

Underway pCO₂ System Description
Laboratory: MBARI

Name/Vintage: SUMAC/ built by Gernot Friederich 2001

Reference

Where installed: R/V Revelle during SOFEX experiment / California coastal upwelling cruises. Previous version based on the same principles has been in use for about ten years for coastal upwelling work and also for high resolution vertical profiling.

Location of Data: MBARI/BOG database

Analyzer: LICOR 6262 infrared CO₂/H₂O analyzer with internal pressure sensor

Method of analysis: Absolute measurement with dry CO₂ free air in reference cell. Air in reference cell is circulated in a closed loop with a soda lime/magnesium perchlorate trap. Measures CO₂ and water vapor in the head space that is recirculated through the equilibrator.

Drying method: None

Equilibrator (setup, size, flows): Liqui-Cel[®] Membrane Contactor (2.5" by 8" cartridge or 0.75" by 5" mini module). Water flow is set to about 1 liter per minute for routine operation. For vertical profiling, this equilibrator can be tuned to have response times of less than ten seconds. A one liter volume showerhead style equilibrator has also been used in the past.

Standards (number, concentrations, frequency): Three standards are run hourly. Concentrations are chosen to cover the expected range for a given area. One of the three will be near atmospheric xCO₂. For short coastal cruises, a single standard is used since any non-linearity relative to overall response appears to constant for many years for any given analyzer. Water vapor zero is measured hourly and the absolute response is measured occasionally since an error of several percent in this measurement can be tolerated.

Source of calibration and accuracy: Primary standards are obtained from CMDL. Secondary standards are obtained from Praxair. The secondary standards are then inter-calibrated with the primaries using a LICOR 7000 CO₂/H₂O analyzer. This inter-calibration procedure provides errors of about 0.2 ppm near atmospheric levels and 0.5 ppm when pCO₂ differs from atmospheric values by more than 100 ppm.

Standard consumption: about 200 cc per hour at atmospheric pressure

Operating cycle: Hourly Cycle:

- 1) Closed loop circulation through soda lime/magnesium perchlorate trap to establish zero. (one minute)
- 2) Standard 1 (one minute)
- 3) Standard 2 (one minute)
- 4) Standard 3 (one minute)
- 5) Air sampling (one minute, air sampling pump has been flushing prior to this)
- 6) Equilibrator sampling (55 minutes)

During equilibrator sampling, the headspace is recirculated at about 500 cc per minute. There is a gas ballast vent to atmosphere near the equilibrator inlet. This vent allows for pressure equilibration since the total gas pressure in the equilibrator may not be in balance with the atmosphere.

Parameters recorded/frequency : For sea surface mapping data is gathered every two seconds and ten second averages are recorded. In most cases files are later merged with other data streams for final processing. The following parameters are produced and recorded directly:

- 1) Date.Time
- 2) IR_volts: raw analyzer voltage output
- 3) XCO2: derived mole fraction of CO₂ (includes correction for water vapor and pressure)
- 4) XH₂O: water vapor mole fraction
- 5) IR_temperature: temperature of IR cell
- 6) IR_pressure: pressure of IR measurement cell
- 7) Gas_Flow: flow rate of gas sample stream
- 8) Water_Flow: flow rate of water through the equilibrator
- 9) Water_temperature: temperature of water in the equilibrator
- 10) ID: sample identification
- 11) Error_status: communication and instrument error information

Hardware details

Temperature measurements: RTD positioned in the inflow of the membrane equilibrator or inside the showerhead equilibrator. RTD probe is calibrated against a recently calibrated Seabird probe. Calibration is valid to 0.01 deg.

Pressure measurements: Licor internal pressure sensor.

Circulation pathway: Two Thomas miniature diaphragm pumps (one for air sampling, one for equilibrator circulation). Gas stream is filtered with 1 μ m Acro disk filters. Two Kloehn 6-way stream selection valves are used for gas routing.

Operating software: Agilent VEE 6.0

Computer interface boards and sensors read:

Boards: B&B A/D with RS232 output

Addressable RS232 switch to allow switching between Licor, A/D system and Kloehn valves

Sensors:

Temperature: Omega RTD with Analog Devices signal conditioning unit

Gas Flow: Honeywell mass flow sensor

Water Flow: Omega hall effect turbine flow sensor with Analog Devices frequency to voltage converter

Approximate Size and Footprint:

Computer: any convenient laptop with one serial port

Gas handling and analytical: 14" wide by 8" deep by 14" high (includes Licor)

Equilibrator and associated sensors: 8" wide by 4" deep by 8" high

“Unique” Hardware or operating principles worth highlighting: The membrane equilibrator system can be mounted in-line and does not need to be near a drain. Wet operation eliminates maintenance and this system has been used completely unattended for periods of several weeks. The rapid response that can be obtained is beneficial during the examination of oceanic fronts.

What improvements would you incorporate in this system?

Automatic cleaning of the membrane equilibrator (currently we utilize a showerhead in cases where this might be an issue).