

**Cruise:** WS19266  
**Ship:** R/V Walton Smith  
**Dates:** September 23rd – September 29<sup>th</sup>, 2019  
**Expocode:** 33WA20190923  
**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  
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 Sample\_ID#: 90101, etc.; Station, cast number and Niskin bottle number  
 PI: Dr. Rik Wanninkhof  
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**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

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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<sub>2</sub> correction applied: Salinity correction was applied using TSG salinity.

### **Remarks**

The volume correction was applied due to added HgCl<sub>2</sub> (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**

<b>Sample ID</b>	<b>Station</b>	<b>Bottle #</b>	<b>Temperature °C</b>	<b>Salinity</b>
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 20<sup>0</sup>C at Full Scale (pH 0-14). The pH was reported at 25<sup>0</sup>C.

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 = 2212.23µmol/kg.

CRM #977 Batch 174, Salinity = 33.408, cert. TA = 2212.23µmol/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	ΔCRM
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 pCO<sub>2</sub> data can be found at the following website  
<http://www.aoml.noaa.gov/ocd/ocdweb/occ.html>

### **Nutrients:**

**Analysis Date:** October 7<sup>th</sup> and 8<sup>th</sup>, 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,  $\beta$ -molybdosilicic acid was formed by the reaction of the silicate contained in the sample with molybdate in acidic solution. The  $\beta$ -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).

#### UPDATE:

Between March and June of 2021, all of the data for the discrete samples was put into a uniform format. The supporting information was checked for accuracy, especially the expocode, date, time, and positions.

Additionally, pH results were recalculated to 20 and 25 degrees Celsius.