

Cruise: WS19266
Ship: R/V Walton Smith
Expo Code: 33WA20190923
Dates: September 23rd – September 29th, 2019
Chief Scientist: Dr. Chris Kelble
Equipment: CTD
Total number of stations: 7
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 the CTD/rosette system onboard the R/V Walton Smith by Ian Smith. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

7 locations, 7 samples each 500-ml, no duplicate samples.
 Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
 PI: Dr. Rik Wanninkhof
 Analyzed by: Charles Featherstone and Patrick Mears

pH:

7 locations, 7 samples each 500-ml, no duplicate samples.
 Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
 PI: Dr. Rik Wanninkhof
 Analyzed by: Charles Featherstone and Patrick Mears

TAlk:

7 locations, 7 samples each 500-ml, no duplicate samples.
 Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
 PI: Dr. Rik Wanninkhof
 Analyzed by: Charles Featherstone and Patrick Mears

Sample Analysis

DIC:

| Instrument ID | Date | Certified CRM (µmol/kg) | CRM Value (µmol/kg) | CRM Offset (µmol/kg) | Blank (Counts) | Avg. Sample Analysis Time |
|---------------|------------|-------------------------|---------------------|----------------------|----------------|---------------------------|
| AOML 6 | 10/07/2019 | 2050.56 | 2051.21 | 0.65 | 12.0 | 9 |

Analysis date: 10/07/2019
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 977 was used and with an assigned value of (includes both DIC and salinity):
Batch 174, c: 2050.56 $\mu\text{mol/kg}$, S: 33.408
CRM values measured: AOML 6: offset 0.65 $\mu\text{mol/kg}$ (2051.21 $\mu\text{mol/kg}$).
Average run time, minimum run time, maximum run time: 9, 8 and 9 min.

Reproducibility: (# samples and average difference): No duplicate samples were collected.

CRM, salinity and HgCl_2 correction applied: Salinity correction was applied using TSG salinity.

Remarks

The volume correction was applied due to added HgCl_2 (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.

DIC samples were analyzed on a new coulometer 5017-O from UIC. Inc.

pH:

Analysis date: 10/07/2019
A CRM was analyzed before sample analysis.
CRM #1052, Batch 174 pH = 7.8578

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed

| Sample ID | Station | Bottle # | Temperature⁰C | Salinity |
|------------------|----------------|-----------------|---------------------------------|-----------------|
| CRM174_1052 | CRM | 1052 | 20.030 | 33.408 |
| 54 | 54 | 127 | 20.023 | 29.210 |
| 55 | 55 | 126 | 20.01 | 31.260 |
| 56 | 56 | 125 | 20.002 | 32.440 |
| 57 | 57 | 128 | 20.018 | 33.058 |
| 571 | 57.1 | 129 | 20.014 | 34.386 |
| 572 | 57.2 | 130 | 20.007 | 35.465 |
| 573 | 57.3 | 131 | 20.022 | 35.480 |

Reproducibility: (# samples and average difference): No duplicates were collected.

Remarks

The equations of Liu et al, 2011 formulated using the purified m-cresol purple indicator was used to determine pH of the samples. pH samples were analyzed at 20⁰C at Full Scale (pH 0-14). The pH was reported at 25⁰C.

Temperature for each sample was measured before analysis using a Hart Scientific Fluke 1523 reference thermometer.

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

Talk:

Analysis date: 10/07/2019

Titration system used: Open cell

CRM #1052 Batch 174, Salinity = 33.408, cert. TA = 2212.23 μ mol/kg.

CRM #977 Batch 174, Salinity = 33.408, cert. TA = 2212.23 μ mol/kg

On 10/07/2019 CRM #1052, Batch 174 was analyzed before sample analysis on System 1.

On 10/07/2019 CRM #977, Batch 174 was analyzed at the end of sample analysis on System 1.

The TA for the water samples was corrected using the daily averaged ratios between the certified and measured values of the CRMs run on system 1 cell. The following table shows the CRM measurements for each day and cell.

| Cell System | Date | Time | Bottle # | TA | \u0394CRM |
|-------------|------------|----------|----------|---------|-----------|
| 1 | 10/07/2019 | 10:29:41 | 1052 | 2209.55 | 3.68 |
| 1 | 10/07/2019 | 14:54:34 | 977 | 2213.21 | 0.98 |

Reproducibility: No duplicates were collected.

Remarks

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 number for the discrete samples.

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

Nutrients:

Analysis Date: October 7th and 8th, 2019

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).