

Cruise: WS18120
Ship: R/V Walton Smith
Expo Code: 33WA20180430
Dates: April 30th – May 3rd, 2018
Chief Scientist: Chris Kelble
Equipment: CTD and Flow Through (FT)
Total number of stations: 16
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 Chris Kelble. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

16 locations, 16 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:

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Talk:

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 PI: Dr. Rik Wanninkhof
 Analyzed by: Dr. Leticia Barbero, 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 5	08/10/2018	2042.41	2043.27	0.86	20.0	8
AOML 6	08/10/2015	2042.41	2043.40	0.99	20.0	9

Analysis date: 08/10/2018
Coulometer used: DICE–CM5011- AOML 5
Blanks: 12.7, 20.0 counts/min
CRM # 665 was used and with an assigned value of (includes both DIC and salinity):
Batch 173, c: 2042.41 $\mu\text{mol/kg}$, S: 33.414
CRM values measured: AOML 5: offset 0.86 $\mu\text{mol/kg}$ (2043.27 $\mu\text{mol/kg}$).
Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 08/10/2018
Coulometer used: DICE–CM5011- AOML 6
Blanks: 12.0, 20.0 counts/min
CRM # 723 was used and with an assigned value of (includes both DIC and salinity):
Batch 173, c: 2042.41 $\mu\text{mol/kg}$, S: 33.414
CRM values measured: AOML 6: offset 0.99 $\mu\text{mol/kg}$ (2043.40 $\mu\text{mol/kg}$).
Average run time, minimum run time, maximum run time: 9, 7 and 17 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.

The blank on AOML 5 (08/10/2018) was raised from 12.7 to 20.0 before running the CRM.

The blank on AOML 6 (08/10/2018) was raised from 12.0 to 20.0 before running the CRM.

pH:

Analysis date: 08/10/2018
A CRM was analyzed before sample analysis.
CRM #536, Batch 173 pH = 7.8787

Spectrophotometer used: HP Agilent 8453

Salinity and temperature of pH samples analyzed.

Sample ID	Station	Bottle #	Salinity	Temperature
CRM-173-536	CRM	536	33.414	20.038
54	54	9	32.773	20.032
55	55	10	34.468	20.039
56	56	11	35.84	20.046
57	57	12	36.343	20.044
58	58	13	36.453	20.050
59	59	17	36.469	20.053
60	60	18	36.042	20.027
61	61	19	35.856	20.046
62	62	20	35.89	20.038
63	63	21	35.58	20.045
65	65	22	35.54	20.041
66	66	23	36.65	20.041
67	67	24	37.06	20.044
57.1	57.1	16	36.351	20.041
57.2	57.2	15	36.464	20.034
57.3	57.3	14	36.265	20.044

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: 08/17/2018

Titration system used: Open cell

CRM #41 Batch 153, Salinity = 33.357, cert. TA = 2225.59 μ mol/kg.

CRM #739 Batch 150, Salinity = 33.343, cert. TA = 2214.71 μ mol/kg

On 08/17/2018 CRM #41, Batch 153 was analyzed before the samples and CRM #739,

Batch 150 was run at the end of 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	Δ CRM
1	08/17/2018	09:28:20	41	2229.30	3.71
1	08/17/2018	19:57:15	739	2215.77	1.06

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 FT sample salinity and temperature were collected from the ship's TSG.

The Sample ID is the sample station, cast number and Niskin bottle 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: May 22nd, 2018

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).