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, 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 identified the following problem areas requiring improvement to the existing SAMI-CO_2 design in our grant proposal:

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.

2) **Electronic drift –** The current design requires very high gain (~10^9) 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.

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.

4) **Calibration complexity –** The calibration set-up is complicated and expensive. Users cannot perform calibrations 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.

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, 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.

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

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.

WORK COMPLETED

1) **Reagent and Blank Flushing –** Testing of a new larger bore (1.0 mm) optical cell in the Z-cell configuration has been completed. Combined with larger bore back pressure tubing, the Z-cell produces fewer bubbles and allows for flushing of bubbles in just 2-3 pumps. Large diameter silicon rubber tubing was briefly tested but contamination problems led to more testing of our standard bore tubular membrane.

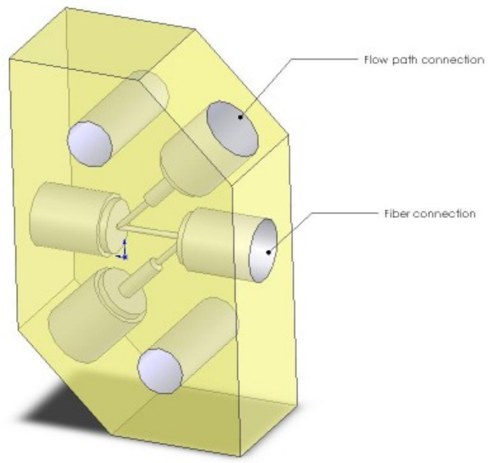


Figure 1: Z-cell design reduces bubble trapping and dead volume problems inherent to current 90° flow cell design.

This testing has shown that the Delrin and PEEK optical cells may be leaching an acidic contaminant into our reagent, changing the SAMI response (RCO_2) when the SAMI is operated with different off-times. Testing has also shown that the rubber fittings inside our pump may be a basic contaminant. This type of error can be corrected for in calibration, which is why it was probably not discovered until recently. It does make operation of the SAMI-CO_2 less flexible, and calibration more time consuming. Further investigation should resolve this and may lead to different material specifications for parts in contact with the reagent.

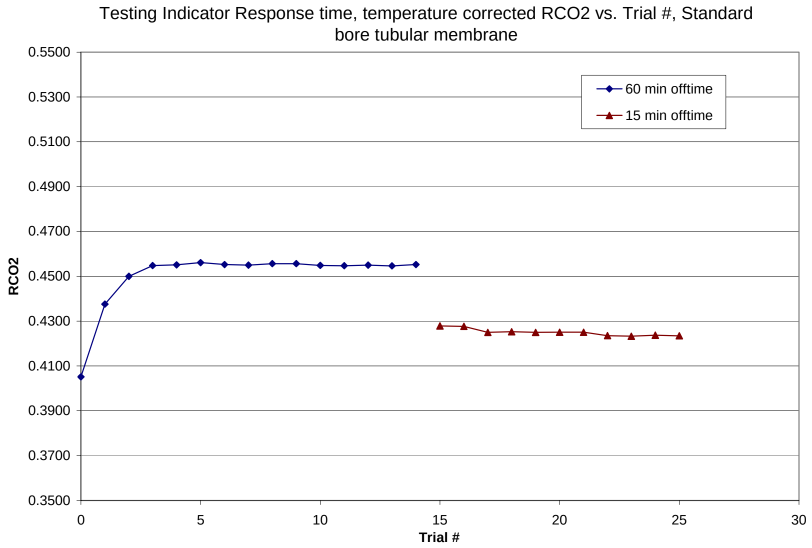


Figure 2: Testing has revealed that sampling time of the current system is affecting the RCO_2 response. Contamination by materials in the flow path are being investigated.

2) **Electronic drift -** The original intent of this objective was to address the current design's shortcomings. In the grant proposal we proposed to make improvements to the existing design and manufacturing techniques, using dual op-amp IC's. We have achieved this goal and are using the LT1462 op-amp in current builds on an analog board that is half the size of the original. Beyond this, however, we have embarked on a much more ambitious effort to redesign the entire electrical system. While the current system uses a tungsten white light source, we have designed an LED based system that should greatly simplify the overall design of the system. In

the new optical design, two LED's at the wavelengths of maximum absorbance (434 nm and 620 nm) are alternately shone through the sample into a single detector (Figure 3). A separate light path to another detector is used as a reference for the drift of the light sources. The system rectifies the two signals and the two references into DC voltages. A hardware based version of this has been built and tested, while a microprocessor based system is almost finished.

The microprocessor based system will be part of an entirely new data logger and power supply. We had entertained the idea of going to a custom data logger early in the year but decided to delay that development. Then Onset, the company that manufactures our current data logger the TFX-11, announced it would end production of the TFX-11. We decided at that point to move forward with a custom data logger. A prototype, including firmware and a simple software client, is very close to being finished. The end product will be a surface mounted printed circuit board that will do the job of 4 separate circuit boards in the current design, and use approximately 70% less space. Other advantages include the ability to upgrade firmware in the field, which is impossible with the current system.

These developments should allow the SAMI-CO_2 to be a much smaller, easier to manufacture instrument. The figure below represents a possible design for the flow cell and optics of such a system.

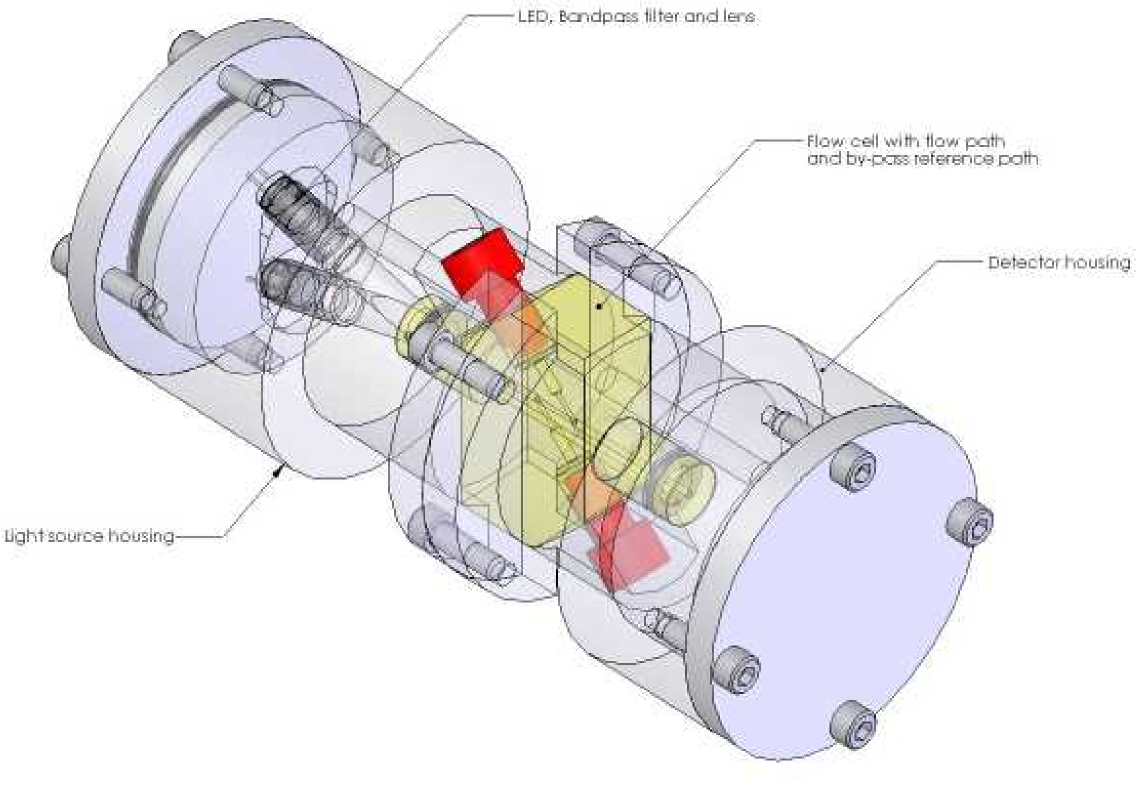


Figure 3: Initial design of the submersible optoelectronic vessel containing flow cell, light source (LED's), and photodetectors. Work is underway to incorporate a planar equilibrator into the design.

3) **Optical cell complexity and performance –** The new Z-cell optical cell design (Figure 1) is much easier to assemble than the 90° design. Flat bottomed fibers are easier to insert and the glass windows separating the reagent from the fibers allow for much quicker flushing of bubbles.

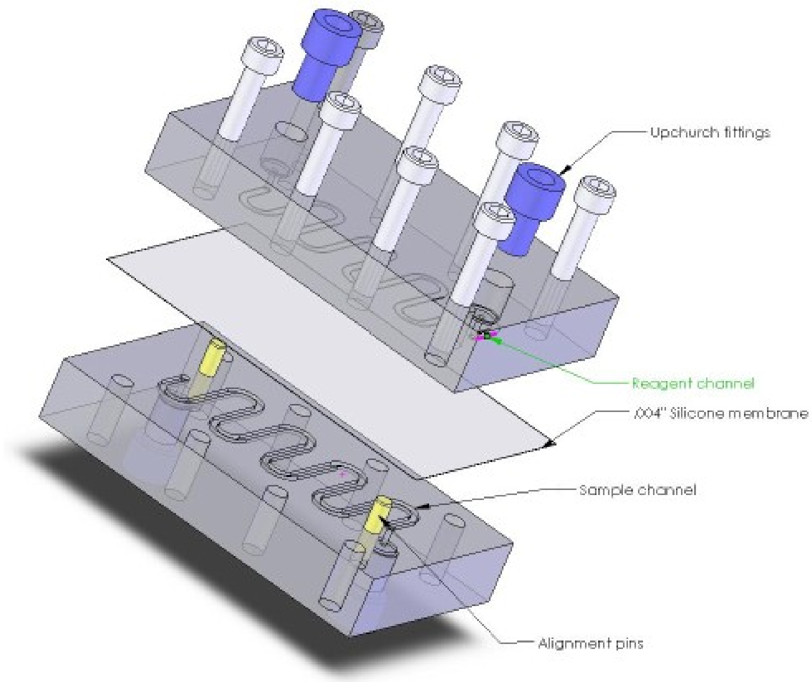
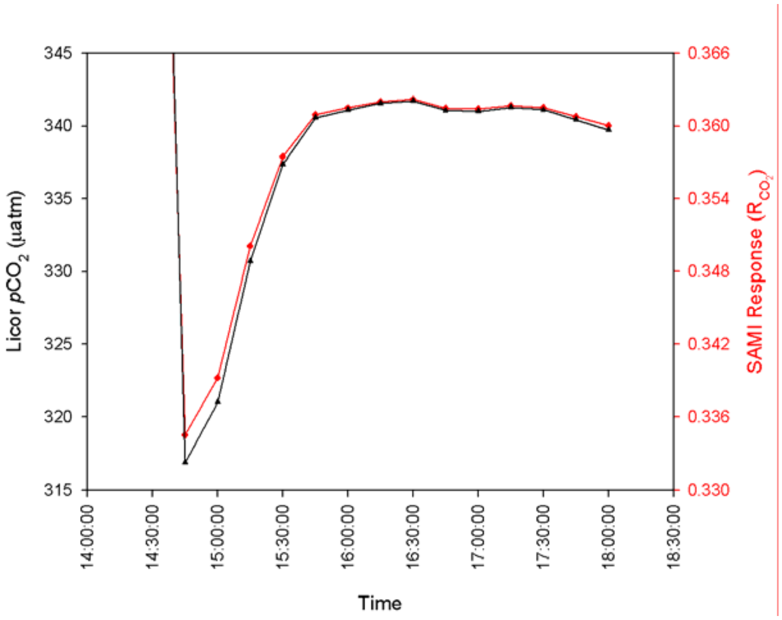


Figure 4 : Prototype flat membrane equilibrator. Silicone membrane is stretched between two plates with flow channels. Design and assembly are much simpler than the current tubing equilibrator.

The first planar membrane design, shown in Figure 4, has also performed well (Figure 5). Both flushing and bubble performance look very good. The planar membrane cell was calibrated and tested for response time using both silicone rubber and Teflon membranes. Both materials showed similar responses, although the silicone rubber membrane is easier. In the prototype design, the reagent is pumped on one side of the membrane and sample is pumped on the other, through shallow serpentine channels. In refining the design we will make it smaller, and will investigate a design that does not require a sample pump.

Figure 5: Response of SAMI-CO_2 using a flat membrane equilibrator (red curve) compared to a Licor infrared CO_2 measurement (black curve).



4) **Calibration complexity** – A jacketed gas cell, which encloses the tubular membrane and attaches to the new Z-cell optical cell, was designed and tested. The new cell performed similarly to the jacketed cell used for our 90° optical cell. A calibration program, written in LabView, was developed to automatically control the varying gas flows used in a calibration. Calibrations are now significantly faster because standards can be changed automatically rather than waiting for a technician to change concentrations during the day. We are working to develop this system to the point that customers can do their own calibrations. Automating the system is a very large step in this direction.

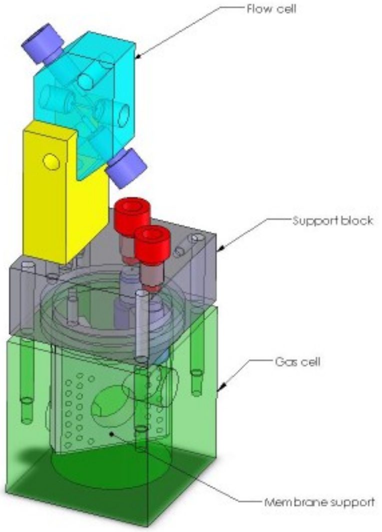
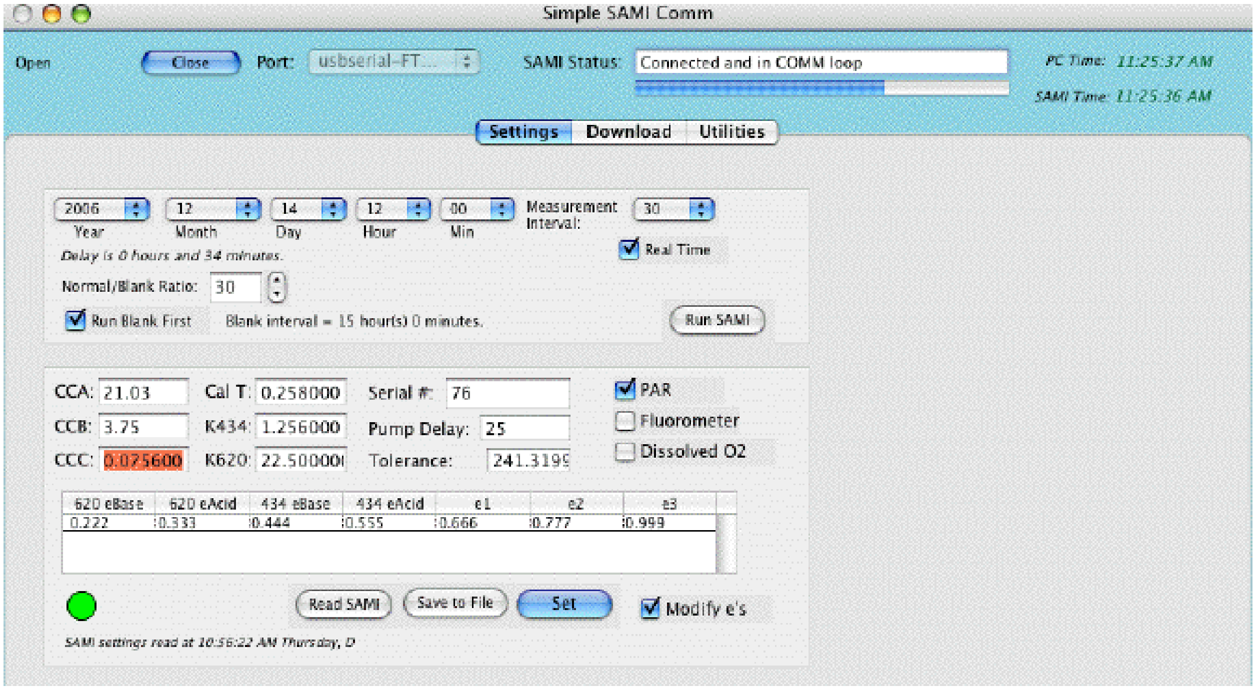


Figure 6: Drawing of the membrane equilibrator and flow-cell with the jacketed gas cell (green). Tubing and fibers are not shown.

5) **Software** - New client software and firmware was developed for the existing SAMI-CO_2. This software allows users to program the instrument and download the data and is much more user-friendly than the current software. The client of the new software, shown below, will be



Port: usbserial-FT...

SAMI Status: Connected and in COMM loop

PC Time: 11:25:37 AM

SAMI Time: 11:25:36 AM

Year: 2006
Month: 12
Day: 14
Hour: 12
Min: 00

Measurement Interval: 30

☑ Real Time

Delay is 0 hours and 34 minutes.

Normal/Blank Ratio: 30

☑ Run Blank First

Blank interval = 15 hour(s) 0 minutes.

CCA: 21.03
CCB: 3.75
CCC: 0.075600
Cal T: 0.258000
K434: 1.256000
K620: 22.50000
Serial #: 76
Pump Delay: 25
Tolerance: 241.3199

☑ PAR
☐ Fluorometer
☐ Dissolved O2

620 eBase	620 eAcid	434 eBase	434 eAcid	e1	e2	e3
0.222	0.333	0.444	0.555	0.666	0.777	0.999

☑ Modify e's

SAMI settings read at 10:56:22 AM Thursday, D

Figure 7: Front screen of the new SAMI-CO_2 client software. It allows the user to program the start-time, sampling interval, and various other parameters. It also allows real-time display

adapted to work with the new data logger as soon as the firmware is finished. Most of the difference between the two will be the communication protocols and should not take much effort to complete.

6) **Documentation –** The existing SAMI-CO_2 is now well documented with extensive PDF based instructions, including diagrams and digital photos to assist users in troubleshooting, etc. The documentation is included with every shipment on a CD. It is also available from our website: (www.sunburstsensors.com).

7) **Optimization of size, power and manufacturing cost –** This is well underway as discussed in sections 1, 2, and 3 above and described in Figures 3 and 4. In terms of power use, we are estimating a full year's operation using only 7 D-size alkaline batteries, as compared to 18 D-cells in the current system. Beyond the obvious power savings, this is also a greater than 60% savings in weight and volume of the battery packs. The LED design, which does not require significant warm-up of the amps or light sources, is responsible for this improvement. The combination of the multiple printed circuit boards into one will also allow a large reduction in the volume.

8) **Environmental testing** - We hope to begin environmental testing of some of the various subsystems in the first quarter of 2007 and continue as the entire product comes together through the year.

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.