DISSOLVED INORGANIC CARBON (DIC)

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Sample collection:

Samples for DIC measurements were drawn (according to procedures outlined in the PICES Publication, *Guide to Best Practices for Ocean CO2 Measurements*) from Niskin bottles into 294 ml borosilicate glass bottles using silicone tubing. The flasks were rinsed once and filled from the bottom with care not to entrain any bubbles, overflowing by at least one-half volume. The sample tube was pinched off and withdrawn, creating a 6 ml headspace, followed by 0.12 ml of saturated HgCl2 solution which was added as a preservative. The sample bottles were then sealed with glass stoppers lightly covered with Apiezon-L grease and were stored at room temperature for a maximum of 12 hours.

Equipment:

The analysis was done by coulometry with two analytical systems (AOML 3 and AOML 4) used simultaneously on the cruise. Each system consisted of a coulometer (CM5017 UIC Inc.) coupled with a Dissolved Inorganic Carbon Extractor (DICE). The DICE system was developed by Esa Peltola and Denis Pierrot of NOAA/AOML and Dana Greeley of NOAA/PMEL to modernize a carbon extractor called SOMMA (Johnson et al. 1985, 1987, 1993, and 1999; Johnson 1992).

The two DICE systems (AOML 3 and AOML 4) were set up in a seagoing container modified for use as a shipboard laboratory on the aft main working deck of the *R/V Thomas G. Thompson.*

DIC Analysis:

In coulometric analysis of DIC, all carbonate species are converted to CO2 (gas) by addition of excess hydrogen ion (acid) to the seawater sample, and the evolved CO2 gas is swept into the titration cell of the coulometer with pure air or compressed nitrogen, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. In this process, the solution changes from blue to colorless, triggering a current through the cell and causing coulometrical generation of OH- ions at the anode. The OH- ions react with the H+, and the solution turns blue again. A beam of light is shone through the solution, and a photometric detector at the opposite side of the cell senses the change in transmission. Once the percent transmission reaches its original value, the coulometric titration is stopped, and the amount of CO2 that enters the cell is determined by integrating the total change during the titration.

DIC Calculation:

Calculation of the amount of CO2 injected was according to the CO2 handbook (DOE 1994). The concentration of CO2 *([CO2])* in the samples was determined according to:

*[CO2] = Cal. Factor \* (Counts – Blank \* Run Time)\* K µmol/count*

*pipette volume \* density of sample*

where *Cal. Factor* is the calibration factor, *Counts* is the instrument reading at the end of the analysis, *Blank* is the counts/minute determined from blank runs performed at least once for each cell solution, *Run Time* is the length of coulometric titration (in minutes), and *K* is the conversion factor from counts to micromoles.

The instrument has a salinity sensor, but all DIC values were recalculated to a molar weight (µmol/kg) using density obtained from the CTD’s salinity. The DIC values were corrected for dilution due to the addition of 0.120 ml of saturated HgCl2 used for sample preservation. The total water volume of the sample bottles was 294 ml (calibrated by Esa Peltola, AOML). The correction factor used for dilution was 1.00041. A correction was also applied for the offset from the CRM. This additive correction was applied for each cell using the CRM value obtained at the beginning of the cell. The average correction was

1.26 µmol/kg for AOML 3 and 1.58 µmol/kg for AOML 4.

The coulometer cell solution was replaced after 24 – 28 mg of carbon was titrated, typically after 9 – 12 hours of continuous use. The blanks ranged from 12 -35.

Calibration, Accuracy, and Precision:

The stability of each coulometer cell solution was confirmed three different ways.

1. Gas loops were run at the beginning of each cell
2. CRM’s supplied by Dr. A. Dickson of SIO, were analyzed at the beginning of the cell before sample analysis.
3. Duplicate samples from the same niskin, were measured near the beginning; middle and end of each cell.

Each coulometer was calibrated by injecting aliquots of pure CO2 (99.999%) by means of an 8-port valve (*Wilke et al., 1993*) outfitted with two calibrated sample loops of different sizes (~1ml and ~2ml). The instruments were each separately calibrated at the beginning of each cell with a minimum of two sets of these gas loop injections.

The accuracy of the DICE measurement is determined with the use of standards (Certified Reference Materials (CRMs), consisting of filtered and UV irradiated seawater) supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO). The CRM accuracy is determined manometrically on land in San Diego and the DIC data reported to the data base have been corrected to this batch 187 CRM value. The CRM certified value for this batch is 2002.85 µmol/kg.

The precision of the two DICE systems can be demonstrated via the replicate samples. Approximately 11% of the niskins sampled were duplicates taken as a check of our precision. These replicate samples were interspersed throughout the station analysis for quality assurance and integrity of the coulometer cell solutions. The average absolute difference of these replicates was 1.74 (AOML 3) and 1.38 (AOML 4) µmol/kg - No major systematic differences between the replicates were observed.

The pipette volume was determined by taking aliquots of distilled water from volumes at known temperatures. The weights with the appropriate densities were used to determine the volume of the pipettes.

Calibration data during this cruise:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| UNIT | Ave Gas Cal Factor | Pipette | Ave CRM | Std Dev | Ave Difference  Dupes |
| AOML 3 | 1.00448 | 27.990 ml | 2003.23, N= 42 | 0.67 | 1.74 |
| AOML 4 | 1.00422 | 29.387 ml | 2004.32, N = 43 | 1.27 | 1.38 |

Instrument Repairs

AOML 3 had a relay switch failure before Station 17. The relay switch and micro acid pump were replaced and the instrument functioned well for the rest of the cruise. AOML 4 had the 5V power supply fail during Station 65. The power supply was replaced with a new one and the instrument functioned well for the remainder of the cruise.

Underway DIC Samples

Underway samples were collected from the flow thru system in the hydro-lab during transit. Discrete DIC samples were collected approximately every 4 hours before the line of 90 CTD stations commenced with duplicates every fifth sample. A total of 38discrete DIC samples including duplicates were collected while underway. The average difference for replicates of underway DIC samples was 0.68 µmol/kg and the average STDEV was 0.30.

Summary:

The overall performance of the analytical equipment was good during the cruise.

Including the duplicates, a total of 2245 samples were analyzed from 90 CTD casts for dissolved inorganic carbon (DIC), which equates to a DIC value for 68% of the niskins tripped. A total of 38 discrete DIC samples including duplicates were collected from the underway system and analyzed while in transit. The DIC data reported to the database directly from the ship are to be considered preliminary until a more thorough quality assurance can be completed shore side.

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