

Development and Testing of New Dissolved Gas Sensor Technologies for Monitoring Air-Sea Gas Exchange

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Abstract. This project prepared a Pro-Oceanus Systems, Inc. gas tension device (GTD) for deployment at the Martha's Vineyard Observatory in collaboration with Dr. Wade McGillis (WHOI). It will be deployed sometime during the week of August 15, 2001. This provides an important new communication technology for dissolved gas sensors. Data will be collected real-time *via* the internet. This project also examined the properties of an oxygen absorbent used in new dissolved oxygen/nitrogen sensors. Experiments were performed on the absorbent by injecting research grade oxygen into a nitrogen chamber in AirWare vacuum tight glassware submerged in a temperature bath. The time constant for the removal of oxygen was determined to be 31 ± 2 seconds, and all of the oxygen was removed in the nitrogen environment. The time constant of the absorbent was found to be limited by the chemical reactions. These new dissolved gas sensor technologies will be used to develop more stable and reliable instruments for measuring dissolved gases in seawater.

1. Introduction

1.1. Background

Current climate change trends are raising critical questions about the future of our planet. Understanding the role of the oceans in climate change is a necessary step towards predicting future climates. Studying air-sea interactions, especially gas exchange rates and mechanisms, better quantify the importance of the oceans in sequestering green house gases, and ultimately provide knowledge and predictive capabilities through modeling efforts.

Current *in-situ* dissolved gas measurement techniques are lacking in the technology to be able to remain stable over measurement times of years. Instruments also need to be able to withstand severe storms, as it is thought that significant gas exchange occurs during storms. Automated oxygen probes are subject to bio-fouling, and drift significantly over long deployments. Analysis of dissolved oxygen using the Winkler Titration Method is limited to shipboard samples, which also becomes costly.

It is necessary to develop new sensors that are more stable over time and can operate and withstand extreme oceanic conditions. The objective of this project is to develop new gas tension device (GTD) technologies by communicating real time with a deployed GTD using a RS-232 serial connection, and to study the properties of an oxygen absorbent which will be used in a new nitrogen/oxygen sensor.

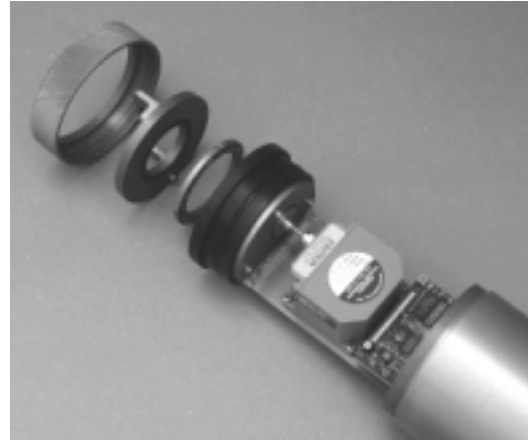


Figure 1. Pro-Oceanus Systems, Inc. Gas Tension Device. Image courtesy of Pro-Oceanus Systems, Inc. (Halifax, N.S., Canada).

1.2. Theory – Gas Tension Device

Figure 1 shows a Pro-Oceanus Systems, Inc. Gas Tension Device (GTD) developed by McNeil et. al. The GTD works on the principle of diffusion of gases through a semi-permeable membrane. A sample volume of air inside the GTD is allowed to equilibrate with the water, and since the membrane is permeable only to gases, at steady state the pressure sensor inside the GTD reads the gas tension of the water. Gas tension, P_T , is the total pressure of dissolved air, composed primarily of nitrogen, pN_2 (~78%), oxygen, pO_2 (~21%), water vapor, pH_2O (~1%), and residual trace gases, mainly argon, p_r , or:

$$P_T = pN_2 + pO_2 + pH_2O + p_r. \quad (\text{Eq 1})$$

In situ gas concentrations, c , can be related to the partial pressures of the gases by using solubility coefficients, β , which are known functions of water temperature, T , and salinity, S [Weiss, 1970].

The effects of bio-fouling can be minimized by placing small amounts of high molecular weight, low molecular diffusivity, anti-fouling agents on the air interface of the membrane. The anti-fouling agent slowly diffuses through the membrane and minimizes bio-fouling problems.

1.3. Theory – Nitrogen/Oxygen Sensor

The newest technology in dissolved gas sensors is a nitrogen sensor. This operates on the same principal as a GTD, except that an oxygen absorbent is added in the air chamber to remove all the oxygen. The internal pressure sensor thus measures the partial pressure of nitrogen,

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$$P_T = pN_2 + pH_2O + p_r. \quad (\text{Eq 2})$$

By assuming, with negligible error [McNeil et al., 1995], that trace gases are air saturated with respect to the mean water column properties we may calculate pN_2 from Equation (2), as water vapor is a known function of temperature and salinity.

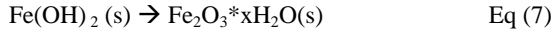
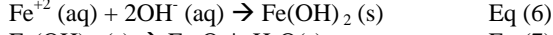
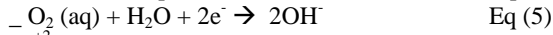
If an independent measurement of the total gas tension (i.e.: with a GTD) is also made, the partial pressure of oxygen in the seawater can also be measured directly by subtracting equation 2 from equation 1.

An important part of developing the oxygen/nitrogen sensor is finding the right absorbent. The absorbent must remove all of the oxygen, as well as have a short time constant for absorbing the oxygen compared to the time constant for equilibrating the GTD. Further, the absorbent must remain stable and not become liquid in the presence of moist air. The residual oxygen pressure in the air chamber is a function of the ratio of the time constants,

$$P_{\text{residual}} \sim \tau_{\text{absorbent}} / \tau_{N_2\text{chamber}} * \Delta P_{O_2}, \quad (\text{Eq 3})$$

where $\tau_{\text{absorbent}}$ is the time constant for absorption of oxygen by the absorbent, $\tau_{N_2\text{chamber}}$ is the time to equilibrate the air chamber inside the nitrogen sensor with the sea water, and ΔP_{O_2} is the pressure difference of oxygen across the membrane, approximately 200 mbar.

The absorbent being tested in this experiment is proprietary to Pro-Oceanus Systems, Inc., however key ingredients include activated charcoal and iron filings. The oxygen is removed by a catalyzed process of rusting, following the chemical reactions [Brady, 1981]:



The activated black carbon provides a very large surface area on which the above reactions can occur.

Developing an oxygen/nitrogen sensor requires an understanding of the absorbent used to remove the oxygen. Pertinent questions include: does the absorbent remove all the oxygen?; what is the time constant for the reaction?; what is the time constant a function of? A series of experiments were performed on the absorbent to address these questions. We expected the time constant of this absorbent to be governed by the chemical reactions given in equations 4-7, rather than a function of the amount of absorbent present or the volume of oxygen injected.

2. Methods

2.1. Gas Tension Device – Laboratory Testing

A GTD made by Pro-Oceanus Systems, Inc. was prepared for deployment at Martha’s Vineyard Observatory in Massachusetts, in collaboration with Dr. Wade McGillis of Woods Hole Oceanographic Institute. Preparation included assembling the instrument and completing a series of tests to ensure that the instrument was functioning properly and had no leaks. The GTD was equipped with a membrane of thickness 0.005 in., a ParoScientific pressure sensor, and a RS-232 Serial connector. The first test was conducted in the pressure tanks at the University of Rhode Island Graduate School of Oceanography Equipment Development Laboratory. The pressure sensor and circuit board were removed from the canister before it was sealed to ensure no damage would be incurred should the instrument housing leak. The instrument was first subjected to a hydrostatic pressure of 70 dbar for 2 minutes. The pressure was then decreased to 10dbar, and the instrument was left for 2 hours.

A second test was performed to ensure no internal air leaks. The pressure sensor and circuit board were replaced in the canister, and the GTD was left submerged in a Hart Scientific precision temperature bath at 20.00°C for a day. The GTD was connected to a

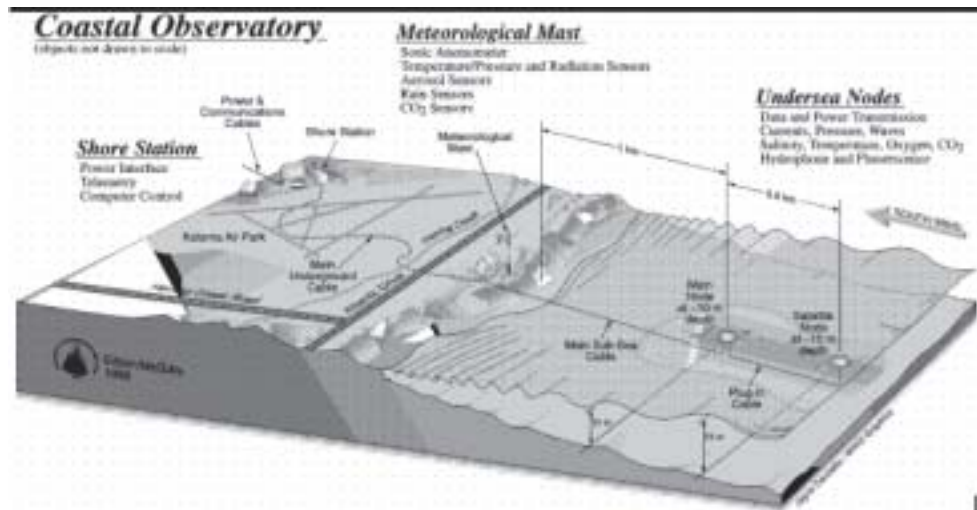


Figure 2. Martha’s Vineyard Coastal Observatory. The GTD will be wet-plugged at the main node, 1 km off shore at a depth of 10m. Image courtesy of Dr. Wade McGillis. [http://adcp.whoi.edu/MV_OBSERVATORY/index.html].

computer, which recorded the output from the pressure sensor.

2.2 Gas Tension Device – Deployment

The GTD will be deployed at the Martha's Vineyard Observatory on August 15th, 2001. It will be wet-plugged into the node 1km off shore at a depth of 10m (figure 2) and it will remain at the site for six months to a year. Data will be accessed real-time via the Internet on a web-site designed to retrieve the data.

2.3 Absorbent

Experiments were performed on oxygen absorbents in vacuum tight AirWare Glassware assembled in the configuration shown in figure 3. The glassware between valves A, B, and C is the oxygen chamber. The pressure of the oxygen chamber was set to near atmospheric pressure (1000 mbar). The glassware between valve C and valve D serves as the nitrogen chamber. The pressure was measured in this chamber by a ParoScientific pressure sensor. A large nitrogen volume compared to the pressure sensor volume was needed to minimize the diffusion of oxygen into and out of the pressure sensor. The nitrogen pressure was reduced by evacuation to 850mbar to simulate atmospheric conditions and mimic the conditions encountered by the absorbent in a useful nitrogen sensor operating in the ocean. The glassware was first flushed with research grade nitrogen for 5 minutes, then evacuated and sealed between valves C and D. Research grade oxygen was then flushed through the glassware from valve A to valve B for 5 minutes. Oxygen injections were done by opening and closing valve C. All experiments were done while submerged in a Hart Scientific precision temperature bath set to 20.00°C to minimize the effect of temperature fluctuations.

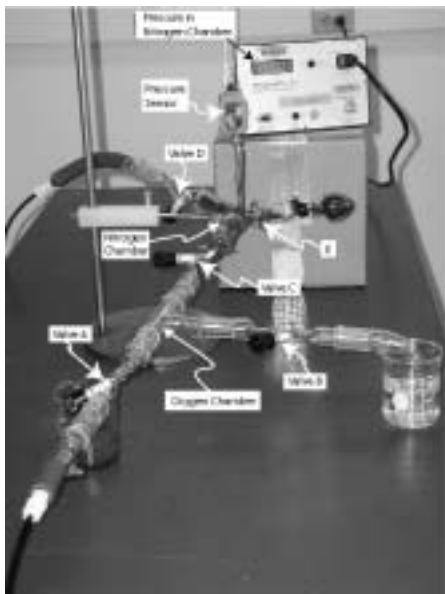


Figure 3. Glassware configuration used to test the absorbent. Valve C was opened to inject oxygen into the nitrogen chamber.

2.4. Steady State (As $t \rightarrow \infty$)

In order to investigate the properties of the absorbent as time goes to infinity, a small amount of absorbent was placed in a 125ml flask. The 125ml flask was attached to point E (fig 2) with approximately 16g of the absorbent. The entire setup was submerged in the temperature bath, and an oxygen volume of approximately 16mbar was injected into the nitrogen chamber. Data was recorded over a few hours.

2.5. $\tau_{\text{absorbent}}$

To investigate the properties of the absorbent, an experimental apparatus was assembled to measure the time constant of the reaction. The setup for the steady state experiment needed to be modified because the diffusion time of oxygen through the glassware was the governing time constant, namely:

$$\tau = z^2 / \varphi \quad \text{Eq (8)}$$

where z is the length of the glassware, and φ is the diffusivity of oxygen ($\sim 30\text{cm}^2\text{s}^{-1}$), and $\tau \sim 30$ min.

Therefore, the entire nitrogen chamber, from valve C to valve D was packed with absorbent (approximately 92g), as shown in figure 4. The 125ml flask was exchanged for a 25ml flask at point E. Multiple injections of oxygen of various volumes were then injected into the nitrogen chamber.

3. Observation and Results

3.1. GTD

The GTD was determined to be leak proof, both outside and inside. The GTD is scheduled for deployment sometime during the week of August 15, 2001. The time constant for equilibration of the GTD is expected to be ten to twenty minutes.

3.2. Absorbent

Figure 5 shows the results of the steady state experiment. Three hours after the injection of 15 mbar of oxygen, the pressure of the nitrogen chamber was

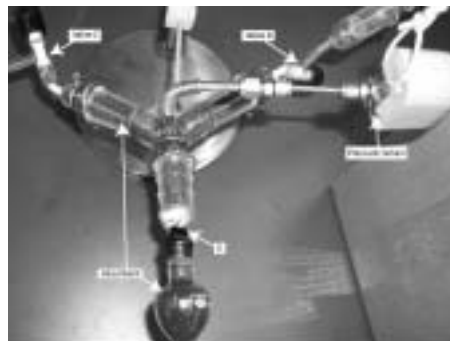


Figure 4. Experimental setup used to determine the time constant of the absorbent. The nitrogen chamber is packed with absorbent to reduce the effects of oxygen diffusion through the glassware.

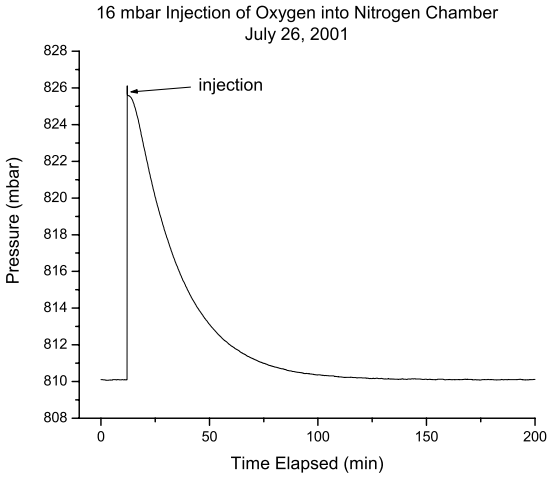


Figure 5. A 16mbar injection of research grade oxygen to determine the steady state residual pressure of oxygen in a nitrogen atmosphere. The spike in the pressure at $t=0$ is due to the effects of closing valve C during the injection.

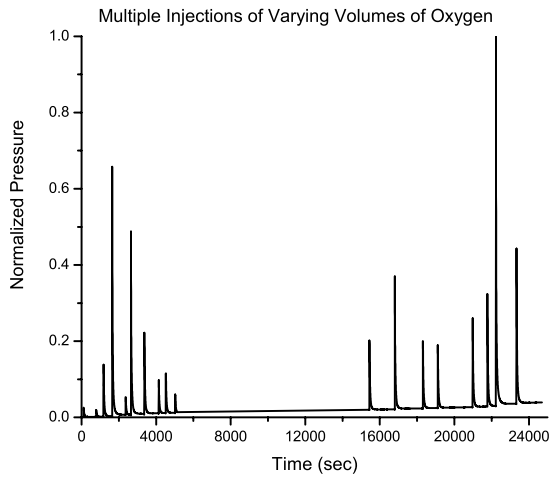


Figure 6. Oxygen injections of varying volumes into a chamber of nitrogen packed with absorbent. The gradual increase in initial pressure over time was determined to be a leak and did not significantly alter the results of these data.

within 0.013 mbar of the initial pressure. We find that the oxygen is removed from the chamber to $P_{\text{residualO}_2} = 0.01 \pm 0.02 \text{ mbar}$, verifying our assumption that the absorbent does indeed remove all available oxygen within the absorbent chamber in the presence of a nitrogen atmosphere.

3.3. $\tau_{\text{absorbent}}$

Seventeen oxygen injections of various volumes were injected into the absorbent-packed nitrogen chamber. These injections are shown in figure 6. The gradual increase in the initial pressure over the course of injections was determined to be caused by a small leak in the valves or pressure sensor, however the leak rate is

small and has an insignificant influence on these set of results. Figure 7 shows the normalized pressure versus the time elapsed after the injection. After fitting an exponential curve to each normalized injection, we found that the time constant varied slightly with the amount of oxygen injected, as shown in Figure 8. The mean time constant was found to be $\tau_{\text{absorbent}} = 34 \pm 2$ seconds for 5ml of oxygen. Extrapolation to steady state conditions (no net oxygen) yields $\tau_{\text{absorbent}} = 31 \pm 2$ seconds.

4. Discussion

Results from these experiments yield a $\tau_{\text{absorbent}}$ value in-situ of 31 ± 2 seconds. The equilibration time for a nitrogen sensor is expected to be much larger than the equilibration time for a GTD due to the increased volume acquired by adding an absorbent chamber. Assuming that the equilibration time for the nitrogen sensor is on the order of a few hours, the residual

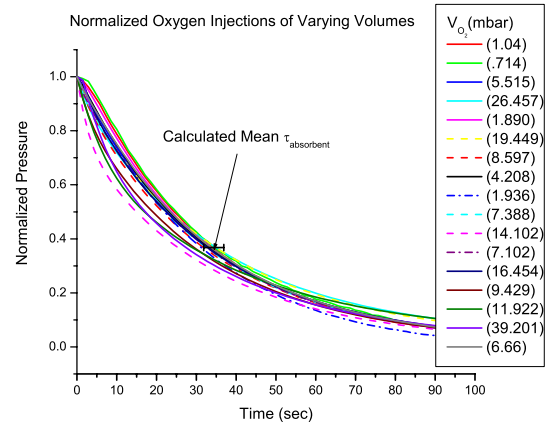


Figure 7. Normalized oxygen injections of varying volumes. The mean time constant was determined to be approximately $34 \text{ sec} \pm 2 \text{ sec}$ for an oxygen injection volume of 5mbar.

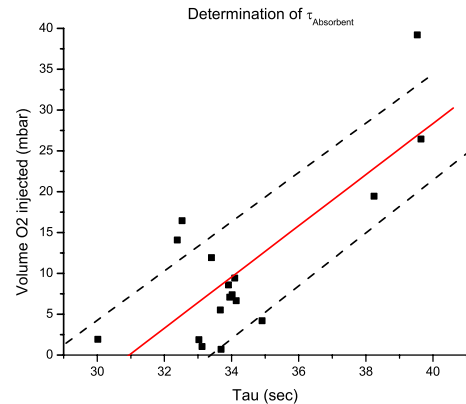


Figure 8. Time constants for the seventeen injections plotted against the injection volume of oxygen. The time constant for equilibrium (no net oxygen) is 31 ± 2 seconds.

pressure of oxygen in the sensor can be calculated using equation 3. This yields a residual pressure of oxygen in the nitrogen sensor of $P_{\text{residualO}_2}=0.805\text{mbar}$. Either increasing the time constant for the nitrogen sensor or decreasing the time constant of the absorbent will decrease the residual pressure of oxygen in the chamber.

The new Pro-Oceanus Systems, Inc. nitrogen sensors are stable to within 0.01% per year, as per manufacturer specifications. This is comparable to the Winkler titration method, which has analytical precision of 0.05% [Knapp, et. al., 1989]. The nitrogen sensors are also more stable than the Sea-Bird Electronics, Inc dissolved oxygen sensor over long deployments, which has a stability of 2% per 1000 hours, or 17.52% per year [<http://www.seabird.com>].

5. Conclusions

After deployment on the 15th of August, the new RS-232 recording system in a GTD will have been tested. This will pave the way for real-time ultra-stable dissolved gas measurement systems.

The results from tests on the absorbent indicate that it will be possible to build a reliable and useful new dissolved oxygen/nitrogen sensor.

Future work will include refining the chemical composition of the absorbent to absorb oxygen faster, and experimenting with different membrane thickness'

to increase the time constant for the nitrogen sensor, which will decrease the total residual pressure of oxygen in the sensor. Long term testing of the absorbent will also be performed. Results of the in-situ oxygen/nitrogen sensor will be intercompared with results from a mass spectrometer. Finally, these new instrument technologies will be employed to collect data for future air-sea gas exchange studies.

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