

**Cruise:** EX1507  
**Ship:** Explorer of the Seas  
**Expo Code:** 33KF20150212  
**Dates:** February 12<sup>th</sup> – 19<sup>st</sup>, 2015  
**Chief Scientist:** Kevin Sullivan  
**Equipment:** TSG-Flow thru system  
**Total number of stations:** 20  
**Location:** Port Canaveral, FL to Willemstad, Curacao

**Sample Collection**

The discrete samples were collected from the TSG-flow thru system onboard the Royal Caribbean ship Explorer of the Seas by Kevin Sullivan. The date and time listed in the data file are UTC when each sample bottle was collected.

**DIC:**

20 locations, 20 samples each 500-ml, 4 duplicate samples.  
 Sample\_ID#: 301, etc.; Sample bottle number  
 PI: Dr. Rik Wanninkhof  
 Analyzed by: Charles Featherstone

**pH:**

20 locations, 20 samples each 500-ml, 4 duplicate samples.  
 Sample\_ID#: 301, etc.; Sample bottle number  
 PI: Dr. Rik Wanninkhof  
 Analyzed by: Charles Featherstone

**TAlk:**

20 locations, 20 samples each 500-ml, 4 duplicate samples.  
 Sample\_ID#: 301, etc.; Sample 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 (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 3	03/05/2015	2016.65	2021.75	5.10	12.0	8

Analysis date: 03/05/2015  
 Coulometer used: DICE-CM5015- AOML 3  
 Blanks: 12.0 counts/min

CRM # 0965 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 5.10  $\mu\text{mol/kg}$  (2021.75  $\mu\text{mol/kg}$ ).  
 Average run time, minimum run time, maximum run time: 8, 8 and 10 min.

**Reproducibility:** (# samples and average difference): 4 sets of duplicate samples,  
 average difference 5.45  $\mu\text{mol/kg}$  (0.15-11.37), average STDEV of 3.86 (0.11-8.04).

Instrument ID	Sample ID	Bottle #	Corrected DIC ( $\mu\text{mol/kg}$ )		Difference	STDEV
				Average		
AOML3	304	304	2020.06			
AOML3	305	305	2025.79	2022.93	5.73	4.05
AOML3	308	308	2002.80			
AOML3	309	309	2014.18	2008.49	11.37	8.04
AOML3	316	316	2001.34			
AOML3	317	317	2001.19	2001.26	0.15	0.11
AOML3	319	319	2039.95			
AOML3	320	320	2035.40	2037.68	4.55	3.22
Average					5.45	3.86

CRM, salinity and  $\text{HgCl}_2$  correction applied: Salinity correction was applied using TSG salinity.

### **Remarks**

The volume correction was applied due to added  $\text{HgCl}_2$  (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. End blank (AOML 3 =12.0).

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 1.5 minutes apart from the ships TSG flow thru system.

### **pH:**

Analysis date: 03/05/2015  
 Spectrophotometer used: HP Agilent 8453

**Reproducibility:** (# samples and average difference): 4 sets of duplicate samples, average difference 0.0018 (0.0002-0.0048), average STDEV of 0.0013 (0.0002-0.0034).

System	Bottle #	Sample ID	pH	Average	Difference	STDEV
HP Agilent 8453	304	304	8.1028			
HP Agilent 8453	305	305	8.1076	8.10521	0.0048	0.0034
HP Agilent 8453	308	308	8.1075			
HP Agilent 8453	309	309	8.1063	8.10687	0.0012	0.0008
HP Agilent 8453	316	316	8.0898			
HP Agilent 8453	317	317	8.0888	8.08931	0.0010	0.0007
HP Agilent 8453	319	319	8.0857			
HP Agilent 8453	320	320	8.0855	8.08562	0.0002	0.0002
Average					0.0018	0.0013

### **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<sup>0</sup>C 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 1.5 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: 03/10/2015

Titration system used: Open cell

CRM batch: 129, S = 33.361, certified TA = 2237.32 μmol/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	ΔCRM
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1	3/10/2015	09:23:23	533	2221.96	
1	3/10/2015	15:52:53	601	2223.04	1.08
2	3/10/2015	09:59:22	533	2214.91	
2	3/10/2015	16:26:57	601	2214.36	0.55
				Average	0.82
				Std. Dev.	0.37

**Reproducibility:** 4 sets of duplicate samples were run in the same cell, with an average absolute difference of 5.74  $\mu\text{mol/kg}$  (0.6 – 11.91), and a Standard Deviation of 5.84. The duplicates were sampled 1 to 1.5 minutes apart from the ships TSG flow thru system.

Bottle #	System	Date	Time	S	TA	Difference	Comments
304	1	3/10/2015	10:50:25	36.03	2360.55	9.54	
305	1	3/10/2015	11:39:50	36.04	2351.01		
308	1	3/10/2015	12:39:54	35.57	2333.49	11.91	
309	1	3/10/2015	12:58:58	35.59	2345.40		
316	1	3/10/2015	14:26:55	35.49	2330.18	0.6	
317	1	3/10/2015	14:50:45	35.49	2330.78		
319	1	3/10/2015	15:09:26	36.03	2359.54	0.92	
320	1	3/10/2015	15:28:59	36.04	2358.62		
						Average	5.74
						Std. Dev.	5.84

### **Remarks**

The two systems behaved well during the analyses.

Duplicates were sampled 1 to 1.5 minutes apart from the ships TSG flow thru system and reproducibility was affected by this.

### **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.