

Commercialization of autonomous sensor systems for quantifying pCO₂ 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-CO₂, a sensor developed for autonomous measurements of the partial pressure of CO₂ (pCO₂) in seawater. The SAMI-CO₂ 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 pCO₂ measurements reliably over long time periods in widespread ocean locations on many different ocean platforms.

PROGRESS

Work has focused on completing the re-design. Two major hurdles have been to test the LED light source, and to isolate and eliminate the temporal drift of R_{CO_2} to allow for varying sample intervals without re-calibration.

LED LIGHT SOURCE

The SAMI electronics were re-designed so that light emitting diodes (LED) can be used as the light source. A 621 nm LED (Lite-on Electronics, Inc.) and a 430-435 nm LED (Roithner Lasertechnik) were modulated at 512 Hz and 256 Hz, filtered with 620 and 435.8 nm bandpass filters (Intor), coupled to a 2×2 optical fiber bundle (Fiber Tech Optica) with 720- μm input bundles and 250- μm and 1000- μm output bundles that coupled to a reference photodiode and a black Delrin™ optical flow cell, respectively.

Temperature dependence. Individual components of the LED SAMI were evaluated for temperature effects as follows. 1) The emission intensity and spectra were measured at temperatures between 5° and 35° C with the LEDs encased in an aluminum housing and immersed in a water bath; 2) intensity of light passing through the optical flow cell was measured at temperatures between 10° and 30°C with the flow cell immersed in a water bath; and 3) measurements were taken with the LED SAMI electronics encased in the SAMI PVC housing which effectively thermostats the electronics over time periods <5 hours because of the time required for the air inside the housing to equilibrate to the temperature outside the housing. The conclusions from these experiments were that each component causes a temperature-dependent light signal. As shown in Figure 1, if the SAMI electronics are at the same temperature as the optical flow cell, the reference signal behaves similarly to the sample signals, and therefore subtracting the reference absorbance from the sample absorbance at each wavelength (indicated by corrected signals in Figure 1) largely removes the temperature dependence of the signal. However, when the electronics are enclosed in the SAMI housing, they remain at a relatively stable temperature while the flow cell is exposed to changing temperatures. In this case, the reference signal is very stable but the sample signal changes with temperature. The reference signal therefore cannot be used to correct for the temperature-dependence of the sample signal. The difference between the reference and sample temperatures could potentially be a problem in the field since the SAMI electronics must be enclosed in the housing to keep them dry. A possible solution is to use housing material that allows more rapid temperature equilibration.

Absorbance precision. Absorbance precision was calculated as 1 standard deviation of the signals measured over 4 hours at a stable temperature. Precision was calculated from light signals measured every 10 seconds in a dry flow cell and every 5 minutes after pumping 50 μL of $5 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$ bromothymol blue (BTB) solution buffered at pH 7.4. As shown in Table 1, pumping the BTB solution caused about an order of magnitude increase in signal noise. However, even with the higher noise of the BTB solution the precision is close to that required to achieve an overall measurement precision of $\pm 2 \mu\text{atm pCO}_2$, which is approximately 0.0016 AU at 436 nm and 0.0012 AU at 620 nm if signals at the two signals diverge; if the two signals covary the noise can be higher.

LED SAMI calibration. The LED SAMI was immersed in a 20°C water bath, molar absorptivities at 436 and 620 nm were measured, and the SAMI was calibrated 4 times. Three of the calibrations included 5 pCO_2 levels, from ~200 – 600 μatm , while one calibration included

only 4 pCO₂ levels, from ~200 – 450 μatm. Three of the calibrations started with the highest pCO₂ level and ended at the lowest level, while one calibration started with the lowest level. Parts of the detection system were disassembled and re-assembled between the first and

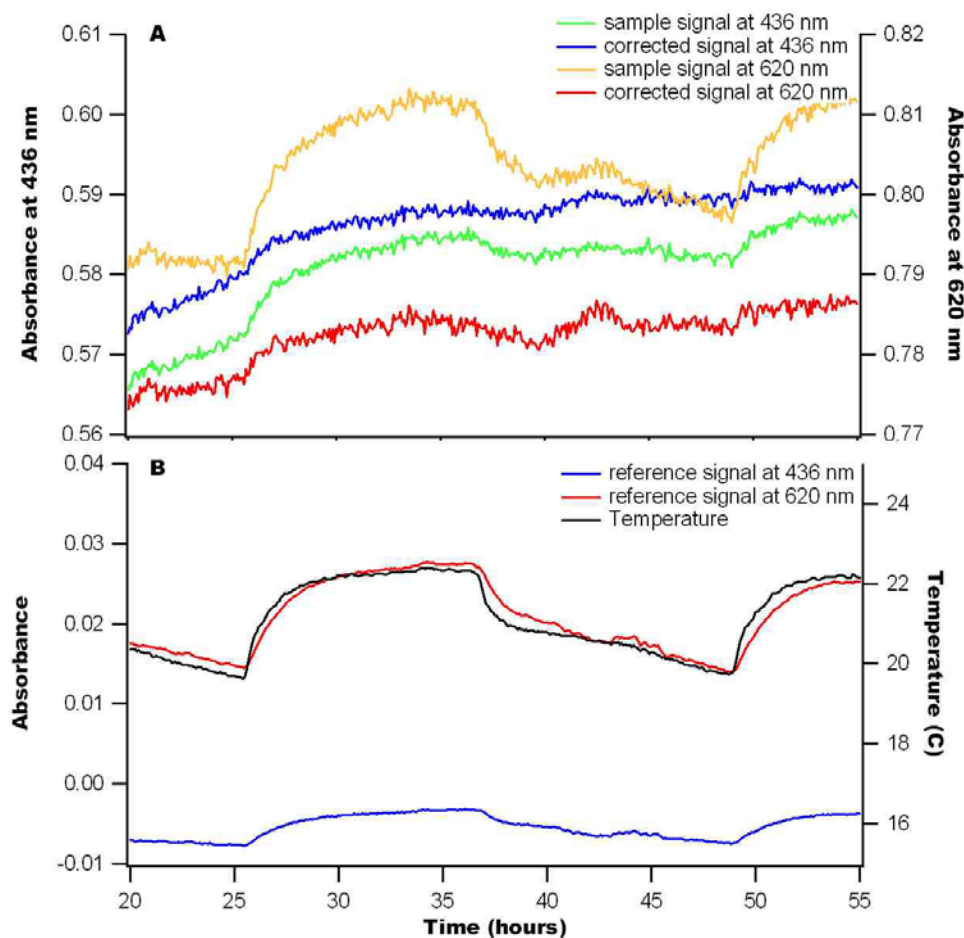


Figure 1. A) Raw and corrected (raw absorbance – reference absorbance) absorbances from the sample signals, and B) absorbances from the reference signals, at 436 nm and 620 nm, for a solution of $5 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$ BTB solution, buffered at pH 7.4. Fifty microliters of BTB were pumped every 5 minutes and an absorbance reading was taken ~10 sec after the pump pulse.

Table 1. Average signals and absorbance precision for the LED SAMI with a dry flow cell and with $5 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$ BTB pumping through the cell at 5-min intervals.

Wavelength	Gain	Flow Cell Contents	Average Signal	Absorbance Precision
436 nm	2.4×10^7	air	22000 ± 6	0.00011
620 nm	2.4×10^7	air	38000 ± 5	0.00008
436 nm	9.4×10^6	BTB	5200 ± 21	0.0018
620 nm	9.4×10^6	BTB	4500 ± 14	0.0014

second calibrations. The LED SAMI calibration curves are compared to a theoretical calibration curve and 4 traditional SAMI calibration curves in Figure 2. All R_{CO_2} values were corrected to 19.98°C. The LED SAMI curves are positively offset from the theoretical curve and show greater divergence from the theoretical curve at lower pCO_2 than at higher pCO_2 . The difference between the LED SAMI and the traditional SAMI calibration curves could be due to different band width and center wavelength of the light sources.

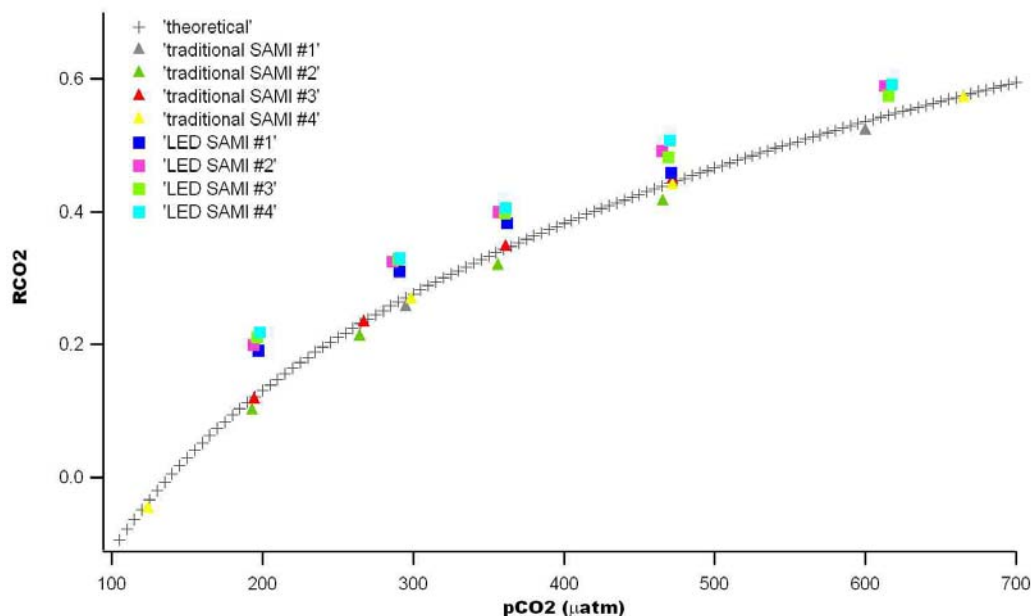


Figure 2. Comparison of calibration curves from 4 traditional SAMIs, 4 replicate calibrations from the LED SAMI, and a theoretical calibration curve. R_{CO_2} is calculated from the absorbances at 436 nm and 620 nm and the molar absorptivity values of the acid and base forms of BTB at the same wavelengths (DeGrandpre et al., 1995).

R_{CO_2} TEMPORAL DRIFT

Recent studies have found that the responses of SAMI- CO_2 sensor (R_{CO_2}) differ significantly between the measurements based on 15-minute interval and those based on 60-minute interval. R_{CO_2} is directly related to pCO_2 of the sample solution and indicates how far away the indicator pH is from the indicator pK_a . As shown in Figure 3, the difference between measurements at 15-minute and 60-minute intervals can be at least 0.02, which corresponds to 20 ppm CO_2 . Further experiments have discovered that the acidic contamination from the flow cell material leads to higher R_{CO_2} at a 60-minute interval. We have bubbled the same BTB indicator with the same concentration CO_2 , and then measured R_{CO_2} of the well-equilibrated indicator solution with a glass cuvet on a spectrophotometer. The response R_{CO_2} was very stable (<0.005 for an hour) during the hourly measurement period.

Several separate efforts have been made to minimize the acidic contamination from the cell material. First, NaCl was added to the BTB indicator to increase ionic strength and suppress ionic exchange between the cell surface and the indicator solution. Second, BTB indicator was dissolved in 10% methanol solution since methanol may help flush the contamination more efficiently. Third, the more soluble pH indicator Cresol Red (CR) replaced the current BTB

indicator to reduce the indicator adsorption on the cell surface. Fourth, the chemically inert material PTFE Teflon was used to make the flow cell. Fifth, both PTFE Teflon and white Delrin cells were silanized with SIGMACOTE (Sigma, Inc.) to suppress the ion exchange between the indicator and the $-OH$ group on the cell surface. Last, a Teflon AF-2400 based liquid core waveguide, which combines the membrane and flow cell into one unit due to its gas permeability and internal light reflection, was used on the test, as well. Unfortunately, none of the above efforts have ever eliminated the measurement errors between 15-minute and 60-minute intervals.

Recently, we have changed the flow cell ID from $1000\ \mu\text{m}$ to $600\ \mu\text{m}$ for smaller internal volume and better flush efficiency. As shown in Figure 4, the difference has fallen within ± 0.004 between 15-minute interval and 60-minute interval, corresponding to $\sim 4\ \mu\text{atm}$ error. Further efforts to eliminate the contamination problem are ongoing.

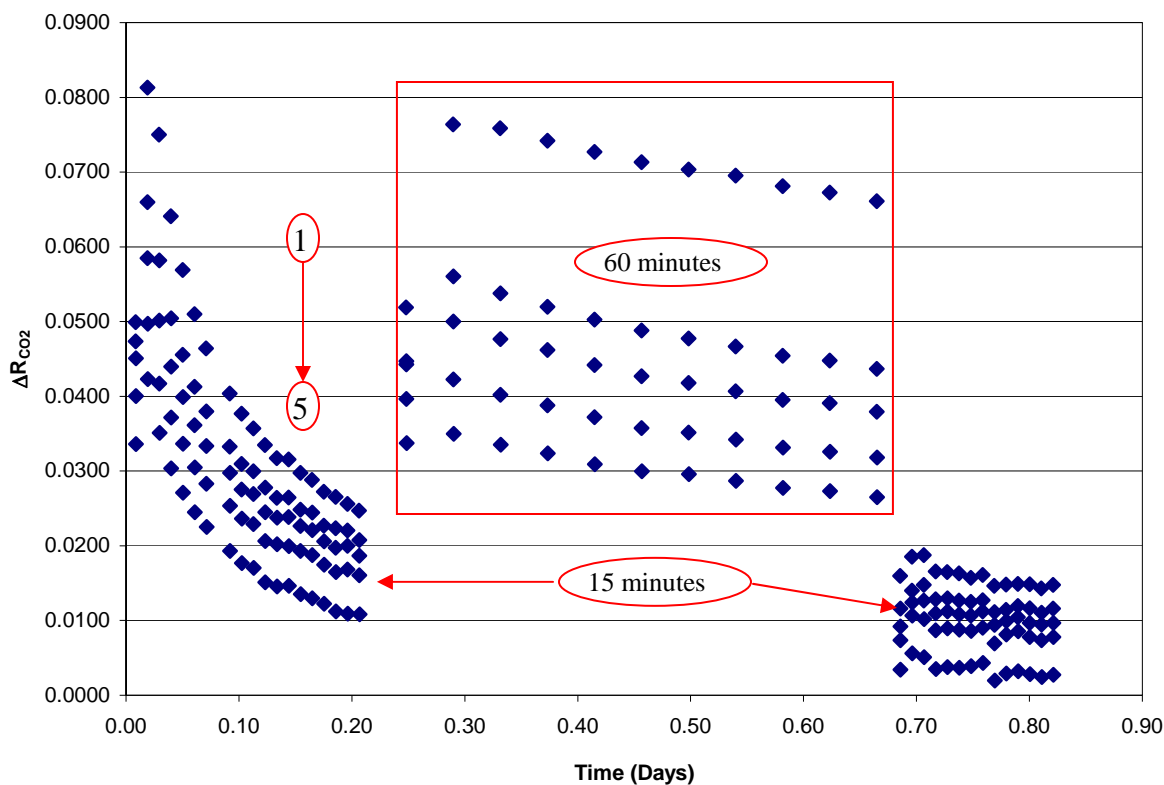


Figure 3. Normalized responses of the SAMI- CO_2 sensor (ΔR_{CO_2} at two different measurement intervals (15 and 60 minutes) with five measurements taken at each time interval (5 pump pulses). The flow cell is white Delrin Z-cell with $1000\ \mu\text{m}$ optical pathlength. $p\text{CO}_2$ is about 360 ppm and the silicone membrane is about 38" long with 0.02" ID and 0.037" OD. BTB indicator is $5.55 \times 10^{-5}\ \text{mol kg}^{-1}$ with $8 \times 10^{-5}\ \text{mol kg}^{-1}$ NaOH for the measurements. For each five measurements, R_{CO_2} decreases from the first to the fifth measurement.

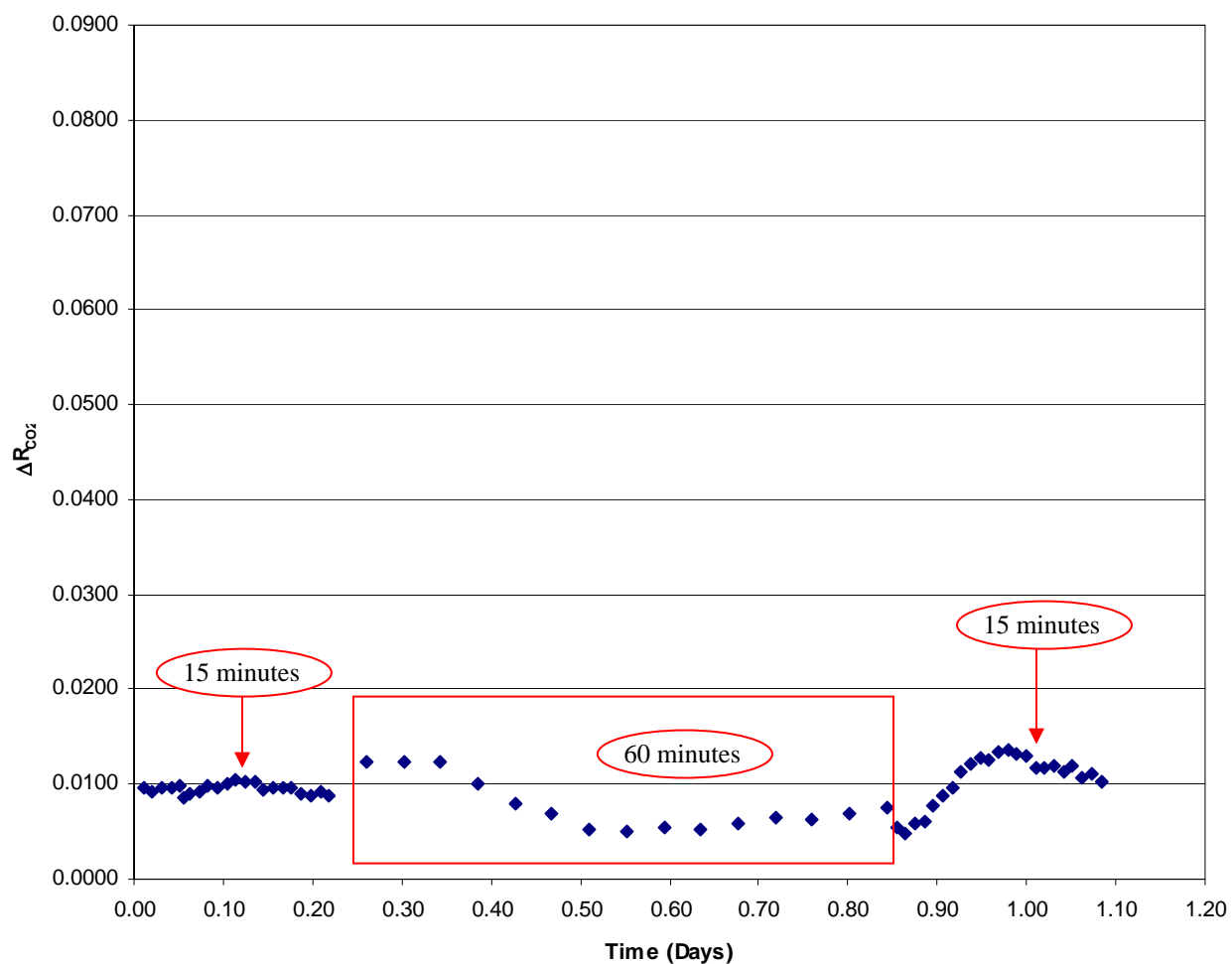


Figure 4. Normalized responses of the SAMI-CO₂ sensor (ΔR_{CO_2} at two different measurement intervals (15 and 60 minutes) with one measurement plotted on the same scale as Figure 3. The flow cell is a white Delrin cell with 600 μm optical pathlength. $p\text{CO}_2$ is about 360 ppm and the silicone membrane is about 22" long with 0.02" ID and 0.037" OD. BTB indicator is $5.6152 \times 10^{-5} \text{ mol kg}^{-1}$ with $8.047 \times 10^{-5} \text{ mol kg}^{-1}$ NaOH for the measurements (same as Figure 3 data).

IMPACT AND APPLICATIONS

Economic Development

This research and development will help make the SAMI-CO₂ a robust, less-expensive means of measuring seawater $p\text{CO}_2$. 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 CO₂ measurements and industrial applications.

References.

DeGrandpre, M. D.; Hammar, T. R.; Smith, S. P.; Sayles, F. L. **In situ measurements of seawater pCO₂**. *Limnology and Oceanography* (1995), 40(5), 969-75.