CO_2 Sensors

Ocean Optics CO_2 Sensors provide a quick and easy way to monitor levels of Dissolved Carbon Dioxide in a variety of environments. While the importance of medical and biochemical applications dominate the CO_2 detection landscape, recent years have revealed a growing demand for environmental monitoring of CO_2, particularly sweet/sea water analysis. Ocean optics fiber optic CO_2 sensor features a wide dynamic range and a high sensitivity required for medical, biochemical, and environmental applications.

About CO_2 Sensors

The following sections contain information about Ocean Optics' Fiber Optic CO_2 Sensors:

Principle of Fiber Optic CO_2 Sensors

Ocean Optics' CO_2 sensor is based on a proprietary sol-gel film (composed of Aluminum silicate co-polymer) that is coated on the tip of optical fibers. We immobilize the sol-gel film with a highly stable pH sensitive fluorescence molecule (8-hydroxypyrene-1,3,6-trisulfonic acid, HPTS). We then protect the sol-gel film with a hydrophobic silicone coating that is permeable to CO_2 and impermeable to H^+. The immobilized sol-gel film creates a pH sensitive solid-state (semi-aqueous) microenvironment at the tip of the fiber.

The sol-gel formulation and process is designed to keep the HPTS indicator in its deprotinated form in the absence of CO_2. The ambient CO_2 diffuses through the hydrophobic silicone coating into the sol-gel film and change the equilibrium between the HPTS protinated and deprotinated forms. An Ocean Optics miniature spectrometer monitors the fluorescence of the deprotinated form (at 515 nm maximum, excited at 470 nm), and the changes in fluorescence intensity are correlated with the CO_2 partial pressure.

Advantages of Sol-gel Technology

Sol-gel is an inorganic glass with high thermal and thermomechanical stability and optical transparency compared to organic polymers. These features makes the Ocean Optics sol-gel based CO_2 sensor more stable at high temperatures compared to CO_2 sensors using polymers for encapsulation of HPTS. Additionally, flexibility when immobilizing high concentrations of indicators as well as the presence of multiple indicators is much higher than polymers. Lastly, glasses such as sol-gel have a higher photochemical stability than polymers.

CO_2 Sensor System Components

Hardware

The CO_2 sensor hardware is similar to FOXY, with the exception of the 450 nm shortpass filter in front of the blue LED. Most FOXY probe designs can also be used for CO_2 sensor. However, the sol-gel coating on these probes must be changed.

Software

The software is going to be part of OOISensors. It will be similar to FOXY, with some minor modifications.

Using the CO_2 Sensor System

The following sections provide information on handling and using Ocean Optics Fiber Optic CO_2 Sensors.

Handling CO_2 Sensors

Avoid bringing the CO_2 sensor into contact with hard objects. The CO_2 sensor has a layer of soft, black silicone coated on the outside of its tip that can be damaged by excess pressure or contact with hard objects.

Precondition the CO_2 sensor before use. Submerge and suspend the tip of the sensor in water for approximately two hours. Ensure that the tip of the sensor is not in contact with any other substance except for the water during this preconditioning to prevent damage to the silicone tip. All CO_2 sensors must be preconditioned prior to use.

Note: After each use, submerge and suspend the tip of the CO_2 sensor in water. By keeping the sensor in a preconditioned state, you can use it whenever it is needed. If you take the sensor out of water after use, you must precondition the sensor prior to using it again.

Using CO_2 Sensors

Follow the steps below to use the CO_2 Sensors:

Configuring a Single Point Calibration

1. Open the CO_2 Sensors software.
2. Select **Calibrate | Oxygen/CO_2, Single Temperature** from the menu. The Single Temperature Calibration window appears.
3. Select **Multi Point** as the calibration type, if necessary, from the Calibration Type options located on the top of the screen.
4. Insert the Calibration floppy disk that came with your precalibrated CO_2 sensor into the floppy disk drive.
5. Select **File | Open Calibration Table**, and then select the calibration table stored on the floppy disk.
6. Click the **Curve Fit** button located on the right side of the window.
7. Click the **Update Channel Calibration** button.

Performing a Single Point Calibration

1. Select **Single Point** from the Calibration Type box on the screen.
2. Place the CO_2 sensor in a solution with a known CO_2 concentration that falls within the precalibrated concentration range.
3. Enter the known concentration in the Concentration box.
4. Select the **Continuous** check box on the right side of the screen, if necessary.
5. Press the **Scan Standard** button on the right side of the screen.
6. Allow the intensity signal on the Intensity box to stabilize. This will take approximately 10 minutes.
7. Press the **Scan Standard** button again to stop the scan.
8. Press the **Curve Fit** button.
9. Press the **Update Channel Calibration** button and click the OK button when the pop-up window appears.
10. Select **File | Close** to exit the Single Temperature Calibration window.

Beginning a Scan

1. Select the **Cont.** option on the Scan switch located at the bottom right of the screen.
2. Click the **Scan** switch up to begin scanning.

Storing CO_2 Sensors

When not using your CO_2 sensors, store the sensor probe submerged in water. The probe tip should be submerged in water for at least two days before testing.

In order to preserve the life of the sensor, you should turn the excitation light off when not using the sensor to avoid photobleaching.

CO_2 Standard Solutions

The following equations comprise the CO_2 standard solutions:

Henry's coefficient, H = 10^1.464 = 29.107 [(atm*L)/mol] at 25 ^{o} and 1 atm pressure.

How to Make CO_2 Standard Solutions:

If we make solutions of known $NaCO_3$ concentrations and keep the solution at low pH (~3) then all the CO_2 is dissolved. The CO_2 partial pressure can be calculated using Henry's Coefficient.

@ 25 ^{o}C, 1 atm

H = CO_2 fugacity [atm]/ CO_2 concentration [mole/L] = 10^1.464 [(atm*L)/mole]

X mol% = (partial pressure / total pressure) * 100

Example:

@ 25 ^{o}C, 1 atm

10^-4 [mol/L] in solution □ 0.29 [mol %] in gas □ 0.0029 atm partial pressure

10^-3 [mol/L] in solution □ 2.9 [mol %] in gas □ 0.029 atm partial pressure

2 E –3 [mol/L] in solution □ 5.8 [mol %] in gas □ 0.058 atm partial pressure

4 E –3 [mol/L] in solution □ 11.6 [mol %] in gas □ 0.116 atm partial pressure

Pre-calibrated CO_2 Range

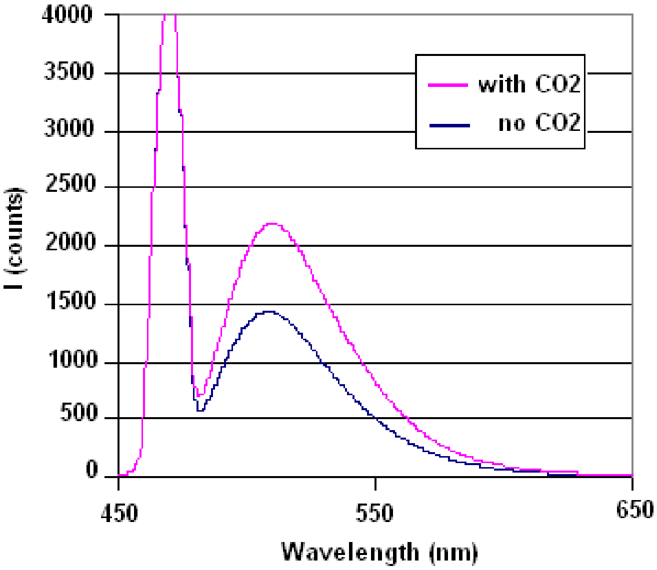
Mole % CO_2	Partial Pressure (atm)
0	0
4.4	0.044
6.5	0.065
9.6	0.096
12.9	0.129

CO_2 Sensor Specifications

The following charts illustrate the various responses of the CO_2 sensor in differing situations:

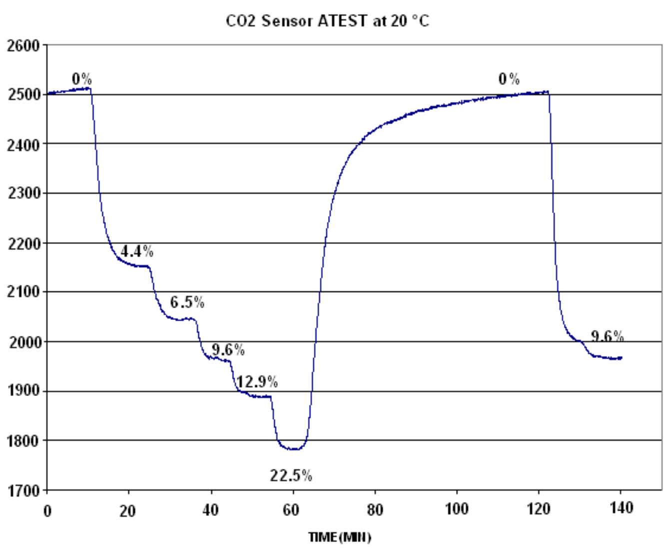
Sensor Spectra

The following figure illustrates the sensor spectrum, which shows the back reflection of excitation light at 470 nm and fluorescence of HPTS at 515 nm. This graphic clearly shows how CO_2 quenches the fluorescence intensity.



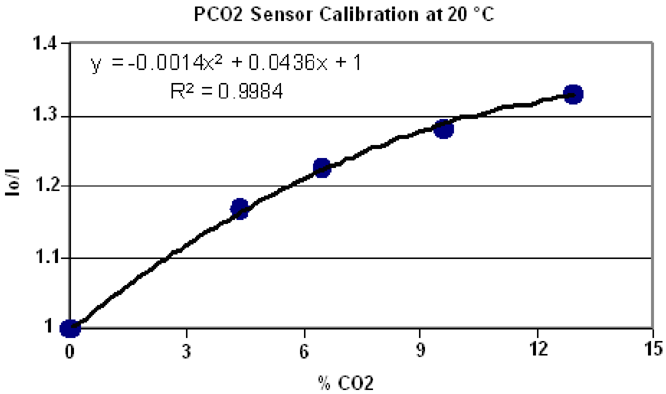
Dynamic Response

The graphic below illustrates the dynamic response of the CO_2 sensor (CO_2 % V.S.I.). It illustrates the reproducibility as well as the reversibility of the sensor. The sensor is sensitive to CO_2 from 0% to 100%, with higher sensitivity readings at lower concentrations. The practical range of CO_2 detection is from 0-25%.



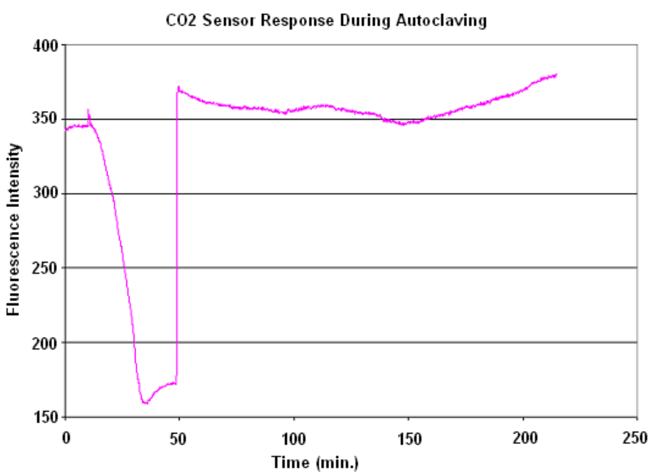
Calibration

The figure below illustrates sensor calibration between 0 and 12.5% CO_2. The calibration data fits a second-order polynomial relation between the inverse of fluorescence intensity and CO_2 concentrations.



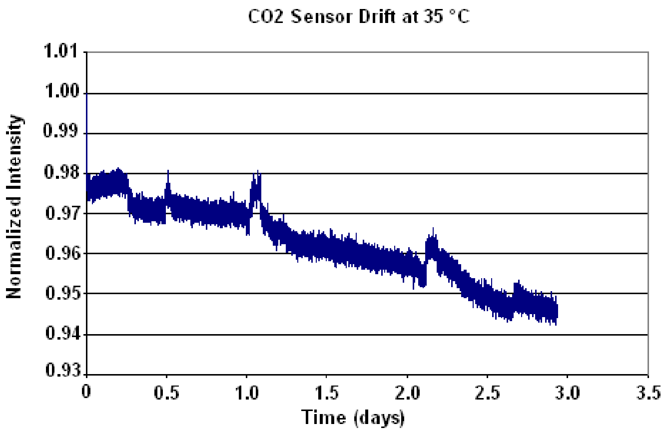
Sensor Sterilization

Our CO_2 fiber optic sensor can be sterilized at 121 C and 15 PSI as shown in the following Figure. This figure shows the sensor fluorescence time line during sterilization for about half hour. The graph shows the full recovery of fluorescence after sterilization.



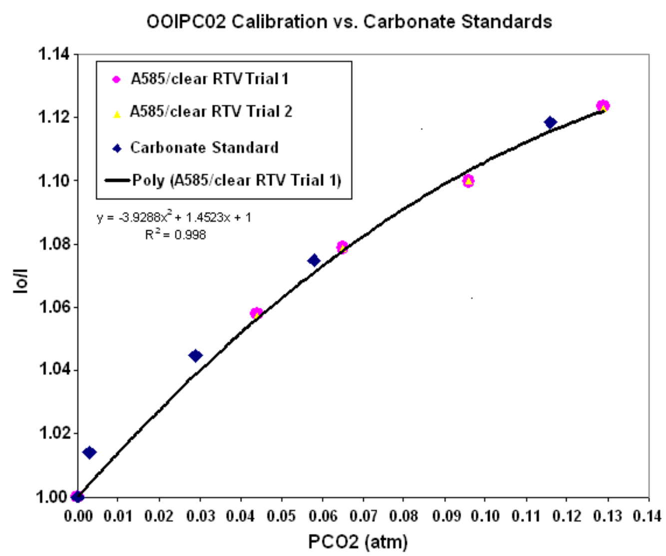
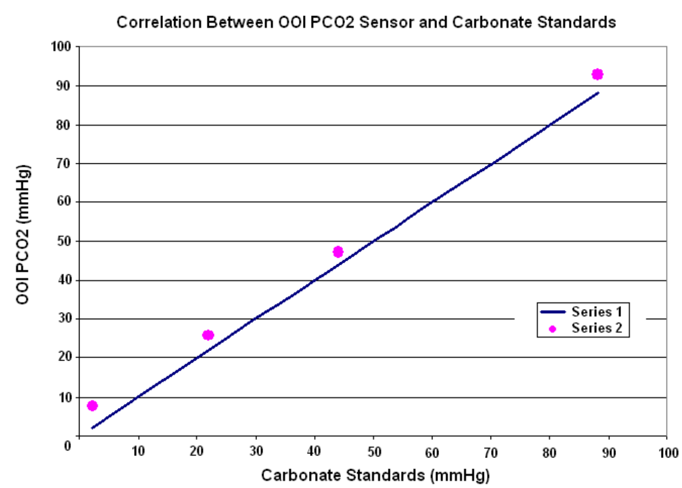
Sensor drift

Sensor signal drift is primarily caused by the photobleaching of the HPTS. The sensor drift was about 5% of actual intensity reading in 3 days which corresponds to 0.01% CO_2 (absolute reading of CO_2 concentration). The Figure bellow shows the sensor drift in 3 days. You can minimize the signal drift by reducing the LED intensity. Maximum LED intensity (20 mA) was used in this experiment. Previous experiments with oxygen sensors (FOXY) indicate that a reduction of the LED current to 5 mA reduces the photobleaching effectively.



Carbonate Standards Comparison

The following graphics illustrate the correlations between Ocean Optics CO_2 Sensors and carbonate standards:

	
Calibration compared to carbonate standards	***Correlation between OOIPCO$_2$ sensors and carbonate standards***

General Specifications

Measurement	PCO_2
Range	1-100% at atmospheric pressure (760 mm Hg) 0-25% practical range
Resolution	0.003% (30 µatm) at low concentrations 0.03% (300 µatm) at high concentrations
Lowest detectable limit	0.003% (30 µatm)
Response time	Average of 10 minutes for large CO_2 changes Less than 10 minutes for less than 1% changes (under 3% CO_2) **Note**: Delay in response time is due to the thick silicone coating on the sensor. Using thinner coatings can reduce response time.
Sensor lifetime	To be determined
Sterilization	Autoclavable (121 °C, 15 PSI)
Operating temperature	To be determined (currently tested up to 120 °C)
Calibration	Single point and Multi-point calibration (contact an Application Scientist for calibration procedures). The preferred reference is a CO_2-free water (for example, a water saturated with N2).
Temperature calibration	To be determined
Probe information	1/16 " OD probe (1000 µm core diameter) in a stainless steel ferule with SMA termination
Disposable probes	Disposable sensor tips will be available in future. The disposable CO_2 tips can be attached to a reflective probe
Recommended spectrometer configuration	SF2000 or USB2000 with the USB-LS-450-C Blue LED Pulsed Light Source and a new band pass filter
Storage	Store in water for a few hours before using.