

Cruise: WS20231
Ship: R/V Walton Smith
Expo Code: 33WA20200818
Dates: August 18th – August 22nd, 2020
Chief Scientist: Ian Smith
Equipment: CTD and Flow-Through (FT)
Total number of stations: 45
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 and Flow-Through system onboard the R/V Walton Smith by Ian Smith and Charles Featherstone. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

45 locations, 75 samples each 500-ml, 7 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:

45 locations, 75 samples each 500-ml, 7 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:

45 locations, 75 samples each 500-ml, 7 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 5 | 09/02/2020 | 2017.88 | 2021.71 | 3.83 | 25.0 | 8 |

| | | | | | | |
|--------|------------|---------|---------|------|------|----|
| AOML5 | 09/03/2020 | 2017.88 | 2018.12 | 0.24 | 20.0 | 10 |
| AOML 6 | 09/01/2020 | 2017.88 | 2025.44 | 7.56 | 12.0 | 8 |
| AOML 6 | 09/02/2020 | 2017.88 | 2021.99 | 4.11 | 12.0 | 9 |
| AOML 6 | 09/03/2020 | 2017.88 | 2022.02 | 4.14 | 12.0 | 9 |

Analysis date: 09/02/2020

Coulometer used: DICE-CM5011-AOML 5

Blanks: 25.0 counts/min

CRM # 594 was used and with an assigned value of (includes both DIC and salinity):

Batch 150, c: 2017.88 $\mu\text{mol/kg}$, S: 33.343

CRM values measured: AOML 5: offset 3.83 $\mu\text{mol/kg}$ (2021.71 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 8, 7 and 9 min.

Analysis date: 09/03/2020

Coulometer used: DICE-CM5011-AOML 5

Blanks: 20.0 counts/min

CRM # 1166 was used and with an assigned value of (includes both DIC and salinity):

Batch 150, c: 2017.88 $\mu\text{mol/kg}$, S: 33.343

CRM values measured: AOML 5: offset 0.24 $\mu\text{mol/kg}$ (2018.12 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 10, 8 and 12 min.

Analysis date: 09/01/2019

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 1234 was used and with an assigned value of (includes both DIC and salinity):

Batch 150, c: 2017.88 $\mu\text{mol/kg}$, S: 33.343

CRM values measured: AOML 6: offset 7.56 $\mu\text{mol/kg}$ (2025.44 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 8, 7 and 11 min.

Analysis date: 09/02/2019

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 9280 was used and with an assigned value of (includes both DIC and salinity):

Batch 150, c: 2017.88 $\mu\text{mol/kg}$, S: 33.343

CRM values measured: AOML 6: offset 4.11 $\mu\text{mol/kg}$ (2021.99 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 8 and 10 min.

Analysis date: 09/03/2019

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 862 was used and with an assigned value of (includes both DIC and salinity):

Batch 150, c: 2017.88 $\mu\text{mol/kg}$, S: 33.343

CRM values measured: AOML 6: offset 4.14 $\mu\text{mol/kg}$ (2022.024 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 8 and 11 min.

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Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.44 (0.13-2.83) and average STDEV of 0.89 (0.09-2.00).

| Sample ID | DIC ($\mu\text{mol/kg}$) | Average | Difference | STDEV |
|-----------|-------------------------------|---------|------------|-------|
| 57101012 | 1643.29 | | | |
| 57101012 | 1643.16 | 1643.22 | 0.13 | 0.09 |
| 620000 | 1702.36 | | | |
| 620000 | 1705.19 | 1703.78 | 2.83 | 2.00 |
| BG401012 | 2045.85 | | | |
| BG401012 | 2044.90 | 2045.37 | 0.95 | 0.67 |
| EB201012 | 2037.19 | | | |
| EB201012 | 2037.41 | 2037.30 | 0.22 | 0.16 |
| RP201012 | 2018.34 | | | |
| RP201012 | 2016.98 | 2017.66 | 1.35 | 0.09 |
| KW401012 | 2019.01 | | | |
| KW401012 | 2016.65 | 2017.83 | 2.35 | 1.67 |
| 320000 | 2078.27 | | | |
| 320000 | 2076.05 | 2077.16 | 2.22 | 1.57 |
| Average | | | 1.44 | 0.89 |

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 on AOML 6 were analyzed on a new coulometer 5017-O from UIC. Inc.

pH:

Analysis date: 09/01/2020, 09/02/2020 and 09/03/2020

A CRM was analyzed before sample analysis.

09/01/2020, Batch 150, CRM #50, pH = 7.9260

09/02/2020, Batch 150, CRM #304, pH = 7.9395
09/03/2020, Batch 150, CRM #550, pH = 7.9391

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

| Sample ID | Sample BTL # | Salinity | Analysis T (°C) |
|-------------|--------------|----------|-----------------|
| CRMB150_050 | 50 | 33.343 | 20.123 |
| CRMB150_304 | 304 | 33.343 | 20.038 |
| CRMB150_550 | 550 | 33.343 | 20.048 |
| 470000 | 81 | 33.683 | 20.086 |
| 4901012 | 82 | 32.744 | 20.087 |
| 5101012 | 83 | 34.617 | 20.088 |
| 5401012 | 84 | 34.427 | 20.079 |
| 5501012 | 85 | 34.046 | 20.076 |
| 5601012 | 86 | 34.628 | 20.082 |
| 5701012 | 87 | 35.249 | 20.083 |
| 57101012 | 88 | 35.496 | 20.072 |
| 57101012 | 89 | 35.496 | 20.080 |
| 6001012 | 90 | 35.71 | 20.074 |
| 610000 | 91 | 36.176 | 20.078 |
| 620000 | 92 | 36.176 | 20.079 |
| 620000 | 93 | 36.176 | 20.086 |
| 6301012 | 94 | 36.784 | 20.075 |
| 6801012 | 95 | 35.954 | 20.072 |
| GP50101 | 173 | 35.393 | 20.031 |
| GP50105 | 174 | 35.941 | 20.034 |
| GP501012 | 175 | 35.942 | 20.045 |
| BG40101 | 176 | 35.92 | 20.038 |
| BG401012 | 177 | 35.932 | 20.027 |
| BG401012 | 178 | 35.932 | 20.023 |
| BG30101 | 179 | 35.618 | 20.035 |
| BG301012 | 180 | 35.627 | 20.042 |
| BG20101 | 181 | 34.733 | 20.041 |
| BG201012 | 182 | 34.798 | 20.051 |
| BG10101 | 183 | 34.442 | 20.045 |
| BG101012 | 184 | 31.287 | 20.046 |
| EB10101 | 185 | 34.645 | 20.046 |
| EB101012 | 186 | 34.647 | 20.045 |
| EB20101 | 187 | 35.771 | 20.045 |

| | | | |
|-----------|-----|--------|--------|
| EB201012 | 188 | 35.774 | 20.056 |
| EB201012 | 189 | 35.774 | 20.054 |
| 410000 | 190 | 32.694 | 20.055 |
| 390000 | 191 | 27.898 | 20.052 |
| 4501012 | 192 | 34.992 | 20.049 |
| CAL60101 | 401 | 36.195 | 20.063 |
| CAL601012 | 402 | 36.066 | 20.072 |
| CAL50101 | 403 | 35.399 | 20.067 |
| CAL501012 | 404 | 35.411 | 20.075 |
| CAL40101 | 405 | 35.856 | 20.079 |
| CAL401012 | 406 | 35.856 | 20.072 |
| CAL30101 | 407 | 35.557 | 20.080 |
| CAL301012 | 408 | 35.558 | 20.078 |
| CAL20101 | 409 | 34.687 | 20.084 |
| CAL201012 | 410 | 34.683 | 20.079 |
| CAL101012 | 411 | 33.491 | 20.080 |
| RP10101 | 412 | 35.127 | 20.076 |
| RP101012 | 413 | 35.081 | 20.082 |
| RP20101 | 414 | 35.188 | 20.082 |
| RP201012 | 415 | 35.194 | 20.080 |
| RP201012 | 416 | 35.194 | 20.098 |
| RP30101 | 417 | 35.593 | 20.083 |
| RP301012 | 418 | 35.576 | 20.085 |
| RP40101 | 419 | 35.699 | 20.084 |
| RP401012 | 420 | 35.705 | 20.083 |
| UKOFF0000 | 461 | 36.348 | 20.044 |
| UKMID0000 | 462 | 36.387 | 20.052 |
| UKIN0000 | 463 | 36.444 | 20.057 |
| KW10101 | 464 | 36.19 | 20.049 |
| KW101012 | 465 | 36.194 | 20.051 |
| KW20101 | 466 | 36.115 | 20.056 |
| KW201012 | 467 | 36.116 | 20.063 |
| KW40101 | 468 | 36.236 | 20.050 |
| KW401012 | 469 | 36.237 | 20.050 |
| KW401012 | 470 | 36.237 | 20.064 |
| 300101 | 471 | 35.728 | 20.056 |
| 3001012 | 472 | 35.922 | 20.057 |
| 3050000 | 473 | 36.1 | 20.050 |
| 310101 | 474 | 36.071 | 20.041 |
| 3101012 | 475 | 36.075 | 20.065 |
| 320000 | 476 | 35.392 | 20.050 |

| | | | |
|---------|-----|--------|--------|
| 320000 | 477 | 35.392 | 20.057 |
| 330101 | 478 | 35.018 | 20.040 |
| 3301012 | 479 | 35.034 | 20.052 |
| 340000 | 480 | 34.034 | 20.056 |

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.01564 (0.0005-0.0334) and an average STDEV of 0.01106 (0.0003-0.0236).

| Instrument | Sample ID | Bottle # | pH @20deeg C | Average | STDEV | Difference |
|-----------------|-----------|----------|-----------------|---------|---------|------------|
| HP Agilent 8453 | 57101012 | 88 | 8.15738 | | | |
| HP Agilent 8453 | 57101012 | 89 | 8.15910 | 8.15824 | 0.0012 | 0.0017 |
| HP Agilent 8453 | 620000 | 92 | 8.13575 | | | |
| HP Agilent 8453 | 620000 | 93 | 8.15402 | 8.14489 | 0.0129 | 0.0183 |
| HP Agilent 8453 | BG401012 | 177 | 8.13336 | | | |
| HP Agilent 8453 | BG401012 | 178 | 8.09205 | 8.11270 | 0.0292 | 0.0413 |
| HP Agilent 8453 | EB201012 | 188 | 8.13492 | | | |
| HP Agilent 8453 | EB201012 | 189 | 8.13542 | 8.13517 | 0.0003 | 0.0005 |
| HP Agilent 8453 | RP201012 | 415 | 8.14795 | | | |
| HP Agilent 8453 | RP201012 | 416 | 8.14954 | 8.14875 | 0.0011 | 0.0016 |
| HP Agilent 8453 | KW401012 | 469 | 8.10566 | | | |
| HP Agilent 8453 | KW401012 | 470 | 8.07227 | 8.08896 | 0.0236 | 0.0334 |
| HP Agilent 8453 | 320000 | 476 | 8.03000 | | | |
| HP Agilent 8453 | 320000 | 477 | 8.04272 | 8.03636 | 0.0090 | 0.0127 |
| Average | | | | | 0.01106 | 0.01564 |

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 20⁰C.

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: 09/03/2020 and 09/04/2020

Titration system used: Open cell

Batch 150, CRM #304 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

Batch 150, CRM #417 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

Batch 150, CRM #1108 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

Batch 150, CRM #928 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

Batch 150, CRM #550 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

Batch 150, CRM #234 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

On 09/03/2020 CRM #304 was analyzed before sample analysis on System 1.

On 09/03/2020 CRM #417 was analyzed after sample analysis on System 1.

On 09/04/2020 CRM #1108 was analyzed before and after sample analysis on System 1.

On 09/03/2020 CRM #928 was analyzed before sample analysis on System 2.

On 09/03/2020 CRM #550 was analyzed after sample analysis on System 2.

On 09/04/2020 CRM #234 was analyzed before and after sample analysis on System 2.

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 and 2 cells. The following table shows the CRM measurements for each day and cell.

| Cell System | Date | Time | Bottle # | TA | ΔCRM |
|-------------|------------|----------|----------|---------|-------|
| 1 | 09/03/2020 | 08:50:00 | 304 | 2201.06 | 13.65 |
| 1 | 09/03/2020 | 18:42:46 | 417 | 2215.92 | 1.21 |
| 1 | 09/04/2020 | 08:23:46 | 1108 | 2214.13 | 0.58 |
| 1 | 09/04/2020 | 15:48:38 | 1108 | 2214.23 | 0.48 |
| 2 | 09/03/2020 | 13:04:23 | 928 | 2212.49 | 2.22 |
| 2 | 09/03/2020 | 18:33:52 | 550 | 2214.44 | 0.27 |
| 2 | 09/04/2020 | 08:48:23 | 234 | 2213.74 | 0.97 |
| 2 | 09/04/2020 | 15:40:38 | 234 | 2214.03 | 0.68 |

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.81 (0.08-1.71) and an average STDEV of 0.46 (0.06-1.21).

| Station | Sample ID | TA ($\mu\text{mol/kg}$) | Average | Difference | STDEV |
|---------|-----------|---------------------------|---------|------------|-------|
| 57.1 | 57101012 | 1927.15 | | | |
| 57.1 | 57101012 | 1888.27 | 1907.71 | 38.87 | 27.49 |
| 62 | 620000 | 2007.05 | | | |
| 62 | 620000 | 2006.47 | 2006.76 | 0.58 | 0.41 |
| BG4 | BG401012 | 2380.80 | | | |
| BG4 | BG401012 | 2382.12 | 2381.46 | 1.32 | 0.93 |
| EB2 | EB201012 | 2379.62 | | | |
| EB2 | EB201012 | 2379.54 | 2379.58 | 0.08 | 0.06 |
| RP2 | RP201012 | 2340.58 | | | |
| RP2 | RP201012 | 2341.58 | 2341.08 | 1.00 | 0.71 |
| KW-4 | KW401012 | 2352.03 | | | |
| KW-4 | KW401012 | 2351.87 | 2351.95 | 0.17 | 0.12 |
| 32 | 320000 | 2386.31 | | | |
| 32 | 320000 | 2388.02 | 2387.16 | 1.71 | 1.21 |
| Average | | | | 0.81 | 0.46 |

Remarks

The first duplicate 57101012 was bad and not included in the overall average and STDEV of the TA duplicates. The first duplicate value was the TA value reported.

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 station number, cast number and niskin number.

Corresponding UW pCO₂ data can be found at the following website

<http://www.aoml.noaa.gov/ocd/ocdweb/occ.html>

Nutrients:

Analysis Date: 09/15/2020

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).

Chlorophyll and Phaeophytin:

Analysis Date: 09/04/2020

Chlorophyll-a concentrations are determined via a standardized filtration-extraction method using a 60:40 mixture of 90% acetone and dimethyl sulfoxide. The fluorescence of each sample is measured before and after acidification in order to correct for phaeophytin on a TD-700 fluorometer. Samples are stored in the dark at -80°C until analysis. A sample duplicate is analyzed with each sample.

Shoaf, W.T. and Lium, B.W. (1976). Improved extraction of chlorophyll-a and b from algae using dimethyl sulfoxide. *Limnology and Oceanography* 21: 926-928.

EPA Method 445 (1997) In vitro determination of chlorophyll-a in marine and freshwater algae by fluorescence.