

Cruise: WS20342
Ship: R/V Walton Smith
Expo Code: 33WA20201207
Funding Project Title: Surface OA Observations on Ships of Opportunity
Funding Project ID: SOOP-OA
Dates: December 7th – December 12th, 2020
Chief Scientist: Ian Smith
Equipment: CTD and Flow-Through
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/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, 6 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, 6 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, 6 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	01/04/2021	2017.88	2026.82	8.94	16.0	10
AOML5	01/05/2021	2063.31	2063.78	0.47	12.0	9
AOML 6	01/04/2021	2017.88	2025.31	7.43	24.0	7
AOML 6	01/05/2021	2063.31	2069.76	6.45	13.0	9

Analysis date: 01/04/2021

Coulometer used: DICE–CM5011-AOML 5

Blanks: 16.0 counts/min

CRM # 358 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 8.94 $\mu\text{mol/kg}$ (2026.82 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 8 and 13 min.

Analysis date: 01/05/2021

Coulometer used: DICE–CM5011-AOML 5

Blanks: 12.0 counts/min

CRM # 145 was used and with an assigned value of (includes both DIC and salinity):

Batch 169, c: 2063.31 $\mu\text{mol/kg}$, S: 33.581

CRM values measured: AOML 5: offset 0.47 $\mu\text{mol/kg}$ (2063.78 $\mu\text{mol/kg}$).

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

Analysis date: 01/04/2021

Coulometer used: DICE–CM5017O-AOML 6

Blanks: 24.0 counts/min

CRM # 42 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 7.43 $\mu\text{mol/kg}$ (2025.31 $\mu\text{mol/kg}$).

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

Analysis date: 01/05/2021

Coulometer used: DICE–CM5017O-AOML 6

Blanks: 13.0 counts/min

CRM # 209 was used and with an assigned value of (includes both DIC and salinity):

Batch 169, c: 2063.31 $\mu\text{mol/kg}$, S: 33.581

CRM values measured: AOML 6: offset 6.45 $\mu\text{mol/kg}$ (2069.76 $\mu\text{mol/kg}$).

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

Reproducibility: (# samples and average difference): 6 duplicate samples were collected with an average difference of 1.02 (0.24-2.191) and average STDEV of 0.72 (0.17-1.55).

DIC				
Sample ID	($\mu\text{mol/kg}$)	Average	STDEV	Difference
CAL10112	2131.7			
CAL10112	2129.8	2130.7	1.38	1.94

V10112	2099.16			
V10112	2101.35	2100.3	1.55	2.19
AMI10112	2144.70			
AMI10112	2143.96	2144.3	0.52	0.74
580112	2027.54			
580112	2026.92	2027.2	0.44	0.62
KW40101	2010.33			
KW40101	2010.58	2010.5	0.17	0.24
KW10112	1946.89			
KW10112	1947.27	1947.1	0.26	0.37
Average			0.72	1.02

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 on AOML 6 were analyzed on a new coulometer 5017-O from UIC. Inc.

pH:

Analysis date: 01/04/2021 and 01/05/2021

A CRM was analyzed before sample analysis.

01/04/2021, Batch 169, CRM #265, pH = 7.807815

01/05/2021, Batch 169, CRM #116, pH = 7.812945

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

Sample ID	Sample BTL #	Salinity	Analysis T (°C)
CRM_B169_265	265	33.518	19.983

CRM_B169_397	397	33.518	19.999
CAL60101	430	35.760	20.011
CAL60112	431	35.756	20.002
CAL50101	21	34.836	19.976
CAL50112	22	34.701	19.992
CAL40101	23	34.222	19.991
CAL40112	24	34.121	20.003
CAL30101	25	31.579	20.017
CAL30112	26	31.724	20.025
CAL20112	27	29.528	20.025
CAL10112	28	27.567	20.035
CAL10112	29	27.567	20.033
RP10112	30	33.786	20.033
RP20112	31	34.286	20.026
RP30101	32	34.565	20.019
RP30112	33	34.562	20.029
RP40101	34	35.309	20.026
RP40112	35	35.309	20.027
GP50101	36	35.968	20.029
GP50112	37	35.971	20.033
BG40101	38	35.580	20.030
BG40112	39	35.549	20.028
BG30101	40	34.803	20.036
BG30112	441	34.789	19.998
BG20101	442	34.163	19.998
BG20112	443	34.161	19.999
BG10112	444	33.551	19.991
V10112	445	33.586	20.001
V10112	446	33.586	20.006
V30101	447	34.885	20.000
V30112	448	34.582	20.000
V50101	449	35.444	20.000
V50112	450	35.307	20.005
V70101	451	35.947	20.010
V70112	452	35.836	20.000
V90101	453	35.478	20.007
V90112	454	35.863	20.003
AMI90101	455	35.941	20.007
AMI90112	456	35.943	20.015
AMI70101	457	35.748	20.008
AMI70112	458	35.749	20.002

AMI50101	459	35.397	20.008
AMI50112	460	35.402	19.994
AMI30101	421	34.500	20.006
AMI30112	422	34.503	20.001
AMI10112	423	33.152	20.004
AMI10112	424	33.152	20.000
UKOFF0000	439	36.084	20.005
UKMID0000	1	36.151	19.988
UKIN0000	2	36.128	19.994
680112	3	34.067	19.992
640112	4	27.785	20.014
600112	5	30.943	20.023
580112	6	35.016	20.019
580112	7	35.016	20.036
5730112	8	34.755	20.028
5720112	9	34.836	20.031
5710112	10	32.924	20.035
570112	11	30.483	20.033
560112	12	29.149	20.028
550112	13	27.597	20.034
540112	14	21.904	20.032
510112	15	32.296	20.027
490112	16	30.452	20.043
410112	17	33.846	20.037
310101	18	34.747	20.030
310112	19	34.624	20.032
330112	20	33.470	20.035
TB10112	425	32.774	20.005
TB30101	426	34.523	20.004
TB30112	427	34.375	20.004
TB50101	428	35.385	20.007
TB50112	429	35.268	19.996
300101	432	35.591	20.010
300112	433	35.354	20.011
KW40101	434	35.546	20.003
KW40101	435	35.546	20.011
KW40112	436	34.377	20.017
KW10112	437	34.778	20.021
KW10112	438	34.778	20.006

Reproducibility: (# samples and average difference): 6 duplicate samples were collected with an average difference of 0.00151 (0.00020-0.00332) and an average STDEV of 0.00106 (0.00014-0.00235).

Instrument	Sample ID	Bottle #	pH @20 °C	Average	STDEV	Difference
HP Agilent 8453	CAL10112	28	7.99955			
HP Agilent 8453	CAL10112	29	7.99935	7.99945	0.00014	0.00020
HP Agilent 8453	V10112	445	8.02520			
HP Agilent 8453	V10112	446	8.02664	8.02592	0.00101	0.00143
HP Agilent 8453	AMI10112	423	8.00134			
HP Agilent 8453	AMI10112	424	8.00287	8.00210	0.00108	0.00153
HP Agilent 8453	580112	6	8.06506			
HP Agilent 8453	580112	7	8.06661	8.06584	0.00110	0.00155
HP Agilent 8453	KW40101	434	8.11094			
HP Agilent 8453	KW40101	435	8.10762	8.10928	0.00235	0.00332
HP Agilent 8453	KW10112	437	8.03223			
HP Agilent 8453	KW10112	438	8.03123	8.03173	0.00070	0.00099
Average					0.00106	0.00151

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). The pH was reported at 20°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: 01/06/2021 and 01/07/2021

Titration system used: Open cell

Batch 150, CRM #209 Salinity = 33.343, cert. TA = 2214.71µmol/kg.

Batch 150, CRM #365 Salinity = 33.343, cert. TA = 2214.71µmol/kg.

Batch 169, CRM #96 Salinity = 33.581, cert. TA = 2207.03 μ mol/kg.

Batch 169, CRM #397 Salinity = 33.581, cert. TA = 2207.03 μ mol/kg.

Batch 169, CRM #16 Salinity = 33.581, cert. TA = 2207.03 μ mol/kg.

On 01/06/2021 CRM #209 was analyzed before sample analysis on System 1.

On 01/06/2021 CRM #365 was analyzed after sample analysis on System 1.

On 01/07/2021 CRM #96 was analyzed before and after sample analysis on System 1.

On 01/06/2021 CRM #397 was analyzed before and after sample analysis on System 2.

On 01/07/2021 CRM #16 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	Δ CRM
1	01/06/2021	11:03:36	209	2216.75	2.04
1	01/06/2021	18:15:47	365	2217.44	0.27
1	01/07/2021	10:14:58	96	2214.78	7.75
1	01/07/2021	17:44:20	96	2211.47	4.44
2	01/06/2021	10:52:24	397	2213.46	6.43
2	01/06/2021	18:26:44	397	2207.60	0.57
2	01/07/2021	10:05:25	16	2202.85	4.18
2	01/07/2021	17:33:50	16	2203.16	3.87

Reproducibility: (# samples and average difference): 6 duplicate samples were collected with an average difference of 1.85 (0.21-4.28) and an average STDEV of 1.31 (0.15-3.02).

TA		Average	STDEV	Difference
Sample ID	(μ mol/kg)			

CAL10112	2340.18			
CAL10112	2337.92	2339.0	1.60	2.26
V10112	2347.56			
V10112	2345.73	2346.6	1.29	1.82
AMI10112	2381.44			
AMI10112	2377.17	2379.3	3.02	4.28
580112	2305.73			
580112	2307.09	2306.4	0.96	1.36
KW40101	2305.84			
KW40101	2306.05	2305.9	0.15	0.21
KW10112	2190.83			
KW10112	2189.63	2190.2	0.84	1.19
Average			1.31	1.85

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: 01/05/2021

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, 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:** 01/05/2021**PI:** Dr. Christopher Kelble**Analyzed by:** Ian Smith

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.