

Cruise: WS21093
Ship: R/V Walton Smith
Expo Code: 33WA20210403
Funding Project Title: Near-shore Carbonate Sampling
Funding Project ID: Near-Shore-OA
Dates: April 3rd – April 9th, 2021
Chief Scientist: Ian Smith
Equipment: CTD-Niskin and Flow-Through (FT)
Total number of stations: 50
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-Niskin/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:

50 locations, 73 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:

50 locations, 73 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:

50 locations, 73 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
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AOML 5	04/23/2021	2063.31	2064.58	1.27	12.0	9
AOML5	04/26/2021	2063.31	2064.38	1.07	14.8	8
AOML 5	05/10/2021	2063.31	2068.38	5.07	17.8	10
AOML 6	04/26/2021	2063.31	2068.20	4.89	12.0	9

Analysis date: 04/23/2021

Coulometer used: DICE-CM5017O-AOML 5

Blanks: 12.0 counts/min

CRM # 385 was used and with an assigned value of (includes both DIC and salinity):

Batch 169, c: 2063.31 $\mu\text{mol/kg}$, S: 33.518

CRM values measured: AOML 5: offset 1.27 $\mu\text{mol/kg}$ (2064.58 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 7 and 11 min.

Analysis date: 04/26/2021

Coulometer used: DICE-CM5017O-AOML 5

Blanks: 14.8 counts/min

CRM # 758 was used and with an assigned value of (includes both DIC and salinity):

Batch 169, c: 2063.31 $\mu\text{mol/kg}$, S: 33.518

CRM values measured: AOML 5: offset 1.07 $\mu\text{mol/kg}$ (2064.38 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 05/10/2021

Coulometer used: DICE-CM5017O-AOML 5

Blanks: 17.8 counts/min

CRM # 1071 was used and with an assigned value of (includes both DIC and salinity):

Batch 169, c: 2063.31 $\mu\text{mol/kg}$, S: 33.518

CRM values measured: AOML 5: offset 5.07 $\mu\text{mol/kg}$ (2068.38 $\mu\text{mol/kg}$).

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

Analysis date: 04/26/2021

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 442 was used and with an assigned value of (includes both DIC and salinity):

Batch 169, c: 2063.31 $\mu\text{mol/kg}$, S: 33.518

CRM values measured: AOML 6: offset 4.89 $\mu\text{mol/kg}$ (2068.20 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 7 and 12 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.95 (0.10-3.01) and average STDEV of 0.67 (0.07-2.13).

Sample ID	DIC			
	($\mu\text{mol/kg}$)	Average	Difference	STDEV
540112	2542.32			
540112	2542.23	2542.28	0.10	0.07

CAL50112	2119.54			
CAL50112	2120.34	2119.94	0.80	0.56
RP40112	2105.77			
RP40112	2104.84	2105.31	0.93	0.66
V70112	2105.34			
V70112	2107.08	2106.21	1.75	1.24
300112	2104.06			
300112	2104.08	2104.07	0.02	0.01
21-LK0112	2001.89			
21-LK0112	2001.92	2001.90	0.03	0.02
MR0112	2006.74			
MR0112	2009.75	2008.24	3.01	2.13
Average			0.95	0.67

CRM, salinity and HgCl₂ correction applied: Salinity correction was applied using TSG salinity.

Remarks

The volume correction was applied due to added HgCl₂ (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 new coulometers 50170 from UIC. Inc.

pH:

Analysis date: 04/23/2021, 04/26/2021 and 05/10/2021
No CRMs was analyzed before sample analysis.

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

Sample ID	Sample BTL #	Salinity	Analysis T (°C)
UK-MID0000	421	36.729	20.121
UK-OFF0000	1	36.309	20.139

UK-IN0000	2	36.995	20.105
700000	3	33.814	20.119
680112	4	34.778	20.122
650112	5	32.862	20.121
600112	6	35.178	20.138
580112	7	35.367	20.133
5730112	8	35.288	20.165
5720112	9	35.170	20.168
5710112	10	34.907	20.185
570112	11	34.926	20.165
540112	12	32.290	20.172
540112	13	32.290	20.166
550112	14	34.187	20.156
560112	15	34.913	20.162
510112	16	34.606	20.167
450112	17	34.921	20.156
410112	18	35.119	20.168
310112	19	35.809	20.255
330112	20	35.141	20.356
CAL50101	21	35.727	20.776
CAL50112	22	35.726	20.949
CAL50112	23	35.726	20.957
CAL40101	24	35.541	20.848
CAL40112	25	35.502	20.864
CAL30101	26	34.872	20.885
CAL30112	27	34.874	20.952
CAL20112	28	34.602	20.968
CAL10112	29	34.124	20.986
RP10112	30	34.345	20.992
RP20112	31	35.239	21.007
RP30112	32	35.503	21.038
RP40101	33	35.001	21.029
RP40112	34	35.962	21.068
RP40112	35	35.962	21.085
GP50101	36	35.916	21.062
GP50112	37	35.931	21.083
BG40112	38	35.942	21.099
BG40101	39	35.962	21.064
BG30101	40	35.763	21.11
BG30112	422	35.602	21.147
BG20112	423	35.287	21.115

BG10112	424	34.071	21.132
V10112	425	35.309	21.156
V30101	426	35.761	21.211
V30112	427	35.745	21.278
V50101	428	35.720	21.322
V50112	429	35.750	21.305
V70101	430	35.900	21.332
V70112	431	35.768	21.382
V70112	432	35.768	21.332
V90101	433	35.987	21.373
V90112	434	36.032	21.357
AMI90112	435	36.143	21.293
AMI90101	436	36.164	21.286
AMI50101	437	35.827	21.26
AMI50112	438	35.851	21.298
AMI10112	439	34.376	21.287
TB10112	440	33.279	21.359
TB40101	441	35.612	21.375
TB40112	442	35.457	21.343
TB100101	443	36.013	21.414
TB100112	444	35.918	21.587
300101	445	36.079	21.647
300112	446	36.073	21.698
300112	447	36.073	21.807
KW40101	448	35.741	21.745
KW40112	449	35.741	21.795
KW20101	450	35.373	21.809
KW20112	451	35.371	20.474
KW10112	452	35.248	20.467
WS0101	453	36.409	20.471
WS0112	454	36.262	20.479
21-LK0101	455	36.328	20.504
21-LK0112	456	36.286	20.507
21-LK0112	457	36.286	20.494
MR0101	458	36.300	20.511
MR0112	459	36.287	20.509
MR0112	460	36.287	20.548

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.00106 (0.0006-0.0013) and an average STDEV of 0.00075 (0.0005-0.0012).

Instrument	Sample ID	Bottle #	pH @20deeg C	Average	STDEV	Difference
HP Agilent 8453	540112	12	8.013646			
HP Agilent 8453	540112	13	8.015358	8.01450	0.0012	0.0017
HP Agilent 8453	CAL50112	22	8.078089			
HP Agilent 8453	CAL50112	23	8.079760	8.07892	0.0012	0.0017
HP Agilent 8453	RP40112	34	8.095104			
HP Agilent 8453	RP40112	35	8.094935	8.09502	0.0001	0.0002
HP Agilent 8453	V70112	431	8.075412			
HP Agilent 8453	V70112	432	8.076188	8.07580	0.0005	0.0008
HP Agilent 8453	300112	446	8.096751			
HP Agilent 8453	300112	447	8.095588	8.09617	0.0008	0.0012
HP Agilent 8453	21-LK0112	456	8.143535			
HP Agilent 8453	21-LK0112	457	8.144804	8.14417	0.0009	0.0013
HP Agilent 8453	MR0112	459	8.130014			
HP Agilent 8453	MR0112	460	8.129366	8.12969	0.0005	0.0006
Average					0.00075	0.00106

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 and 25⁰C.

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: 04/21/2021, 04/27/2021, 05/10/2021 and 06/09/2021

Titration system used: Open cell

Batch 169, CRM #385 Salinity = 33.518, cert. TA = 2207.03 μ mol/kg.

Batch 169, CRM #442 Salinity = 33.518, cert. TA = 2207.03 μ mol/kg.

Batch 169, CRM #758 Salinity = 33.518, cert. TA = 2207.03 μ mol/kg.

Batch 169, CRM #1071 Salinity = 33.518, cert. TA = 2207.03 μ mol/kg.

Batch 169, CRM #514 Salinity = 33.518, cert. TA = 2207.03 μ mol/kg.

Batch 169, CRM #203 Salinity = 33.518, cert. TA = 2207.03 μ mol/kg.

On 04/21/2021 CRM #385 was analyzed before and after sample analysis on System 2.

On 04/27/2021 CRM #442 was analyzed before sample analysis on System 2.

On 04/27/2021 CRM #758 was analyzed after sample analysis on System 2.

On 05/10/2021 CRM #1071 was analyzed before and after sample analysis on System 1.

On 06/09/2021 CRM #514 was analyzed before sample analysis on System 1.

On 02/09/2021 CRM #203 was analyzed after 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 and 2 cells. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	\u0394CRM
1	05/10/2021	10:44:39	1071	2213.78	6.75
1	05/10/2021	16:40:08	1071	2213.10	6.07
1	06/09/2021	09:46:51	514	2193.41	13.62
1	06/09/2021	19:08:56	203	2242.16	35.13
2	04/21/2021	10:02:46	385	2210.40	3.37
2	04/21/2021	20:25:56	385	2208.32	1.29
2	04/27/2021	09:50:18	442	2210.40	3.37
2	04/27/2021	19:45:04	758	2220.01	12.98

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 3.21 (1.07-4.90) and an average STDEV of 2.27 (0.76-3.46).

Station	Sample ID	TA (umol/kg)	Average	Difference	STDEV
54	540112	2807.1			
54	540112	2811.8	2809.43	4.66	3.29

CAL5	CAL50112	2402.1				
CAL5	CAL50112	2401.0	2401.53	1.07	0.76	
RP4	RP40112	2388.6				
RP4	RP40112	2390.4	2389.47	1.80	1.27	
V7	V70112	2388.8				
V7	V70112	2393.7	2391.29	4.90	3.46	
30	300112	2395.8				
30	300112	2397.6	2396.74	1.81	1.28	
21LK	21LK0112	2370.0				
21LK	21LK0112	2374.4	2372.24	4.41	3.12	
MR	MR0112	2375.6				
MR	MR0112	2371.7	2373.63	3.87	2.74	
Average				3.21	2.27	

Remarks

None

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: 04/16/2021

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:** 04/18/2021

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.