

Cruise: S11802
Ship: R/V Hugh R. Sharp
Expo Code: 33H520181102
Dates: November 2, 2018 – November 12, 2018
Chief Scientist: Jerry Prezioso
Equipment: CTD Rosette
Total number of stations: 12
Location: U.S. Mid-Atlantic and New England coastal region

The samples were run for Chris Melrose of the NEFSC as part of our coastal ocean acidification monitoring project.

Sample Collection

The discrete samples were collected from Niskin bottles attached to a 24 bottle configured rosette onboard the R/V Hugh R. Sharp by the survey tech Christopher Taylor. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

12 locations, 40 samples each 500-ml, 4 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:

12 locations, 40 samples each 500-ml, 4 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:

12 locations, 40 samples each 500-ml, 4 duplicate samples.
 Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
 PI: Dr. Rik Wanninkhof
 Analyzed by: Leticia Barbero, Charles Featherstone and 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	02/04/2019	2017.88	2021.13	3.25	18.0	8.0

AOML 6	02/04/2019	2017.88	2025.61	7.73	16.0	7.0
AOML 6	02/04/2019	2020.88	2025.06	4.18	16.0	7.0

Analysis date: 02/04/2019
 Coulometer used: DICE–CM5011- AOML 5
 Blanks: 18.0 counts/min
 CRM # 846 was used and with an assigned value of (includes both DIC and salinity):
 Batch 150, c: 2017.88 µmol/kg, S: 33.343
 CRM values measured: AOML 5: offset 3.25 µmol/kg (2021.13 µmol/kg).
 Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 02/04/2019
 Coulometer used: DICE–CM5011- AOML 6
 Blanks: 16.0 counts/min
 CRM # 528 was used and with an assigned value of (includes both DIC and salinity):
 Batch 150, c: 2017.88 µmol/kg, S: 33.343
 CRM values measured: AOML 6: offset 7.73 µmol/kg (2025.61 µmol/kg).
 Average run time, minimum run time, maximum run time: 7, 7 and 12 min.

Analysis date: 02/04/2019
 Coulometer used: DICE–CM5011- AOML 6
 Blanks: 16.0 counts/min
 CRM # 947 was used and with an assigned value of (includes both DIC and salinity):
 Batch 152, c: 2020.88 µmol/kg, S: 33.371
 CRM values measured: AOML 6: offset 4.18 µmol/kg (2025.06 µmol/kg).
 Average run time, minimum run time, maximum run time: 7, 7 and 12 min.

Reproducibility: (# samples and average difference): 4 duplicate samples were collected with an average difference 0.71 µmol/kg (0.12 – 1.85) and an average STDEV of 0.50 (0.09 – 1.31).

SAMPLE DUPLICATES

Instrument	Sample ID	DIC (umol/kg)	Average	Difference	STDEV
AOML5	10101	1968.94			
AOML5	10101	1969.07	1969.00	0.12	0.09
AOML5	90212	2001.40			
AOML5	90212	2001.16	2001.28	0.24	0.17
AOML5	270701	2186.02			
AOML5	270701	2187.88	2186.95	1.85	1.31
AOML5	561112	2034.29			
AOML5	561112	2034.92	2034.60	0.64	0.45
Average				0.71	0.50

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.

A new CRM was run on AOML 6 after the first one had a difference of 7.73 µmol/kg from the certified value.

pH:

Analysis date: 02/04/2019

Spectrophotometer used: HP Agilent 8453

09/24/2018 CRM #230, Batch 150 had a pH value of 7.9408

Reproducibility: (# samples and average difference): 4 duplicate samples were collected with an average difference 0.002 (0.0003 – 0.0046) and an average STDEV of 0.002 (0.0002 – 0.0032).

System	Sample ID	Sample Bottle #	S	t	pH	Average	Difference	STDEV
HP Agilent 8453	10101	1	31.908	20.033	7.98127			
HP Agilent 8453	10101	2	31.908	20.032	7.98158	7.9814	0.0003	0.0002
HP Agilent 8453	90212	7	34.0501	20.034	8.09168			
HP Agilent 8453	90212	8	34.0501	20.042	8.09312	8.0924	0.0014	0.0010
HP Agilent 8453	270701	21	35.0613	20.049	7.74291			
HP Agilent 8453	270701	22	35.0613	20.044	7.74047	7.7417	0.0024	0.0017
HP Agilent 8453	561112	36	32.7786	20.062	7.89869			
HP Agilent 8453	561112	37	32.7786	20.061	7.90325	7.9010	0.0046	0.0032
Average							0.002	0.002

Temperatures measured during pH analysis

Sample ID	Station #	Bottle #	Temp
CRM150_230	CRM150_230	CRM150_230	20.024
10101	1	1	20.033

10101	1	2	20.032
10104	1	3	20.036
10108	1	4	20.026
90201	9	5	20.037
90206	9	6	20.043
90212	9	7	20.034
90212	9	8	20.042
100301	10	9	20.038
100304	10	10	20.040
100312	10	11	20.031
140401	14	12	20.035
140405	14	13	20.051
140409	14	14	20.050
190502	19	15	20.037
190506	19	16	20.041
190512	19	17	20.050
220601	22	18	20.050
220606	22	19	20.045
220609	22	20	20.050
270701	27	21	20.049
270701	27	22	20.044
270702	27	23	20.051
270712	27	24	20.052
290701	28	25	20.043
290704	28	26	20.047
290712	28	27	20.051
340901	34	28	20.043
340905	34	29	20.050
340912	34	30	20.043
411001	41	31	20.057
411007	41	32	20.056
411012	41	33	20.051
561101	56	34	20.060
561106	56	35	20.052
561112	56	36	20.062
561112	56	37	20.061
601201	60	38	20.051
601202	60	39	20.049
601212	60	40	20.051

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.

A CRM was run for pH before analysis of samples.

pH values are reported at 25°C in the data spreadsheet.

Talk:

Analysis date: 02/06/2019, 02/13/2019, 02/14/2019 and 02/15/2019

Titration system used: Open cell

CRM Batch 152, Salinity = 33.371, cert. TA = 2216.94 µmol/kg.

On 02/06/2019, 02/13/2019, 02/14/2019 and 02/15/2019 one CRM was analyzed before the samples and a different CRM from the same Batch number 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	\Delta CRM
2	02/06/2019	10:18:18	869	2207.55	
2	02/06/2019	18:50:38	1225	2231.81	24.25
2	02/13/2019	12:20:35	185	2232.87	
2	02/13/2019	17:56:35	239	2254.78	21.91
2	02/14/2019	11:13:45	439	2229.71	
2	02/14/2019	14:59:21	751	2220.61	9.10
2	02/15/2019	10:22:35	1059	2228.51	7.28
2	02/15/2019	17:51:19	309	2221.23	

Reproducibility: (# samples and average difference): 4 duplicate samples were collected with an average difference µmol/kg 3.10 (0.11-7.73) and an average STDEV of 2.19 (0.08-5.47).

System	Sample ID	TAlk	Average	Difference	STDEV
2	10101	2151.31			
2	10101	2143.58	2147.45	7.73	5.47
2	90212	2270.93			
2	90212	2266.72	2268.83	4.20	2.97
2	270701	2312.08			
2	270701	2312.19	2312.14	0.11	0.08
2	561112	2194.31			
2	561112	2193.97	2194.14	0.34	0.24
Average				3.10	2.19

Remarks

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

The first duplicate with sample ID 10101 had a large difference which contributed to the overall high average for the difference and STDEV of all the samples.

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 Sample ID is the sample station, cast number and Niskin bottle number for the discrete samples.

No corresponding UW pCO₂ data – no pCO₂ system was on the ship.