Integration of an Emerging Highly Sensitive Optical CO_2 Sensor for Ocean Monitoring on an Existing Data Acquisition System SeaKeeper 1000™
Annual Report for FY11 (Oct 1, 2010 – Sep 30, 2011)

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LONG-TERM GOALS

Develop a high-performance pCO_2 sensor that is affordable enough to be deployed in geat numbers to autonomously monitor the overall patterns of CO_2 emissions and ocean acidification.

OBJECTIVES

- Meet the challenging requirements for ocean pCO_2 monitoring using an innovative sensor design based on high sensitivity fluorescence detection.
- Assemble the system with low-cost optics and electronics in order to make it affordable enough (target cost <$1,000) to be deployed in greater numbers.
- Make the entire system drift and calibration free by perfecting a patch renewal process using an innovative microfluidics-based approach.
- Integrate the system into an existing platform system, the Seakeeper 1000™, to leverage already proven deployment systems readily amenable to autonomous operation.
- Test the reliability and robustness of the prototype system in the lab and open waters with our partners NOAA and Seakeepers International.
- Commercialize sensors with our industrial partner Fluorometrix Corporation.

APPROACH AND WORK PLAN

- Scientific and/or technical approach

The novelly designed optical sensor for autonomous ocean monitoring works on equilibrium principles. When the pH-sensitive reagent solution sitting behind a gas-permeable membrane is exposed to seawater, the CO_2 molecules present in the seawater diffuse across the membrane into the reagent and induce a pH change. After equilibrium is reached, the fluorescence is measured and the pCO_2 data are recovered from a calibration curve. A specific feature of our measurement technique is the use of excitation ratiometric approach. A violet LED (Light Emitting Diode) and a blue LED are used to excite the sensing reagent through an excitation filter and the pCO_2 dependent emission is measured through an emission filter by a photodiode. This approach is especially valuable from stability point of view – the chemical part that the sensor is based on is

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practically insensitive to the changes in temperature. Besides the ratiometric feature, the system also has a lot of other novel features including the ideal 90° separation between excitation and emission, the mirrored cavity, the beam combiner, and the renewal of the sensing reagent, etc. To greatly improve the sensitivity of the sensor, we ideally separated the excitation and the emission, leading to significantly reduced scattered light reaching the detector, thereby increasing the signal to noise ratio. The sensing reagent was placed in a mirrored cavity, allowing the excitation light to uniformly excite the dye. To address the photobleaching of the sensing reagent, we used a technique that automatically renews the sensing reagent after every measurement. This makes the measurements totally calibration-free.

- The key individuals participating in this work

Govind Rao, Ph.D., Professor, overall project management.
Yordan Kostov, Ph.D., Research Associate Professor, electronics and optics design.
Xudong Ge, Ph.D., Research Assistant Professor, reagent formulation and microfluidics design.
Robert Henderson, Graduate Student, system preparation and test etc.
Nick Selock, Graduate Student, system preparation and test etc.

- Work plans for the upcoming year

We will optimize the system to further improve its performance. We will miniaturize the device so that it is small enough to be integrated on available data acquisition platforms.

WORK COMPLETED

- Designed and built the excitation and read out system with low-cost optics and electronics.
- Designed and built the microfluidic system including the equilibrium chamber and the measurement chamber.
- Optimized the sensing patch formulation, found the best dye or dye combinations to meet the requirements for measuring ranges, found the optimal dye and base concentrations to satisfy the required sensitivity, and found the best semipermeable material for pCO_2 sensing.
- Prototype systems were presented and examined at NOAA's AOML location.

RESULTS

- Optoelectronics

The optical unit and the read out system were debugged and optimized in this report fiscal year. After being built, the system was tested in realistic conditions to evaluate its accuracy, precision, temperature drifts, and other metrological parameters. The efficiency of the excitation, the decoupling between excitation and emission, and the novel algorithms for noise and drift-suppression were studied.

LEDs are fairly sensitive to temperature, with their brightness decreasing ~3% with every 1°C increase. Furthermore, different types of LEDs (i.e. violet vs. blue) have different sensitivity to temperature. As this was expected, we provided referenced reading of the LED brightness and attempted corrections based on the measured brightness. However, we still did not achieve the required stability of the reading. Therefore, we set to investigate whether the spectrum of the LEDs changes with the temperature shift. It was found that blue LED did not exhibit significant changes in spectrum; however, the violet LED (emission maximum 405 nm) exhibited changes in both intensity and spectrum with temperature - approximately 0.1 nm/°C. The shifts were large enough to shift the calibration curve and cause fluctuations of ~ 7 ppm CO_2. Furthermore, not only the spectrum peak position changed, but also the shape of the spectral emission varied. Therefore, it was determined that the best approach (except using different types of dyes) was to place the instrument in a thermostated environment. We have developed such a system by using off-the-shelf components. At present, the accuracy of the temperature setting is 0.1% and it seems to result in significant improvement of sensor repeatability.

Another problem that we were facing was the relatively low signal to noise ratio (~2000:1) of the measurements. This ratio was found to be valid for the lowest end of the measurement range (150 ppm CO_2); it further deteriorated to 700:1 at the highest end (750 ppm CO_2). Such signal-to-noise ratios resulted in measurement uncertainty of ±4 ppm. Investigation of the reasons for the relatively low signal to noise ratio (SNR) revealed that the measurement was timed inadequately when the signal was still rising. Based on that finding we just recently were able to achieve SNR on the order of 8000:1. We are still evaluating to what extent this resulted in increased sensitivity and less measurement uncertainty.

- Fluid mechanics

The final design of the equilibrium chamber is shown in Figure 1. It has an easily manufacturable outer shell and common HPLC internal connections for the Teflon AF membrane tubing. The outer shell consists of common, store bought PVC fittings used in plumbing. The membrane tubing is a capillary tube (0.032” OD and 0.024” ID) made from Teflon AF 2400. Teflon AF 2400 was used as our exchange membrane tubing due to its exceptional gas permeability. The tubing is five feet long and wound around a central support structure in such a way that the winding minimizes both the contact of the tubing with itself and with the support structure. Due to the thin nature of this tubing and the small geometries involved, the response time to various fugacities of CO_2 is very quick. The 90% response time of a CO_2 free dye to a gas phase on the other side with a CO_2 fugacity of ~214 µAtm is only 3.75 minutes.

After the equilibrium chamber was built, a residence time distribution test (RTD) was performed to determine the real residence time within the baffled equilibration chamber. In the RTD testing, the pumprate using a peristaltic pump was set at 0.26 Liters/minute, and the light absorbant tracer was injected at t=0 seconds. Figure 2 shows the residence time distribution of the seawater through the equilibrium chamber at 0.26 L/min. It can be seen that the equilibrium chamber behaves between a plug flow tubular vessel and a well-mixed tank. There is no dead volume observed.

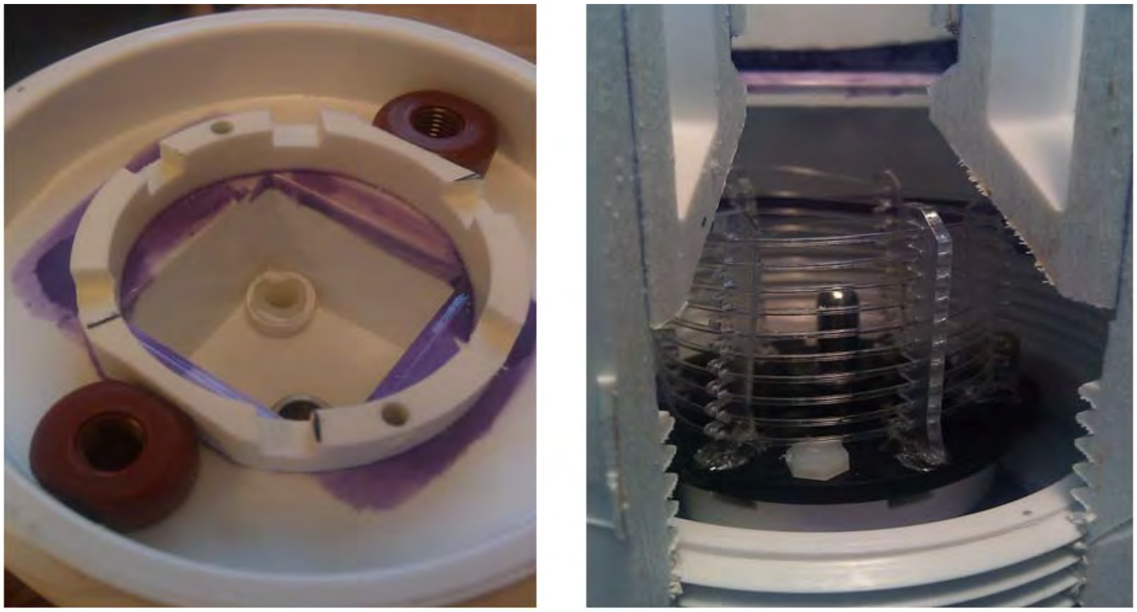

Figure 1. The final design of the equilibrium chamber.

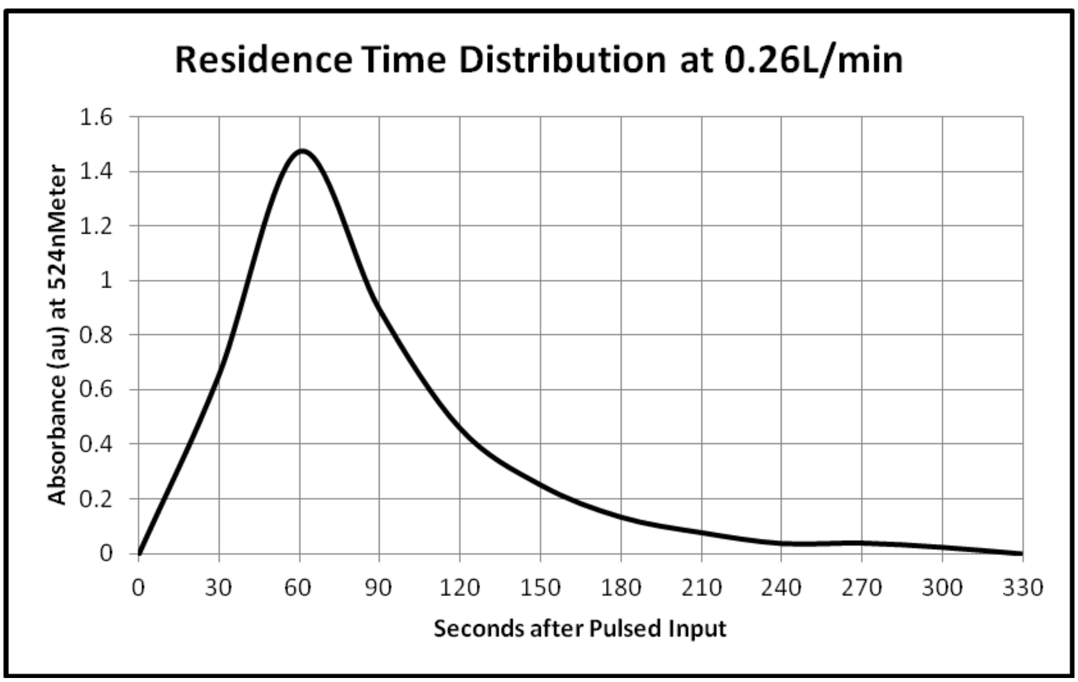

Figure 2. The residence time distribution of the seawater through the equilibrium chamber at 0.26 L/min.

- System calibration

The system was calibrated by using 4 standards that contain 200, 300, 400, and 500 ppm CO_2. The setup is shown in Figure 3. Each of the standards was prepared by blending a pure N_2 supply with a certified gas mixture containing 998 ppm CO_2 in N_2. Two mass flow controllers controlled the flow rate of the gas sources creating a controllable, blended gas. This gas passed through an H_2O scrubber, a particulate filter, and then into a LiCor 820. After the LiCor, the gases passed into the PreEQ bottle for water vapor saturation and then into the dye bottle. A 50-μL solenoid pump from Lee Co. was procured to handle pumping the dye solution through the micro flow cell. The pump was attached inline but downstream from the flow cell to prevent bubble formation in the flow cell due to possible pump cavitation. A LabVIEW program controlled the frequency and number of pumping for this testing by manipulating an external transistor attached to the pump. The uFluidic Fluorometer measured the normalized fluorescence intensity until the readings stabilized. The results in Figure 4 show that the device responded to different CO_2 levels very well. Based on the calibration data, single digit ppm resolution was obtained. Figure 4 also shows that different devices had different calibrations. This is because the LEDs used to build the devices had different optical properties. Actually, no two LEDs generate light with the same intensity when operated at the same current. The intensities may differ up to 100% even though they are considered to be identical by the company that produces them. Study on the further improvement of the precision is still going on. As described in the Optoelectronics Section, we have just boosted the SNR to 8000:1. At this SNR level, 1-ppm resolution is easily attainable.

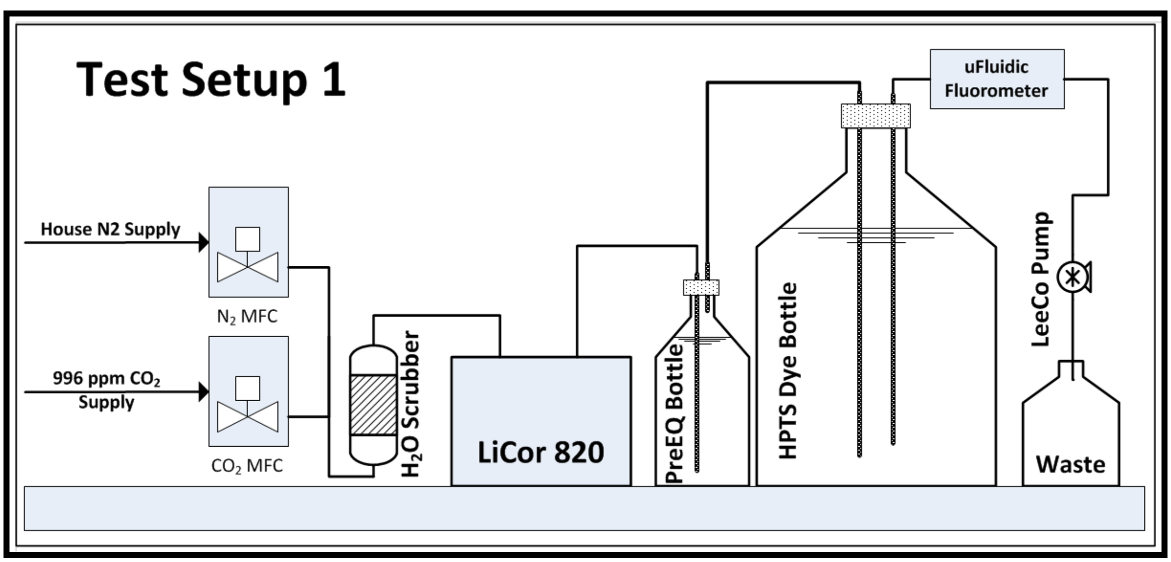

Figure 3. Setup for system tests.

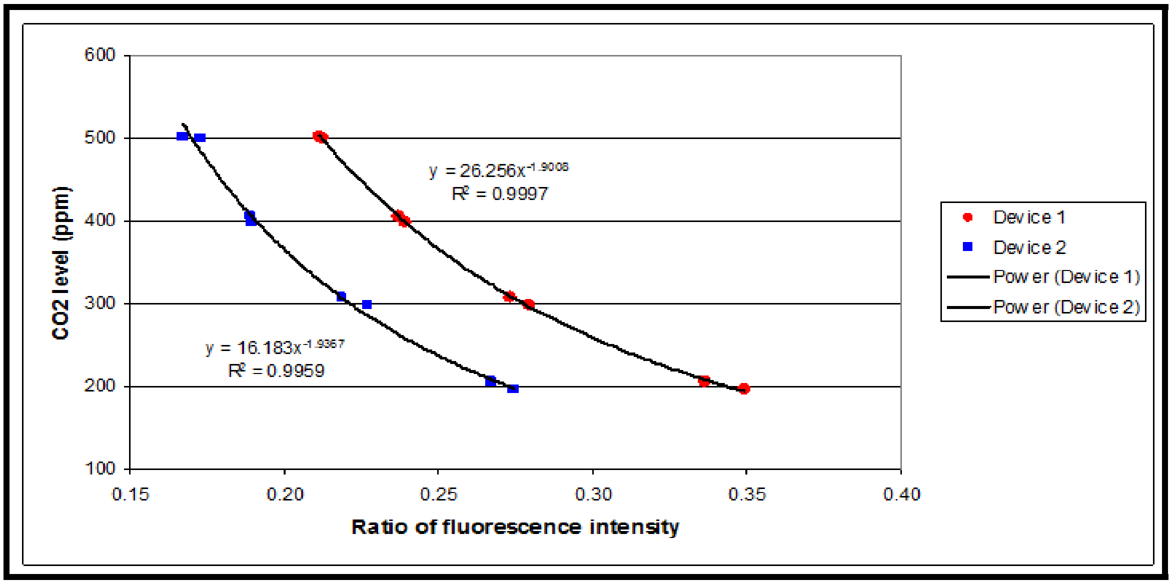

Figure 4. Response of two different detectors to different levels of CO_2 measured in the micro fluidic chip. The data can be fitted to a power function.

IMPACT AND APPLICATIONS

National Security

Global warming caused by increasing amount of CO_2 discharged into the environment by human activity is usually characterized as an environmental threat, but now it has been realized that it is also an issue of national security. Unchecked global warming could raise the sea levels, change the amount and pattern of precipitation, and increase the intensity of extreme weather events and change the agricultural yields, leading to large-scale migrations, increased border tensions, the spread of disease and conflicts over food and water. All could lead to direct involvement by the United States military. The pCO_2 sensor being developed will likely have a great impact on understanding and mitigating global warming. As the sensor being developed will be highly sensitive, and highly stable, yet affordable enough to be deployed in great numbers, the overall pattern of greenhouse gas emissions in an area can be monitored autonomously. Accurately and precisely measuring is the first critical step to control global warning and to alleviate the severity of its effects.

Economic Development

The economic sector most affected by global warming will be the agricultural sector because global warming will seriously affect the number of rainfall. In some regions, the overall frequency of droughts will become longer and more intense. While in other areas, there will be too much rainfall, leading to flooding. Another globally important economic activity most affected by global warming will be fisheries. Due to their primitive nature, the output of fisheries is directly and strongly affected by variations in natural conditions. The pCO_2 sensor being developed will monitor the pCO_2 levels and help alleviate its harmful effects.

Quality of Life

Fisheries are closely tied to human health and species health across the globe. Widespread changes in quality of life will occur if global warming continues at its current pace. More frequent heat waves and a significant increase in days with poor air quality could endanger humans, particularly the elderly and children.

TRANSITIONS

Economic Development

Discussions are underway with a major manufacturer of environmental sensors to fast-track deployment of the pCO_2 sensors.

PUBLICATIONS

Xudong Ge, Yordan Kostov, Robert Henderson, Govind Rao. A low-cost high-performance fluorescence detector for measurements of pCO_2 in seawater (submitted).

PATENTS

A new US Patent Provisional Application was filed this year. The application is entitled "Analyte Sensing System and Method Utilizing Separate Equilibrium and Measurement Chambers" and the Application Serial No. is 51/388,219.