

Cruise: WS17086
Ship: R/V Walton Smith
Expo Code: 33WS20170327
Dates: March 27th – 31st, 2017
Chief Scientist: Dr. Chris Kelble
Equipment: CTD Rosette
Total number of stations: 9
Location: Southwest Florida Gulf of Mexico coastal region

Samples were collected for Dr. Leticia Barbero for the Ocean Acidification Program during the South Florida Project (SFP) water quality cruises in the SW Gulf of Mexico lead by Dr. Chris Kelble.

Sample Collection

The discrete samples were collected from Niskin bottles attached to a 24 bottle configured rosette onboard the R/V Walton Smith by Patrick Mears. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

6 locations, 9 samples, each 500-mL, 0 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Patrick Mears

pH:

6 locations, 9 samples, each 500-mL, 0 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Patrick Mears

Talk:

6 locations, 9 samples, each 500-mL, 0 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Patrick Mears

Sample Analysis

DIC:

| Instrument ID | Date | Certified CRM ($\mu\text{mol/kg}$) | CRM Value ($\mu\text{mol/kg}$) | CRM Offset ¹ ($\mu\text{mol/kg}$) | Blank (Counts) | Avg. Sample Analysis Time |
|---------------|-----------|--------------------------------------|----------------------------------|--|----------------|---------------------------|
| AOML4 | 4/11/2017 | 2031.53 | 2029.63 | 1.90 | 28 | 11 |

Analysis date: 04/11/2017
 Coulometer used: DICE–CM5015- AOML 4
 Blanks: 10.0 counts/min and raised to 28.0 counts/min before CRM analysis
 CRM # 1216 was used and with an assigned value of
 Batch 144, TCO₂: 2031.53 μmol/kg, S: 33.571
 CRM values measured: AOML 4: offset 1.90 μmol/kg (2029.63 μmol/kg).
 Average run time, minimum run time, and maximum run time: 11, 8 and 13 min.

Reproducibility: No duplicate samples were collected.

CRM, salinity and HgCl₂ correction applied: Salinity correction was applied using CTD salinity.

Remarks

The volume correction was applied due to added 0.2mL of HgCl₂ (Measured DIC*1.00037). The first CRM of each cell was used for a CRM correction.

The DIC instruments were stable: the gas loop and CRM values did not change significantly throughout the life span of each cell.

The samples were analyzed using the DICE (AOML 4) and a UIC, Inc. coulometer model CM5015 with CM5011 emulation software.

pH:

Analysis date: 04/11/2017
 Spectrophotometer used: HP Agilent 8453

Reproducibility: No duplicate samples were collected.

Temperature measured during pH analysis

| Sample ID | Sample BTL # | BTL Temp (°C) | Start Cell (°C) | End Cell (°C) | Differ Start to End Cell (°C) |
|-----------|--------------|---------------|-----------------|---------------|-------------------------------|
| 57.2 | 12I | 19.745 | 19.914 | 20.214 | 0.300 |
| 57.1 | 13I | 19.848 | 19.854 | 20.438 | 0.584 |
| 57 | 19I19I | 19.783 | 20.307 | 20.594 | 0.287 |
| 56 | 15I | 19.759 | 20.073 | 20.306 | 0.233 |
| 55 | 16I | 19.945 | 20.141 | 20.417 | 0.276 |
| 54 | 17I | 19.906 | 20.239 | 20.470 | 0.231 |
| 57.1b | 18I | 19.794 | 20.037 | 20.262 | 0.225 |
| 57b | 19I | 19.905 | 19.995 | 20.566 | 0.571 |
| 54b | 20I | 19.797 | 20.261 | 20.677 | 0.416 |
| Average | | 19.831 | 20.091 | 20.438 | 0.347 |

Remarks

The equations of Liu et al, 2011 formulated using the purified m-cresol purple indicator was used to determine pH of the samples. The pH samples were analyzed at ~20°C at Full Scale (pH 0-14).

Temperature for each sample was measured before and after analysis using a Hart Scientific Fluke 1523 reference thermometer. The end cell temperature was used in the calculation of the pH.

Approximately 80 mL of sample was extracted from each DIC sample bottle by syringe before DIC analysis to determine the pH.

The pH was also reported at 25°C

Talk:

Analysis dates: 04/26/2017

Titration system used: Open cell

CRM Batch 153, Salinity = 33.357, cert. TA = 2225.59 $\mu\text{mol/kg}$.

CRM Batch 144, Salinity = 33.571, cert. TA = 2238.60 $\mu\text{mol/kg}$.

On 04/26/2017 one CRM was analyzed before the samples and another CRM was run at the end of analysis for each system.

The TA for the water samples run on System 1 on 04/26/2017 was corrected using the ratio of the ending CRM (Batch 153). The TA for the water samples run on System 2 were corrected using the averaged ratios between the certified and measured values of the CRM (Batch 144). The following table shows the CRM measurements.

| Cell System | Date | Time | Bottle # | TA | \Delta CRM |
|-------------|-----------|----------|----------|---------|------------|
| 1 | 4/26/2017 | 12:10:17 | 410 | 2212.23 | |
| 1 | 4/26/2017 | 17:29:07 | 1153 | 2219.37 | 7.14 |
| 2 | 4/26/2017 | 13:41:04 | 410 | 2235.4 | |
| 2 | 4/26/2017 | 17:21:44 | 1153 | 2229.1 | 6.3 |

Reproducibility: No duplicate samples were collected.

Remarks

For unknown reasons the difference between the beginning and ending CRM values are

higher than desired.

Comments

The latitude, longitude, date, and time reported with the DIC, pH and TALK measurements were taken from the sample field log. The field log values are provided for reference; no post-cruise assurance of accuracy has been done to this data. The Niskin bottles are approximately one half meter above the CTD sensors on the rosette. Therefore, Temp and Sal are bin-averaged CTD values representing the next shallower depth from that recorded by the CTD (CTD Depth) at the time the Niskin bottles were fired with the exception of the surface values, which are the same as the CTD Depth values (as per the log sheet).

The Sample ID is the sample station, cast number and Niskin bottle number for the discrete samples. No cast or niskin number was recorded – the sample ID is the sample station number.

The salinity and temperature were taken from the CTD system. These CTD salinities were used in the DIC, Talk and pH calculations.

Corresponding UW pCO₂ data can be found at the following website
<http://www.aoml.noaa.gov/ocd/ocdweb/occ.html>

Nutrients:

Analysis Date: April 17, 2017

Nutrient samples were analyzed using a Seal Analytical high resolution digital colorimeter auto-analyzer 3 (AA3). A series of standards for each method were run before sample analysis to obtain a calibration curve for data reduction.

Method 353.4 was used to determine the concentration of nitrate and nitrite for each station (Zhang et al., 1997b). This method used automated, gas-segmented, continuous flow colorimetry for the analysis of nitrate and nitrite. Samples were first passed through a copper-coated cadmium reduction column. Nitrate was reduced to nitrite in a buffer solution. The nitrite was then determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a color azo dye. The absorbance measured at 550 nm is linearly proportional to the concentration of nitrite + nitrate in the sample. Nitrate concentrations are obtained by subtracting nitrite values, which have been separately determined without the cadmium reduction procedure, from the nitrite + nitrate values.

Method 365.5 was used to determine the concentration of orthophosphate for each station (Zimmermann and Keefe, 1997; Zhang et al., 2001). This method used automated colorimetric and continuous flow analysis for the determination of low-level orthophosphate concentrations. Ammonium molybdate and antimony potassium tartrate react in an acidic medium with orthophosphate to form an antimony-phospho-molybdate complex. This complex was reduced to a blue-colored complex by ascorbic acid. The absorbance measured at 880 nm is proportional to the phosphate concentration in the

sample.

Method 366.0 was used to determine the concentration of soluble silica for each station (Zhang and Berberian, 1997). This method used automated, gas-segmented, continuous flow colorimetry for the analysis of dissolved silicate concentration. In this method, β -molybdosilicic acid was formed by the reaction of the silicate contained in the sample with molybdate in acidic solution. The β -molybdosilicic acid was then reduced by ascorbic acid to form molybdenum blue. The absorbance of the molybdenum blue, measured at 550 nm, is linearly proportional to the concentration of silicate in the sample.

Zhang, J.-Z. and Berberian, G.A. (1997). Determination of dissolved silicate in estuarine and coastal waters by gas segmented flow colorimetric analysis, *U.S. Environmental Protection Agency, (EPA Method 366.0)*, EPA-600-R-97-072.

Zhang, J.-Z., Fischer, C.J. and Ortner, P.B. (2001). Continuous flow analysis of phosphate in natural waters using hydrazine as a reductant. *Intern. J. Environ. Anal. Chem.* 80(1): 61-73.

Zimmermann, C.F., and C.W. Keefe (1997). Determination of orthophosphate in estuarine and coastal waters by automated colorimetric analysis. *U.S. Environmental Protection Agency (EPA method 365.5)*, EPA-600-R-97-072.

Zhang, J.-Z., Ortner, P.B. and Fischer, C.J. (1997b). Determination of nitrate and nitrite in estuarine and coastal waters by gas segmented continuous flow colorimetric analysis. *U.S. Environmental Protection Agency (EPA Method 353.4)*, EPA-600-R-97-072.

Operation Manual (2008), AutoAnalyzer 3 high resolution, Seal Analytical. *Publication No. MB7-31EN-02*, (February 2008).