Report on the Development of CO_2 Monitoring Systems to be Included in an Autonomous Data Gathering System.

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The goal of this project was to miniaturize an existing pCO_2 monitoring system and it's attendant water gas equilibrator, for deployment on yachts, buoys and other platforms of opportunity as a component of the SeaKeepers Ocean and Weather Monitoring System. The requirements for the system were to develop a small, light weight, energy efficient instrument package that could be operated automatically for extended periods of time.

The objectives of the first phase, completed six months ago, were:

1. to modify a compact, less expensive commercial non-dispersive infrared detector (NDIR) CO_2 sensor to monitor pressure and temperature of CO_2.
2. to calibrate and make stability tests for the compact NDIR CO_2 sensor
3. to fabricate a miniaturized showerhead equilibrator
4. to perform laboratory bench tests of the new instrument against a reference unit
5. and to perform at sea tests of the new instrument against a reference unit

Figure 1 illustrates schematically the principal components of a pCO_2 sensor. A closed loop of air is passed through a equilibrating chamber, where water with the unknown CO_2 concentration is sprayed from a shower head to maximize surface contact between the water droplets and the air. This allows the CO_2 concentration in the air to equilibrate with the CO_2 concentration in the seawater. The air stream is then passed through a (NDIR) to measure the change in the CO_2 concentration in the air. The concentration of dissolved carbon dioxide in seawater is a function of temperature and salinity.

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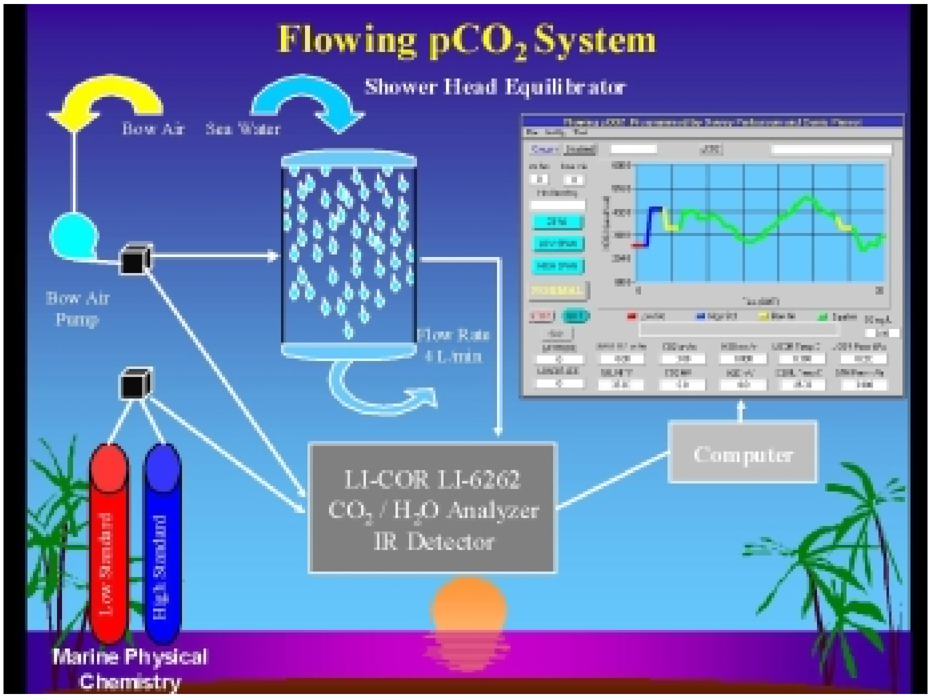

Figure 1. Generalized scheme for measuring pCO2 in seawater.

Stand-alone pCO_2 instruments have become common in oceanographic research on the total carbon cycle and its implications for global warming.. They typically have been large systems, requiring large volumes of continuously flowing seawater and high pressure cylinders of calibration gases.   Efforts have been underway in our laboratory to reduce the size and complexity of the instrumentation. Figure 2 shows the equipment used by Millero to make these measurements on research vessels. The photograph does not show the 40-liter waterfall equilibrator, which is the active part of the system. Although smaller than those used by others, it is still considerably larger than the permitted SeaKeepers footprint or the space available in a monitoring buoy.

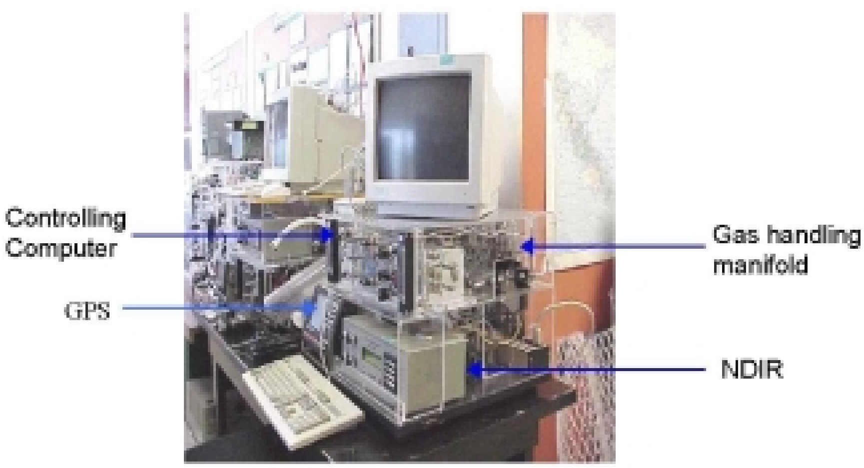

Figure 2. Research pCO2 monitoring system for field work.

The SeaKeepers modules were designed to provide a complete monitoring system in a compact modular format, so that sensors could be interchanged as research projects required. The system is contained in two stainless steel NEMA-4 enclosures, which are together 48 inches high, 16 inches wide and 10 inches deep. The enclosures can be separated and mounted in a variety of configurations to fit the available space. The instrumentation module has a manifold to support five discrete instrument packages in independent submodules of 4x8x12 inches (Figure 3). The ultimate goal is to develop a pCO_2. sensor that will fit in a submodule.

Figure 3. Instrument module with pump, manifold and 3 sensor submodules: Turbidity/CDOM, CTD (temperature, conductivity, dissolved oxygen, pH, Eh), and a prototype trace metals analyzer.

An inter-comparison between the “standard” detector (the Li-6262) and the smaller Li-800 gas analyzer proposed for this application is shown in figure 4. While it is clear that absolute calibration shifts are occurring, the similarity in the shapes of the curves and their response times are encouraging.

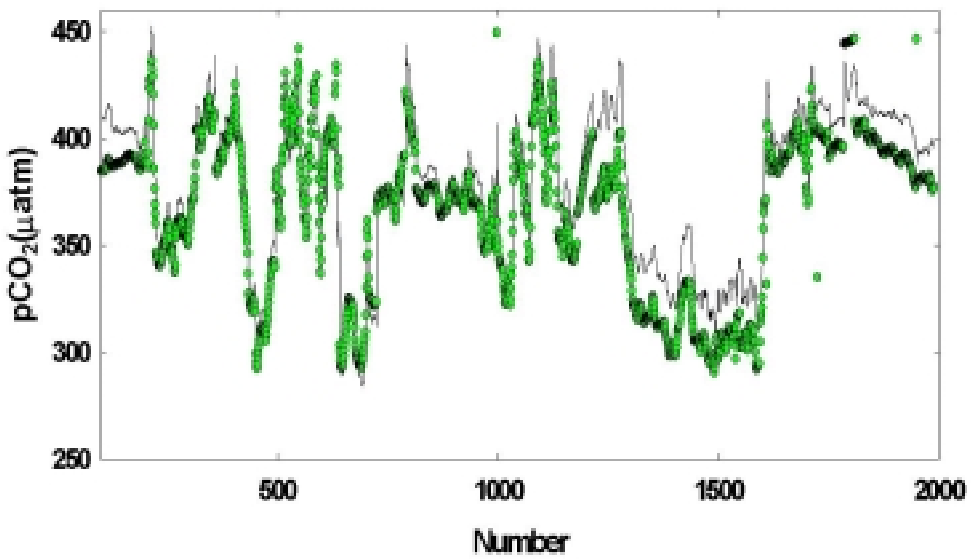

Figure 4. Intercomparison between the Li-6262 and the Li-800 NDIR detectors

A wide range calibration of the detector yielded a standard deviation of 4.3 micro-atmospheres, which indicates the possibility of achieving the research criterion of +/- 1 micro-atmosphere over the more limited ambient observed range. Stability measurements made with the smaller detector gave a standard deviation of 1.06, which is again very encouraging.

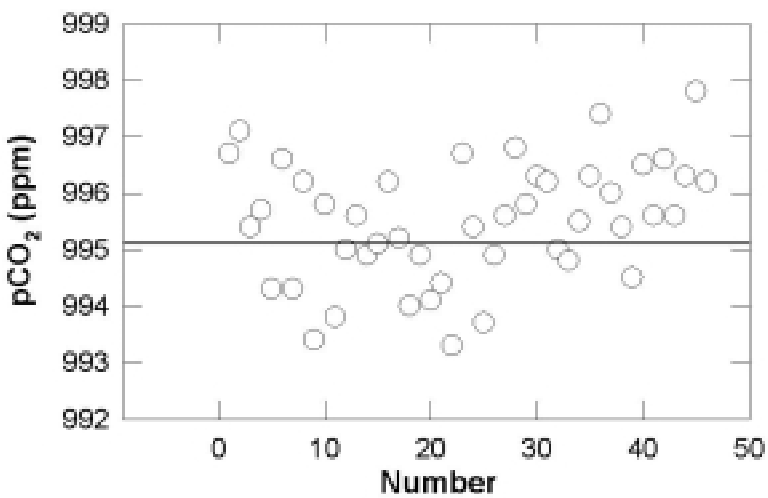

Figure 5. Li-800 stability with time. $\sigma = 1.08$

The Li-800 NDIR may be adequate for the intended use, and has the advantages of being smaller and less expensive than the Li.-6262

There remains an instrumental design problem to be resolved. Water is pumped through the system and returned to the source, while air of known concentration is pumped through the equilibrator (Figure 6). It is critical that the water level in the equilibrator remain constant, so the air circulation is a closed loop. If the liquid level drops in the equilibrator, the system can draw in outside air which can change the concentration of CO_2 in the air and the equilibrium values of the system, independent of the exchange with the sample water. On the other hand, if the water is allowed to overflow freely with little or no retention time, air will be lost as entrained bubbles. The air loss problem increases in severity and complexity as the volume of the equilibrator is decreased. It was decided to attempt to design a system which would continuously control the water level while using bubble traps to minimize bubble air loss.

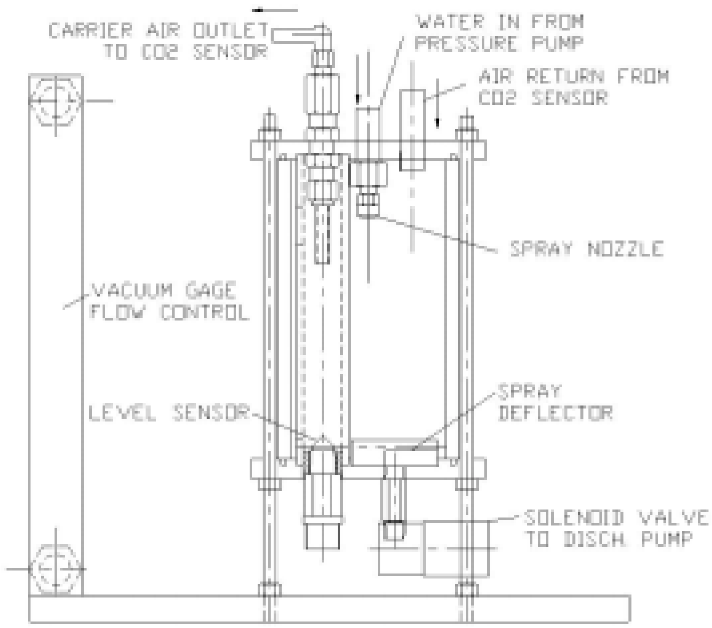

Figure 6. Schematic of the prototype pCO2 equilibrator.

Figure 7. Equilibrator and control system in SeaKeepers submodule

In a bench top comparison between the research grade instrument and the prototype, response and tracking appear to be in good agreement (Figure 8). There is a clear calibration offset and perhaps a systematic drift in the prototype that could be attributable to loss of equilibrated air and replacement with fresh air. The addition of a water level control in the next version may resolve these issues.

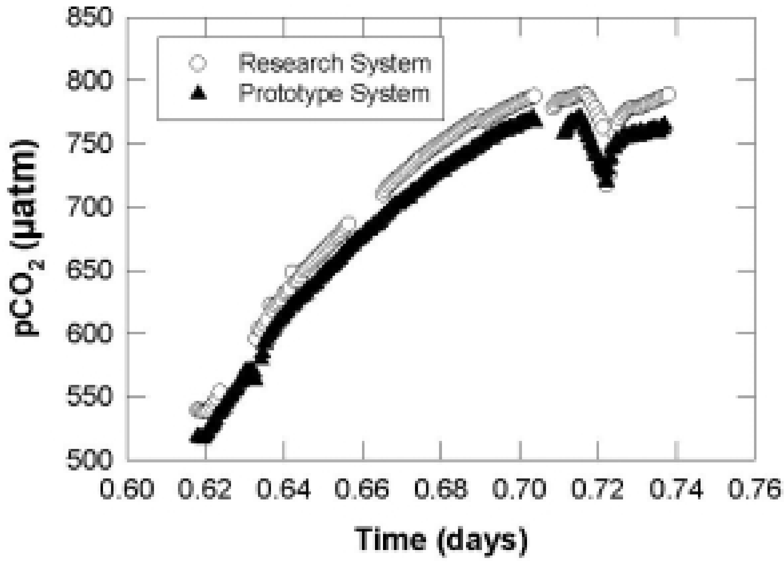

Figure 8. Bench top comparison of the two systems

During a one week cruise of the R/V F. G. Walton Smith, an informal inter-comparison was made between the research grade sensor and the prototype (figure 9).

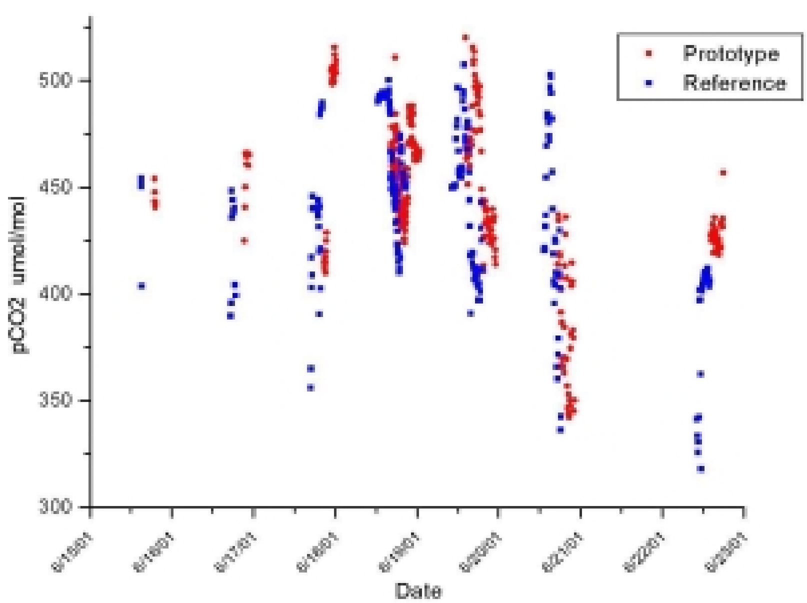

Figure 9. Field trial of the prototype, compared to a research system.

The results, while encouraging, are far from the desired accuracy of one micro-atmosphere. Additional funding was been obtained to further develop the miniaturized pCO2 analyzer and to deploy it on platforms of opportunity such as SeaKeepers member yachts, piers, buoys and commercial ships.

Another parameter, besides pCO_2, which is routinely measured to characterize the CO_2 system is total dissolved inorganic CO_2 (TCO_2). Currently, TCO_2 measurements involve acidifying the seawater sample with phosphoric acid and measuring the amount of CO_2 evolved by either coulometry or infrared detectors. A new and promising technique for measuring TCO2 has been developed in cooperation between Idronaut Srl, (Milan, Italy) and the University of Rome (figure 10). The system uses peristaltic pumps to fill a mixing chamber with an unknown sample of seawater. The differential pH sensors are normalized by passing this sample through both channels. A buffer solution is then added to the sample in one channel, stirred and the change in pH measured relative to the untreated sample. The volumes used of seawater and buffer are miniscule,

The differential pH sensors rely upon beautifully constructed capillary electrodes. Differential repeatability to the fourth decimal place has been observed. A unit in the third decimal place is equivalent to one micro-atmosphere.

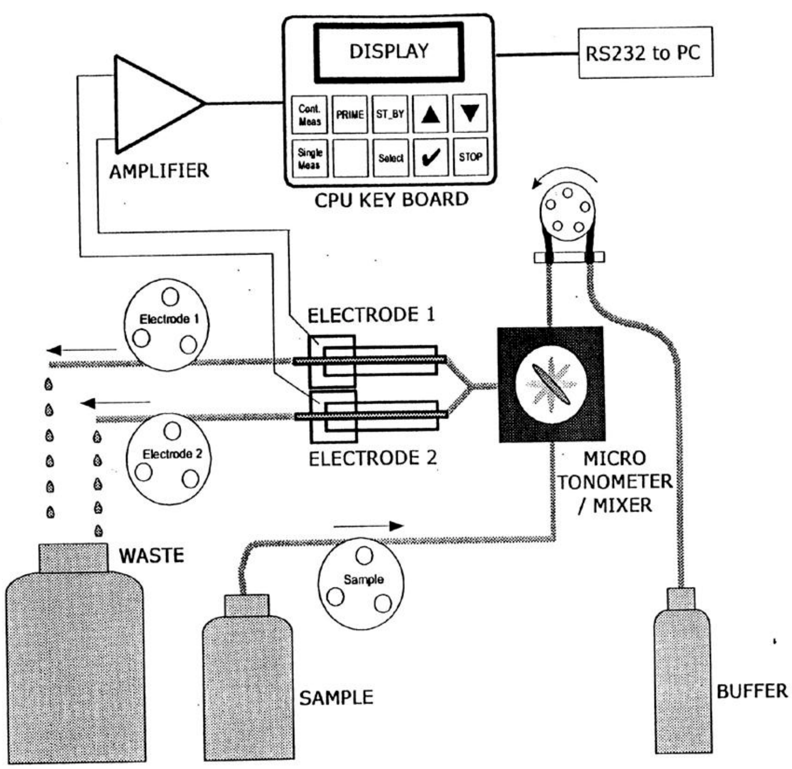

Figure 10. Prototype TCO_2 instrument

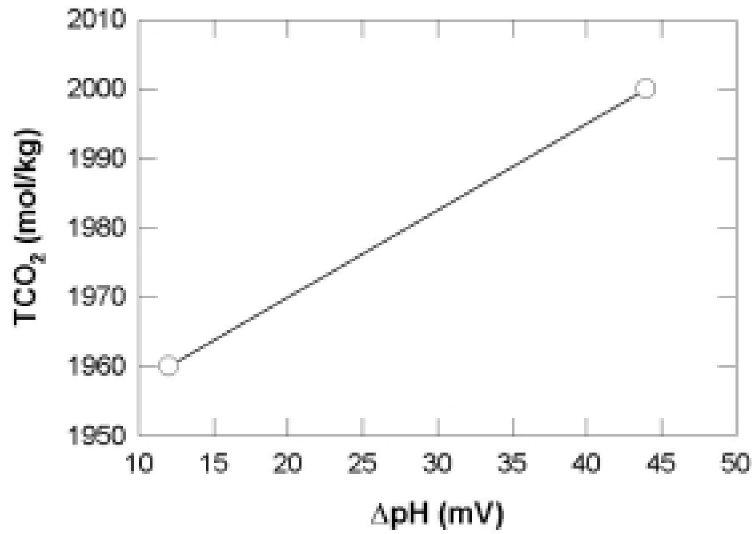

Figure 11. TCO_2 calibration curve