Extrapolated pH measurements of CRMs

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Project
» Improving Accuracy and Precision of Marine Inorganic Carbon Measurements (Inorganic Carbon Meaurements)

Contributors	Affiliation	Role
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Abstract
The temperature dependence of spectrophotometric pH measurements was determined and compared to values calculated from total alkalinity and dissolved inorganic carbon using different combinations of the required dissociation constants. Spectrophotometric measurements were made on two batches of CRMS (179 and 189) between -1.7 and 40 ˚C. This dataset contains the extrapolated pH measurements of CRMs.

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Dataset Description

Extrapolated pH measurements of CRMs.

Methods & Sampling

The temperature dependence of spectrophotometric pH measurements was determined and compared to values calculated from total alkalinity and dissolved inorganic carbon using different combinations of the required dissociation constants. Spectrophotometric measurements were made on two batches of CRMS (179 and 189) between -1.7 and 40 ˚C.

A custom designed spectrophotometric pH system was used similar to the system described in Carter et al. (2013). It consists of an Agilent 8454 UV-Vis spectrophotometer with a Kloehn v6 syringe pump to rinse, fill, and add the indicator dye to a 10 cm quartz microvolume spectrophotometer cell. A batch of ~2 millimolar Purified meta-cresol purple indicator dye (provided by Robert H. Byrne, University of South Florida) prepared in ~0.7 molar NaCl was used. The pH on the total scale was calculated using the equations of Liu et al. (2011). The dye perturbation was accounted for by making 20 measurements at each temperature with varying amounts of dye and extrapolating to zero dye added. Both the final pH values and the raw absorbances are available from BCO-DMO. Further details of the methods can be found in Woosley (2020).

Data Processing Description

The pH was adjusted to account for dye perturbation by extrapolation to 0 dye added.

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Data Files

File
pH.csv (Comma Separated Values (.csv), 492 bytes) MD5:008bc1158a17658c9d9651522482e054 Primary data file for dataset ID 822386

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Related Publications

Carter, B. R., Radich, J. A., Doyle, H. L., & Dickson, A. G. (2013). An automated system for spectrophotometric seawater pH measurements. Limnology and Oceanography: Methods, 11(1), 16–27. doi:10.4319/lom.2013.11.16
Methods

Liu, X., Patsavas, M. C., & Byrne, R. 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
Methods

Woosley, R. J. (2020). Evaluation of the temperature dependence of dissociation constants for the marine carbon system using pH and certified reference materials. Marine Chemistry, 103914. doi:10.1016/j.marchem.2020.103914
Results

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Parameters

Parameter	Description	Units
Batch	CRM batch number	unitless
Temperature	Temperature	degrees Celsius
pH	pH on the total scale	total scale
Standard_Error	Standard error	unitless

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Instruments

Dataset-specific Instrument Name	Agilent 8454 UV-Vis Spectrophotometer
Generic Instrument Name	Spectrophotometer
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

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Project Information

Improving Accuracy and Precision of Marine Inorganic Carbon Measurements (Inorganic Carbon Meaurements)

Coverage: Lab studies

NSF Award Abstract:
The oceans absorb about one third of the CO2 humans release into the atmosphere from the burning of fossil fuels and other activities. While ocean uptake of CO2 slows its rate of increase in the atmosphere, it comes with costs for the oceans and the organisms that live there. Once in seawater, CO2 reacts with water to produce bicarbonate and hydrogen ions. The increase in hydrogen ions lowers the pH in a process called ocean acidification. Not all areas of the ocean are affected equally. The solubility of CO2 is greater in the cold waters of the Arctic making them more prone to ocean acidification. However, due to the low temperatures and low salinities in the Arctic, the uncertainties in pH values are much larger there than for the other oceans. This project evaluates pH at low temperatures and salinities, and develops best practice recommendations to improve the ability to compare measurements among laboratory groups and studies and reduce overall uncertainty in the measurements. The project provides training for an undergraduate student and promotes awareness of ocean acidification through public outreach.

Having highly accurate and precise measurements are important for monitoring changes to pH and CO2 uptake through time and the effects on marine life. In order to improve pH measurements for polar waters, several different experiments will be conducted. The temperature dependence of pH will be determined from 30˚C to near freezing for low salinity waters. The results will be compared to current chemical models to quantify offsets and biases. Recommendations will be made for the best physical chemical model to use for low temperature and salinity seawater. Moreover, pH is measured spectrophotometrically using an indicator dye. Preparation and calibration of the indictor is important to standardize studies across space and time and ensure comparability. Indicator quality is essential for detecting ocean acidification, but its stability is currently unknown. If the dye degrades after production, biases or artifacts in pH measurements may result as the dye ages. Experiments will be undertaken using batches of dyes from weeks to over 10 years old to resolve its degradation characteristics. The experiments will establish how long a batch of dye remains valid once it is prepared without biasing the measurements. This is particularly important for long term studies such as extended research expeditions and autonomous systems where a batch of dye may be used over a year. Together, by both investigating the validity of chemical models for seawater pH at low temperature and salinity and examining the stability of the pH indicator dye, methodological uncertainties can be reduced to permit better monitoring of changes in global ocean pH.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1923312

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