Underway pCO_2 System Description
Laboratory: Princeton University

Name/Vintage: Disc Equilibrator/1995

Reference:

Sabine, C.L. and R.M. Key, *A new instrument design for continuous determination of oceanic pCO_2*, Tech. Rep. #96-12, Ocean Tracer Laboratory, Dept. of Geosciences, Princeton Univ., Princeton, NJ, 20 pp., 1996.

Sabine, C.L. and R.M. Key, *Surface Water and Atmospheric Underway Carbon Data Obtained During the World Ocean Circulation Experiment Indian Ocean Survey Cruises (R/V Knorr, December 1994-January 1996), ORNL/CDIAC-103, NDP-064,* Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge TN, 89 pp., 1997.

Where installed: Not currently assigned to permanent ship, but operated for several years on R/V Knorr.

Location of Data: CDIAC

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 1 m Nafion drying tube before going through a 10 cm column half filled with $Mg(ClO_4)_2$ and half filled with Aquasorb. The outer gas for the Nafion dryer came from the reference gas after it was vented from the LiCor.

Equilibrator (setup, size, flows): The disk equilibrator is an acrylic cylinder, 8" in diameter and 24" long, with 60 disks mounted on a stainless steel shaft that runs along the axis of the chamber. The 0.0625" thick disks are 7.5" in diameter and are rotated at 135 RPM by a gear reduction motor connected to the disk shaft with a flexible universal coupler. On the motor end of the equilibrator, the disk shaft passes through the endplate of the cylinder. Gas and water leakage around the shaft is prevented by compressible teflon seals. On the other end of the cylinder the shaft is mounted in a permanently lubricated brass sleeve bearing. The equilibrator is fitted with a high precision absolute pressure transducer (Setra model 270), a calibrated platinum resistance thermometer, a precision mercury thermometer and a water level float switch.

Seawater from the ship's bowpump is run through an acrylic bypass chamber at the fastest rate possible to minimize the residence time between the equilibrator and the bowpump and to assure that sufficient water is available whenever the system demands. The bypass chamber is fitted with a valve from which discrete water samples can be collected. Water is pumped from the bypass chamber into the equilibrator using a belt driven impeller pump. The pump is powered by a 1/3 HP - 1725 RPM electric motor.

Water flows through the equilibrator at 8-18 l/min with the rate being determined by the available supply from the bowpump and regulated by varying pulley diameter ratios on the pump and pump motor. The pump is automatically turned on and off by a float switch to maintain a constant water level in the equilibrator. Both the water inlet and drain lines of the equilibrator are fitted with flow control valves mounted adjacent to the equilibrator chamber. By changing the water pump pulleys and adjusting the flow control valves, the system can be adjusted to work with a very wide range of water delivery rates from the bowpump. Once water flow is established through the equilibrator it is simple to balance the flow so that the water pump runs almost all the time. In normal operation, the equilibrator chamber remains approximately half-full resulting in a water residence time in the equilibrator of one minute or less. The rotating disks develop a thin layer of water on both sides thus increasing the exposed surface area of the water 20 fold. Because the disks rotate, the amount of water directly exposed to air per unit time, is increased by a factor much greater than 20. Air is recirculated through the top half of the chamber (approximately 6 liters) in the opposite direction to the water at a rate of approximately 6 l/min resulting in an air residence time in the chamber of approximately 1 min. The high water flow coupled with the very high effective water surface area exposure and the relatively low rate of air flow to the detector (about 0.03 l/min) results in an extremely rapid equilibration rate. The small amount of air removed from the equilibrator for measurement is replaced by a vent line extending from the equilibrator air circulation plumbing to the outside. The vent line is fitted with a baffle volume to minimize air surging in this line caused by the air circulation pump.

Standards (number, concentrations, frequency): In the Indian Ocean we ran the system with a 200 ppm reference gas and 3 standards at approximately 250, 350, and 450 ppm. Previous cruises were run using a zero references, but we found that by using a reference gas with a non-zero concentration, the dynamic range of the instrument could be significantly increased. Full calibrations, including running the reference gas as a standard, were done every 3 hours.

Source of calibration and accuracy: All of the reference and calibration gases used with this instrument were calibrated to an accuracy of 0.3 ppm by R. Weiss against his standards and primary standards measured and prepared by C. D. Keeling.

Standard consumption: 6 tanks a year of reference gas; <1 tank a year for higher standards.

Operating cycle: Any time the gas selector valve changes, the computer waits a preset minimum “delay time” prior to saving any datum (3 minutes for standards and samples, 5 minutes for reference gas). For samples as well as standards, the delay time is set sufficiently long to allow the “new” gas to completely flush the “old” gas and for the detector response to stabilize. Once data collection begins for any sample, the time separation between points is determined by the time required for the signal to stabilize after closing and opening the solenoid valves. When the solenoid valves are closed - in order to take the actual measurement under no flow conditions at atmospheric pressure - gas pressure builds up behind the solenoid. When the solenoids are opened it takes a finite amount of time for the resulting pressure surge to dissipate. The detector is sensitive to these pressure fluctuations. The time for this pressure surge to pass is significantly less than the initial delay time.

Based on present knowledge of system performance at sea, a complete calibration is run every three hours. Each calibration consists of collecting a preset number, N (generally 5-10), of data points for each of the standard gases and the reference gas (which acts as a fourth standard). The three hour time interval begins at the end of a calibration run. During the three hours between calibrations the system alternates between equilibrator gas (20 readings) and marine air sampling (5 readings).

Parameters recorded/frequency : Sampling frequency is based on a dynamic stability tester, but the long-term average was ~2.5 minutes between water samples.

Hardware details

Temperature measurements: The temperature of the water inside the equilibrator was monitored with a Rosemont ultra linear platinum temperature sensor (PRT). The PRT was calibrated prior to the first leg of the survey, by the Scripps Ocean Data Facility (ODF) using standard CTD calibration techniques. Estimated accuracy is +/- 0.003 °C on the ITS90 scale. A secondary check on the accuracy of the equilibrator temperature readings was made by frequently comparing temperature readings from a mercury thermometer, located in the equilibrator, to values recorded from the PRT.

Pressure measurements: Setra model 270 pressure transducer

Circulation pathway: The input gas going to the detector is selected with an electronically actuated 6-port valve (Valco model no. ESD6M). Prior to entering the selector valve, sample gases (marine air and equilibrator air) are filtered through stainless steel filter elements with a 0.5 mm pore size. After exiting the selector valve and before entering the detector, both standard and sample gasses are passed through a hygroscopic, ion exchange membrane (Nafion) and a small column with 50% magnesium perchlorate and 50% Aquasorb to remove water vapor. All gases are adjusted to flow through the detector at a rate of ~0.04 l/min. The standard and reference gas flow rates are adjusted using a combination of pressure, which is set at the tank by high purity two stage regulators, and needle valves located near the detector inlet ports. Solenoid valves are located adjacent to the detector inlets on both the reference and sample gas lines to stop the gas flow prior to taking a measurement. Zero gas flow during actual measurement was found to yield significantly better results than trying to precisely control the gas flow rate.

Operating software: Lab Windows

Computer interface boards and sensors read:

Boards: National Instruments A/D board (model PC+)

Sensors: as noted above

Approximate Size and Footprint

Electronics package ~ 2' x2' x2'

Equilibrator and associated hardware ~ 5' x 2' x2'

Water pump housing ~ 1' x1' x2'

“Unique” Hardware or operating principles worth highlighting:
Laboratory measurements demonstrated that the temperature corrected Li-Cor response was still reacting to the ambient temperature fluctuations. This is the reason that the entire detector rack was thermally insulated. To further ameliorate ambient temperature changes a 60 watt flexible silicone rubber heater was placed inside the detector rack. Air inside the rack is circulated with muffin fans. The air temperature inside the rack is measured and controlled with an Omega (model CN76130) temperature controller connected to a fast response platinum resistance thermometer and the heater. The thermometer monitors the air temperature adjacent to the Li-Cor air vent opening. This temperature controller is rated to ±0.1°C, however during shipboard operation we have not been able to regulate the detector temperature to better than approximately ±0.15°C on a daily basis.

The efficiency of the disk equilibrator determines how quickly the system responds to changes in the seawater CO2 concentration and to what extent the system is influenced by the introduction of air through a leak in the system (e.g. the replacement air vent line). Schink et al. (1970) examined the efficiency of the disk extractor design using an oxygen electrode in the effluent stream, oxygen saturated water as the test solution, and an oxygen free extraction gas. They found that at least 99% of the oxygen was extracted under a wide range of conditions. The extraction was essentially independent of the liquid level from 1/4 to 1/2 full and gas flow rates up to 2.5 l/min. The gas removal was sensitive to liquid flow rates, with complete extraction up to 1.6 l/min dropping to 75% extraction at 2 l/min. Schink and coworkers tested the efficiency of the stripper at removing radon by hooking three strippers in series and treating the gas from each stripper as a separate sample. They found that the first extractor removed 96% of the radon gas from seawater with a water flow rate of 1.6 l/min and a helium flow rate of 1.0 l/min. With the rotating disks in equilibrator mode, the response to an instantaneous change in the CO_2 of the water is an exponential mixing function. Laboratory and "at sea" tests indicate that the e-folding time for this system is approximately one minute.

What improvements would you incorporate in this system?