Underway pCO₂ System Description Laboratory: NOAA/AOML

Name/Vintage: System 3.0, built by Craig Neill in 1999

Reference: general operating principle described in Wanninkhof and Thoning (1992) and Feely et al. (1998)

Where installed: NOAA ship Ronald H. Brown

Location of Data: <u>www.aoml.noaa.gov/ocd/oaces</u>. Data generally released within 2 weeks of completion of cruise

Analyzer: LICOR 6252 (analog output) infrared (IR) analyzer

Method of analysis: Differential analyses relative to the low standard gas which flows continuously through the Licor reference cell. Measures dried air and equilibrator headspace gas. Gas flow is stopped prior to IR readings.

Drying method: Bow air and equilibrator headspace gas pass through a water trap cooled to 5 C and subsequently through column of $Mg(ClO_4)_{2}$.

Equilibrator (setup, size, flows): Equilibrator purchased from Scripps Institution of Oceanography and patterned after a design by Weiss, with 17 liter water reservoir and 12 liter gaseous headspace. Water flow rate is 10 l/min. Headspace gas is recirculated @ 250 ml/min.

Standards (number, concentrations, frequency): Three standards are used with approximate concentrations of 300, 360, and 420 ppm. In certain areas, a high standard of approximately 520 ppm is used instead of 420. All standards are run once an hour.

Source of calibration and accuracy: All standards come from NOAA's Climate Monitoring and Diagnostics Laboratory (CMDL) and are traceable to the WMO scale. Stated accuracy of the standards is 0.07 ppm from 330 to 420 ppm and 0.2 ppm for higher or lower standards.

Standard consumption: 2 tanks a year of low/reference standard; less than 1 tank a year for mid and high standards.

Operating cycle: Hourly cycle with sequence:

Three gas standards (3.5 minute flush @ 50 ml/min, 15 second wait (stop flow), 10 second analysis with average of 5 readings)

4 samples from equilibrator headspace (4 minute flush @ 250 ml/min, 15 second wait (stop flow), 10 second analysis with 5 IR readings averaged)

3 samples of bow air (3.5 minute flush @ 300 ml/min, 15 second wait (stop flow), 10 second analysis with average of 5 readings)

4 samples from equilibrator headspace (4 minute flush, 15 second wait (stop flow), 10 second analysis with 5 IR readings averaged)

During the head space gas measurement phases, gas is recirculated from the Licor sample output back to the equilibrator. During standard and air measurement phases, the sample output is vented to the atmosphere.

Parameters recorded/frequency : At the end of each phase (≈4.25 minutes) the following is recorded to disk resulting in a data file of less than 1.5 Megabytes per month

PHASE: water, air or standard

PC_DATE PC_TIME

YEAR_DAY

LATITUDE: from shipboard computer system (SCS)

LONGITUDE: from SCS

IR_VOLTS: analyzer voltage CO2 channel

IR_CONC: concentration determined from 2nd order polynomial fit of preceding standards

PRESSURE: pressure in laboratory

YSI_TEMP: temperature measured by separate YSI sensor in shunt water flow near equilibrator

YSI_SAL: salinity measured by separate YSI sensor in shunt water flow near equilibrator (poor quality)

YSI_DO: oxygen measured by separate YSI sensor in shunt water flow near equilibrator (no good)

EQ_VOLTS: resistance of thermistor in equilibrator

EQ_TEMP: temperature determined from an empirical polynomial function determined from laboratory calibration for thermistor in equilibrator

SCS_TEMP: temperature from thermosalinograph in bow (from SCS)

SCS_SAL: salinity from thermosalinograph (from SCS)

WIND_SPD_ABS: absolute wind speed (from SCS)

WIND_DIR_ABS: absolute wind direction (from SCS)

WIND_SPD_REL: relative wind speed (from SCS - corrected for ship speed/direction) WIND_DIR_REL: relative wind direction (from SCS)

EQ_MFM_VOLTS: voltage output from water flow meter in front of equilibrator

EQ_MFM_FLOW: flow (L/min) from water flow meter in front of equilibrator

PRE_MFM_REF_VOLTS: voltage output from reference gas flow meter in front of IR before flow is stopped prior to analysis

PRE_MFM_REF_FLOW: flow (from algorithm with voltage provided by manufacturer) PRE_MFM_SMP_VOLTS: voltage output from gas flow meter gas sample line in front of IR before flow is stopped prior to analysis

PRE_MFM_SMP_FLOW: flow (from algorithm with voltage provided by manufacturer) POST_MFM_REF_VOLTS: voltage output from reference gas flow meter in front of IR after flow is stopped prior to analysis

POST_MFM_REF_FLOW: flow (from algorithm with voltage provided by manufacturer)

POST_MFM_SMP_VOLTS: voltage output from gas flow meter gas sample line in front of IR after flow is stopped prior to analysis POST_MFM_SMP_FLOW: flow (from algorithm with voltage provided by manufacturer) SCS_DATE: date stamp from shipboard computing system SCS_TIME: time stamp (GMT) from shipboard computing system. IR_TEMP_VOLTS: Licor temperature output IR_TEMP: Licor temperature output FLUORO: Output of Turner 10-AU fluorometer (from SCS)

<u>Hardware details</u>

Temperature measurements: Thermistor positioned in bottom of equilibrator, calibrated against a Hart thermometer once a year

Pressure measurements: Setra model 350 pressure transducer

Circulation pathway: Two KNF pumps (one for head space gas, one for bow air) routed through 1 μ m Acro disks and a Valco 6-port valve. The Licor sample output is routed through a solenoid that allows it to be directed back to the equilibrator or to the atmosphere. This line also has a 1 μ m Acro disk.

Operating software: Labview Version 5.1

Computer interface boards and sensors read:

Boards: National Instruments ATMIO 16 XE-50, National Instruments ER-8 relay board **Sensors:** A/D 16 bit- voltage LICOR CO₂ channel (0-5 V)

A/D 16 bit- voltage LICOR temperature (0-5 V)

A/D 16 bit- Data Industrial water flow meter (0-5 V)

A/D 16 bit- Aalborg gas flow meter on reference side of Licor (0-5 V)

A/D 16 bit- Aalborg gas flow meter on sample side of Licor (0-5 V)

A/D 16 bit- resistance, constant current – thermistor equilibrator

A/D 16 bit- Setra model 350 (0-5 V)

YSI thermosalinograph is read via RS-232 port

Position, Thermosalinograph, fluorometer, wind speed and wind direction are read via RS-232 port from shipboard computing system

Approximate Size and Footprint

Computer and interface boards- box of 18" wide by 18 " deep by 30" high Equilibrator: on stand over a drain pan size 18" wide by 15 " deep by 40" high Box with valves and LICOR: box of 24" wide by 18 " deep by 24" high Water cooling bath: 20" wide by 24" deep by 30" high Condensor box: 14" wide by 14" high by 4" deep

"Unique" Hardware or operating principles worth highlighting:

- a. Magnetic float and reed switch that will turn off pumps if condenser fills with water.
- b. Automatic water drains for condensor (operate every 5 hours during standard cycle

- **c.** Short vent lines of equilibrator are in an open chamber flushed with excess bow air
- d. YSI thermosalinograph installed in shunt water flow near equilibrator

What improvements would you incorporate in this system?

Decrease size; improve ease of installation; improve drying to decrease the frequency of changing of Mg(ClO₄)₂; decrease standard gas consumption; correct for lag in response between TSG input and equilibrator. That is, correct for residence time for water in tubes on ship (≈ 3 minutes). Change timing of solenoid that recirculates head space gas to equilibrator.