

P16S - 2014 - Alkalinity

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Sample Collection

Samples for alkalinity measurements were taken at all P16S Stations (1-90). The Niskin bottles chosen for sampling matched those chosen for Dissolved Inorganic Carbon measurements. Two Niskins at each station were sampled twice for duplicate measurements. Using silicone tubing, the alkalinity samples were drawn from Niskin bottles into 250 mL Pyrex bottles, making sure to rinse the bottles and Teflon sleeved glassed stoppers at least twice before the final filling. A headspace of approximately 5 mL was removed and 0.12 mL of saturated mercuric chloride solution was added to each sample for preservation. After sampling was completed, each sample's temperature was equilibrated to approximately 20°C using a Thermo Scientific RTE water bath.

Summary

Samples were dispensed using a Sample Dispensing System (SDS) consisting of a volumetric pipette and various relay valves and air pumps controlled using LabVIEW 2012. Before filling the jacketed cell with a new sample for measurement, the volumetric pipette was cleared of any residual from the previous sample with the aforementioned air pumps. The pipette is then rinsed with new sample and filled, allowing for overflow and time for the sample temperature to equilibrate. The temperature inside the drawing bottle was measured using a DirecTemp thermistor probe and the pipette temperature was measured using a DirecTemp surface probe placed on the pipette. These temperature measurements were used to convert the sample volume to mass for analysis.

During instrument set up it was discovered that the Pipette A SDS board was dispensing more than the calibrated volume due to a weak valve. This was confirmed by running titrations using a calibrated manual pipette to dispense reference seawater of known alkalinity and measuring correct alkalinity values compared to the Pipette A SDS board that was providing incorrect alkalinity values with the same reference seawater. As a result, the Pipette B SDS board was switched in and maintained its calibrated volume of 92.190 mL for the entire P16S Line.

Samples were analyzed using an open cell titration procedure using two 250 mL jacketed cells. One sample was undergoing titration while the second was being prepared and equilibrating to 20°C for analysis. After an initial aliquot of approximately 2.3-2.4 mL of standardized hydrochloric acid (~0.1M HCl in ~0.6M NaCl solution), the sample was stirred for 5 minutes and had air bubbled into it at a rate of 200 scc/m to remove any liberated carbon dioxide gas. A Metrohm 876 Dosimat Plus was used for all standardized hydrochloric acid additions. After equilibration, 19 aliquots of 0.04 ml were added. Between the pH range of 3.5 to 3.0, the progress of the titration was monitored using a pH glass electrode/reference electrode cell, and the total alkalinity was computed from the titrant volume and e.m.f. measurements using a non-linear least-squares approach (Dickson, et.al., 2007). An Agilent 34970A Data Acquisition/Switch Unit with a 34901A multiplexer was used to read the voltage measurements

from the electrode and monitor the temperatures from the sample, acid, and room. The calculations for this procedure were performed automatically using LabVIEW 2012.

Quality Control

Throughout P16S, empty pre-weighed glass bottles with rubber stoppers and metal caps were filled with deionized water and then crimped shut. Upon return to shore, these bottles were re-weighed to observe the dispensed volume throughout the cruise. It was determined that the Pipette B SDS board actually gave a volume of 92.179 mL instead of 92.190 mL. The volume of 92.179 mL remained constant throughout the cruise. All measurements were corrected for this volume difference.

Dickson laboratory Certified Reference Material (CRM) Batch 135 was used to determine the accuracy of the Alkalinity analyses. The certified alkalinity value for Batch 135 is $2226.33 \pm 0.63 \mu\text{mol kg}^{-1}$. This reference material was analyzed 208 times throughout P16S. The preliminary B135 measured value average for P16S is 2225.84 ± 0.76 . After the aforementioned volume correction, the final B135 average is 2226.10 ± 0.76 .

Twice per station, a single Niskin was sampled twice to conduct duplicate analyses. A total of 178 Niskins were sampled for Duplicate analyses and gave a pooled standard deviation of $0.67 \mu\text{mol kg}^{-1}$.

2749 Niskins were sampled for alkalinity analyses. The provided Alkalinity data is considered final because any and all corrections for pipette volume adjustments, CRMs and mercuric chloride additions have been performed. No shifts in the pipette volume were observed after the Pipette B SDS board was installed into the system so no additional volume correction was needed once the P16S Line began.

Each P16S 2014 station's alkalinity measurements were compared to measurements taken from the neighboring P16S 2014 stations and the P16S 2005 stations of similar if not identical coordinates.

Reference

Dickson, Andrew G., Chris Sabine and James R. Christian, editors, "Guide to Best Practices for Ocean CO₂ Measurements", Pices Special Publication 3, IOCCP Report No. 8, October 2007, SOP 3b, "Determination of total alkalinity in sea water using an open-cell titration"