

Cruise: Equinox_0315
Ship: Equinox
Expo Code: MLCE20150306
Dates: March 6th – March 11th, 2015
Chief Scientist: Dr. Denis Pierrot
Equipment: TSG-Flow thru system
Total number of stations: 19
Location: Ft. Lauderdale, FL and the US, Virgin Islands

Sample Collection

The discrete samples were collected from the TSG-flow thru system onboard the ship of opportunity Royal Caribbean Equinox by Dr. Denis Pierrot. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

19 locations, 19 samples each 500-ml, 6 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

pH:

19 locations, 19 samples each 500-ml, 6 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

Talk:

19 locations, 19 samples each 500-ml, 6 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero and Charles Featherstone

Sample Analysis

DIC:

Instrument ID	Date	Certified CRM (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 3	03/24/2015	2016.65	2017.60	0.95	15.2	13

Analysis date: 03/24/2015
Coulometer used: DICE-CM5015- AOML 3
Blanks: 15.2 counts/min

CRM # 0793 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 0.95 $\mu\text{mol/kg}$ (2017.60 $\mu\text{mol/kg}$).
 Average run time, minimum run time, maximum run time: 13, 8 and 20 min.

Reproducibility: (# samples and average difference): 6 sets of duplicate samples,
 average difference 6.01 $\mu\text{mol/kg}$ (0.65-12.21), average STDEV of 4.25 (0.46-8.63).

Instrument ID	Sample ID	Bottle #	Corrected DIC ($\mu\text{mol/kg}$)	Average	Difference	STDEV
AOML3	1	1	2047.81			
AOML3	2	2	2045.96	2046.89	1.85	1.31
AOML3	6	6	2069.12			
AOML3	7	7	2074.75	2071.93	5.63	3.98
AOML3	12	12	2052.74			
AOML3	13	13	2040.54	2046.64	12.21	8.63
AOML3	14	14	2046.04			
AOML3	15	15	2037.81	2041.93	8.23	5.82
AOML3	16	16	2025.35			
AOML3	17	17	2032.85	2029.10	7.51	5.31
AOML3	18	18	2030.73			
AOML3	19	19	2030.08	2030.40	0.65	0.46
Average					6.01	4.25

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. End blank (AOML 3 =27.5).

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

Duplicates were sampled 1 to 3 minutes apart from the ships TSG flow thru system.

pH:

Analysis date: 03/24/2015

Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): 6 sets of duplicate samples, average difference 0.089 (0.0016-0.0193), average STDEV of 0.0063 (0.0012-0.0137).

System	Bottle #	Sample ID	pH	Average	Difference	STDEV
HP Agilent 8453	1	1	8.0903			
HP Agilent 8453	2	2	8.1004	8.0953	0.0101	0.0072
HP Agilent 8453	6	6	8.1279			
HP Agilent 8453	7	7	8.1134	8.1206	0.0146	0.0103
HP Agilent 8453	12	12	8.1084			
HP Agilent 8453	13	13	8.1127	8.1106	0.0044	0.0031
HP Agilent 8453	14	14	8.1131			
HP Agilent 8453	15	15	8.1147	8.1139	0.0016	0.0012
HP Agilent 8453	16	16	8.1092			
HP Agilent 8453	17	17	8.1059	8.1075	0.0032	0.0023
HP Agilent 8453	18	18	8.1094			
HP Agilent 8453	19	19	8.1288	8.1191	0.0193	0.0137
Average					0.0089	0.0063

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.

Duplicates were sampled 1 to 3 minutes apart from the ships TSG flow thru system.

Talk:

The results posted are analyses from the same sample bottles used for DIC and pH.
 Analysis dates: 03/25/2015
 Titration system used: Open cell
 CRM batch: 129, S = 33.361, certified TA = 2237.32 $\mu\text{mol}/\text{kg}$

2 CRM samples were run on each cell, before and after the seawater samples. The TA for the water samples was corrected using the 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 cell.

Cell System	Date	Time	Bottle #	TA	\Delta CRM
1	3/25/2015	11:58:09	201	2219.28	
1	3/25/2015	16:38:22	795	2222.28	3.00
2	3/25/2015	12:08:25	201	2211.12	
2	3/25/2015	16:38:54	795	2214.66	3.54
				Average	3.27
				Std. Dev.	0.38

Reproducibility: 5 sets of duplicate samples were run in the cell 1 and one set of duplicates was run on cell 2, with an average absolute difference of 1.68 $\mu\text{mol}/\text{kg}$ (0.03 – 2.96), and a Standard Deviation of 1.06. The duplicates were sampled 1 to 3 minutes apart from the ships TSG flow thru system.

Bottle #	System	Date	Time	S	TA	\text{Difference}	Comments
1	2	3/25/2015	12:39:09	36.38	2378.04	1.67	
2	2	3/25/2015	13:01:10	36.36	2379.71		
6	1	3/25/2015	12:16:44	36.66	2398.27	0.03	
7	1	3/25/2015	12:40:53	36.66	2398.30		
12	1	3/25/2015	13:03:00	36.14	2369.52	2.96	
13	1	3/25/2015	13:25:40	36.17	2372.48		
14	1	3/25/2015	13:52:44	36.13	2370.84	2.70	
15	1	3/25/2015	14:17:48	36.16	2373.54		
16	1	3/25/2015	14:41:17	35.88	2354.90	1.48	

17	1	3/25/2015	15:04:36	35.88	2356.38	
18	1	3/25/2015	15:26:18	35.89	2355.31	1.26
19	1	3/25/2015	15:55:31	35.88	2356.57	
					Average	1.68
					Std. Dev.	1.06

Remarks

The two systems behaved well during the analyses.

Duplicates were sampled from the ships TSG flow thru system 1 to 3 minutes apart.

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.

Cruise: Equinox_1505
Ship: Equinox
Expo Code: MLCE20150427
Dates: April 28th, 2015 – May 6th, 2015
Chief Scientist: Dr. Denis Pierrot
Equipment: TSG-Flow thru system
Total number of stations: 35
Location: Ft. Lauderdale, FL to Lisbon, Portugal

Sample Collection

The discrete samples were collected from the TSG-flow thru system onboard the ship of opportunity Royal Caribbean Equinox by Dr. Denis Pierrot. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

35 locations, 40 samples each 500-ml, 5 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Robert Castle

TALK:

35 locations, 40 samples each 500-ml, 5 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero and Dr. Denis Pierrot

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	07/26/2015	2031.53	2031.34	0.19	30.0	8
AOML 3	07/26/2015	2031.53	2030.74	0.79	24.0	10

Analysis date: 07/26/2015

Coulometer used: DICE-CM5015- AOML 3

Blanks: 12.0 counts/min and raised to 30.0 counts/min before CRM analysis

CRM # 889 was used and with an assigned value of (includes both DIC and salinity):

Batch 144, c: 2031.53 $\mu\text{mol/kg}$, S: 33.571

CRM values measured: AOML 3: offset 0.19 $\mu\text{mol/kg}$ (2031.34 $\mu\text{mol/kg}$).

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

Analysis date: 07/26/2015

Coulometer used: DICE–CM5015- AOML 3

Blanks: 12.0 counts/min and raised to 24.0 counts/min before CRM analysis

CRM # 889 was used and with an assigned value of (includes both DIC and salinity):

Batch 144, c: 2031.53 $\mu\text{mol/kg}$, S: 33.571

CRM values measured: AOML 3: offset 0.79 $\mu\text{mol/kg}$ (2030.74 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 10, 9 and 12 min.

Reproducibility: (# samples and average difference): 5 sets of duplicate samples, average difference 1.96 $\mu\text{mol/kg}$ (0.00-4.34), average STDEV of 1.39 (0.00-3.07).

Instrument ID	Sample ID	Bottle #	Corrected DIC ($\mu\text{mol/kg}$)	Average	Difference	STDEV
AOML3	1	1	2034.70			
AOML3	2	2	2039.04	2036.87	4.34	3.07
AOML3	6	6	2063.58			
AOML3	7	7	2064.88	2064.23	1.30	0.92
AOML3	19	19	2087.01			
AOML3	20	20	2087.01	2087.01	0.00	0.00
AOML3	28	28	2093.09			
AOML3	29	29	2093.63	2093.36	0.54	0.38
AOML3	30	30	2094.18			
AOML3	31	31	2097.82	2096.00	3.64	2.57
Average					1.96	1.39

CRM, salinity and HgCl_2 correction applied: Salinity correction was applied using TSG salinity.

Remarks

The volume correction was applied due to added HgCl_2 (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 samples were analyzed using the DICE (AOML 3) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

Duplicates were sampled 3 to 5 minutes apart from the ships TSG flow thru system.

Talk:

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

Analysis dates: 07/29/2015 – 07/30/2015

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	ΔCRM
1	07/29/15	11:03:14	289	2227.13	
1	07/29/15	17:57:49	868	2232.75	6.62
1	07/30/15	10:55:22	43	2224.34	
1	07/30/15	19:55:07	95	2227.56	3.22
2	07/29/15	11:06:02	289	2218.82	
2	07/29/15	17:56:47	868	2222.51	3.69
2	07/30/15	10:49:05	43	2219.71	
2	07/30/15	19:48:25	95	2221.13	1.42
				Average	3.49
				Std. Dev.	1.73

Reproducibility: 5 sets of duplicate samples were run in the same cell, with an average absolute difference of 1.67 $\mu\text{mol/kg}$ (0.31-3.32), and a Standard Deviation of 1.10.

Bottle #	System	Date	Time	S	TA	Difference	Comments
1	1	6/2/2014	16:07:29	35.218	2370.61		
2	1	6/2/2014	17:01:03	35.218	2373.93	3.32	
6	1	6/3/2014	15:42:16	33.372	2396.51		
7	1	6/3/2014	16:07:07	33.372	2395.28	1.23	

19	1	6/4/2014	12:52:22	32.532	2388.41	0.31
20	1	6/4/2014	13:39:37	32.532	2388.10	
28	1	3/6/2014	16:58:56	32.892	2361.64	1.88
29	1	3/6/2014	17:21:40	32.892	2359.76	
30	1	3/6/2014	16:58:56	32.892	2368.39	1.59
31	1	3/6/2014	17:21:40	32.892	2366.80	
					Average	1.67
					Std. Dev.	1.10

Remarks

The two systems behaved correctly during the analyses.
 Duplicates were sampled 3 to 5 minutes apart from the ships TSG flow thru system.

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 bottle number for these underway samples.

Cruise: Equinox1604
Ship: Royal Caribbean Equinox
Expo Code: MLCE20160415
Dates: April 15th – April 25th, 2016
Chief Scientist: Dr. Denis Pierrot
Equipment: TSG-Flow thru system
Total number of stations: 36
Location: Ft. Lauderdale, FL to Lisbon, Portugal

Sample Collection

The discrete samples were collected from the TSG-flow thru system onboard the ship of opportunity Royal Caribbean Equinox by Dr. Denis Pierrot. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

36 locations, 40 samples each 500-ml, 4 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

pH:

36 locations, 40 samples each 500-ml, 4 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

TAlk:

36 locations, 40 samples each 500-ml, 4 duplicate samples.
Sample_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero and Charles Featherstone

Sample Analysis

DIC:

Instrument ID	Date	Certified CRM (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 3	07/18/2016	2031.53	2031.26	0.27	26.0	15
AOML 3	07/19/2016	2031.53	2033.04	1.51	26.0	14
AOML 4	07/18/2016	2031.53	2028.56	2.97	28.0	13

Analysis date: 07/18/2016

Coulometer used: DICE–CM5015- AOML 3

Blanks: 14.4 counts/min and raised to 26.0 counts/min before CRM analysis

CRM # 1235 was used and with an assigned value of (includes both DIC and salinity):

Batch 144, c: 2031.53 $\mu\text{mol/kg}$, S: 33.571

CRM values measured: AOML 3: offset 0.27 $\mu\text{mol/kg}$ (2031.26 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 15, 12 and 19 min.

Analysis date: 07/19/2016

Coulometer used: DICE–CM5015- AOML 3

Blanks: 12.0 counts/min and raised to 26.0 counts/min before CRM analysis

CRM # 1110 was used and with an assigned value of (includes both DIC and salinity):

Batch 144, c: 2031.53 $\mu\text{mol/kg}$, S: 33.571

CRM values measured: AOML 3: offset 1.51 $\mu\text{mol/kg}$ (2033.04 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 14, 11 and 16 min.

Analysis date: 07/19/2016

Coulometer used: DICE–CM5015- AOML 4

Blanks: 23.9 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 236 was used and with an assigned value of (includes both DIC and salinity):

Batch 144, c: 2031.53 $\mu\text{mol/kg}$, S: 33.571

CRM values measured: AOML 4: offset 2.97 $\mu\text{mol/kg}$ (2028.56 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 13, 12 and 16 min.

Reproducibility: (# samples and average difference): 4 sets of duplicate samples, average difference 5.00 $\mu\text{mol/kg}$ (3.62-6.03), average STDEV of 3.54 (2.56-4.26).

Instrument ID	Sample ID	Bottle #	Corrected DIC ($\mu\text{mol/kg}$)	Average	Difference	STDEV
AOML3	10000	1	2036.64			
AOML4	20000	2	2042.53	2039.59	5.88	4.16
AOML4	80000	8	2081.93			
AOML3	90000	9	2085.55	2083.74	3.62	2.56
AOML3	260000	26	2115.68			
AOML3	270000	27	2109.65	2112.66	6.03	4.26
AOML3	820000	82	2123.00			
AOML3	830000	83	2118.53	2120.76	4.47	3.16
Average					5.00	3.54

CRM, salinity and HgCl_2 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 samples were analyzed using the DICE (AOML 3 & AOML 4) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

Duplicates were sampled 2 to 4 minutes apart from the ships TSG flow thru system.

pH:

Analysis date: 07/18/2016 and 07/19/2016
Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): 4 sets of duplicate samples, average difference 0.0055 (0.0001-0.0131), average STDEV of 0.0039 (0.0001-0.0092).

System	Sample ID	Bottle #	pH	Average	Difference	STDEV
HP Agilent 8453	10000	1	8.1135			
HP Agilent 8453	20000	2	8.1175	8.1155	0.004	0.0028
HP Agilent 8453	80000	8	8.0889			
HP Agilent 8453	90000	9	8.0889	8.0889	0.0001	0.0001
HP Agilent 8453	260000	26	8.0093			
HP Agilent 8453	270000	27	8.0043	8.0068	0.005	0.0035
HP Agilent 8453	820000	82	7.9985			
HP Agilent 8453	830000	83	7.9854	7.9920	0.0131	0.0092
Average					0.0055	0.0039

Temperature measured during pH analysis

Sample ID	Sample BTL #	Btl. Temp	Start Cell (°C)	End Cell (°C)	Differ Start to End Cell (°C)
10000	1	19.821	20.918	21.648	0.730
20000	2	19.802	20.712	21.509	0.797
30000	3	20.004	20.907	21.694	0.787
40000	4	20.009	20.949	21.862	0.913
50000	5	19.986	20.789	21.911	1.122
60000	6	20.303	20.965	21.582	0.617

70000	7	20.070	20.898	21.798	0.900
80000	8	19.958	20.927	21.926	0.999
90000	9	19.974	20.886	21.735	0.849
100000	10	19.951	20.828	21.939	1.111
110000	11	20.004	20.855	21.962	1.107
120000	12	20.068	20.901	21.736	0.835
130000	13	20.126	20.952	21.618	0.666
140000	14	20.012	20.961	21.952	0.991
160000	16	20.152	20.951	21.804	0.853
200000	17	19.960	20.932	21.922	0.990
170000	18	19.985	20.865	21.810	0.945
220000	19	20.029	20.986	21.880	0.894
190000	20	19.916	20.849	21.703	0.854
210000	21	19.964	20.805	21.714	0.909
230000	22	19.954	20.982	21.972	0.990
250000	23	20.003	20.987	21.933	0.946
270000	24	20.002	20.892	21.919	1.027
310000	25	20.024	20.838	21.796	0.958
240000	26	20.037	20.838	21.916	1.078
260000	27	19.957	20.808	21.779	0.971
290000	29	19.949	20.904	21.753	0.849
350000	31	20.109	21.076	21.963	0.887
370000	33	20.043	20.947	21.674	0.727
390000	35	20.07	21.054	21.927	0.873
330000	37	19.863	20.815	21.699	0.884
810000	39	20.131	20.962	21.896	0.934
820000	81	19.897	20.877	21.594	0.717
830000	82	18.896	20.695	21.680	0.985
880000	83	20.024	20.935	21.723	0.788
890000	88	20.045	20.957	21.826	0.869
900000	89	19.956	20.822	21.630	0.808
910000	90	20.044	20.862	21.655	0.793
1740000	91	19.987	20.818	21.740	0.922
180000	174	19.984	20.708	21.686	0.978
Average		19.977	20.890	21.787	0.896

Remarks

Duplicates were sampled 2 to 4 minutes apart from the ships TSG flow thru system.

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:

Analysis date: 7/28/2016

Titration system used: Open cell

CRM Batch 120, Salinity = 33.072, cert. TA = 2208.34 $\mu\text{mol/kg}$.

On 7/28/2016 one CRM was analyzed before the samples and another CRM was run at the end of analysis 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\text{CRM} $
1	07/28/2016	11:26:45	434	2207.70	
1	07/28/2016	19:57:20	434	2211.51	3.81
2	07/28/2016	11:19:11	268	2182.56	
2	07/28/2016	19:50:56	268	2183.19	0.63

Reproducibility: (# samples and average difference): 4 duplicate samples were collected with an average difference 3.78 $\mu\text{mol/kg}$ (0.34 – 9.89) and an average STDEV of 2.67 (0.24 – 6.99).

System	Sample ID	Talk	Average	Difference	STDEV
System 2	10000	2368.62	2373.56	9.89	6.99
System 1	20000	2378.51			
System 1	80000	2400.61	2401.45	1.68	1.19
System 2	90000	2402.29			
System 1	260000	2377.77	2376.16	3.21	2.27
System 2	270000	2374.56			
System 2	820000	2365.48	2365.65	0.34	0.24
System 1	830000	2365.83			

Average	3.78	2.67
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Remarks

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

Duplicates were sampled 2 to 4 minutes apart from the ships TSG flow thru system.

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.

The salinity and temperature were taken from the UW pCO₂ system. The salinities were used in the DIC, TAlk and pH calculations.

Corresponding UW pCO₂ data can be found at the following website
<http://www.aoml.noaa.gov/ocd/ocdweb/occ.html>

Cruise: Equinox1610
Ship: Royal Caribbean Equinox
Expo Code: MLCE20161030
Dates: October 30th – November 11th, 2016
Chief Scientist: Dr. Denis Pierrot
Equipment: TSG-Flow thru system
Total number of stations: 35
Location: Ft. Lauderdale, FL to Lisbon, Portugal (Trans-Atlantic)

Sample Collection

The discrete samples were collected from the TSG-flow thru system onboard the ship of opportunity Royal Caribbean Equinox by Dr. Denis Pierrot. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

35 locations, 38 samples each 500-ml, 3 duplicate samples.
 Sample_ID#: 301, etc.; Sample bottle number
 PI: Dr. Rik Wanninkhof
 Analyzed by: Charles Featherstone

pH:

35 locations, 38 samples each 500-ml, 3 duplicate samples.
 Sample_ID#: 301, etc.; Sample bottle number
 PI: Dr. Rik Wanninkhof
 Analyzed by: Charles Featherstone

TAlk:

35 locations, 38 samples each 500-ml, 3 duplicate samples.
 Sample_ID#: 301, etc.; Sample bottle number
 PI: Dr. Rik Wanninkhof
 Analyzed by: Dr. Leticia Barbero and Charles Featherstone

Sample Analysis

DIC:

Instrument ID	Date	Certified CRM (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 3	11/09/2016	2022.04	2023.53	1.49	28.0	20
AOML 4	11/08/2016	2022.04	2021.29	0.75	26.0	17
AOML 4	11/09/2016	2022.04	2020.94	1.10	28.0	17
AOML 4	11/10/2016	2022.04	2022.90	0.86	35.0	12

Analysis date: 11/09/2016
 Coulometer used: DICE–CM5015- AOML 3
 Blanks: 23.2 counts/min and raised to 28.0 counts/min before CRM analysis
 CRM # 625 was used and with an assigned value of (includes both DIC and salinity):
 Batch 123, c: 2022.4 $\mu\text{mol/kg}$, S: 33.384
 CRM values measured: AOML 3: offset 1.49 $\mu\text{mol/kg}$ (2023.53 $\mu\text{mol/kg}$).
 Average run time, minimum run time, maximum run time: 20, 19 and 20 min.

Analysis date: 11/08/2016
 Coulometer used: DICE–CM5015- AOML 4
 Blanks: 10.4 counts/min and raised to 26.0 counts/min before CRM analysis
 CRM # 560 was used and with an assigned value of (includes both DIC and salinity):
 Batch 123, c: 2202.04 $\mu\text{mol/kg}$, S: 33.384
 CRM values measured: AOML 4: offset 0.75 $\mu\text{mol/kg}$ (2021.29 $\mu\text{mol/kg}$).
 Average run time, minimum run time, maximum run time: 17, 11 and 20 min.

Analysis date: 11/09/2016
 Coulometer used: DICE–CM5015- AOML 4
 Blanks: 12.3 counts/min and raised to 28.0 counts/min before CRM analysis
 CRM # 292 was used and with an assigned value of (includes both DIC and salinity):
 Batch 123, c: 2202.04 $\mu\text{mol/kg}$, S: 33.384
 CRM values measured: AOML 4: offset 1.10 $\mu\text{mol/kg}$ (2020.94 $\mu\text{mol/kg}$).
 Average run time, minimum run time, maximum run time: 17, 11 and 20 min.

Analysis date: 11/10/2016
 Coulometer used: DICE–CM5015- AOML 4
 Blanks: 27.4 counts/min and raised to 35.0 counts/min before CRM analysis
 CRM # 18 was used and with an assigned value of (includes both DIC and salinity):
 Batch 123, c: 2022.04 $\mu\text{mol/kg}$, S: 33.384
 CRM values measured: AOML 4: offset 0.86 $\mu\text{mol/kg}$ (2022.90 $\mu\text{mol/kg}$).
 Average run time, minimum run time, maximum run time: 12, 9 and 15 min.

Reproducibility: (# samples and average difference): 3 sets of duplicate samples, average difference 4.52 $\mu\text{mol/kg}$ (1.14-7.54), average STDEV of 3.19 (0.81-5.33).

Instrument ID	Sample ID	Bottle #	Corrected DIC ($\mu\text{mol/kg}$)	Average	Difference	STDEV
AOML4	620000	62	2112.27			
AOML4	630000	63	2117.14	2114.71	4.87	3.44
AOML4	730000	73	2114.45			
AOML4	740000	74	2115.59	2115.02	1.14	0.81
AOML3	1770000	177	2078.62			

AOML3	1780000	178	2086.16	2082.39	7.54	5.33
Average					4.52	3.19

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

Duplicates were sampled 1 to 2 minutes apart from the ships TSG flow thru system.

pH:

Analysis date: 11/08/2016, 11/09/2016 & 11/10/2016

Spectrophotometer used: HP Agilent 8453

CRM Batch 123 pH results

System	Analysis Date	Certified CRM pH	CRM Value pH	CRM Offset
HP Agilent 8453	11/08/2016	8.00	7.9082	0.0910
HP Agilent 8453	11/09/2016	8.00	7.9199	0.0801
HP Agilent 8453	11/10/2016	8.00	7.9242	0.0758

Reproducibility: (# samples and average difference): 3 sets of duplicate samples, average difference 0.0063 (0.0021-0.0144), average STDEV of 0.0044 (0.0001-0.0102).

System	Sample ID	Bottle #	pH	Average	Difference	STDEV
HP Agilent 8453	620000	62	8.0507	8.0579	0.0144	0.0102
HP Agilent 8453	630000	63	8.0651			
HP Agilent 8453	730000	73	8.0824	8.0823	0.0002	0.0001
HP Agilent 8453	740000	74	8.0822			

HP Agilent 8453	1770000	177	8.1161	8.1182	0.0043	0.0030
HP Agilent 8453	1780000	178	8.1203			
Average					0.0063	0.0044

Temperature measured during pH analysis

Sample ID	Sample BTL #	Btl. Temp	Start Cell (°C)	End Cell (°C)	Differ Start to End Cell (°C)
610000	61	20.230	21.125	21.258	0.133
620000	62	20.030	21.088	21.463	0.375
630000	63	19.978	20.544	21.207	0.663
640000	64	20.130	21.205	21.898	0.693
650000	65	19.839	20.773	21.308	0.535
660000	66	20.096	21.162	21.655	0.493
670000	67	20.055	21.181	21.939	0.758
680000	68	20.079	21.165	21.864	0.699
690000	69	20.306	21.246	21.994	0.748
700000	70	20.049	20.679	21.459	0.780
710000	71	19.829	20.389	20.990	0.601
720000	72	19.983	20.965	21.510	0.545
730000	73	20.048	20.783	21.662	0.879
740000	74	19.978	20.857	21.530	0.673
750000	75	19.925	20.882	21.699	0.817
760000	76	19.858	20.678	21.501	0.823
770000	77	19.893	20.505	21.305	0.800
780000	78	19.962	20.766	21.343	0.577
790000	79	19.975	20.829	21.551	0.722
800000	80	19.984	20.550	21.271	0.721
1750000	175	20.055	20.689	21.554	0.865
1760000	176	20.015	20.776	21.737	0.961
1770000	177	20.078	20.982	21.865	0.883
1780000	178	19.865	20.769	21.371	0.602
1790000	179	20.051	20.856	21.698	0.842
1800000	180	19.924	20.594	21.436	0.842
1810000	181	19.836	20.613	21.309	0.696
1820000	182	19.941	20.839	21.160	0.321
1830000	183	20.202	21.338	21.727	0.389
1840000	184	19.811	20.330	20.874	0.544
1850000	185	19.868	20.530	20.873	0.343
1860000	186	19.827	20.502	21.035	0.533
1870000	187	19.828	20.515	21.007	0.492
1880000	188	19.904	20.651	21.568	0.917

1890000	189	19.844	20.837	21.359	0.522
1900000	190	19.982	21.628	22.258	0.630
1910000	191	19.78	20.407	21.017	0.610
1920000	192	19.761	20.287	20.850	0.563
CRM 350	CRM 350	19.831	20.672	21.415	0.743
CRM 568	CRM 568	19.87	20.543	21.486	0.943
CRM 75	CRM 75	19.809	20.143	20.443	0.300
Average			20.777	21.426	0.648

Remarks

Duplicates were sampled 1 to 2 minutes apart from the ships TSG flow thru system.

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:

Analysis date: 11/17/2016, 11/18/2016 & 11/22/2016

Titration system used: Open cell

CRM Batch 123, Salinity = 33.384, cert. TA = 2225.21 $\mu\text{mol/kg}$.

On 11/17/2016, 11/18/2016 & 11/22/2016 one CRM was analyzed before the samples and another CRM or same CRM was run at the end of analysis 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	11/17/2016	08:49:58	185	2227.46	
2	11/17/2016	16:05:32	185	2222.63	4.83
2	11/18/2016	09:03:06	129	2222.31	
2	11/18/2016	16:39:16	1062	2217.03	5.28
2	11/22/2016	08:21:52	953	2223.31	
2	11/22/2016	17:14:52	953	2224.52	1.21

Reproducibility: (# samples and average difference): 3 duplicate samples were collected with an average difference 2.03 $\mu\text{mol/kg}$ (0.80 – 2.75) and an average STDEV of 1.44 (0.57 – 1.95).

System	Bottle #	Sample ID	Talk	Average	Difference	STDEV
System 2	62	190504	2418.77	2417.49	2.55	1.80
System 2	63	190504	2416.22			
System 2	73	200601	2423.59	2424.97	2.75	1.95
System 2	74	200601	2426.34			
System 2	177	200611	2412.48	2412.88	0.80	0.57
System 2	178	200611	2413.28			
Average					2.03	1.44

Remarks

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

Duplicates were sampled 1 to 2 minutes apart from the ships TSG flow thru system.

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 bottle number for the discrete samples.

The salinity and temperature were taken from the UW pCO₂ system. The salinities were used in the DIC, Talk and pH calculations.

Corresponding UW pCO₂ data can be found at the following website
<http://www.aoml.noaa.gov/ocd/ocdweb/occ.html>