

**Cruise:** WS17135 , cuba, CIOERT2017

**Ship:** Walton Smith

**Dates:** May 15, 2017 – June 13, 2017

**Expocode:** 33WA20170515

**Chief Scientist:** Dr. Mingshun Jiang

**Equipment:** CTD

**Total number of stations:** 22

**Location:** Coastal areas around Cuba

The samples were run for Dr. Mingshun Jiang to provide calibration data for pCO<sub>2</sub> and pH sensors installed on a glider during the CIOERT cruise.

### **Sample Collection**

The discrete samples were collected from the CTD/Rosette onboard the Walton Smith by Dr. Mingshun Jiang and Denis Ilias. The date and time listed in the data file are UTC when each sample bottle was collected.

#### **DIC:**

22 locations, 99 samples, each 500-ml, 0 duplicate samples.

Sample\_ID#: 101, etc.; Sample bottle number

PI: Dr. Leticia Barbero

Analyzed by: Charles Featherstone and Patrick Mears

#### **pH:**

22 locations, 99 samples, each 500-ml, 0 duplicate samples.

Sample\_ID#: 101, etc.; Sample bottle number

PI: Dr. Leticia Barbero

Analyzed by: Charles Featherstone and Patrick Mears

#### **TAlk:**

22 locations, 99 samples, each 500-ml, 0 duplicate samples.

Sample\_ID#: 101, etc.; Sample bottle number

PI: Dr. Leticia Barbero

Analyzed by: 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 3	10/02/2017	2017.95	2019.14	1.19	28.0	11
AOML 4	10/02/2017	2017.95	2013.92	4.03	28.0	12
AOML 3	10/03/2017	2017.95	2019.11	1.16	28.0	8
AOML 4	10/03/2017	2017.95	2014.64	3.31	28.0	10
AOML 3	10/04/2017	2017.95	2019.20	1.25	28.0	9
AOML 4	10/04/2017	2017.95	2010.48	7.47	28.0	11

Analysis date: 2 October, 2017

Coulometer used: DICE–CM5015- AOML 3

Blanks: 12.0 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 1099 was used and with an assigned value of (includes both DIC and salinity):

Batch 153, c: 2017.95 $\mu\text{mol/kg}$ , S: 33.357

CRM values measured: AOML 3: offset 1.25  $\mu\text{mol/kg}$  (2019.2  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 11, 9 and 16 min.

Analysis date: 2 October, 2017

Coulometer used: DICE–CM5015- AOML 4

Blanks: 12.0 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 216 was used and with an assigned value of (includes both DIC and salinity):

Batch 153, c: 2017.95 $\mu\text{mol/kg}$ , S: 33.357

CRM values measured: AOML 4: offset 4.03  $\mu\text{mol/kg}$  (2013.92  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 12, 8 and 18 min.

Analysis date: 3 October, 2017

Coulometer used: DICE–CM5015- AOML 3

Blanks: 12.0 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 761 was used and with an assigned value of (includes both DIC and salinity):

Batch 153, c: 2017.95 $\mu\text{mol/kg}$ , S: 33.357

CRM values measured: AOML 3: offset 0.68  $\mu\text{mol/kg}$  (2017.03  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 3 October, 2017

Coulometer used: DICE–CM5015- AOML 4

Blanks: 17.9 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 432 was used and with an assigned value of (includes both DIC and salinity):

Batch 153, c: 2017.95 $\mu\text{mol/kg}$ , S: 33.357

CRM values measured: AOML 4: offset 3.13  $\mu\text{mol/kg}$  (2014.64  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 10, 8 and 15 min.

Analysis date: 4 October, 2017

Coulometer used: DICE–CM5015- AOML 3

Blanks: 12.0 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 98 was used and with an assigned value of (includes both DIC and salinity):

Batch 153, c: 2017.95 $\mu$ mol/kg, S: 33.357

CRM values measured: AOML 3: offset 1.74  $\mu$ mol/kg (2018.09  $\mu$ mol/kg).

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

Analysis date: 4 October, 2017

Coulometer used: DICE–CM5015- AOML 4

Blanks: 16.4 counts/min and raised to 28.0 counts/min before CRM analysis

CRM # 1015 was used and with an assigned value of (includes both DIC and salinity):

Batch 153, c: 2017.95 $\mu$ mol/kg, S: 33.357

CRM values measured: AOML 4: offset 7.47  $\mu$ mol/kg (2010.48  $\mu$ mol/kg).

Average run time, minimum run time, maximum run time: 11, 8 and 17 min.

**Reproducibility:** (# samples and average difference): 0 sets of duplicate samples.

### **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.

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

### **pH:**

Analysis date: 2-4 October, 2017

Spectrophotometer used: HP Agilent 8453

**Reproducibility:** (# samples and average difference): 0 sets of duplicate samples.

### **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) and reported at 25<sup>0</sup>C.

Temperature for each sample was kept constant with a water bath connected, jacketed cell. Temperature was measured in the return flow to the water bath using a Hart Scientific Fluke 1523 reference thermometer after a 1.5 minute equilibration period. An experimentally determined temperature offset was applied to the measured temperature.

A CRM (Batch 153) was measured before each set of samples for the day to help

determine day to day variability.

Approximately 80 mL of sample was extracted from each DIC sample bottle by an automated syringe immediately before DIC analysis to determine the pH.

**Talk:**

Analysis dates: 12-13 October, 2017, 16-17 October, 2017

Titration system used: Open cell

CRM Batch 153, Salinity = 33.325, cert. TA = 2225.59 $\mu$ mol/kg.

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	\u0394CRM
1	10/12/2017	15:39:41	197	2213.16	
1	10/02/2017	20:09:05	328	2034.63	13.6
1	10/13/2017	14:17:11	447	2226.49	
1	10/13/2017	21:05:23	447	2232.59	6.1
1	10/16/2017	11:30:12	1136	2224.06	
1	10/16/2017	15:52:16	1136	2219.85	4.2
1	10/17/2017	08:34:23	593	2222.72	
1	10/17/2017	10:14:13	593	2222.42	0.3
2	10/12/2017	13:52:14	135	2221.21	
2	10/12/2017	20:06:33	375	2219.05	2.16
2	10/13/2017	13:14:02	67	2217.32	
2	10/13/2017	21:04:12	1205	2217.49	0.17

**Reproducibility:** (# samples and average difference): 0 duplicate samples were collected.

**Remarks**

The CRM measurement for each day was used to correct the data for that day only. Reproducibility of junk waster samples on System 2 was not able to be achieved from 10/16/2017 onward, and the remaining samples were moved to System 1.

### 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.

The salinities and temperatures were collected from the CTD and provided by the field log. Due to the uncertainty in the salinity provided for stations 15-19, these salinities were calculated using a densitometer using 2 averaged measurements at 20°C. These salinities were used in the DIC, Talk and pH calculations.

It was noted that several bottles were improperly sampled, and that the majority of the bottles had little to no headspace as well as excessive application of grease. Bottle # 161 had a paper slip inside the sample, the cap on bottle #101 was secured upside down, and the rubber bands on bottle# 121 and 122 were not properly put on, and as a result slipped off before samples were run.

The samples marked with a QC Flag of 3 should be viewed with suspicion as they deviate from the expected relationship between carbon properties.

### 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.