

**Cruise:** WS20006  
**Ship:** R/V Walton Smith  
**Dates:** January 6<sup>th</sup> – January 11<sup>th</sup>, 2020  
**Expocode:** 33WA20200106  
**Chief Scientist:** Dr. Chris Kelble  
**Equipment:** CTD and Flow-Through  
**Total number of stations:** 24  
**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. The date and time listed in the data file are UTC when each sample bottle was collected.

#### **DIC:**

24 locations, 39 samples each 500-ml, 0 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:**

24 locations, 39 samples each 500-ml, 0 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:**

24 locations, 39 samples each 500-ml, 0 duplicate samples.  
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 5	02/03/2020	2017.88	2020.49	2.61	25.0	7

Analysis date: 02/03/2020

Coulometer used: DICE-CM5011-AOML 5

Blanks: 25.0 counts/min

CRM # 221 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 2.61  $\mu\text{mol/kg}$  (2020.49  $\mu\text{mol/kg}$ ).

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

Analysis date: 02/03/2019

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 16.0 counts/min

CRM # 184 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 0.86  $\mu\text{mol/kg}$  (2018.74  $\mu\text{mol/kg}$ ).

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

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

CRM, salinity and  $\text{HgCl}_2$  correction applied: Salinity correction was applied using TSG salinity.

### **Remarks**

The volume correction was applied due to added  $\text{HgCl}_2$  (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: 02/03/2020

A CRM was analyzed before sample analysis.

02/03/2020, Batch 150, CRM #556, pH = 7.9410

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed

Station	Sample ID	Bottle #	Salinity	Temperature $^{\circ}\text{C}$
CRM150_556	CRM150_556	CRM150_556	33.343	20.001

RP3	1	1	34.661	20.025
RP3	2	2	34.661	20.022
RP4	3	3	35.603	20.035
RP4	4	4	35.603	20.039
GP5	5	5	36.077	20.041
GP5	6	6	36.077	20.033
BG4	7	7	35.529	20.039
BG4	8	8	35.526	20.034
BG3	9	9	34.944	20.038
BG2	10	10	34.546	20.042
BG2	11	11	34.598	20.037
57.2	12	12	35.21	20.034
57.2	13	13	35.21	20.034
57.1	14	14	35.066	20.031
57.1	15	15	35.068	20.040
57	16	16	34.48	20.037
57	17	17	34.48	20.038
56	18	18	33.689	20.035
55	19	19	31.766	20.033
54	20	20	30.495	20.028
UK_OFF	21	21	35.99	20.038
UK_MID	22	22	36.155	20.035
UK_IN	23	23	36.003	20.039
7	24	24	36.109	20.026
7	25	25	36.107	20.030
30	26	26	36.018	20.045
33	27	27	34.278	20.041
33	28	28	34.278	20.028
CAL6	29	29	35.986	20.028
CAL6	30	30	35.986	20.031
CAL5	31	31	35.188	20.038
CAL5	32	32	35.19	20.033
CAL3	33	33	33.915	20.026
CAL3	34	34	33.915	20.029
CAL1	35	35	31.502	20.035
RP1	36	36	33.899	20.029
RP1	37	37	33.849	20.034
RP2	38	38	34.281	20.034
RP2	39	39	34.281	20.040

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**Reproducibility:** (# samples and average difference): No duplicate samples 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 and pH at temperature analyzed.

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: 02/04/2020 and 02/05/2020

Titration system used: Open cell

Batch 150, CRM #221 Salinity = 33.343, cert. TA = 2214.71μmol/kg.

Batch 150, CRM #556 Salinity = 33.343, cert. TA = 2214.71μmol/kg.

Batch 150, CRM #494 Salinity = 33.343, cert. TA = 2214.71μmol/kg.

On 02/04/2020 CRM #221 was analyzed before sample analysis on System 2.

On 02/04/2020 CRM #556 was analyzed after sample analysis on System 2.

On 02/05/2020 CRM #494 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
2	02/04/2020	09:57:48	221	2221.52	6.81
2	02/04/2020	17:59:48	556	2216.09	1.38
2	02/05/2020	09:53:33	494	2223.18	8.47
2	02/05/2020	17:08:08	494	2219.31	4.60

**Reproducibility:** (# samples and average difference): No duplicate samples 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 bottle number for the discrete samples.

Sample Bottle #26 was broken after DIC/pH analysis, no sample water left for TA analysis.

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:** January 15<sup>th</sup>, 2020

**PI:** Dr. Jia-Zhong Zhang

**Analyzed by:** Ian Smith

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).