

Cruise: PC_1405
Ship: R/V Pisces
Expo Code: 334B20141103
Dates: 11/04/2014 – 11/21/2014
Chief Scientist: Jerry Prezioso
Equipment: CTD Rosette
Total number of stations: 24
Location: US Mid-Atlantic coastal region (ECOMON cruise)

The samples were run for Dr. Jon Hare 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 Pisces by Christopher Taylor. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

24 locations, 80 samples each 500-ml, 9 duplicate samples.
Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

pH:

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Talk:

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Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero, Dr. Denis Pierrot and Charles Featherstone

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 3	01/13/2015	2016.65	2014.13	2.52	28.3	12
AOML 3	01/14/2015	2016.65	2013.16	3.49	29.1	9
AOML 3	01/15/2015	2016.65	2014.64	2.01	12.0	11
AOML 4	01/13/2015	2016.65	2019.08	2.43	28.0	17

AOML 4	01/14/2015	2016.65	2021.30	4.65	35.0	16
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Analysis date: 01/13/2015

Coulometer used: DICE –CM5015- AOML 3

Blanks: 32.8, 28.3 counts/min

CRM # 0459 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 3: offset 2.52 $\mu\text{mol/kg}$ (2014.13 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 12, 8 and 20 min.

Analysis date: 01/14/2015

Coulometer used: DICE –CM5015- AOML 3

Blanks: 32.6, 29.1 counts/min

CRM # 0408 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 3: offset 3.49 $\mu\text{mol/kg}$ (2013.16 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 8 and 12 min.

Analysis date: 01/15/2015

Coulometer used: DICE –CM5015- AOML 3

Blanks: 12.0 counts/min

CRM # 0144 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 2: offset 0.35 $\mu\text{mol/kg}$ (2016.30 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 11, 8 and 20 min.

Analysis date: 01/13/2015

Coulometer used: DICE –CM5015- AOML 4

Blanks: 19.5, 28.0 counts/min

CRM # 0535 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 4: offset 2.43 $\mu\text{mol/kg}$ (2019.08 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 17, 12 and 20 min.

Analysis date: 01/14/2015

Coulometer used: DICE –CM5015- AOML 4

Blanks: 40.4, 33.6, 35.0 counts/min

CRM # 0210 was used and with an assigned value of (includes both DIC and salinity):

Batch 129, c: 2016.65 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 4: offset 4.65 $\mu\text{mol/kg}$ (2021.3 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 16, 11 and 20 min.

Reproducibility: (# samples and average difference): 9 sets of duplicate samples, average difference 3.44 $\mu\text{mol/kg}$ (0.02-8.85), average STDEV of 2.43 (0.02-6.26).

Instrument ID	Sample ID	Bottle #	Corrected DIC ($\mu\text{mol/kg}$)	Average	Difference	STDEV
AOML3	1640411	11	2070.76			

AOML4	1640411	12	2071.10	2070.93	0.34	0.24
AOML3	490705	20	2153.27			
AOML3	490705	22	2149.34	2151.30	3.93	2.78
AOML3	550903	23	2085.86			
AOML3	550903	26	2084.56	2085.21	1.30	0.92
AOML3	721406	28	2150.78			
AOML3	721406	30	2156.11	2153.44	5.33	3.77
AOML4	871802	31	2178.06			
AOML4	871802	34	2186.47	2182.27	8.41	5.95
AOML4	952107	36	2099.20			
AOML4	952107	38	2100.42	2099.81	1.22	0.86
AOML4	1112403	42	2190.64			
AOML3	1112403	45	2192.22	2191.43	1.58	1.12
AOML3	1332709	54	2062.20			
AOML3	1332709	55	2062.23	2062.22	0.02	0.2
AOML3	1483007	60	2094.65			
AOML3	1483007	62	2085.80	2090.23	8.85	6026

Average 3.44 2.43

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. The end blank for AOML 3 (57.4) and AOML 4 (36.4) on 01/13/2015 were higher than the starting blank. All other days of analysis the end blank was under 30 counts for both systems.

The samples were analyzed using the DICE (AOML 3 and 4) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

The pipette on AOML 4 did not fill completely while analyzing sample bottles 42 and 51.

Samples were re-analyzed on AOML 3. The clamp for the sample bottle for AOML 4 was replaced and no further issues with the pipette filling properly were encountered.

pH:

Analysis date: 01/13/2015; 01/14/2015; 01/15/2015

Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): 9 sets of duplicate samples, average difference 0.0052 (0.0013-0.0115), average STDEV of 0.0037 (0.0009-0.0081).

Instrument	Sample ID	Bottle #	pH_20deeg	Average	STDEV	Difference
HP Agilent 8453	160411	11	8.0655			
HP Agilent 8453	160411	12	8.0585	8.0620	0.0050	0.0070
HP Agilent 8453	490705	20	7.6604			
HP Agilent 8453	490705	22	7.6718	7.6661	0.0081	0.0115
HP Agilent 8453	550903	23	7.7765			
HP Agilent 8453	550903	26	7.7714	7.7739	0.0036	0.0050
HP Agilent 8453	721406	28	7.8283			
HP Agilent 8453	721406	30	7.8296	7.8289	0.0009	0.0013
HP Agilent 8453	871802	31	7.7239			
HP Agilent 8453	871802	34	7.7209	7.7224	0.0021	0.0030
HP Agilent 8453	952107	36	7.8327			
HP Agilent 8453	952107	38	7.8301	7.8314	0.0019	0.0027
HP Agilent 8453	1112403	42	7.7448			
HP Agilent 8453	1112403	45	7.7420	7.7434	0.0020	0.0028
HP Agilent 8453	1332709	54	8.0063			
HP Agilent 8453	1332709	55	8.0034	8.0048	0.0021	0.0029
HP Agilent 8453	1483007	60	8.0389			
HP Agilent 8453	1483007	62	8.0498	8.0443	0.0077	0.0109
Average					0.0037	0.0052

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).

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 syringe before DIC analysis to determine the pH.

Talk:

The results posted are duplicate analyses from the same sample bottles used for DIC and pH.

Analysis dates: 02/04/2015 – 02/05/2015

Titration system used: Open cell

CRM batch: 129, S = 33.361, certified TA = 2237.32 $\mu\text{mol/kg}$

2 CRM samples were run daily on each cell, before and after the seawater samples. The TA for the water samples was corrected using the daily averaged ratios between the certified and measured values of the 2 CRMs run on each cell. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	$ \Delta\text{CRM} $
1	2/4/2015	11:38:28	1032	2224.63	
1	2/4/2015	18:23:53	637	2223.68	0.95
1	2/5/2015	09:36:25	456	2221.69	
1	2/5/2015	19:19:14	225	2223.44	1.75
2	2/4/2015	12:20:04	1032	2220.00	
2	2/4/2015	18:21:09	637	2213.23	6.77
2	2/5/2015	09:33:38	456	2216.87	
2	2/5/2015	19:11:37	225	2216.81	0.06
				Average	2.38
				Std. Dev.	3.01

Reproducibility: 9 sets of duplicate samples were run in the same cell, with an average absolute difference of 1.66 $\mu\text{mol/kg}$ (0.16-3.54), and a Standard Deviation of 1.3.

Bottle #	System	Date	Time	S	TA	Difference	Comments
11	1	2/4/2015	13:50:01	35.491	2342.41	2.40	
12	1	2/4/2015	14:13:32	35.491	2340.01		
20	1	2/4/2015	15:39:34	33.36	2234.27	0.16	
22	1	2/4/2015	15:57:21	33.36	2234.11		
23	1	2/4/2015	16:20:32	32.71	2197.87	2.06	
26	1	2/4/2015	16:39:00	32.71	2199.94		
28	1	2/4/2015	17:03:20	34.678	2309.76	0.57	
30	1	2/4/2015	17:22:05	34.678	2309.19		
31	1	2/4/2015	17:43:06	34.644	2294.71	0.59	
34	1	2/4/2015	18:01:52	34.644	2294.12		
36	1	2/5/2015	10:01:38	33.593	2243.60	3.54	
38	1	2/5/2015	10:25:27	33.593	2247.14		
42	1	2/5/2015	11:05:09	35.058	2317.14	2.04	
45	1	2/5/2015	11:46:13	35.058	2315.10		
54	1	2/5/2015	13:29:30	34.335	2276.05	3.28	
55	1	2/5/2015	13:52:40	34.335	2279.33		
60	1	2/5/2015	14:55:39	35.69	2354.11	0.27	
62	1	2/5/2015	15:16:59	35.69	2353.83		
						Average	1.66
						Std. Dev.	1.3

Remarks

The two systems behaved well during the analyses. On February 4th, the values for the CRMs used on system 2 were, one higher than usual and the other lower than usual, resulting in a difference between them of 6.77 umol/kg. However, the average between the 2 is consistent with the values obtained for this system and the correction was done with the average between the two CRMs.

There was a short power outage lasting about one minute on February 5th while one sample was being analyzed (Sample ID 1372903). The power outage interrupted the titration and the process was restarted with the same sample volume that was being

titrated before. The titration file was reconstructed from the two partial titrations and the sample value has been flagged 3.

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.

UPDATE JULY 2015

This datafile has been merged with nutrient data from the same cruise, provided by Dr. Jon Hare's group. Samples for carbon parameters and nutrients were occasionally drawn from different Niskin bottles, so merging has been done based on sample depth, assuming all Niskin bottles tripped at the same depth would have the same (or close enough) nutrient values. We have kept the salinity and temperature values used for the carbon parameter calculations. Comparison with calibrated and corrected salinity values provided by Hare's group indicate that the average salinity difference (absolute difference) between preliminary and corrected values was 0.008 ± 0.01 .

For sample 1302602, the depth listed on our file was wrong. We have corrected it from 40 to 21 meters.

The following columns have been added:

Date.UTC, Depth_station, CTDPRS, Sigma-Theta, CTDOXY, CTDOXYMOL, SILCAT, NITRIT+NITRAT, AMMONIA, PHSPHT, and Niskin_nuts.

UPDATE:

Between March and June of 2021, all of the data for the discrete samples was put into a uniform format. The supporting information was checked for accuracy, especially the expocode, date, time, and positions.

Additionally, pH results were recalculated to 20 and 25 degrees Celsius.