

Underway pCO₂ System Description

Laboratory: Baltic Sea Research Institute Warnemünde (IOW), Marine Chemistry, Dr. Bernd Schneider (The manual version is described. The automatic system is under construction, but some successful tests were done.)

Name/Vintage: Warnemünde pCO₂ system

Reference: General operating principle described in Körtzinger et al. (1996): Körtzinger, A. et al., 1996. At-sea intercomparison of two newly designed underway pCO₂ systems - encouraging results. *Marine Chemistry*, 52(2): 133-145.

Where installed: Currently installed at the IOW. Last used on R/V A. v. Humboldt and R/V Gauss.

Location of Data: Dr. Bernd Schneider, IOW (bernd.schneider@io-warnemuende.de)

Analyzer: LI-COR 6262 (analog output) non-dispersive infrared gas analyzer

Method of analysis: Equilibrated air and air from the top deck were measured by differential analyses relative to nitrogen (in the automatic version it will be clean air, soda lime pallets and Mg(ClO₄)₂). The pCO₂ in seawater is determined by continuous equilibration using a bubble-type equilibrator .

Drying method: No drying method is applied prior to air and headspace gas measurement, the reference gas nitrogen 5.0 is additionally cleaned using gas purification tubes with soda lime pallets and one with Mg(ClO₄)₂.

Equilibrator size, flow and setup: Equilibrator designed by Bernd Schneider, 200 ml water, about 100 ml headspace
Water flow rate: about 1 l/min
Headspace circulated at 500 ml/min

Standards: Two standards of about 300 and 450 ppm

Source of calibration and accuracy: Two standards come from Scott-Marrin, Inc., Riverside, CA, USA with certified CO₂ amount (NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO, USA): 300.97 ppm and 453.02 ppm.

Standard consumption: about 1 tank in 3 years.

Operating cycle:

The 5-way ball valve can be manually switched between zero gas, standard gas 1, standard gas 2, and measurement, respectively. Manual switching between pCO₂ air and pCO₂ water measurements is performed by a three-way valve. The calibration is done in 12 hour intervals. During standard and air measurements, the gas is vented to the atmosphere.

Parameters recorded/frequency : The data collection and preliminary calculations were performed by a windows programme designed to synthesize ship data and data supplied by the LI-COR instrument. Each minute a set of parameters listed below is displayed and stored:

Time and date (UTC)
Local time (PC-clock)
GPS-Longitude
GPS-Latitude
pCO₂-air (μatm)*
pCO₂-water (μatm)*
Surface water salinity (psu)
Surface water temperature T (°C)
Water temperature in the equilibrator (°C)
Molar ratio of CO₂ in dry air (ppm)*
Molar ratio of water vapour (ppt)*
Atmospheric pressure (hPa)
Ambient air temperature (°C)
Relative Humidity of ambient air (%)
Output voltage CO₂ (mV)
Pressure in the detector cell (kPa)
Temperature detector cell (°C)
CO₂-zero
CO₂-span
H₂O-zero
H₂O-span

*either measurement of pCO₂ water or pCO₂ air

Hardware details

Temperature measurements: Pt-100 temperature probe (4-wire technique) positioned in the top of the equilibrator, calibrated

Pressure measurements: Kobold (800-1200 mbar) pressure transducer

Circulation pathway: A membrane pump (WISA 200) routed by a manually actuated Whitey 2-port valve, either pumps air in a closed loop from the headspace of the equilibrator through a flow meter with needle valve, adjusted to 500 mL min⁻¹, through the detector, and back to the headspace, or sucks air from the top deck of the ship through the sample cell and then vents to the atmosphere.

Operating software: Visual basic (Thomas Renger, Bernd Schneider)

Computer interface boards and sensors read:

Temperature modul: Keithley, SmartLink™ KNM-RTD31

Sensors: A/D 16 bit- voltage LI-COR CO₂ channel (0-5 V)
A/D 16 bit- voltage LI-COR temperature (0-5 V)

Approximate Size and Footprint

Computer box of 21" wide by 19 " deep by 32" high

Equilibrator, cooling bath: size 10" wide by 15 " deep by 15" high

Box with valves, flowmeters, pressure transducer, LI-COR, and interface boards: box of 30" wide by 20" deep by 20" high

“Unique” Hardware or operating principles worth highlighting:

Synthesis of pCO₂-measurements, meteorological, and oceanographic data provided by the data-system of the ship, preliminary calculations

What improvements would you incorporate in this system?

Automation