### Dissolved Inorganic Carbon

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#### Sampling

Dissolved inorganic carbon (DIC) samples were the first to be collected once the CTD/rosette was secured on deck. Seawater was collected in glass 250 mL reagent bottles. The sampling tube was connected to the spigot of the Niskin bottle and, by holding the tube above the spigot, was rinsed by flowing approximately one tube volume of sea water through the tube. Any trapped air bubbles were removed by tapping or squeezing the tube. The bottle was filled smoothly from the bottom (tubing touching the bottom of the bottle) and the bottle overflowed by two times its volume. The tubing was withdrawn to the neck and the spigot valve closed or the flow in the tubing squeezed off before the tubing was removed from the bottle. One percent of the stoppered sample volume was removed to leave a headspace (about 1 % of the bottle volume - i.e., 2.5 mL for a 250 mL bottle) by inserting a nylon plug into the bottle. Since all of the samples on this cruise were analyzed post cruise, 100 μL of saturated mercuric chloride solution was added to each samples and glass stoppers greased to seal the bottles for sample preservation. DIC, then alkalinity were measured from the same sample.

#### Analysis

Samples were analyzed at IOS by Marty Davelaar, using a SOMMA analysis system to determine the concentration of dissolved inorganic carbon (or total carbon dioxide). The SOMMA (Single Operator Multi Metabolic Analyzer) is a sea-going, computer-controlled automated system used to measure DIC. This SOMMA was constructed at Woods Hole by Ken Johnson. The SOMMA uses a DOS based PC and GW-Basic software along with a coulometric detector (UIC Coulometrics, model 5011). The SOMMA dispenses and acidifies a known volume of seawater, strips the resultant CO2 from solution, dries it and delivers it to the coulometric detector.

At the start of each day, seawater was run through the system to condition the cell. Next a system blank is started. If the blank is below 1.0 μg Carbon in a ten minute period a Dickson CRM sample is analyzed to confirm the system is working properly. For each analysis (standard or sample) a headspace gas is used to push the sample out of the bottle and into the water-jacketed calibrated pipette. The water from the pipette is then drained into a scrubber compartment to which approximately 1.0 mL of 8.5 % ortho-phosphoric acid had been added. UHP nitrogen is then pushed through a bottom mounted frit, the nitrogen pushes the CO2 which has been stripped from the sample by the acid through a cold trap which is used to keep water vapor from entering the cell where the CO2 is titrated. The coulometer was operated in the μg C mode. The software then uses the μg C total along with the pipette’s temperature, the salinity of the water and other constants to calculate the μmol/kg value of each sample. At the start of each sample or standard, the system performs a “rinse” analysis where the system uses the sample that is currently being analyzed to completely fill the pipette, the water is then drained to the scrubber to which acid has been added and the CO2 is stripped away. So each sample is actually analyzed for DIC twice. The final concentrations are calibrated with the daily measured Dickson CRM where:

*corrected value = raw value \* certified CRM value \* HgCl2 correction factor*

 *daily CRM measured value*

The HgCl2 correction factor is 1.0004 and DIC values are reported in units of µmol/kg.

* + - 1. ***Precision, Standards, and Blanks***

Table 1. Water sample precision and accuracy

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Chemistry Sample** | **Precision (*s*p)** | **Units** | **Number of Replicates (*n*)** | **Outliers removed** | **Minimum Range** | **Maximum Range** | **Accuracy (%recovery)** |
| DIC | n/a | µmol/kg | 1 | n/a | 1767.5 | 2262.2 | 100.03 |

The accuracy of DIC analysis was assured by daily analysis of Dickson CRM sea water (batch 133, S=33.341 psu, concentration 2021.12 µmol/kg; DOE 1994; Dickson 2001; Dickson et al. 2003) supplied by Andrew Dickson (Scripps Institute of Oceanography, San Diego, USA). The mean accuracy (%recovery) was calculated to be 100.00%, ranging from 99.93 to 100.06%. Only once sample was collected in duplicate this year and so, the pooled standard deviation could not be calculated.