**Underway pCO$_2$ 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 pCO$_2$ system

**Reference:** General operating principle described in Körtzinger et al. (1996): Körtzinger, A. et al., 1996. At-sea intercomparison of two newly designed underway pCO$_2$ 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 $Mg(ClO_4)_2$). The pCO$_2$ 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 $Mg(ClO_4)_2$.

**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 CO$_2$ 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 pCO$_2$ 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
$pCO_2$-air          (μatm)*
$pCO_2$-water     (μatm)*
Surface water salinity (psu)
Surface water temperature T (°C)
Water temperature in the equilibrator (°C)
Molar ratio of $CO_2$ 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 $pCO_2$ water or $pCO_2$ air

<u>**Hardware details**</u>
**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, SmartLinkTM KNM-RTD31

**Sensors:** A/D 16 bit- voltage LI-COR $CO_2$ 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 $pCO_2$-measurements, meteorological, and oceanographic data provided by the data-system of the ship, preliminary calculations

**What improvements would you incorporate in this system?**

Automation