

**Cruise:** H24013

**Ship:** R/V Hogarth

**Expo Code:** 33SGDK20240113

**Funding Project Title:** Expanding near-shore carbonate measurements along the East-coast and Gulf of Mexico through multiple collaborations

**Funding Project ID:** 21403

**Dates:** 1/13/2024 to 1/19/2024

**Chief Scientist:** Ian Smith

**Equipment:** CTD-Niskin and Flow-Through (FT)

**Total number of stations:** 54

**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 Hogarth by Rachel Cohn and Ian Smith. The date and time listed in the data file are UTC when each sample bottle was collected.

#### **DIC:**

54 locations, 80 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, Patrick Mears

#### **pH:**

54 locations, 80 samples each 500-ml, 7 duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

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#### **TAlk:**

54 locations, 80 samples each 500-ml, 7 duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Patrick Mears

### Sample Analysis

#### **DIC:**

Instrument ID	Date	Certified CRM ( $\mu\text{mol/kg}$ )	CRM Value ( $\mu\text{mol/kg}$ )	CRM Offset ( $\mu\text{mol/kg}$ )	Blank (Counts)	Avg. Sample Analysis Time
AOML 5	07/17/2024	2048.19	2049.91	1.72	12	9
AOML 5	07/22/2024	2048.19	2048.40	0.21	19	9
AOML 5	07/24/2024	2048.19	2049.72	1.53	12	9
AOML 6	07/17/2024	2048.19	2050.23	2.04	12	9
AOML 6	07/22/2024	2048.19	2049.97	1.78	12	8
AOML 6	07/24/2024	2048.19	2049.79	1.60	15	8

Analysis date: 07/17/2024

Coulometer used: DICE–CM5017O-AOML 5

Blanks: 12.0 counts/min

CRM # 288 was used and with an assigned value of (includes both DIC and salinity):

Batch 201, c: 2048.19  $\mu\text{mol/kg}$ , S: 33.302

CRM values measured: AOML 5: offset 1.72  $\mu\text{mol/kg}$  (2049.91  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 9, 7 and 10 min.

Analysis date: 07/22/2024

Coulometer used: DICE–CM5017O-AOML 5

Blanks: 19.0 counts/min

CRM # 620 was used and with an assigned value of (includes both DIC and salinity):

Batch 201, c: 2048.19  $\mu\text{mol/kg}$ , S: 33.302

CRM values measured: AOML 5: offset 0.21  $\mu\text{mol/kg}$  (2048.40  $\mu\text{mol/kg}$ ).

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

Analysis date: 07/24/2024

Coulometer used: DICE–CM5017O-AOML5

Blanks: 12.0 counts/min

CRM # 467 was used and with an assigned value of (includes both DIC and salinity):

Batch 201, c: 2048.19  $\mu\text{mol/kg}$ , S: 33.302

CRM values measured: AOML 6: offset 1.53  $\mu\text{mol/kg}$  (2049.72  $\mu\text{mol/kg}$ ).

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

Analysis date: 07/17/2024

Coulometer used: DICE–CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 185 was used and with an assigned value of (includes both DIC and salinity):

Batch 201, c: 2048.19  $\mu\text{mol/kg}$ , S: 33.302

CRM values measured: AOML 6: offset 2.04  $\mu\text{mol/kg}$  (2050.23  $\mu\text{mol/kg}$ ).

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

Analysis date: 07/22/2024

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 045 was used and with an assigned value of (includes both DIC and salinity):

Batch 201, c: 2048.19  $\mu\text{mol/kg}$ , S: 33.302

CRM values measured: AOML 6: offset 1.78  $\mu\text{mol/kg}$  (2049.97  $\mu\text{mol/kg}$ ).

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

Analysis date: 07/24/2024

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 15.0 counts/min

CRM # 413 was used and with an assigned value of (includes both DIC and salinity):

Batch 201, c: 2048.19  $\mu\text{mol/kg}$ , S: 33.302

CRM values measured: AOML 6: offset 1.6  $\mu\text{mol/kg}$  (2049.79  $\mu\text{mol/kg}$ ).

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

**Reproducibility:** (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.95 (0.07-2.06) and average STDEV of 0.67 (0.05-1.46).

Sample ID	DIC ( $\mu\text{mol/kg}$ )	Average	STDEV	Difference
CAL50112	2118.03	2117.32	1.01	1.42
CAL50112	2116.61			
CAL50101	2115.93	2116.11	0.25	0.35
CAL50101	2116.29			
580112	2085.66	2085.69	0.05	0.07
580112	2085.73			
300112	2073.81	2074.09	0.40	0.57
300112	2074.37			
AMI10112	2146.00	2145.73	0.38	0.53
AMI10112	2145.46			
TB40101	2104.93	2103.90	1.46	2.06
TB40101	2102.86			

TB40112	2106.12	2105.31	1.15	1.62
TB40112	2104.49			
Average			0.67	0.95

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.

DIC samples were analyzed on new coulometers 5017O from UIC. Inc.

The CRM offset was incorrectly applied in the previous dataset and has since been corrected.

### **pH:**

Analysis date: 07/17/2024, 7/22/2024, and 7/24/2024  
No CRMs were analyzed before sample analysis.

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.			
Sample ID	Sample BTL #	Salinity	Analysis T (°C)
CAL50112	192	36.285	19.937
CAL10112	401	33.233	19.924
CAL20112	402	34.688	19.922
CAL30101	403	35.092	19.924
CAL30112	404	35.092	19.921
CAL40101	405	35.821	19.93
CAL40112	406	35.822	19.935
CAL50101	407	36.284	19.93

CAL50101	408	36.284	19.935
CAL50112	410	36.285	19.931
330112	411	35.692	19.932
310112	412	36.490	19.93
410112	413	34.651	19.922
450112	414	34.859	19.938
490112	415	29.758	19.923
510112	416	33.479	19.924
540112	417	28.718	19.93
550112	418	29.738	19.926
560112	419	32.840	19.918
570112	420	33.479	19.932
57.10112	421	34.969	19.94
57.20112	422	36.610	19.911
57.30112	423	36.616	19.94
580112	424	36.637	19.942
580112	425	36.637	19.94
600112	426	33.882	19.944
650112	427	30.574	19.956
680112	428	34.968	19.952
700000	429	33.036	19.947
160112	430	35.376	19.918
70112	431	35.411	19.926
UK IN0000	432	35.519	19.947
UK MID0000	433	36.159	19.951
UK OFF0000	434	36.054	19.953
100112	435	34.896	19.941
MR0101	436	35.990	19.911
MR0112	437	35.992	19.939
21/LK0101	438	36.106	19.945
21/LK0112	439	36.080	19.943
WS0101	440	36.188	19.922
WS0112	441	36.183	19.924
KW10112	442	36.084	19.934
KW20101	443	36.227	19.919
KW20112	444	36.179	19.93
KW40101	445	36.540	19.929
KW40112	446	36.400	19.932
300101	447	36.515	19.937
300112	448	36.382	19.938
300112	449	36.382	19.92

RP10112	450	32.328	19.939
RP20112	451	32.552	19.935
RP30112	452	34.676	19.936
BG10112	453	33.192	19.935
BG20112	454	33.851	19.926
BG30101	455	35.142	19.938
BG30112	456	35.134	19.946
RP40101	457	35.617	19.924
RP40112	458	35.616	19.94
BG40101	459	35.712	19.936
BG40112	460	35.746	19.925
GP50101	461	36.327	19.931
GP50112	462	36.286	19.939
V90101	463	36.440	19.943
V90112	464	36.404	19.944
V50101	465	36.296	19.945
V50112	466	36.300	19.935
V10112	467	34.101	19.937
AMI90101	468	36.477	19.931
AMI90112	469	36.477	19.943
AMI50101	470	36.361	19.953
AMI50112	471	36.478	19.939
AMI10112	472	34.171	19.934
AMI10112	473	34.171	19.938
TB40101	474	36.241	19.934
TB40101	475	36.241	19.946
TB40112	476	35.944	19.949
TB40112	477	35.944	19.96
TB100101	478	36.486	19.936
TB100112	479	36.480	19.937
TB10112	480	33.718	19.934

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**Reproducibility:** pH @ 20°C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0014 (0.0004– 0.0034) and an average STDEV of 0.0010 (0.0003 – 0.0024).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	CAL50112	192	8.046	8.048	0.0024	0.0034
HP Agilent 8453	CAL50112	410	8.050			

HP Agilent 8453	CAL50101	407	8.043	8.043	0.0013	0.0018
HP Agilent 8453	CAL50101	408	8.042			
HP Agilent 8453	580112	424	8.020	8.021	0.0010	0.0014
HP Agilent 8453	580112	425	8.022			
HP Agilent 8453	300112	448	8.075	8.075	0.0007	0.0010
HP Agilent 8453	300112	449	8.076			
HP Agilent 8453	AMI10112	472	7.976	7.976	0.0003	0.0004
HP Agilent 8453	AMI10112	473	7.976			
HP Agilent 8453	TB40101	474	8.057	8.058	0.0006	0.0009
HP Agilent 8453	TB40101	475	8.058			
HP Agilent 8453	TB40112	476	8.044	8.044	0.0004	0.0006
HP Agilent 8453	TB40112	477	8.045			
Average					0.0010	0.0014

**Reproducibility:** pH @ 25°C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0013 (0.0004– 0.0033) and an average STDEV of 0.0003 (0.0003 – 0.0024).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	CAL50112	192	7.971	7.973	0.0024	0.0033
HP Agilent 8453	CAL50112	410	7.975			
HP Agilent 8453	CAL50101	407	7.968	7.967	0.0013	0.0018
HP Agilent 8453	CAL50101	408	7.967			
HP Agilent 8453	580112	424	7.946	7.946	0.0010	0.0014
HP Agilent 8453	580112	425	7.947			
HP Agilent 8453	300112	448	8.000	8.000	0.0007	0.0010
HP Agilent 8453	300112	449	8.001			
HP Agilent 8453	AMI10112	472	7.902	7.902	0.0003	0.0004
HP Agilent 8453	AMI10112	473	7.902			
HP Agilent 8453	TB40101	474	7.982	7.983	0.0006	0.0009
HP Agilent 8453	TB40101	475	7.983			

HP Agilent 8453	TB40112	476	7.969	7.969	0.0004	0.0006
HP Agilent 8453	TB40112	477	7.970			

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Average					0.0009	0.0013
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### **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 and 25°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: 07/18/2024, 07/23/2024, and 07/25/2024

Titration system used: Open cell

Batch 201, CRM #185 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.

Batch 201, CRM #132 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.

Batch 201, CRM #620 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.

Batch 201, CRM #413 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.

Batch 201, CRM #288 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.

Batch 201, CRM #045 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.

Batch 201, CRM #467 Salinity = 33.302, cert. TA = 2207.56 µmol/kg.

On 07/18/2024 CRM #185 was analyzed before sample analysis on System 1.

On 07/18/2024 CRM #132 was analyzed after sample analysis on System 1.

On 07/23/2024 CRM #620 was analyzed before and after sample analysis on System 1.

On 07/25/2024 CRM #413 was analyzed before and after sample analysis on System 1.

On 07/18/2024 CRM #288 was analyzed before and after sample analysis on System 2.

On 07/23/2024 CRM #045 was analyzed before and after sample analysis on System 2.

On 07/25/2024 CRM #467 was analyzed before and after sample analysis on System 2.

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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
1	07/18/2024	10:07:47	185	2218.71	11.15
1	07/18/2024	16:09:59	132	2216.88	9.32
1	07/23/2024	09:24:21	620	2217.43	9.87
1	07/23/2024	14:51:25	620	2218.2	10.64
1	07/25/2024	10:07:46	490	2215.47	7.91
1	07/25/2024	14:42:09	490	2215.98	8.42
2	07/18/2024	09:35:10	288	2207.19	-0.37
2	07/18/2024	16:19:30	288	2210.52	2.96
2	07/23/2024	09:37:06	45	2204.61	-2.95
2	07/23/2024	14:59:15	45	2205.54	-2.02
2	07/25/2024	09:01:24	467	2219.2	11.64
2	07/25/2024	14:28:29	467	2218.35	10.79

The acid was replaced on system 2 prior to running on 7/25/2024. While the difference in measured and certified CRM values are higher than desired, the calculated TA from DIC and pH match up well with the measured values using these CRM values indicating the acid may have changed in concentration while in storage.

**Reproducibility:** (# samples and average difference): 6 duplicate samples were collected with an average difference of 2.29 (0.21 – 4.06) and an average STDEV of 1.62 (0.15 – 2.87).

Station	Sample ID	TA (umol/kg)	Average	STDEV	Difference
CAL5	CAL50112	2400.19			
CAL5	CAL50112	2396.29	2398.24	2.76	3.9
CAL5	CAL50101	2398.39			
CAL5	CAL50101	2395.47	2441.44	2.07	2.93
58	580112	2352.19			

58	580112	2350.05	2384.17	1.51	2.13
AMI1	AMI10112	2377.48			
AMI1	AMI10112	2377.69	2312.85	0.15	0.21
TB4	TB40101	2387.80			
TB4	TB40101	2391.86	2417.78	2.87	4.06
TB4	TB40112	2380.33			
TB4	TB40112	2378.97	2432.18	0.96	1.36

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Average			1.62	2.29
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### **Remarks**

The average of the CRMs were used to adjust the values of the samples for each day.

It was determined using calculated TA values from DIC and pH that the duplicate sample associated with bottle 449, sample ID, 300112 was bad and was not included in the statistics.

Stations 54, 55, 56, and 57 are known to have historically high TA values and should be considered normal.

### **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 pCO<sub>2</sub> data can be found at the following website  
<http://www.aoml.noaa.gov/ocd/ocdweb/occ.html>

**Nutrients:****Analysis Date:** 1/22/2024, 1/24/2024

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).

### **Remarks**

No remarks.

### **Chlorophyll and Phaeophytin:**

**Analysis Date:** 1/24/2024, 1/25/2024

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.