**Cruise:** EX1403 **Ship:** R/V Okeanos Explorer **Dates:** May 10<sup>th</sup> – May 17<sup>th</sup>, 2014 **Chief Scientist:** Derek Sowers **Equipment:** CTD Rosette **Total number of stations:** 3 **Location:** Northeast Florida region

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 ship by the survey tech. The date and time listed in the data file are UTC when each sample bottle was collected.

#### DIC:

3 locations, 15 samples each 500-ml, no duplicate samples. Sample\_ID#: 90101, etc.; Station, cast number and Niskin bottle number PI: Dr. Rik Wanninkhof Analyzed by: Charles Featherstone

## pH:

3 locations, 15 samples each 500-ml, no duplicate samples. Sample\_ID#: 90101, etc.; Station, cast number and Niskin bottle number PI: Dr. Rik Wanninkhof Analyzed by: Charles Featherstone

## TAlk:

3 locations, 15 samples each 500-ml, no duplicate samples. Sample\_ID#: 90101, etc.; Station, cast number and Niskin bottle number PI: Dr. Rik Wanninkhof Analyzed by: Dr. Leticia Barbero and Dr. Denis Pierrot

*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 2	06/18/14	2016.65	2016.30	0.35	14.4	13

Analysis date: 06/18/2104 Coulometer used: AOML 2 Blanks: 14.4 counts/min CRM # 0144 was used and with an assigned value of (includes both DIC and salinity): Batch 129, c: 2016.65 µmol/kg, S: 33.361 CRM values measured: AOML 2: offset 0.35 µmol/kg (2016.30 µmol/kg). Average run time, minimum run time, maximum run time: 13, 11 and 20 min.

**Reproducibility:** (# samples and average difference): No duplicate samples were collected.

CRM, salinity and HgCl2 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 instrument was stable: CRM values did not change significantly throughout the life span of each cell.

The samples were analyzed using the SOMMA (AOML 2) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

The dry trap was wet and replaced with a new dry trap after running sample bottle 75 (20 minute titration; 4 endpoints).

## pH:

Analysis date: June 18<sup>th</sup>, 2014 Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): No duplicates were collected.

## **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 around.

Temperature for each sample was measured before and after analysis using a Hart Scientific Fluke 1523 reference thermometer. The temperature of the measurement was taken as the average of the before and after values. The pH values reported on the total scale have been calculated at 20  $^{\circ}$ C from the measured values using the measured DIC values and the CO<sub>2</sub>\_Sys program (Pierrot et al., 2006).

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 analyses from the same sample bottles used for DIC and pH. Analysis date: June 19<sup>th</sup>, 2014 Titration system used: Open cell CRM analysis (values in  $\mu$ mol/kg): CRM analyzed:

Batch 123, Salinity = 33.384, cert. TA = 2225.21 µmol/kg.

2 CRM samples were run on each cell, before (CRM-1) and after (CRM-2) 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.

System	Date	Time	Bottle #	ТА	$ \Delta CRM $
1	6/19/2014	14:07:41	064	2215.71	
1	6/19/2014	18:12:42	064	2216.29	0.58
2	6/19/2014	15:27:52	447	2209.35	
2	6/19/2014	18:15:41	447	2208.80	0.55

Reproducibility: No duplicates were collected.

## **Remarks**

System 1 behaved well during the analyses. System 2 was more inconsistent and needed more junk runs before starting with sample analysis but CRM reproducibility was good for both systems.

## **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. Discrete salinity was calculated from density measurements obtained with an Anton Paar densitymeter from leftover water after DIC, pH and TA analyses.

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

#### References

Liu, Xuewu, Patsavas, Mark C., & Byrne, Robert H. (2011). Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements. *Environmental Science & Technology*, 45(11), 4862-4868. doi: 10.1021/es200665d

Pierrot, D. E. Lewis, and D. W. R. Wallace. (2006). MS Excel Program Developed for CO2 System Calculations. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/otg.CO2SYS\_XLS\_CDIAC105a

## UPDATE JULY 2015

This datafile has been merged with nutrient data from the same cruise, provided by Dr. Jon Hare's group. Temperature and salinity values were not available at the time DIC and TA were measured. Values have been recalculated with the CTD values extracted from the nutrients file.

The following columns have been added:

Depth\_station, CTDPRS, CTDSAL, CTDTMP, Sigma-Theta, CTDOXYmg, CTDOXY, SILCAT, NITRIT+NITRAT, AMMONIA, and PHSPHT.