# BioChem - Standard Operating Procedure

## Data Type: pCO2 (Discrete bottle measurements)

## Data Provider/PI: Stephen Punshon/Kumiko Azetsu-Scott

## Data\_Type\_Seq:

## Background:

In this case, pCO2 is defined as the partial pressure of carbon dioxide in moist air in equilibrium with the seawater sample at 22 °C, and the units are micro-atmospheres (μatm). pCO2 samples are collected from rosette casts into 160 mL volume serum bottles using a short length of flexible tubing. The bottles are allowed to overflow by two volumes, immediately preserved by the addition of 50 μL of saturated mercuric chloride solution, then sealed using a Teflon faced butyl rubber septum and crimp seal. The samples are stored in a refrigerator until analysis back at BIO. The preservation protocol does not affect the analysis or results and as the analysis is rarely if ever performed at sea, there is no distinction between “fresh” or “preserved” samples. The analysis is usually performed within two months of collection. pCO2 samples are almost always paired with TIC samples, as TIC data are required, along with temperature, salinity and pressure, to convert the pCO2 values obtained at the analytical temperature of 22 °C to in situ conditions. The analytical method is based on Neill et al. (1997). Samples are thermally equilibrated in a water bath at 22 ± 0.1 °C for one hour whereupon 11 mL of the sample volume is replaced by a headspace gas mixture consisting of 400 ppm CO2 in hydrocarbon free air. The bottles are then shaken for 8 minutes to reach phase equilibrium and the headspace pressure is measured by piercing the septum with a needle connected to a pressure transducer . The headspace gas is then dried and injected into a gas chromatograph equipped with a methanizer where CO2 is quantitatively reduced to methane in the presence of hydrogen and detected by a flame ionisation detector. A post analysis calculation adjusts the CO2 partial pressure to 100% relative humidity. The method is standardised by injections of Certified Primary Gas Mixtures, nominally 400, 800 and 1200 and 2000 ppm CO2.

## Instrument

The analytical instrumentation used for pCO2 comprises an SRI 8610C Gas Chromatograph fitted with two 1/8” x 2 m packed columns (Hayesep D 80/100) in a pre-column back-flush configuration. CO2 eluting from the main column passes through a methaniser held at 380 °C and the resulting methane peak is determined with a Flame Ionisation Detector and a computer running SRI PeakSimple integration software.

## Analysis Protocol:

Neill, Craig, Kenneth M. Johnson, Ernie Lewis, Douglas W. R. Wallace, 1997. Accurate Headspace Analysis of fCO2 in Discrete Water Samples Using Batch Equilibration. Limnology and Oceanography, Vol. 42, No. 8, 1774-1783.

## Quality Assurance Prior to Provision:

The data are flagged using the WOCE data quality flag system (Bottle flag, Laboratory flag, Interpretive flag) prior to provision.

## Standard File Name Convention:

Open to discussion, but in the past we have submitted files as Cruise name\_pCO2.xlsx

## Preservation:

Samples are preserved with a saturated solution of mercuric chloride to give a final concentration of 0.03%.

## Sample Handling:

Unfiltered water (whole water sample)

## Storage Description:

Stored at 4 °C prior to analysis

## Unit of Measure:

μatm

## Detection Limit:

0.5 μatm

## Quality Assurance Prior to Load:

Range check 1 – 5000 μatm