Short description of the first tests for integrating the new CO_2 sensor from Licor (LI7815) into the *p*CO_2 system from General Oceanics

Tobias Steinhoff[1,2], Craig Neill[3]

[1]*NORCE Norwegian Research Centre AS, Bergen/Norway*
[2]*GEOMAR Helmholtz Centre for Ocean Research Kiel/Germany*
[3]*CSIRO Oceans & Atmosphere, Hobart/Australia*

tost@norceresearch.no
Craig.Neill@csiro.au

Last changed: 11. March 2020

Please note: This is a working document. If you have new findings for integration the LI7815 into the GO system, please let me now so that we can add it to the document!

ICOS OTC 2020

Contact Information:
ICOS OTC
Visiting address: Allegaten 70, NO-5007 Bergen, Norway
Postal address: Postbox 7810, NO-5020 Bergen, Norway
Email: icos-otc@uni.no

In June 2019, Licor agreed to provide one of the new CO_2 sensors (LI7815) to the ICOS OTC for a 3-week testing period. The aim of the test was to evaluate the instrument's performance and integration into the pCO2 system from General Oceanics (GO pCO2 System, https://www.generaloceanics.com/pco2-measuring-system-8050.html).

This report gives an overview of the steps that were necessary to integrate the instrument to the GO pCO_2 system and shows the results from the tests that were run during the 3-week evaluation period.

The GO Labview program was adjusted for the following points:

- new top-level Labview VI reads 1 Hz data from the LI7815 using the MQTT protocol and adds data columns to the GO generated text file.
- user can select what data to add to the GO files and what averaging time to use
- change the idle position of the Valco valve to the open port (port 5 on the valve, which shows as 9 on the valve's LED display).
- set to "no stop flow valve" - the Valco valve does not step to stop flow during EQU measurement cycles. Flow is stopped by stopping the EQU air pump and the vent/return solenoid switches to the vent position.
- the equilibrator pump speed is set to 0.

Hardware settings/changes:

- bypass equilibrator air pump
- pressure upstream of the 7815 was measured with the LI6262
- The pressure for the standard gases at the gas regulators was set to 4 PSI. The pressure for the standard gases in the gas stream, when gas was flowing, was adjusted approximately to the pressure measured during equilibrator measurements using the needle valves:
    - The check flow routine for EQU measurements was used with needle valve fully open and the pressure readings (P_{equ}) were noted before the LI7815 (in our case the readings from LI6262)
    - Then the check flow routine was used for all standard gases and the needle valves were adjusted so that the pressure readings are between (P_{equ}+30mbar) and (P_{equ}+100mbar)
    - If the adjusted pressure (by needle valve) is too low, it can happen that the pressure drifts too low, which will result in a pressure drop in the LI7815

The instrument was connected in-line with the LI6262 in the GO system (Figure 1) and first tests were performed. This was mainly to adjust the GO software to deal with the LI7815.

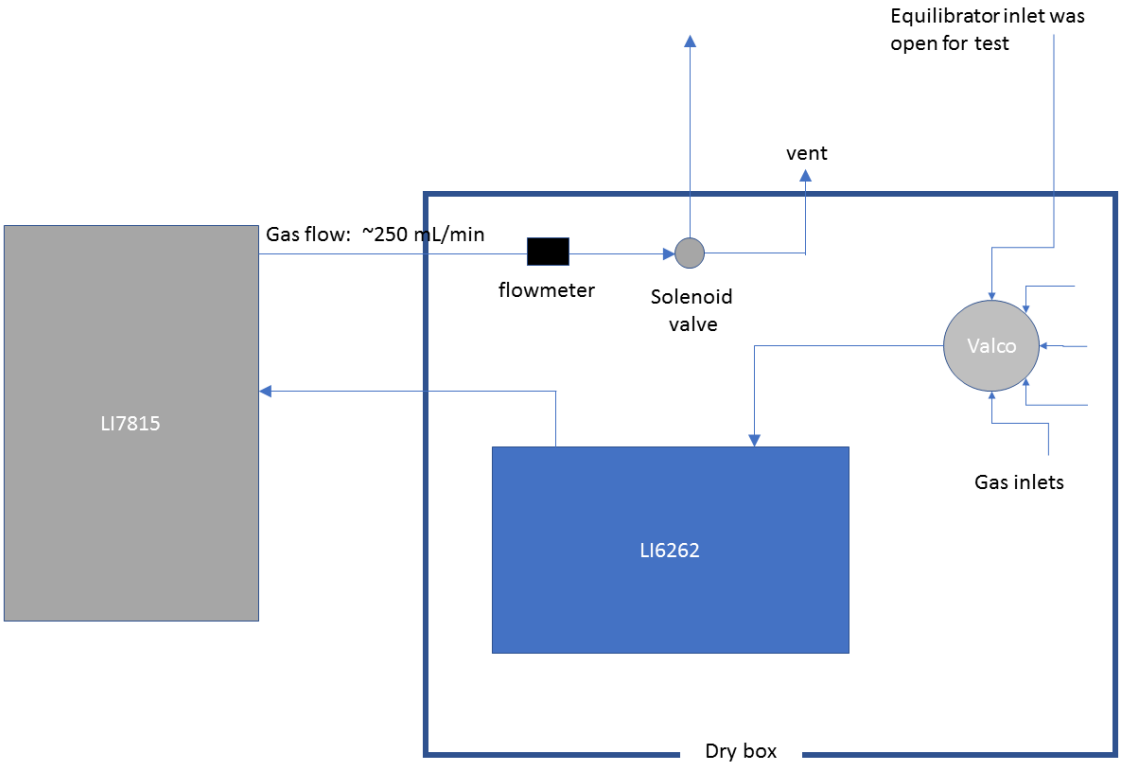

Figure 1: Schematic of connections for the LI7815 within the GO system in series with the LI6262. Please note that, for the beginning of our tests, the dry box was not connected to the wet box.

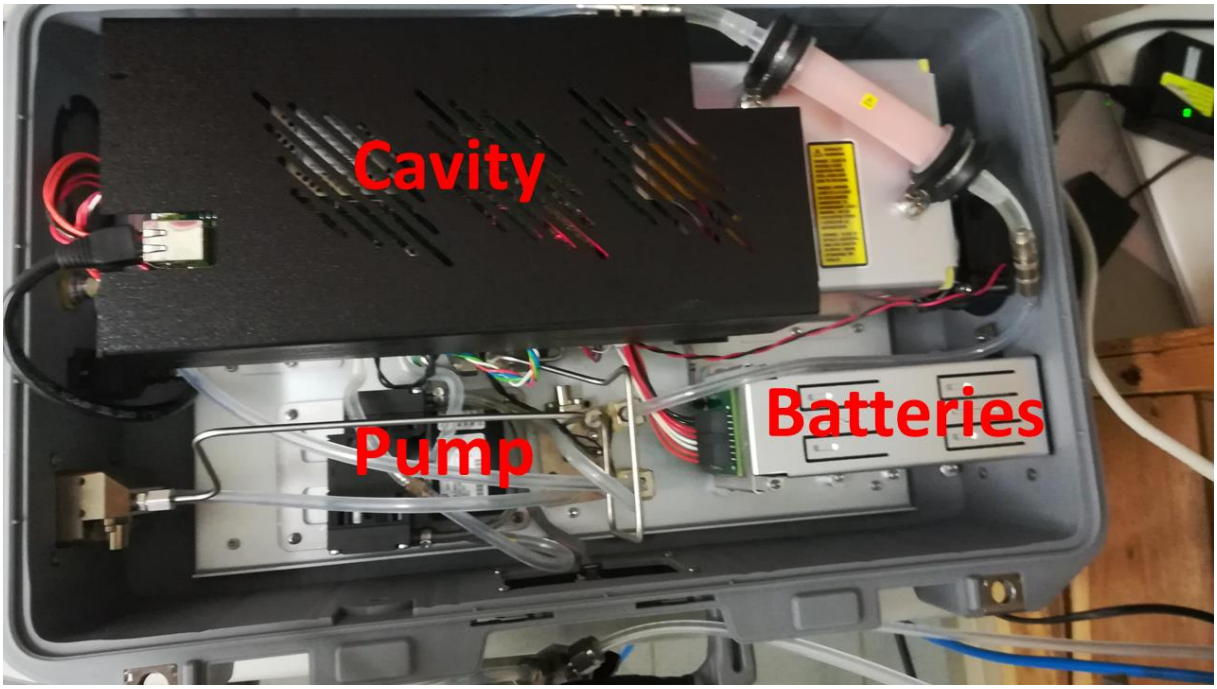

Figure 2: Inside view of LI7815. Each component can be removed separately.

1. Leak tightness

Since the LI7815 works with a cavity that operates at ca. 400 mbar, a vacuum pump is used inside the instrument (see Figure 2). In order to test for leaks in the pump, the LI6262 was connected downstream of the LI7815 to detect leaks in the LI7815 that are behind the cavity. When running the zero gas, we blew inside the dry box and LI7815 to provide a high CO2 atmosphere. The signal at the LI6262 was observed for possible peaks, but it stayed constant. Afterwards, the systems were connected as shown in Figure 1.

2. Influence of ship movement

On June 07, the dry box of the GO system was installed onboard the research ship "Littorina" (length: ca. 30 m). Since the weather was calm, we induced ship roll by maneuvering in a criss-cross pattern through the Kiel bight while measuring 2 standard gases STD1: 0 ppm (CO_2 free air), 512.6 ppm (in natural air). The results are shown in Figure 3.

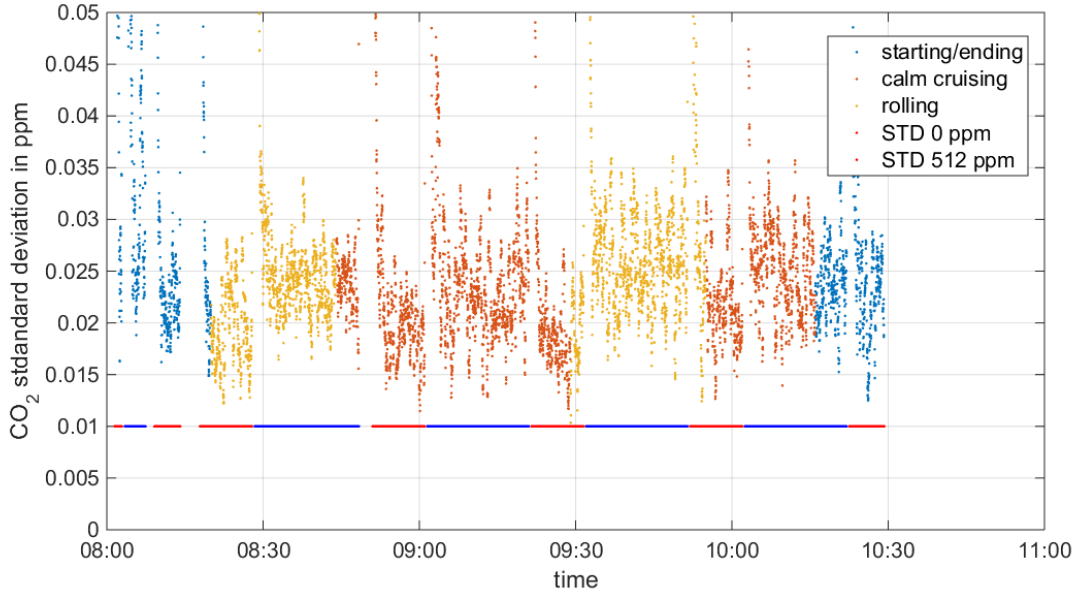

Figure 3: Standard deviation of CO_2 values averaged over 20 seconds during the rolling experiment onboard Littorina. The data are color coded for the periods where the ship was moving out of/into port and for the times where the ship was heavily rolling or calmly sailing. The color code of the line at 0.01 denotes the standard gas that was measured. The higher values above 0.035 ppm are from the period after the standard gas was changed, which typically leads to a higher standard deviation.

3. Multiple day test #1

After the test onboard Littorina, the system was setup in the lab (as shown in Figure 1) and standard gases were connected:

STD1:	0 ppm (CO_2 free air)	
STD2:	349.8 ppm (in air)	aluminum cylinder, ~60bar, last calibration against CMDL using LI7000 in 2006
STD3:	372.3 ppm (in air)	CMDL aluminum cylinder, ~100 bar, last calibration by CMDL in 2006
STD4:	512.6 ppm (in air)	CMDL aluminum cylinder, ~100 bar, last calibration by CMDL in 2006

When the system was measuring ambient air the pressure readings at the LI6262 were ca. 1000 mbar. The standard gas regulators and needle valves were adjusted to give the same pressure at the LI6262.

On **June 7** at 11:30 UTC the instrument was zeroed and spanned. The zero and span of the LI7815 were not changed until **June 14**.

The GO system was started with the following sequence:

0	Zero	1
1	Span	1
2	STD1	3
3	STD2	3
4	STD3	3
5	STD4	3
6	EQU	1
7	Wait	45
8	Loop2	4
9	End	3

The GO program had code in the “wait” function that made the Valco valve turn to a closed position while waiting. This caused the pressure within the Licor cell to decrease to less than 20 mbar. When this was noticed (June 9), all ports where opened immediately and the system pressure went back to normal. The error messages, however, remained and the “phase error” did not recover. The instrument was restarted, and all values went back to normal.

The routine was started again, but instead of “wait” the EQU measurements were set to 60. All went fine, except the Labview routine LI-7815.vi, which reads the data from the LI7815 and hands them to the GO program, stopped after several hours. Thus, no LI7815-data were recorded in the GO program. Data were still available for download from the instrument itself. LI-7815.vi was later modified to re-initialize the MQTT data connection if data are not received, which seems to have improved reliability.

4. Averaging time

To estimate the optimal averaging time, two standard gases were measured for approximately 20 minutes. First the gas with 0 ppm CO_2 was measured and then the gas with 512.9 ppm CO_2. Figure 4 shows Allan plots for both gases. The result compares very well with the Allan plot shown by Licor in their report, which can be found here: https://www.licor.com/env/products/trace_gas/.

The results indicate that for both concentrations an averaging interval of 10 seconds is sufficient to reduce the measurement uncertainty of the instrument below 0.01 ppm.

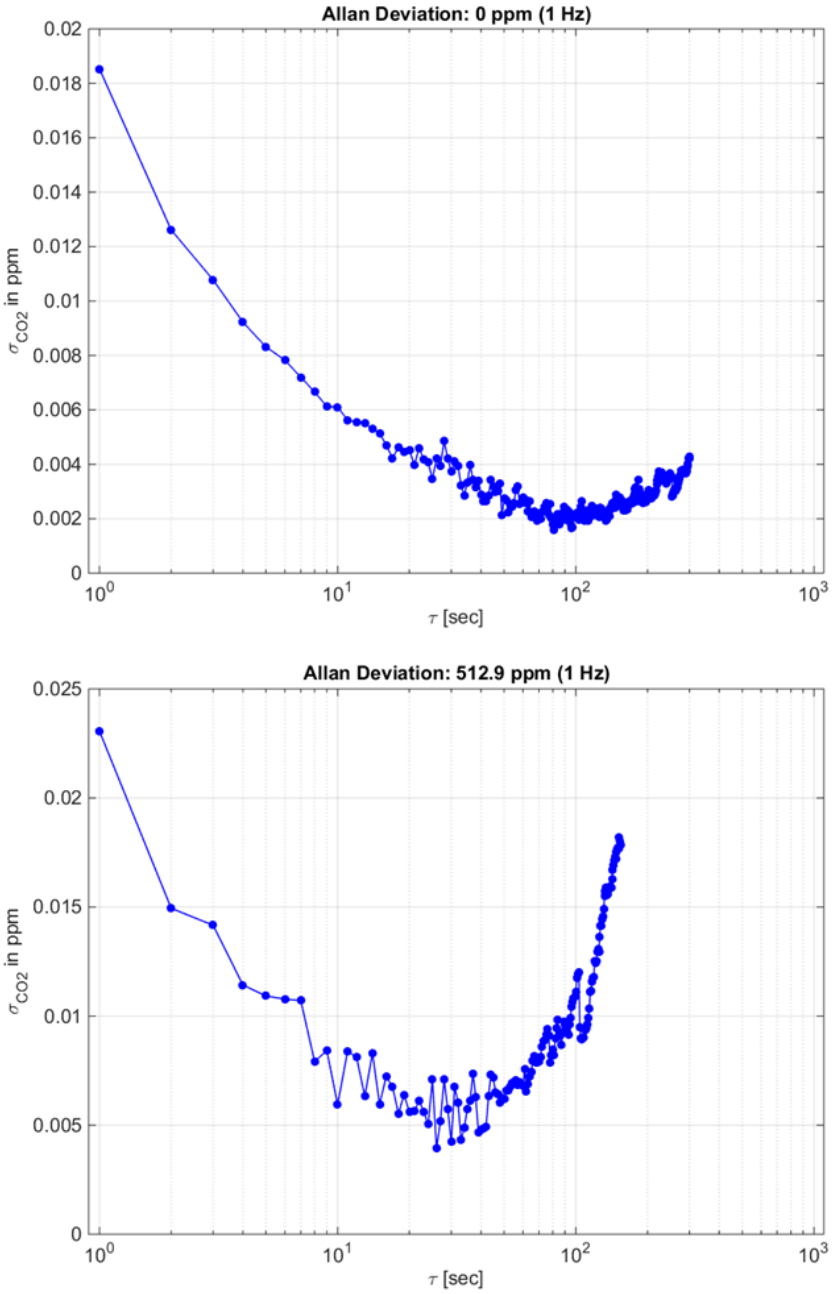

Figure 4: Allan deviation plots for CO_2 measurements at 1 Hz. The upper panel shows data for measuring the zero standard and the lower panel shows data from measuring the standard gas with 512.9 ppm CO_2.

5. Running the instruments in parallel to LI6262

The LI7815 circulates the gas at a flow rate of approximately 250 mL/min. The GO system was originally designed for a gas flow of about 100 mL/min. In order to reduce the flow through the equilibrator and drying unit/Nafions and to reduce the gas flow of the standard gases we connected the two instruments in parallel (Figure 3).

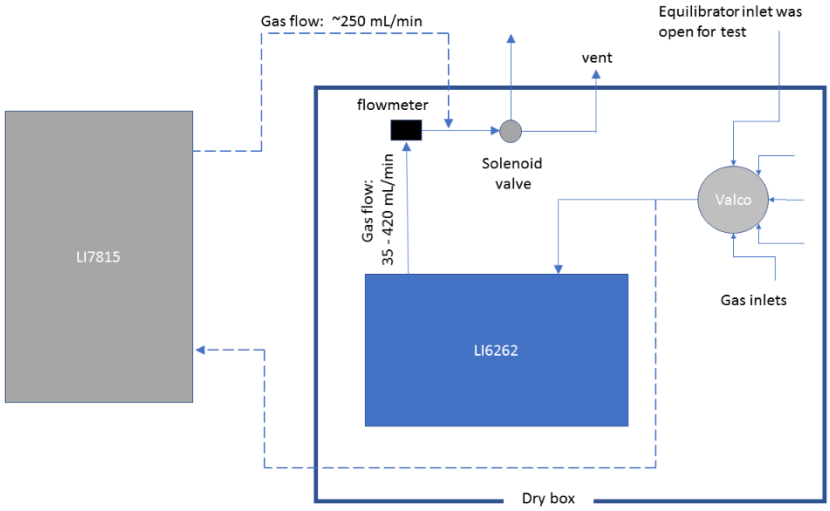

Figure 5: Schematic of connections for the LI7815 to the GO system in parallel configuration. The wet box was not connected.

Zero gas was used for the test and the flow was adjusted using the needle valves before the Valco valve. Figure 6 shows the resulting CO2 readings of the LI7815. As long as the gas flow was smaller or close to the gas flow in the LI7815 (250 mL/min), the system did not reach the zero value. Once the flow was higher than 250 mL/min, the system went to the zero values that were measured before and after this test (i.e. when the instruments were connected in series).

The parallel connection is not a solution, as the gas flow needs to be even higher than 250 mL/min. The instruments were connected, therefore, again in series after this test.

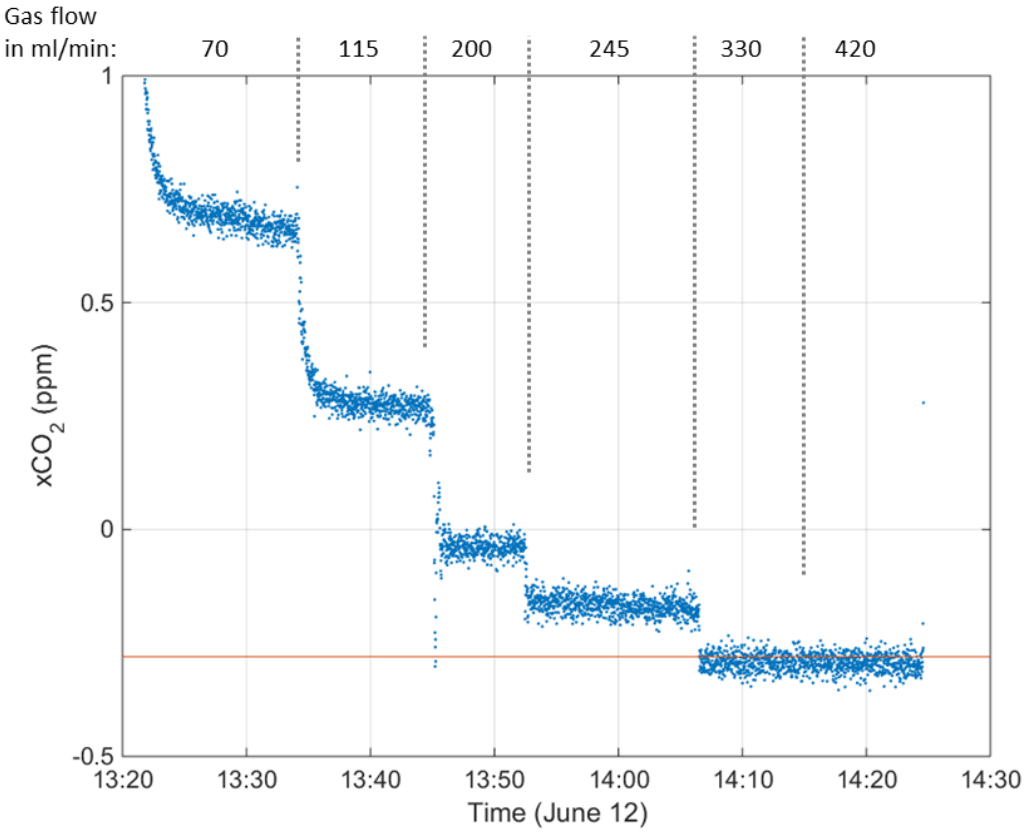

Figure 6: CO_2 readings of the LI7815 for different gas flows at the GO system. Both sensors (LI7815 and LI6262)9 were connected in parallel. The red line shows the approximate values for the zero standard measured before and after this test, when the sensors were connected in series.

6. 10 day test

The wet box was connected to the dry box as shown in Figure 7 to mimic shipboard applications. On **June 14** the zero and span values were readjusted (only minimal changes were done).

- The GO software was set to measure 4 x STD2, 4 x STD3, 4 x STD4 and ca. 3 hours EQU.
- Once a day zero and span was set for the LI6262. **Note**: The daily zero span was only done for the LI6262. The LI7815 was not adjusted for the rest of the time.
- The Labview software reading the LI7815 was set to send 20 second average values to the main GO program.
- The LI6262 was used to adjust the pressure of the standard gases upstream of the LI7815. The pressure was adjusted to approximately 1050 mbar.

The system was turned on in the afternoon of **June 14** and ran without changes until **June 24**.

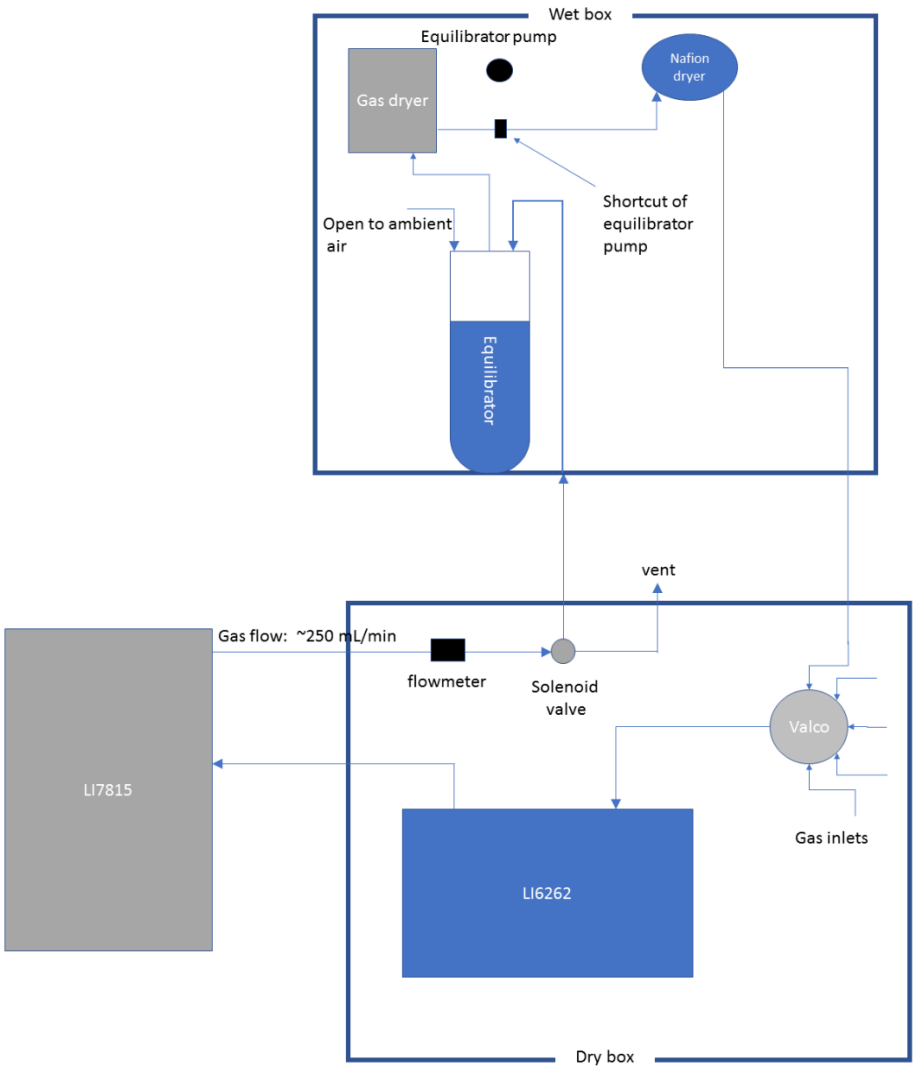

Figure 7: Schematic of connections for the LI7815 to the GO system in serial configuration with the wet box connected. The equilibrator pump of the GO system was bypassed.

Figure 8 shows the pressure readings for the whole test. STD4 shows large deviations from the certified value. The gas bottle was nearly empty (~10 bar left) and the gas regulator was old, so we assume that the regulator was the problem.

The pressure was around 900 mbar when measuring equilibrator air, which was approximately 100 mbar below atmospheric pressure. The standard gases needed to be adjusted well above this level to ensure enough gas flow in case of changing conditions.

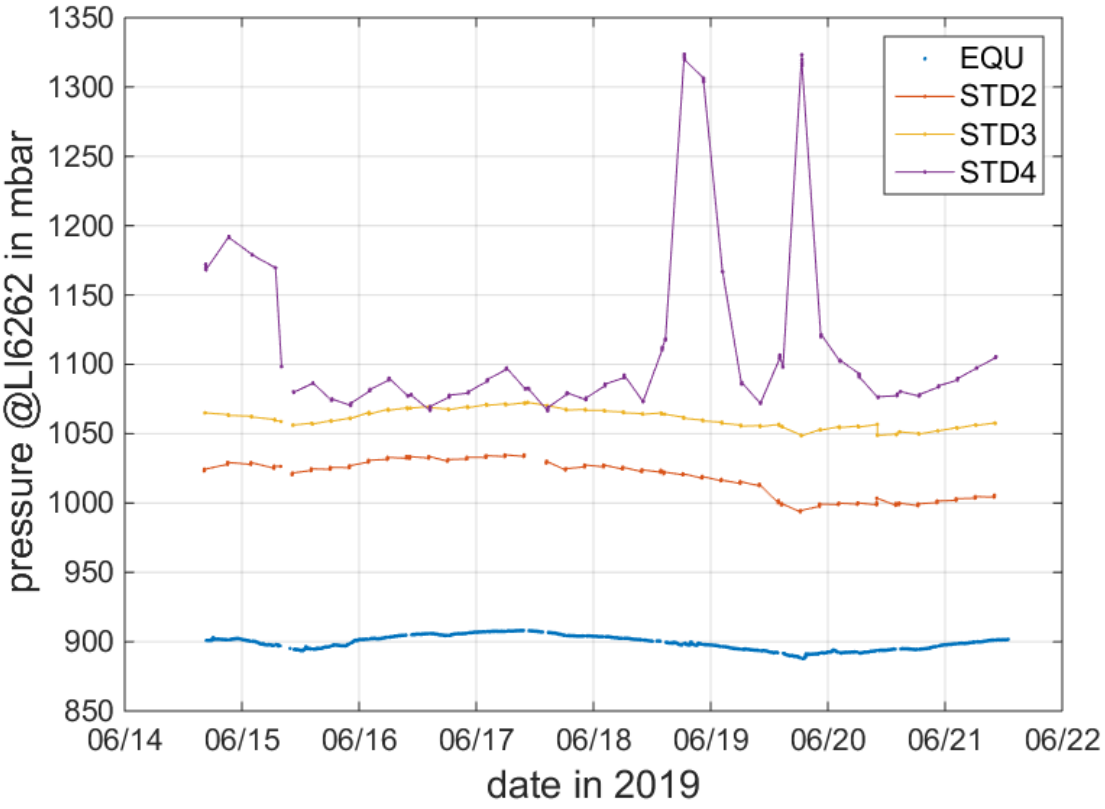

Figure 8: Pressure readings before the LI7815.

The following data were all recorded by the GO software. The data were reduced with the standard Matlab software that is used for pCO2 data reduction (following the recommendations of Pierrot et al., 2009). The data were checked only for obvious outliers and xCO_2 was calibrated using the standard gases. No further calculations were performed.

Figure 9 shows the standard gas measurements with the LI6262 and LI7815. There are 4 consecutive measurements each time a standard gas was measured. The first measurement for the LI7815 was always between 0.04 and 0.09 ppm higher than the last three measurements. As mentioned above, the zero and span of the LI7815 was not adjusted during the time period shown (approximately a week) and the instrument was stable within approximately 0.1 ppm. The standard deviation of the standard gas measurements was for all three gases below 0.03 ppm (see Figure 9). This includes also a possible drift over the week.

Figure 9: Data from standard gas measurements with the LI6262 (upper panel) and LI7815 (lower panel). The difference between the measured and the certified value for all three non-zero standard gases is shown. The standard deviation for measurements with the LI7815 is: σ(STD2) = 0.028 ppm, σ (STD3) = 0.026 ppm, σ (STD4) = 0.022 ppm.

7. Recommendations

- Look at how to mount the LI-7815 components inside the pCO2 dry box. It appears that this will not be difficult if the air pump and spectrometer are mounted separately. Is it okay to leave the battery out completely?
- With greater confidence in H_2O measurements from the LI7815, the system can be simplified by removing the Nafion dryers and associated air pump. This will eliminate the small error from CO2 loss across the Nafion and reduce cost and size.
- This would be a good opportunity to look at redesigning the condenser. The EQU air flow will be 2-3 times higher than previously. It would be good (CCN thinks) if the ATM side of the condenser could handle the full 2-3 litres per minute, allowing the ATM air pump to be plumbed downstream of the condenser in tropical conditions. The condenser could be optional on vessels that only sail in cold waters, but the water trap and overflow sensors should probably be retained. There is probably an OEM condenser available that would work.

8. Further testing

- The linearity of the system should be tested with a larger number of high-quality reference gases. We could run up to 6 gases between zero and 550 ppm in Hobart.
- Test using a pressure controller downstream of the Valco valve, with needle valves open or removed. Try with EQU air pump bypassed and see what pressure setpoint works best – it will be a small negative gauge pressure as the LI-7815's air pump will have to draw the air from the equilibrator, through an Acrodisc filter and a small differential for the pressure controller to operate. Test a slightly larger EQU pump running constantly at full speed to maintain positive pressure in the condenser and Acrodisc.
- Test without the pressure controller or needle valves – the inlet pressure to the 7815 would then be +0.3 bar for reference gases and maybe -0.05 bar for EQU air.
- Run for some time (many days to weeks) with water flowing in the equilibrator, to make sure the equilibrator and condenser can handle the higher air flow.
- Test flushing time with no NDIR in series with the 7815.