Discrete pH Analyses
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Sampling
Samples were collected in 300 mL Pyrex glass bottles and sealed using grey butyl rubber stoppers held in place by aluminum-crimped caps. Each bottle was rinsed a minimum of two times and allowed to overflow by one additional bottle volume. Prior to sealing, each sample was given a 1% headspace and poisoned with 0.02% saturated mercuric chloride ($HgCl_2$). Samples were collected only from Niskin bottles that were also being sampled for both total alkalinity and dissolved inorganic carbon in order to completely characterize the carbon system. This resulted in an overall coverage of greater than 75%. Additionally, two to four duplicate samples were collected from each for quality control purposes.

Analysis
pH was measured spectrophotometrically on the total hydrogen scale using an Agilent 8453 spectrophotometer and in accordance with the methods outlined by Carter et al., 2013. A Kloehn V6 syringe pump was used to autonomously fill, mix, and dispense sample through the custom 10cm flow-through jacketed cell. A Thermo NESLAB RTE-7 recirculating water bath was used to maintain the cell temperature at 20.0°C during analyses, and a YSI 4600 precision thermometer and probe were used to monitor and record the temperature of each sample immediately after the spectrophotometric measurements were taken. The indicator meta-cresol purple (mCP) was used to measure the absorbance of light measured at two different wavelengths (434 nm, 578 nm) corresponding to the maximum absorbance peaks for the acidic and basic forms of the indicator dye. A baseline absorbance was also measured and subtracted from these wavelengths. The baseline absorbance was determined by averaging the absorbances from 725-735nm. The ratio of the absorbances was then used to calculate pH on the total scale using the equations outlined in Liu et al., 2011. The salinity data used was obtained from the conductivity sensor on the CTD. The salinity data was later corroborated by shipboard measurements.

Reagents
The mCP indicator dye was made up to a concentration of 2.0mM and a total ionic strength of 0.7 M. A total of 3 batches were used during the cruise. The pHs of these batches was adjusted to approximately 7.8-7.9 using a pH meter calibrated with NBS buffers and dilute solutions of HCl and NaOH with ionic strengths of 0.7 M. The indicator was provided by Dr. Robert Byrne of the University of South Florida, and was purified using the HPLC technique described by Liu et al., 2011.

Data Processing
An indicator dye is itself an acid-base system that can change the pH of the seawater to which it is added. Therefore it is important to estimate and correct for this perturbation to the seawater's pH for each batch of dye used during the cruise. To determine this correction,

multiple bottles from each station were measured twice. Once with a normal amount of indicator dye and once with double the normal amount of indicator dye. The measured absorbance ratio R, and an isosbestic absorbance A_{iso} were determined for each measurement, where:

$R = (A_{578} - A_{base}) / (A_{434} - A_{base})$ and

$A_{iso} = (A_{488.6} - A_{base})$.

The change in R for a given change in A_{iso}, $\Delta R/\Delta A_{iso}$, was then plotted against the measured R-value for the normal amount of dye and fitted with a linear regression. From this fit the slope and y-intercept (b and a respectively) are determined by:

$\Delta R/\Delta A_{iso} = bR + a$

From this the corrected ratio (R') corresponding to the measured absorbance ratio if no indicator dye were present can be determined by:

$R' = R - A_{iso} (bR + a)$

Standardization/Results

The precision of the data was accessed from measurements of duplicate analyses, replicate analyses (two successive measurements on one bottle), certified reference materials (CRMs) from Batch 135 (provided by Dr. Andrew Dickson, UCSD), and TRIS buffer Batch 20 (provided by Dr. Andrew Dickson, UCSD). CRMs were measured twice a day and bottles of TRIS buffer were measured once a day over the course of the cruise.

In total 2,748 Niskin bottles were sampled and submitted for pH on this cruise. The overall precision determined from duplicate analyses was found to be ±0.0003 for 193 sets. The overall precision determined from replicate analyses was found to be ±0.0003 for 201 sets. Additionally, 211 measurements were made on 59 bottles of Certified Reference Materials and found to have a pH of 7.9293±0.0013 and an average per bottle standard deviation of ±0.0003.

References

Carter, B.R., Radich, J.A., Doyle, H.L., and Dickson, A.G., "An Automated Spectrometric System for Discrete and Underway Seawater pH Measurements," *Limnology and Oceanography: Methods*, 2013.

Liu, X., Patsvas, M.C., Byrne R.H., "Purification and Characterization of meta Cresol Purple for Spectrophotometric Seawater pH Measurements," *Environmental Science and Technology*, 2011.