

**Cruise:** SAV1803  
**Ship:** R/V Savannah  
**Expo Code:** 33H620180308  
**Dates:** March 8<sup>th</sup>, 2018 – March 13<sup>th</sup>, 2018  
**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 Niskin bottles attached to a 12 bottle configured rosette onboard the R/V Savannah. The samples were collected by Dr. Chris Kelble, Ian Smith and Kelly Montenero. 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, 0 duplicate samples.  
 Sample\_ID#: 101, etc.; Bottle number  
 PI: Dr. Rik Wanninkhof  
 Analyzed by: Charles Featherstone and Patrick Mears

**pH:**

7 locations, 7 samples each 500-ml, 0 duplicate samples.  
 Sample\_ID#: 101, etc.; Bottle number  
 PI: Dr. Rik Wanninkhof  
 Analyzed by: Charles Featherstone and Patrick Mears

**TAlk:**

7 locations, 7 samples each 500-ml, 0 duplicate samples.  
 Sample\_ID#: 101, etc.; Bottle number  
 PI: Dr. Rik Wanninkhof and Leticia Barbero  
 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	11/29/2017	2042.41	2043.27	0.86	20.0	7.7

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Analysis date: 08/10/2018

Coulometer used: DICE–CM5011- AOML 5

Blanks: 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: 7.7, 7 and 9 min.

**Reproducibility:**

No duplicate samples were taken

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.

The blank on AOML 5 (08/10/2018) was raised from 12.0 to 20.0 before running the CRM.

The samples were analyzed using the DICE (AOML 5) and a coulometer from UIC, Inc. CM5011 with CM5011 emulation software.

**pH:**

Analysis date: 08/10/2018

Spectrophotometer used: HP Agilent 8453

A CRM #536 from Batch 173 was run before analysis of samples; pH value = 7.8769

**Reproducibility:**

No duplicate samples were taken

Temperature and salinity of pH samples analyzed

Sample ID	Station	Bottle #	Salinity	Temperature
CRM173-536	CRM	536	33.414	20.038
54	54	103	32.113	20.041

55	55	102	34.079	20.031
56	56	101	35.013	20.032
57	57	104	35.79	20.049
571	57.1	105	35.85	20.050
572	57.2	106	35.91	20.036
573	57.3	107	36.01	20.056

**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).

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.

Samples are reported at 25<sup>0</sup>C.

**Talk:**

Analysis date: 8/20/2018

Titration system used: Open cell

CRM Batch 173, Salinity = 33.414, cert. TA = 2210.77  $\mu$ mol/kg.

On 8/20/2018 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 first CRM (bottle # 689) ratio 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
2	8/20/2018	08:36:53	689	2216.60	
2	8/20/2018	15:20:52	575	2221.92	5.31

**Reproducibility:**

No duplicate samples were taken

**Remarks**

The CRM measurement for each day was used to correct the data for that day only.

## **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.

### **Nutrients:**

**Analysis Date:** April 4<sup>th</sup> and 5<sup>th</sup>, 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,  $\beta$ -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).