2004's NOPP Topic 4B "Sensors for Sustained, Autonomous Measurement of Chemical or Biological Parameters in the Ocean" uses the NOPP funding to promote commercialization of the SAMI-CO_2, a sensor developed for autonomous measurements of the partial pressure of CO_2 (pCO_2) in seawater. The SAMI-CO_2 was commercialized in 1999 through an exclusive license from the University of Montana to Sunburst Sensors, a company in Missoula, Montana (see sunburstsensors.com). Field deployments by DeGrandpre and others have demonstrated the excellent long-term stability predicted by the SAMI's well-understood theoretical response. The design, however, was complex and prone to failures, especially by customers who are not trained to operate the SAMI. Incremental changes in the design improved reliability, but a full redesign is required to implement modern electronic and manufacturing technology. The new design will allow individual investigators to make pCO_2 measurements reliably over long time periods in widespread ocean locations on many different ocean platforms.

PROGRESS

Work has focused on completing the redesign and resolving some issues with the basic design. The redesign has been much more comprehensive than originally envisioned so that the only unchanged sub-system is the plumbing (pump-valve and tubing). The new design meets all of the criteria established in our proposal. It is more compact, uses less power, and is more reliable and user friendly. Testing on prototype instruments have given us confidence in the new light emitting diode (LED) based design. A first article prototype is currently being assembled and will be tested over the next few months after which we expect to go into production of the new device.

New Design – Overview

Figure 1 shows an exploded view of the new design. The top chamber holds the optics, electronics and battery pack. Not shown, on top, are bulkhead connectors. One of the bulkheads is for power and serial communication while the other three support external instruments such as a PAR sensor, fluorometer, or oxygen optode.

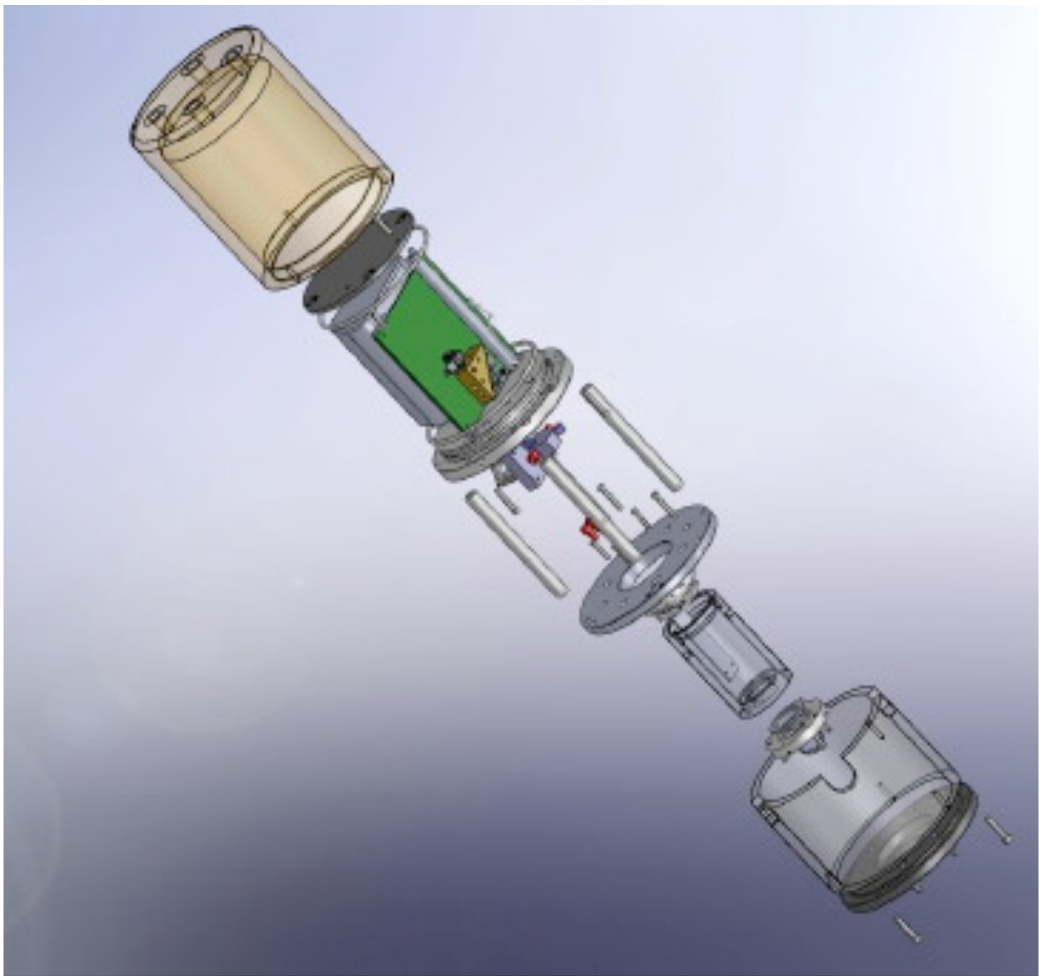

Figure 1: Exploded view of the new SAMI-CO_2 design

In the center section, which is exposed to sea water, is the integrated Z-cell and equilibrator as well as the thermistor (not shown) and cable to the pump-valve housing (not shown). This section will be enclosed in a copper mesh (not shown) for anti-fouling and protection of the tubing and fiber optics.

The bottom section is comprised of a chamber for holding the reagent bags and a housing for the pump-valve assembly. As in the original design, the pump-valve housing is filled with low viscosity silicon oil to match it to ambient pressure.

Figure 2: New design (at right) next to old version

Figure 2 shows a partially assembled prototype of the design next to the original design of the SAMI-CO_2. While they may look fairly similar in size, on the left, notice there is a reagent box that clamps to the exterior of the old design. The reagent bag is now contained in the white chamber at top. Also notice the pump/valve housing, fibers and equilibrator on top of the old instrument. The electronics (4 separate printed circuit boards), lamp, fiber optic splitter, optical filter housing and battery on the left comprise 16.5” of length while on the right the new instrument puts all of this into a 6” section. The new design will be able to use 1 liter bags of reagent versus a 450 ml bag on the old SAMI, a more than two-fold increase in total deployment life.

The new SAMI-CO_2 has many advantages over the original design, most of which are summarized in Table 1. First, with a thicker walled delrin enclosure it will be rated to 500 m depth instead of 100 m depth – a depth rating which will meet the needs of most researchers. We anticipate developing a 3000 m rated version after this version has been thoroughly tested . Because it will be substantially smaller, we can reduce the size of the mooring cage and ship the instrument separately from the mooring cage . (The current design is such that it is typically shipped in its mooring cage, at great expense due to weight and size.) The new design is much more power efficient than the old design, squeezing 4x the life out of 8 D-cells compared to the 18 D-cells in the original design.

Migration to a new data logger was required since the TFX-11 (Onset Computing) used by the SAMI-CO_2 was discontinued over a year ago. By moving to a custom data-logger, developed by Seawell Microsystems, we have consolidated all the necessary electronics on a board approximately ¼ the size of the combined 4 boards used in the old design (Figure 5), while increasing the available memory from 1 MB to 8 MB. Having the electronic board outsourced to a contractor will reduce our build times and significantly reduce costs. With fewer interconnections, reliability should be improved as well. This change also necessitates the migration to new software. While the TFX-11 and its TFBasic programming language did allow flexibility in programming individual devices, it has not been a very reliable platform. Lock-ups of the TFX-11 have resulted in numerous losses of data. Additionally, the client TFTools does not seem to work reliably on some newer computers. The new data-logger will allow firmware updates via a serial connection allowing “in the field” fixes if necessary.

The remainder of this report will focus on the optical sub-system and testing thereof.

Table 1: Summary of major design differences between original and new SAMI-CO_2 designs

	Original SAMI-CO_2	**New SAMI-CO_2 Design**
Depth rating	100 m or 1500 m	500 m or 3000 m (to be developed)
Power	18 D-cells with expected life of 1 year on hourly sampling intervals.	8 D-cells with expected life of 4.5 years on hourly sampling intervals and no ancillary sensors
Electronics – general	3 printed circuit boards built in-house with through hole components	1 printed circuit board with surface mount components
Data logger	TFX-11 by Onset (now discontinued) with 1 MB memory.	Part of main circuit board – 8 MB memory
Light source	Tungsten lamp in housing – 20 s warm up	2 LED's mounted to circuit board– no warm-up time.
Fibers	Fiber from lamp to flow-cell Fiber from flow-cell to bundled 1x3 fiber splitter Splitter to photodiodes	Fiber from LED beam splitter to flow cell Fiber from flow cell to photodiode
Photodiodes and Filters	3 photodiodes with 2 filters per photodiode – 6 filters total on analog board.	2 photodiodes – one for sample signal, oner for reference, one filter per LED – two filters total
Pump/Valve	Lee 50 µl pump and Neptune 3 way valve in silicon oil	No change
Software	TFBasic program on SAMI with TFTools interface (command line)	Custom firmware and GUI client interface.

Optical Subsystem

As discussed in earlier reports, one of the major efforts of this re-design has been to move from a tungsten lamp to LEDs. In the LED design, the two LEDs are turned on alternately for 100 µsec with a 5 msec interval between each sample with averaging of up to 256 samples. The signal is measured for each wavelength separately. Advantages to such a move are reduced power use and higher light throughput with a consequent reduction in noise due to lower amplification requirements. A number of designs were tested and found wanting, due to temperature sensitivity, mechanical instability, inadequate throughput, or complexity. Good results were obtained using a 2x2 fiber optic splitter, but even better throughput was obtained using the beam splitter (Figures 3B and 4). This design has the added advantage of greater simplicity and lower over-all cost.

The original SAMI-CO_2 design used a 600 μm fiber to transmit light (tungsten lamp source) to the flow cell and an optical fiber bundles to split the light coming out of the flow cell into 3 channels which were subsequently filtered with 436 nm, 620 nm, and 740 nm bandpass filters. The use of 2 modulated light emitting diode (LED) sources centered at 435.8 nm and 621 nm with 435.8 and 620 nm bandpass filters (Intor) eliminated the need for the reference wavelength (740 nm), since the light from each wavelength was split and used as a self-reference. This also changed the configuration of the optical fiber bundle to a 2×2 with input from both LEDs which were each evenly distributed to a reference fiber and a fiber that directed light to the flow cell. Data using this optical design was presented in the previous annual report (DeGrandpre et al., 2007). However, the optical fiber bundles were difficult to incorporate into the new SAMI housing design. We therefore replaced the optical fiber bundle with a 50% transmittance:50% reflectance plate beam splitter (Edmund Optics) to split each light source into sample and reference beams and a 0.2 optical density filter (Newport Corp) to attenuate the reference beam. This is shown schematically in Figure 3.

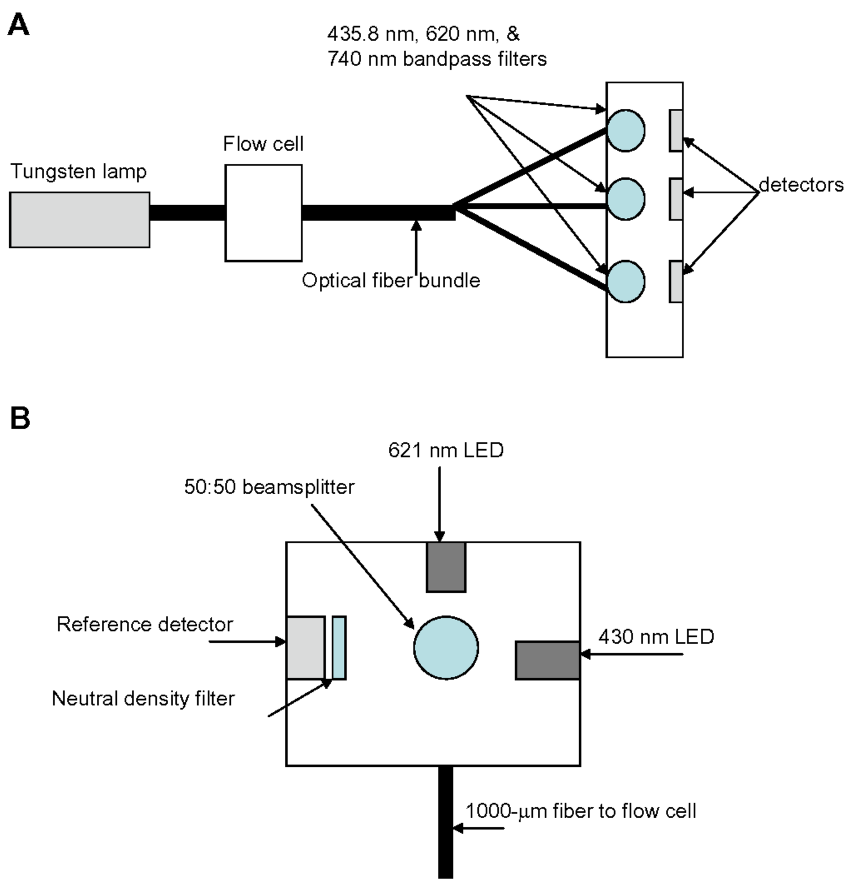

Figure 3: Optical design of **A)** old SAMI; **B)** LED-beam splitter SAMI.

Figure 4 shows how this design was implemented into the over-all design of the SAMI-CO_2 with the beam splitter housing being mounted directly to the new circuit board. The beam splitter housing is 1.5" square. The reference and signal photodiodes are located close together so they can use the same amplification circuitry while reducing noise. (Long signal paths for a small signal invite RF and thermal noise.) Figure 5 shows the first article board that is currently being tested on the bench top to establish design parameters.

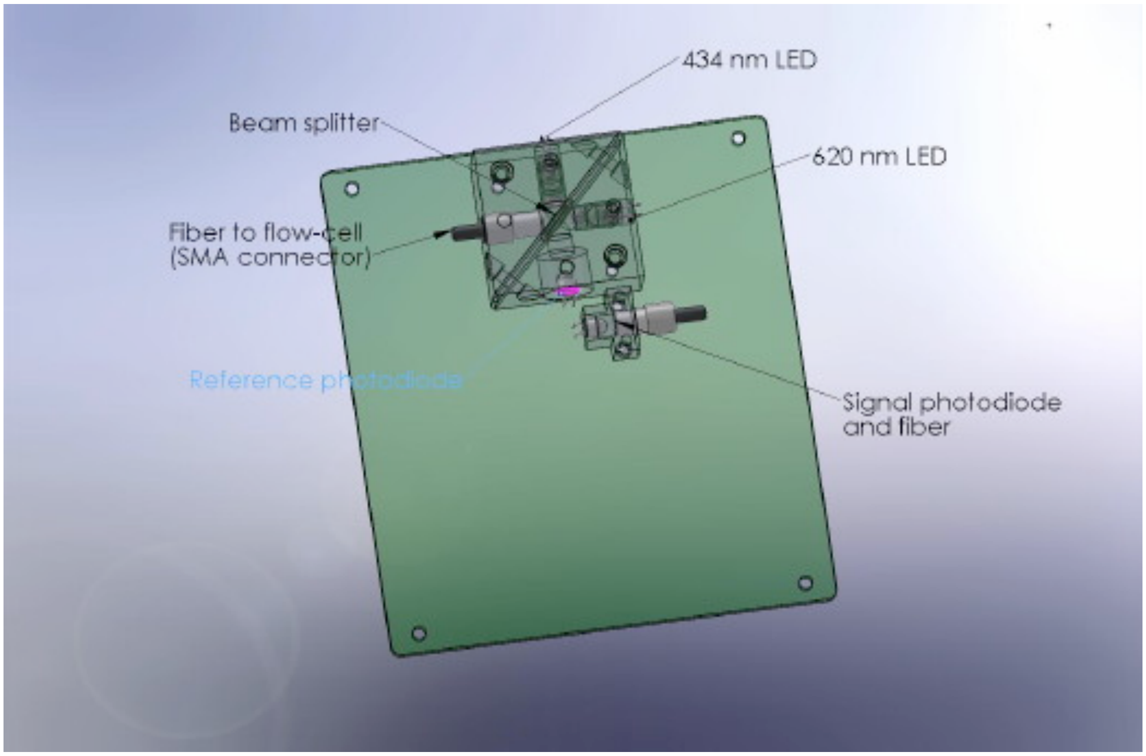

Figure 4: Drawing of the optical subsystem using a beam splitter and LEDs. Fibers not shown.

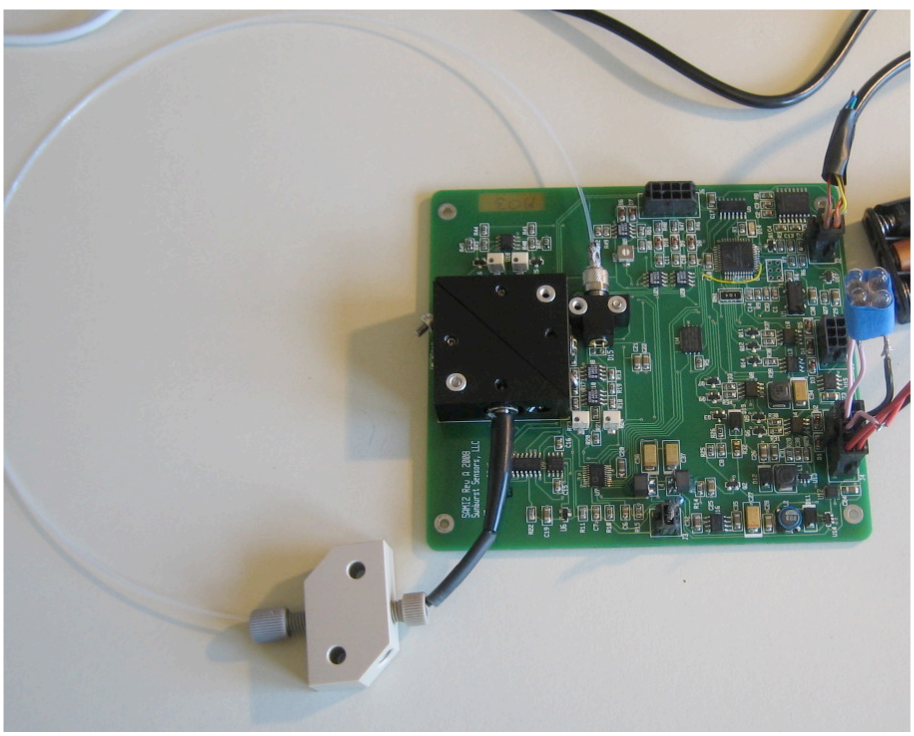

Figure 5: Bench-top testing of new board and optical subsystem.

LED-beam splitter SAMI calibration and comparison to LI-COR. Testing was conducted using the prototype electronics (i.e. breadboard) prior to giving the go-ahead for development of an actual printed circuit board. A test LED-beam splitter SAMI was built with a 0.6 mm i.d. white acetron GP flow cell and a 200-µL membrane, as these components have proven to produce the least amount of acidic contamination in the reagent (DeGrandpre et al., 2007). The test SAMI was fitted with a 20ºC water bath, which immersed the membrane and flow cell, and calibrated at 5 pCO_2 levels, from ~200 – 600 µatm, equilibrated in water and verified by measurements on a Li-6251 (LI-COR Biosciences). Figure 6 shows the LED-beam splitter SAMI calibration curve compared to the theoretical calibration curve and calibration of a SAMI with the same flow path design but the older optical design (Tungsten light source with optical fiber bundle and 3 optical bandpass filters).

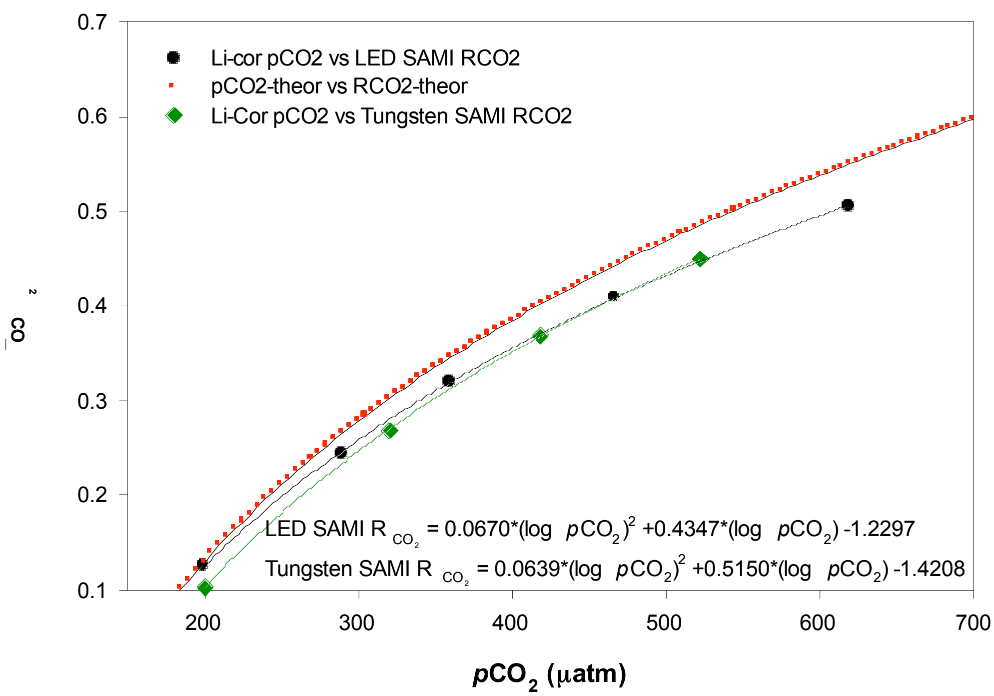

Figure 6: Calibration plots and regression equations for LED-beamsplitter and Tungsten light source SAMIs.

After calibration, the test SAMI was immersed in a ~200-L tank that was connected to a temperature-controlled water bath. A MiniModule (Liqui-Cell Membrana) gas exchanger and a SAMI with the older optical design were also in the test tank. Air equilibrated in the MiniModule with the pCO_2 levels in the tank water and was then dried and directed to a Li-840 (LI-COR Biosciences) for pCO_2 measurement. Figure 7 shows results from 2 weeks of measurements with water temperatures between 8°C and 25°C.

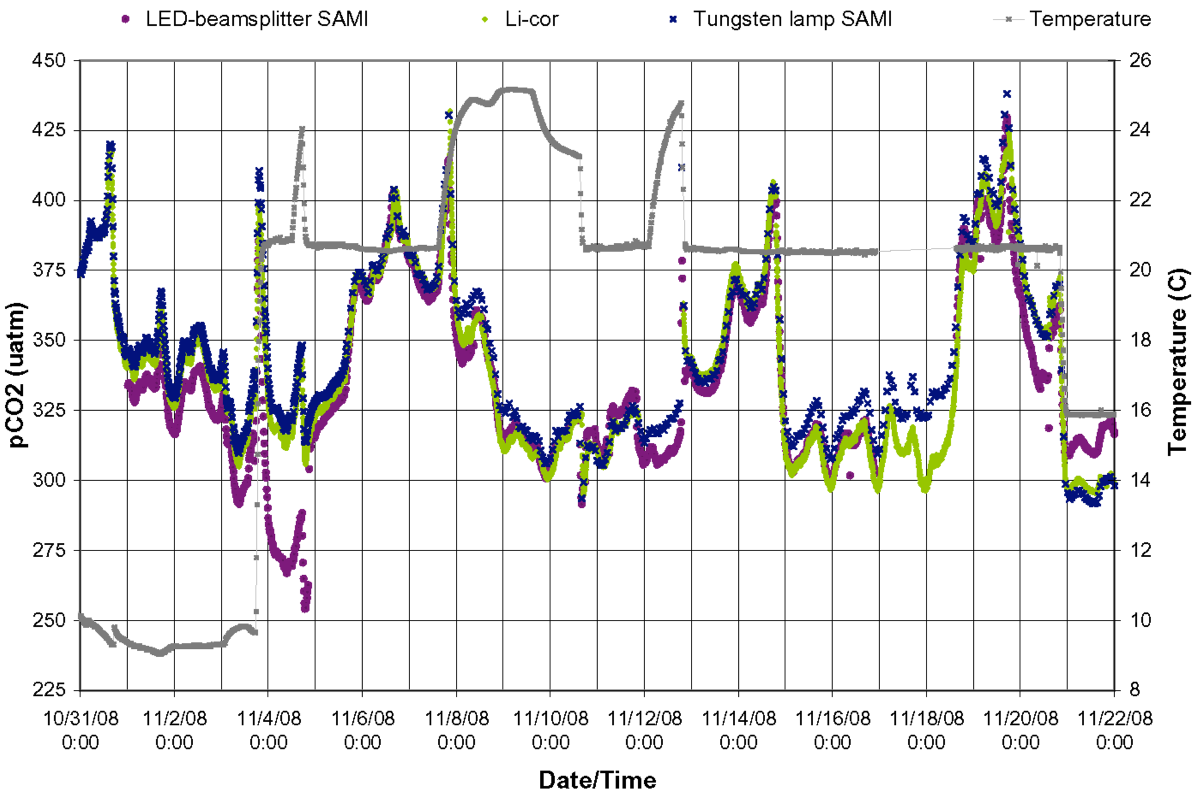

Figure 7: pCO_2 data from LED-beam splitter SAMI, MiniModule membrane contactor/LI-COR, and Tungsten lamp SAMI in a 200-L tank filled with water and thermostated with a circulating water bath.

The signal from the LED light source is more dependent on temperature than that of the Tungsten light source whereas the magnitude of change in the 436 nm signal is similar for both sources. The effect of temperature on blank signal is shown in Figure 8 for the LED-beam splitter SAMI (K_i = (signal through flow cell at wavelength i)/(signal of reference beam at wavelength i) and the SAMI with a Tungsten source (K_i = (signal through flow cell at wavelength i)/(signal through flow cell at 740 nm).

A change in temperature will cause the LED-beam splitter SAMI pCO_2 measurements to be offset from LI-COR measurements (Fig. 3), but after a blank is analyzed at the new temperature the pCO_2 levels will again match the LI-COR. Blanks can be used to back-calculate pCO_2 for all samples at the same temperature. However, the inside of the current SAMI housing (old design) takes at least 5 hours to equilibrate to ambient temperature, so the blank must be analyzed more than 5 hours after the temperature change occurs. When the prototype SAMI with LED-beam splitter optics and new housing is complete, we will thoroughly characterize the blank signal changes due to temperature. This will determine the length of time required for temperature equilibration after a temperature change occurs and the magnitude of temperature change that necessitates blank analysis. The results will be incorporated into the SAMI operating program to dictate when blanks are analyzed in the field.

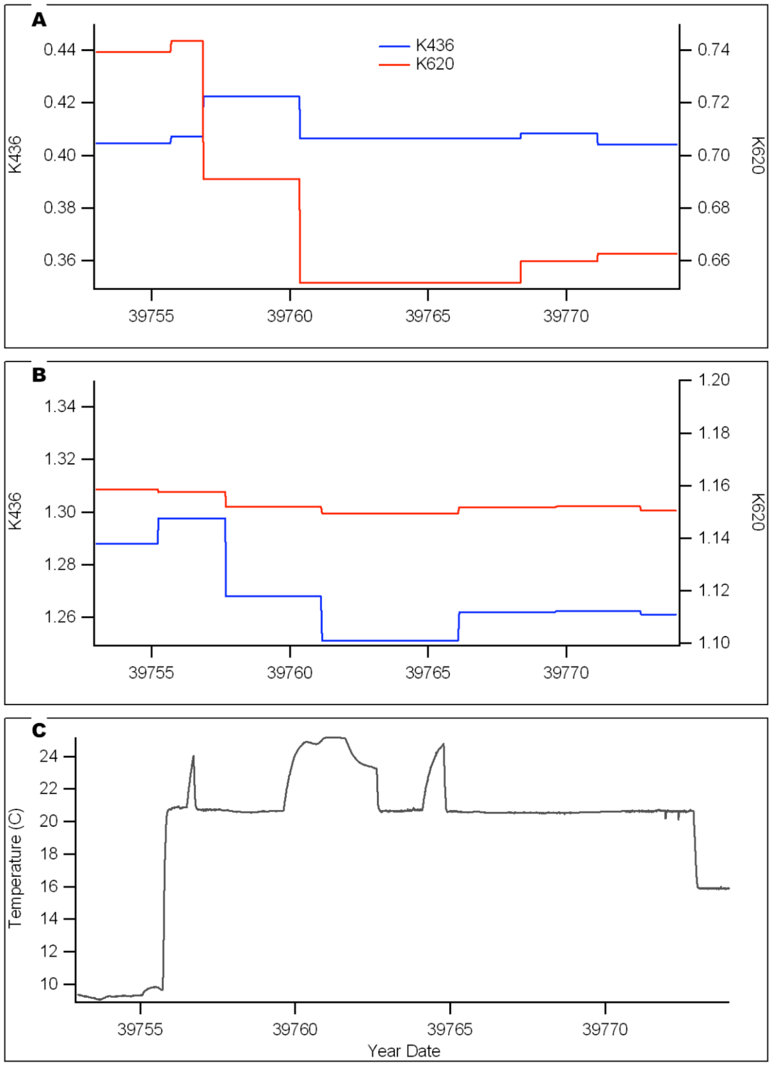

Figure 8: Change in blank signals with changing temperature. **A)** LED-beamsplitter SAMI (K_i = [signal through flow cell at wavelength i]/[signal of reference beam at wavelength i]); **B)** Tungsten light source SAMI (K_i = [signal through flow cell at wavelength i]/[signal through flow cell at 740 nm]); **C)** Temperature.

IMPACT AND APPLICATIONS

Economic Development

This research and development will help make the SAMI-CO_2 a robust, less-expensive means of measuring seawater pCO_2. The high cost and complexity of the current design is a disincentive to sales, and widespread adoption within the oceanographic research community. This work may also be the springboard for moving the technology into other research areas, such as atmospheric CO_2 measurements and industrial applications.

References.

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DeGrandpre, M.D.; Beck, J.C., Hammar, T.R.; Dickenson, A. **Commercialization of autonomous sensor systems for quantifying pCO_2 and total inorganic carbon.** Annual Report to NOPP for award #: OCE-052955 (2007).