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

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LONG-TERM GOALS

Our research efforts are directed toward developing a variety of innovative chemical sensors. In addition to CO_2, we are working toward developing innovative alkalinity and pH sensors and incorporating our technology into autonomous long-term monitors.

OCEAN PLATFORMS. 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). 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, is complex and prone to failures, especially by customers who are not trained to operate the SAMI. Incremental changes in the design have 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.

APPROACH AND WORK PLAN

We have identified the following problem areas requiring improvement to the existing SAMI-CO_2 design (in no particular order) followed by the proposed solution and key individuals:

1) **Reagent and blank flushing** - A variety of minor plumbing problems can lead to measurement errors. For the redesign we are testing or will test 1) larger ID silicone rubber tubing or alternative, e.g. thin-walled Teflon AF tubing, 2) opening up the bore of the cell outlet to allow bubbles to freely pass, 3) new optical cell designs that eliminate the 90^o flow configuration and 4) a separate sensor housing.

   Key to this effort are DeGrandpre, Jim Beck (Sunburst Sensors) and Terry Hammar (WHOI). Progress (see below) has been made in all areas except the design of a separate housing, which will occur in the coming year.

2) **Electronic drift –** The current design requires very high gain ($\sim10^9$) amplification, which is problematic. We have found that poor shielding, solder joints and inconsistent op amp performance lead to drift in the dark signal of the 434 channel. While we proposed to make and have made improvements to the existing design and manufacturing techniques, using dual op-amp IC's, we have also come up with an innovative design which may solve this problem while simplifying the over-all design. (Described in 'Work Completed' below.)

   Key to this effort are DeGrandpre, Jim Beck and Dave Kemple (Sunburst Sensors). Progress (see below) has been made in this area, with considerable work to be completed in the first half of 2006.

3) **Optical cell complexity and performance –** The current optical cell and equilibrator is expensive and difficult to manufacture and maintain. The design readily traps bubbles because of the 90^o entrance channels and the small bore of the optical cell (0.6 mm). Because of the difficulty in assembling the cell correctly, users are discouraged users from troubleshooting this part. We are investigating innovative designs of both the equilibrator and the optical cell to reduce or eliminate these problems.

   Key to this effort are DeGrandpre, Cory Beatty (UM), Jim Beck and Terry Hammar. Progress (see below) has been made in the design and fabrication of a planar equilibrator and an improved flow cell. The coming year will see significant progress in testing and refining these designs.

4) **Calibration complexity –** Calibration set-up is complicated and expensive. Users cannot do it on-site. We will design a jacketed gas cell to enclose the new optical cell to eliminate the need for the large chamber and feed-through used for calibrations. All users with a good quality water bath (e.g. ±0.1 C temperature stability) and 3-5 gaseous CO_2 standards will then be able to calibrate their own instruments.

   Key to this effort are DeGrandpre, Jim Beck and Terry Hammar. No significant progress has been made on this task, but an effort is planned to begin in the second quarter of 2006.

5) **Software –** Both firmware and client software need to be upgraded in terms of reliability, flexibility and user friendliness. We are developing a GUI to simplify control, graphing and

data analysis, and allow easy export of data in spreadsheet or other formats. With a coordinated effort to improve the existing firmware (Onset), the system will also allow troubleshooting of remote units via internet protocols. The software will be adaptable for different modes, e.g. continuous on screen monitoring on a volunteer observing ship, data downloading, setting up instrument parameters, or calibrations.

Key to this effort is Jim Beck. Testing will be performed by UM personnel, including DeGrandpre. Significant progress has been made and we are planning for beta testing of the software for second –third quarter of 2006.

6) **Documentation –** System documentation for users is very poor. Documentation will be an ongoing effort as design improvements are made to the system.

   Key to this effort is Dave Kemple (Sunburst Sensors) who has brought the documentation up to date. Effort here will be ongoing as improvements are incorporated.

7) **Optimization of size, power, and manufacturing cost –** The technology can be more widely used (e.g. in profiling floats) if the package is made smaller, less power hungry and less expensive. Optimization will be driven by developments in the electronics and optical cell designs described above. in items 1, 2 and 3.

8) **Environmental testing** - Because the ‘use-environment’ is very hostile, real-world testing is required to validate improvements. This testing will occur as significant design improvements are adopted. Laboratory testing will be performed by Beatty. Beatty and Kemple will perform the field-testing in Montana. Andrew Dickson will oversee the seawater testing. Undergraduate research assistants will participate in the field-testing and data interpretation. Testing may begin in late 2006.

WORK COMPLETED

1) **Reagent and blank flushing** - Design and fabrication of a larger bore optical cell without the 90° angles and minimal ‘dead volume’ has been completed. Testing of this design has just begun. Testing of larger diameter silicon tubing for an equilibrator is underway, but may be superseded by planar equilibrator discussed below (item 3).

2) **Electronic drift –** A new design using narrow band, high output LED is being developed and tested. Current testing is bench-top. Preliminary testing shows LED’s to be ~250x as bright as current tungsten lamp. Investigating using pulsed LED circuit with feedback to increase output further and to reduce DC drift and noise. Design is lower power since no amp/lamp warm-up is required. Schematic of design is shown in Figure 1.

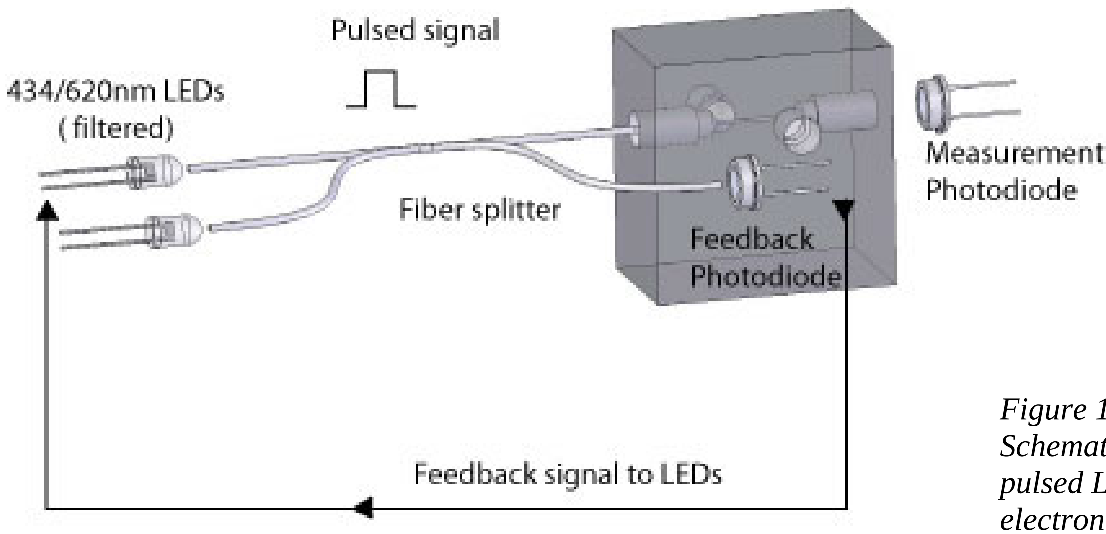


Figure 1: Schematic of pulsed LED electronic design.

3) **Optical cell complexity and performance** – A planar equilibrator has been prototyped and testing has begun to investigate response time. Prototype design uses 'sandwich approach' where very shallow (.005") channel on reagent side of membrane is formed by cutting channel in thin sheet of PEEK and capturing with membrane between two blocks of plastic with plumbing. Channel on opposite side of membrane (seawater side) is deeper and machined. (See Figure 2)

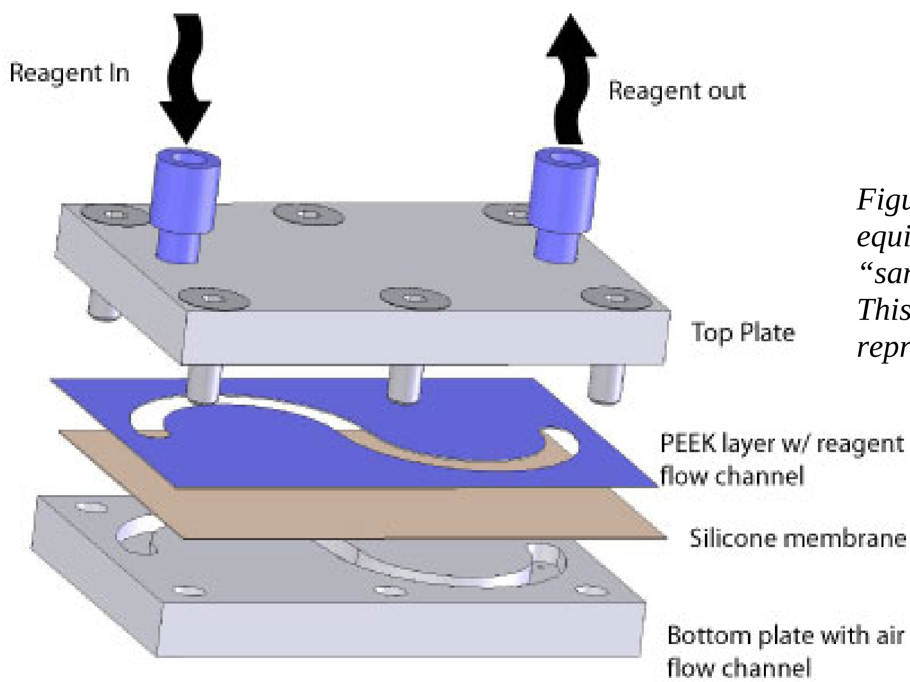


Figure 2: Planar equilibrator using "sandwich" design. This is a schematic representation only.

4) **Calibration complexity –** No significant work accomplished yet. Significant effort planned for 2nd quarter of 2006.

5) **Software -** Graphical user interface software for client approximately 50% complete. Improvements to accompanying firmware also made. Figure 3 shows a sample of the user interface.

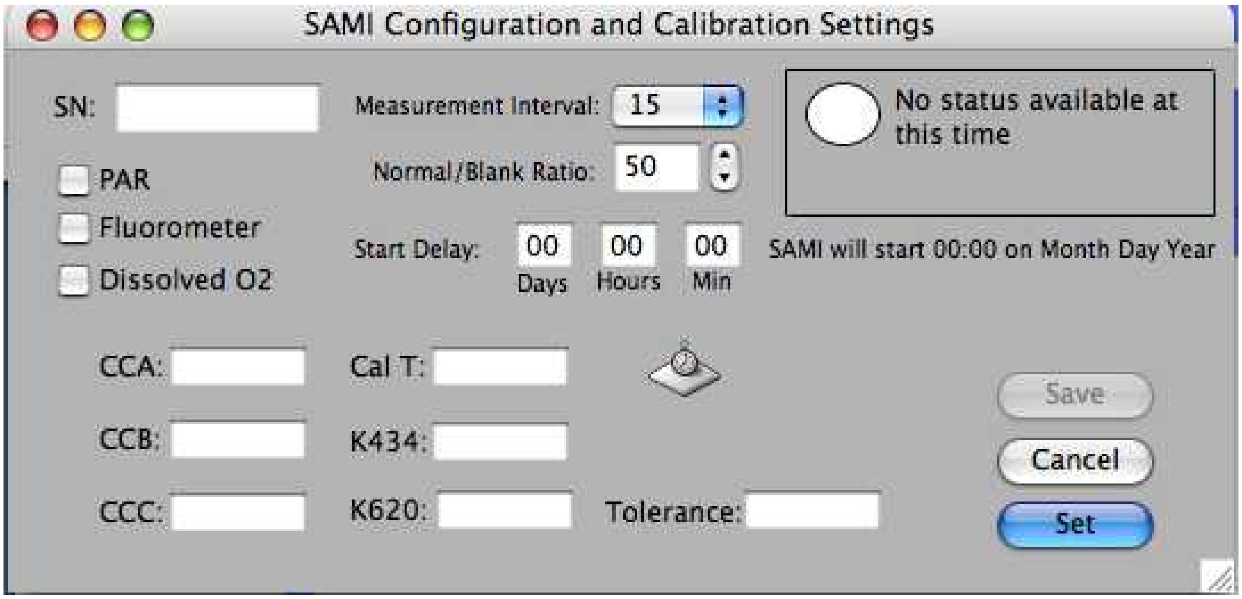


Figure 3: Sample of graphical user interface for SAMI client software.

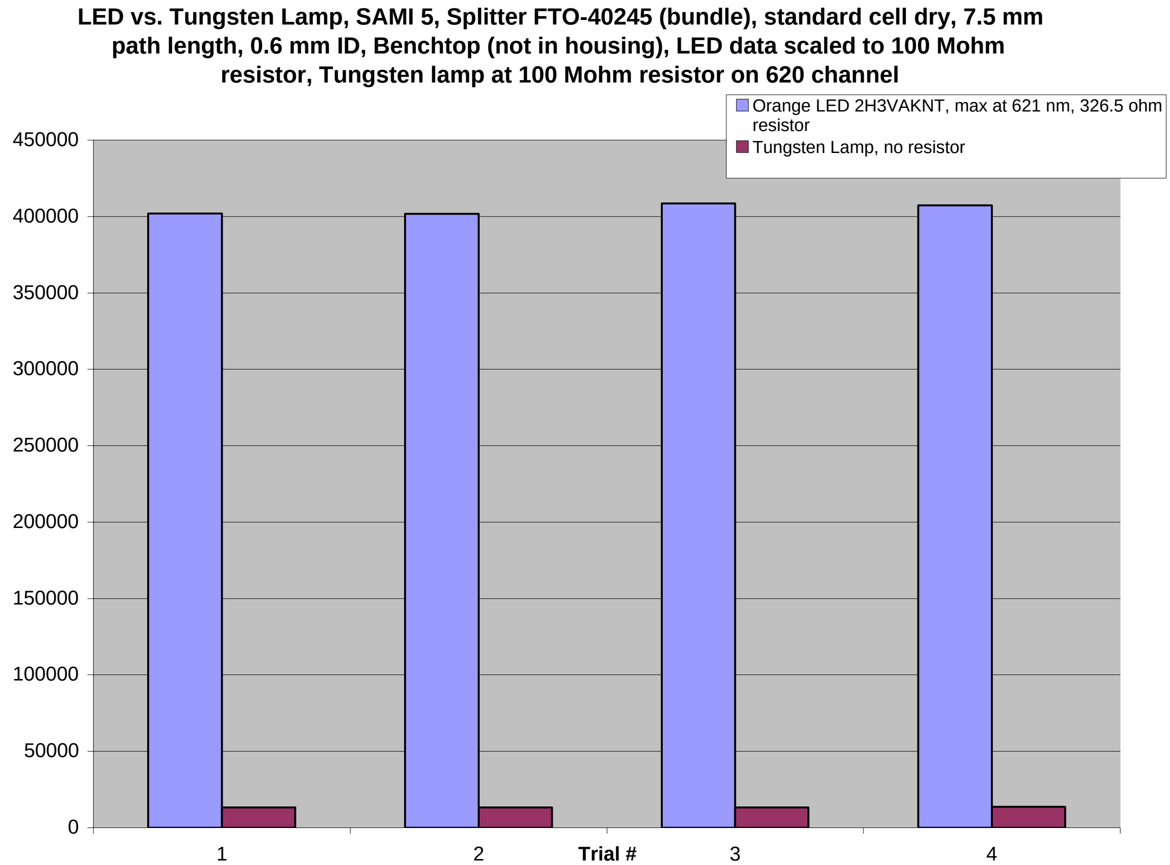
6) **Documentation –** Documentation for existing SAMI completed. Ongoing effort to maintain documentation to reflect design changes.

7) **Optimization of size, power, and manufacturing cost -** Dependent on further development of items 1, 2 and 3 above.

8) **Environmental testing –** None yet. Should be underway in late 2006.

RESULTS

Our most significant finding to date is that narrow band LEDs are significantly brighter than current tungsten lamp at the wavelengths of interest (434 nm, 620 nm). Use of pulsed LEDs may lead to very significant design improvement, not anticipated in proposed work. Figure 4 below shows the output of the 620 nm LED as compared to current lamp. LED output is only ~15% of steady state maximum so actual brightness is close to 200x that of tungsten lamp.



IMPACT AND APPLICATIONS

Economic Development

This research and development will help make the SAMI-CO_2 a robust, less-expensive means of measuring pCO_2. The high cost 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 measurement.