

**Cruise:** WS17282  
**Ship:** R/V Walton Smith  
**Expo Code:** 33WS20171009  
**Dates:** 10/09/2017 – 10/13/2017  
**Chief Scientist:** Chris Kelble  
**Equipment:** CTD Rosette & Ship's Flow Thru (FT)  
**Total number of stations:** 20  
**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 Niskin bottles attached to a 24 bottle configured rosette 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:**

20 locations, 20 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:**

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**Talk:**

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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 3	10/23/2017	2017.95	2017.88	0.07	28.0	9
AOML 4	10/23/2017	2017.95	2009.60	8.35	28.0	14

Analysis date: 10/23/2017  
Coulometer used: DICE–CM5015- AOML 3  
Blanks: 28.0 counts/min  
CRM # 1065 was used and with an assigned value of (includes both DIC and salinity):  
Batch 153, c: 2017.95  $\mu\text{mol/kg}$ , S: 33.357  
CRM values measured: AOML 3: offset 0.07  $\mu\text{mol/kg}$  (2017.88  $\mu\text{mol/kg}$ ).  
Average run time, minimum run time, maximum run time: 9, 8 and 11 min.

Analysis date: 10/23/2017  
Coulometer used: DICE–CM5015- AOML 4  
Blanks: 28.0 counts/min  
CRM # 868 was used and with an assigned value of (includes both DIC and salinity):  
Batch 153, c: 2017.95  $\mu\text{mol/kg}$ , S: 33.357  
CRM values measured: AOML 4: offset 8.35  $\mu\text{mol/kg}$  (2009.60  $\mu\text{mol/kg}$ ).  
Average run time, minimum run time, maximum run time: 14, 8 and 20 min.

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

The blank on AOML 3 (10/23/2017) was raised from 12.0 to 28.0 before running the CRM.

The blank on AOML 4 (10/23/2017) was raised from 12.0 to 28.0 before running the CRM.

The samples were analyzed using the DICE (AOML 3 and 4) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

### **pH:**

Analysis date: 10/23/2017  
Spectrophotometer used: HP Agilent 8453

A CRM was run before sample analysis. CRM 738, Batch 153 had a pH value of 7.9713

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

Temperatures measured during pH analysis

Sample ID	Station	Bottle #	Temp Deg C
CRM 738	CRM	738	19.765
573	57.3	401	19.774
572	57.2	402	19.766
571	57.1	403	19.756
57	57	404	19.757
56	56	405	19.764
55	55	406	19.777
54	54	407	19.778
53	53	408	19.796
51	51	409	19.795
50	50	410	19.774
49	49	411	19.759
47	47	412	19.769
45	45	413	19.761
39	39	414	19.774
40	40	415	19.761
41	41	416	19.775
42	42	417	19.777
33	33	418	19.787
305	30.5	419	19.765
30	30	420	19.794

**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°C at Full Scale (pH 0-14).

Samples were run on an automated system where the temperature was kept constant.

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

Results reported at 25°C.

**Talk:**

Analysis date: 10/24/2017

Titration system used: Open cell

CRM Batch 153, Salinity = 33.357, cert. TA = 2225.59 $\mu$ mol/kg.

On 10/24/2017 one CRM was analyzed before the samples and the same CRM was run at the end of analysis each day for each system.

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

Cell System	Date	Time	Bottle #	TA	\u0394CRM
1	10/23/2017	12:52:15	501	2220.89	
1	10/23/2017	17:13:08	501	2208.50	12.39
2	10/23/2017	13:36:05	1001	2213.98	
2	10/23/2017	17:08:10	1001	2208.46	5.52

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

**Remarks**

The CRM measurement for each day was used to correct the data for that day only. Both systems worked well.

**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, cast number and Niskin bottle 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 18<sup>th</sup> and 19<sup>th</sup>, 2017

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.

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Operation Manual (2008), AutoAnalyzer 3 high resolution, Seal Analytical. *Publication No. MB7-31EN-02*, (February 2008).

