

Development of a Sensor Array for In-situ Real-time Measurement of Deep Ocean and Hydrothermal Vent Chemistry

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Background

The study of dynamic biogeochemical processes in the ocean, especially in the deep ocean or near hydrothermal vents, is a daunting challenge and requires the ability to monitor a variety of chemical species in-situ in real time under extreme conditions. Understanding these dynamic processes is critical to understanding the long-term effects of natural and human impacts on the oceans. The immediate goal of this project was to develop and demonstrate as a proof-of-concept a sensor array capable of providing simultaneous in-situ real-time nM measurements of a variety of ionic species at extreme depths and near vent temperatures in the ocean. The longer-term objective was to enable follow-on research that, with improved detection limits and selectivity, could provide the ocean sciences community with a new tool for in-situ real-time chemical mapping of a broad range of ionic chemical species in seawater. The resulting sensor array device would also be of use to researchers in a variety of related disciplines for studies or monitoring of other bodies of water such as lakes, estuaries, ground water, drinking water, and rivers. The ability to perform such analyses will have a significant and broad impact in the ocean sciences, chemical oceanography, biology, charting ocean circulation, in understanding the effects of pollutants and increased CO₂ levels in the ocean, and the effects of global climate change, to name a few.

ISE Sensor Fabrication

To this point only one previous study has characterized the influence of pressure on the response of a classically configured ISE sensor. The reported nitrate ISE sensor was only tested up to 30 bar, using an internal filling solution, solid contact, and a capillary type reference electrode. The results of that study showed only a minor effect of increased on sensor behavior [1]. However, the tested sensor is not exactly comparable to the sensors developed here. The physical configuration of the ISE will have a direct bearing on its response to pressure changes. In order to ensure the survivability of the ISE sensor array at the proposed deep-ocean pressures of 400 bar, the existing configuration of the sensors originally used for the analyses on Mars [2] was modified to provide a more solid system and stability over a longer period of in seawater. The development and evaluation effort of the high-pressure ISE sensors has been published [3].

The final configuration and fabrication of our ISE sensors is shown in Figure 1. The use of nanoporous carbon as an ion-to-electron transducer, coupled with a symmetric membrane configuration, was shown to maintain or improve on the sensitivity, lifetime and stability of previous solid-contact electrodes. This type of ISE sensor appears extremely stable over long periods of time and is ideally suited for continuous monitoring in seawater at high pressures due to the constant wetting of the membrane without decreased functionality and its solid construction. The use of SM-SC-ISEs allowed for miniaturization of the sensor while maintaining sensitivity, stability and lifetime. As can be seen in **Figure 1**, the sensors unlike

commercially available ISEs, are fabricated from solid materials and contain no gaps or air and thus allows them to be used at extreme pressures.

ISE Sensor Evaluation at High Pressures

In order to test the ISE sensors at the high pressure (HP) found at deep-sea hydrothermal vents, a special custom build HP chamber was assembled from several off-the-shelf components. The HP chamber is constructed of T316 stainless steel and holds a volume of 1.2 L. It is capable of reaching pressures of up to 345 bar and 350°C. As shown in **Figure 2**, the chamber has been integrated with a high pressure HPLC pumping (Figure 2, top right) system which allows injection of solutions under pressure and thus, calibration at high pressures. The chamber is also equipped with a 12-pin feed through to allow for up to eleven ISE and reference electrode. The ISE sensors (Figure 2, right bottom) can be placed directly into the chamber, but typically are placed in a separate beaker inside the chamber. The chamber also allows for stirring of solutions while operating at high pressure. An external programmable unit can control the pressure and temperature as desired. **Figure 3** shows the results of testing a Cl^- , K^+ , and Ca^{2+} sensor at 1, 100, and 160 bar. Each sensor was calibrated over the indicated range at 22°C. The theoretical response of the sensors was as expected and showed little or no effect of the increased pressure.

Sensor Evaluation at STP Using 0-3000 Meter Seawater Samples

In August of 2011, our collaborators (Luther Research Group, University of Delaware) obtained CTD-rosette samples at a Middle Atlantic Bight location (37 03.78 N; 73 02.00 W). These samples provided clean seawater and a range of nitrate and other ionic species concentrations from surface to 3000 meters. The sensor array used for this test consisted of sensors for Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NO_3^- , and pH. As would be the case for in-situ measurements, two calibration points were run and then the samples were each analyzed. The sensor response data from the analysis is shown in **Figure 4**. The sensor calibration data were then used to generate the depth profile data shown in **Figures 5A-H**. In all cases the observed concentrations are reasonable and clearly show a changing concentration with depth. Data for Figures 5I-K were provided by the Luther group. A comparison of the depth profiles for nitrate generated using the Tufts ISE sensors and the PN Sharp autoanalyzer shows similar concentrations but different profiles. Note though that the autoanalyzer data includes $\text{NO}_3 + \text{NO}_2$ while the ISE data is for NO_3 only. In any case, the profiles both show a similar peak at 250m but the ISE NO_3 sensor shows half the concentration for the 200 and 2700m depths.

Calibration of ISE Sensors Prior to Cruise Deployment

During March of 2012, a new set of sensors was fabricated and evaluated for deployment on the April 1-3 cruise in Delaware Bay. The sensor array consisted of ISEs for Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NO_3^- , NH_4^+ , H^+ , F^- , and Cl^- , and pH. The sensors were calibrated two days prior to deployment. The calibration curves are shown in **Figure 6**. All sensors responded as expected with a linear response over a range from 10^{-6} M to 10^{-1} M, though several exhibited lower sensitivities than predicted by theory. The reasons are not clearly understood, though it is suspected that membrane formulation and fabrication is not optimized for seawater. Experiments are underway to optimize and reformulate as necessary.

Cruise Deployment of Sensor Array

The sensor array was mounted on a Sea-Bird SBE 19plus V2 SEACAT CTD. The interface between the sensor array and the CTD electronics was made via two six-channel ADC with high impedance amplifier circuits. The original electronics boards were initially placed in a Plexiglas box which was then filled with a special water proof epoxy. Unfortunately, this step which occurred two weeks prior to deployment, caused overheating during the curing process, cracking the ADC boards and failure of the electronics. Thus, the two weeks leading up to deployment were dedicated to replacing and repotting a new set of electronics boards. This limited our plans for end-to-end testing of the entire system in real seawater and also testing the integrity of the electronics and grounding system. **Figure 7** shows the two Tufts graduate students in the process of calibrating the sensor array just prior to deploying the SBE probe. The sensor array is mounted on the inside portion of the SBE probe as shown in **Figure 8A** with **Figure 8B** showing the sensor array electronics.

Data Acquisition During Cruise Deployment

The R.V. Sharp departed Lewes Delaware April 1st for a three-day survey of Delaware Bay from Marcus Hook, PA to the mouth of the Delaware Bay and 20 km offshore. This salinity-transect sampled every 1 salinity unit until 5 salinity units on the first day to test the sensor array response. The following two days, a salinity transect was performed from freshwater to 32 salinity units at every 2 salinity units. Surface and bottom samples were collected from a CTD for ground truthing of ISE sensors.

The initial data from the sensor array indicated that as soon as the sensors were submersed, they experienced an approximately 1-1.5 volt offset in signal. We now suspect that the replacement of the original electronics and the lack of time to perform an in-situ end-to-end test, resulted in a ground loop problem between the CTD probe and the sensor electronics. The grounding also resulted in increased noise levels. Unfortunately, all attempts to correct these problems during the cruise were unsuccessful. However, we continued to collect data from all 21 stations in the hopes that the offset and noise could be compensated afterwards by a data processing. The data from two of the stations, one in relatively fresh water (**Figure 9**) and the other from the point where there was a mid-depth isocline of fresh and saltwater (**Figure 10**), show that even though the signals for all 12 sensors are noisy and uncalibrated, there are identifiable profiles.

Even though we did not obtain exactly the in-situ data we had hoped for, it was an immensely profitable experience, not only for training of our grad students and debugging the system, but in preparing for the upcoming August cruise to deeper waters and for a useful set of lessons-learned in operating the ISE sensors and high impedance electronics in a real underwater environment. We also collected Niskin bottle samples from each station for later analysis in our labs.

Laboratory Analysis of Delaware Bay Niskin Samples Using the ISE Sensor Array

Analysis was performed on the surface/bottom samples that were collected from the Niskin bottles during the 177 km transect starting 26 km south of Franklin Bridge (Philadelphia PA) and ending 20 km offshore from the mouth of Delaware Bay in open ocean, using the same sensors as used during the cruise. **Figure 11** shows the raw calibration and sample signals for the sensor array and the clear indication that the sensors are responding to a variety of ionic species. **Figure 12** shows the calibration curve for the sensors. Again, their response is well within expected parameters. This data was then used to generate the relationships shown in **Figures 13A-D**. Of most interest is the comparison of the nitrate analyses obtained with the UDel SUNA NO_3^- analyzer and the NO_3^- ISE sensor as a function of distance from the Franklin Bridge. The ISE data shows an excellent correlation in both the gradient and concentration and thus also between each of the analytical techniques as shown in **Figure 13C**. Figure 13D shows the response of the Cl^- ISE sensor, and as would be expected, its good correlation to the CDT salinity measurements.

Conclusion

In conclusion we have successfully met the major proposed goals of the project. As detailed above, we have successfully fabricated a subset of the ion selective (ISE) sensors, tested them in a laboratory setting, at both high pressure and in seawater, and evaluated them during the Delaware Bay cruise over a 177 km transect starting just south of Franklin Bridge and ending 20 km offshore in open ocean. The results showed that the prototype ISE sensors are capable of accurately measuring concentrations of the proposed ionic species under all these conditions and have for the first time demonstrated the potential ability to use ion selective electrodes (ISE) to obtain in-situ concentrations of inorganic ionic species in seawater and, most importantly, shown by comparing them to two other NO_3^- analytical techniques, that we can detect variations of nitrate at ambient concentrations in the micro-molar range in seawater.

References Cited

1. B. Müller and P. C. Hauser, "Effect of pressure on the potentiometric response of ion-selective electrodes and reference electrodes", *Anal. Chim. Acta*, **1996**, 320, 69-75.
2. S. P. Kounaves, et al., "The MECA Wet Chemistry Laboratory on the 2007 Phoenix Mars Scout Lander", *J. Geophys. Res.*, **2009**, 114, E00A19, doi:10.1029/2008JE003084
3. A. W. Weber, G. D. O'Neil, and S. P. Kounaves, "Solid Contact Ion Selective Electrodes for In Situ Measurements at High Pressure" *Anal. Chem.*, **2017**, 89, 4803-4807, doi: 10.1021/acs.analchem.7b00366K.

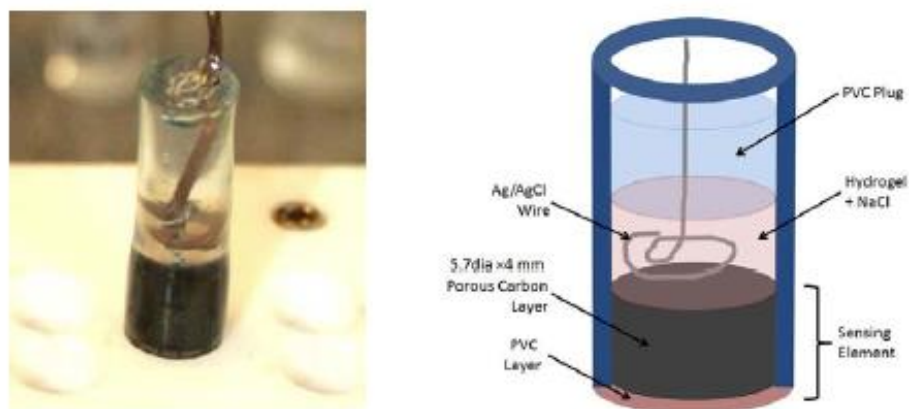


Figure 1. Construction of the ion selective sensors.



Figure 2. The custom built high pressure/temperature chamber for testing the ISE sensors (left). High pressure reagent injector system (top right) and the ISE sensor array (bottom left)

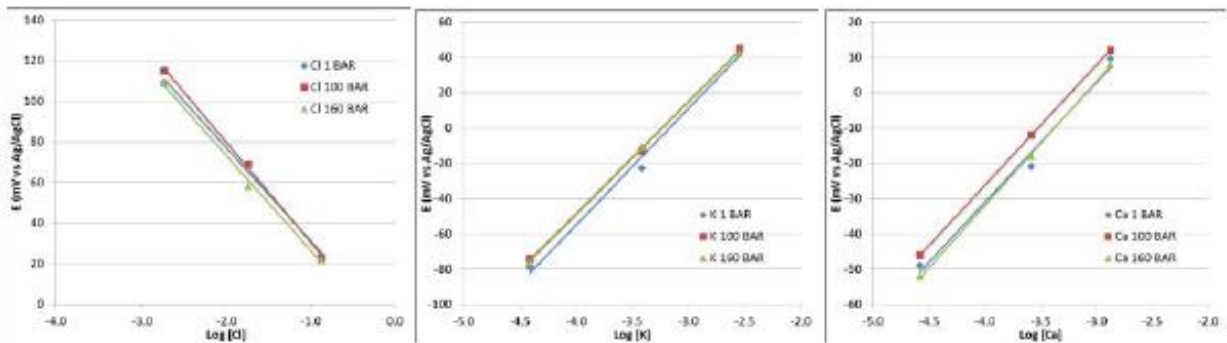


Figure 3. Calibration curves for the Cl^- , K^+ , and Ca^{2+} ISE sensors at 1, 100, and 160 bar pressure.

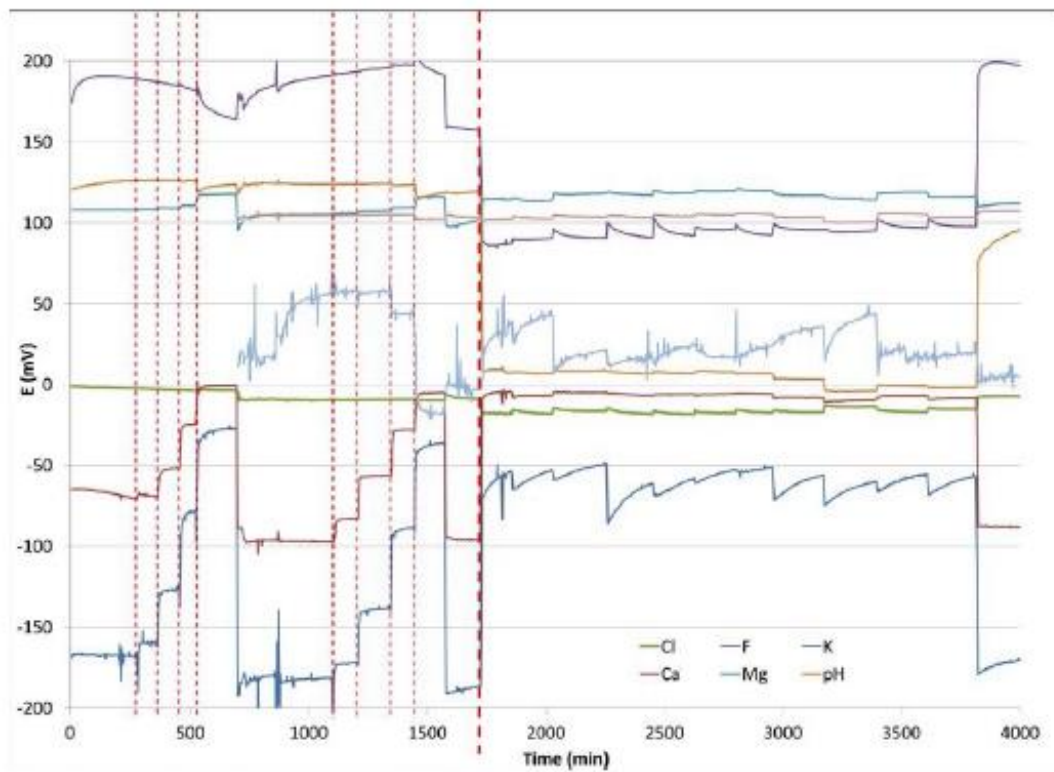


Figure 4. Calibration and subsequent analysis for 12 seawater samples using the indicated ISE sensors obtained from 0 to 2700 m depth.

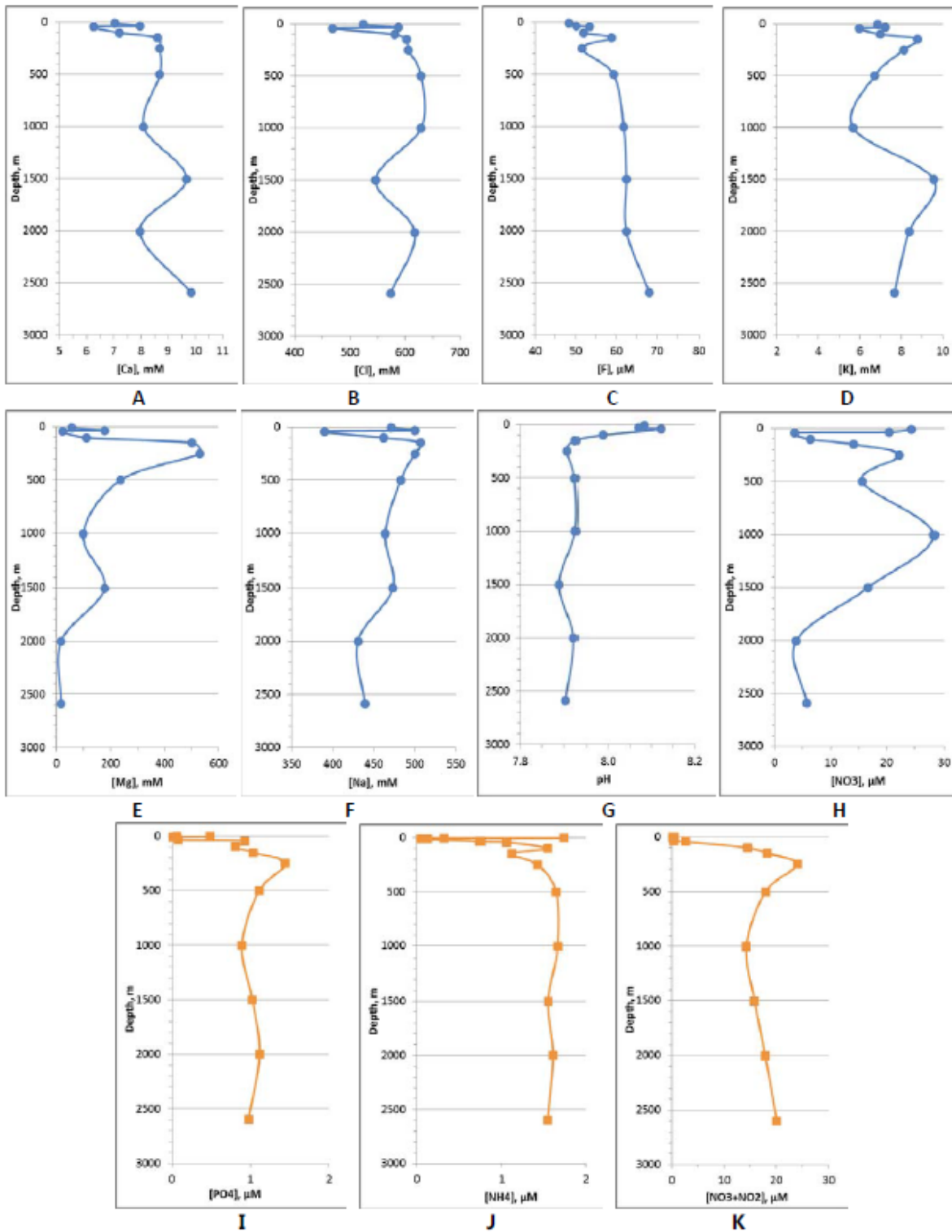


Figure 5. Profiles generated by ISE measurements of 12 samples using indicated sensors, obtained from 0 to 2700 m depth (A-H). Comparison of profiles for NO₃⁻ using ISEs and UD autoanalyzer (H & K).

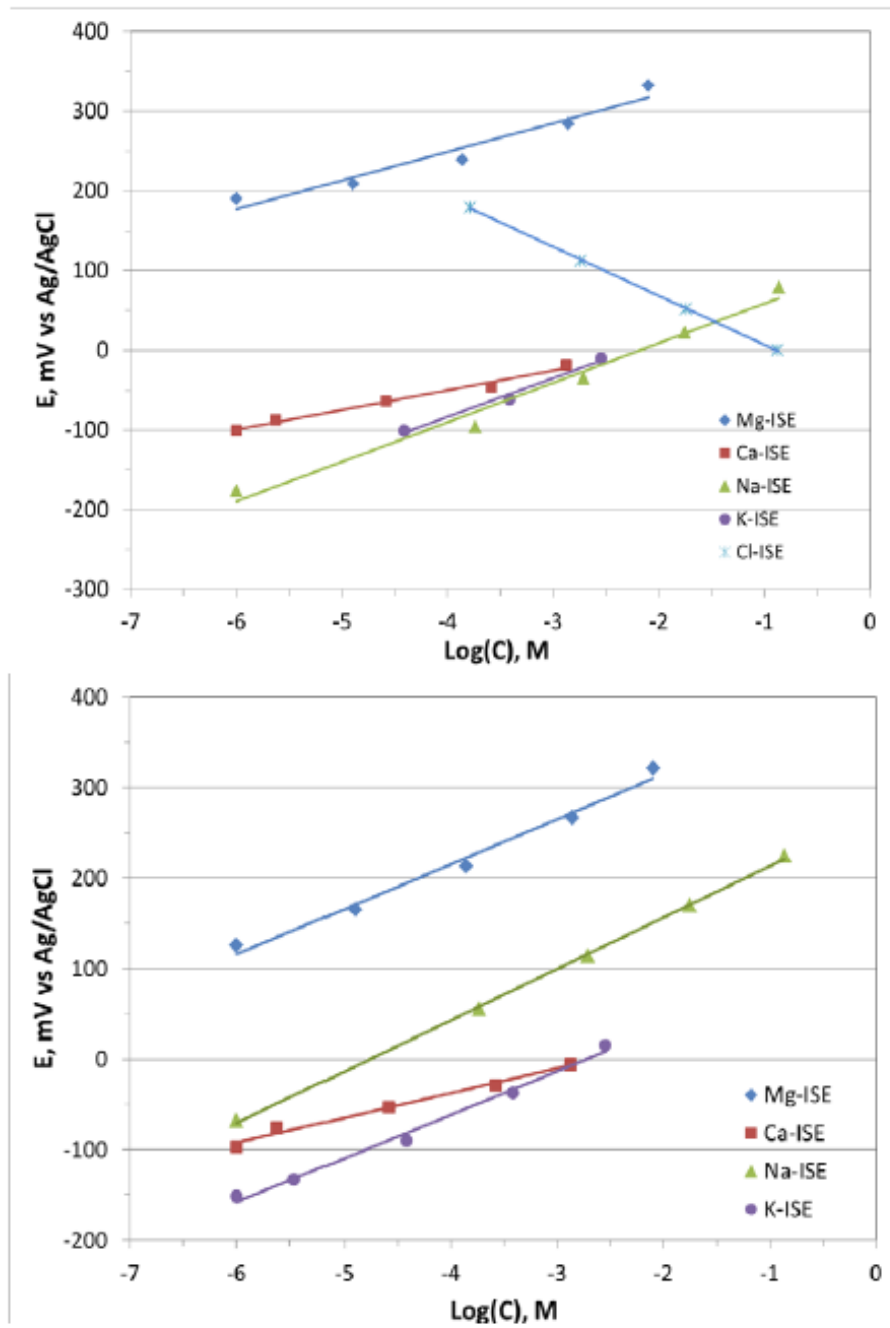


Figure 6. Calibration of indicated sensors two days prior to deployment for Delaware Bay cruise.



Figure 7. Two Tufts University students calibrating sensor array prior to being deployed.

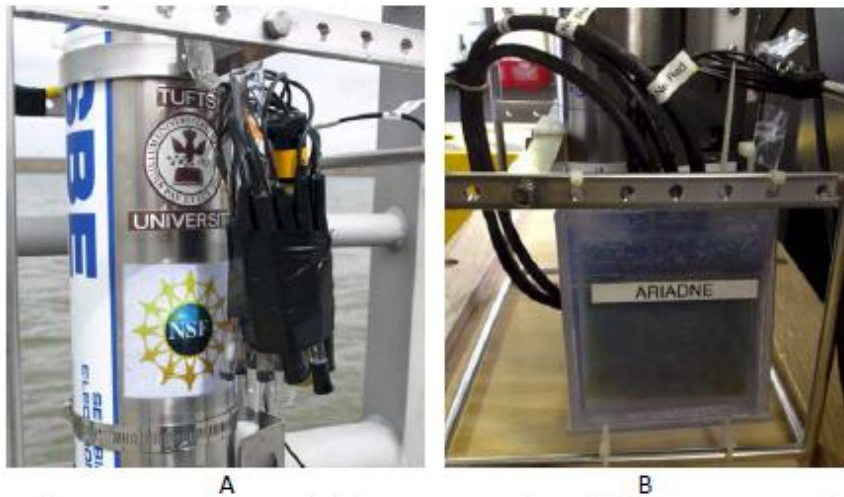


Figure 8. (A) ISE sensor array attached to SBE CTD probe and (B) measurement electronics.

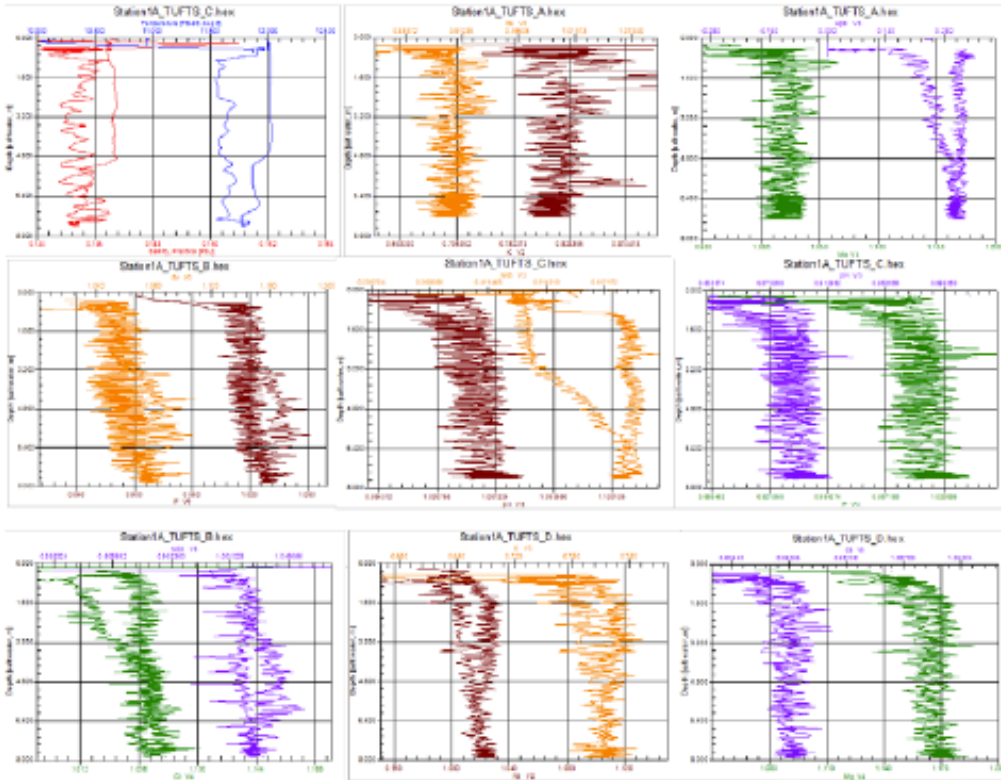


Figure 9. In-situ ISE sensor array data from Station 6 (26 km from Franklin Bridge)

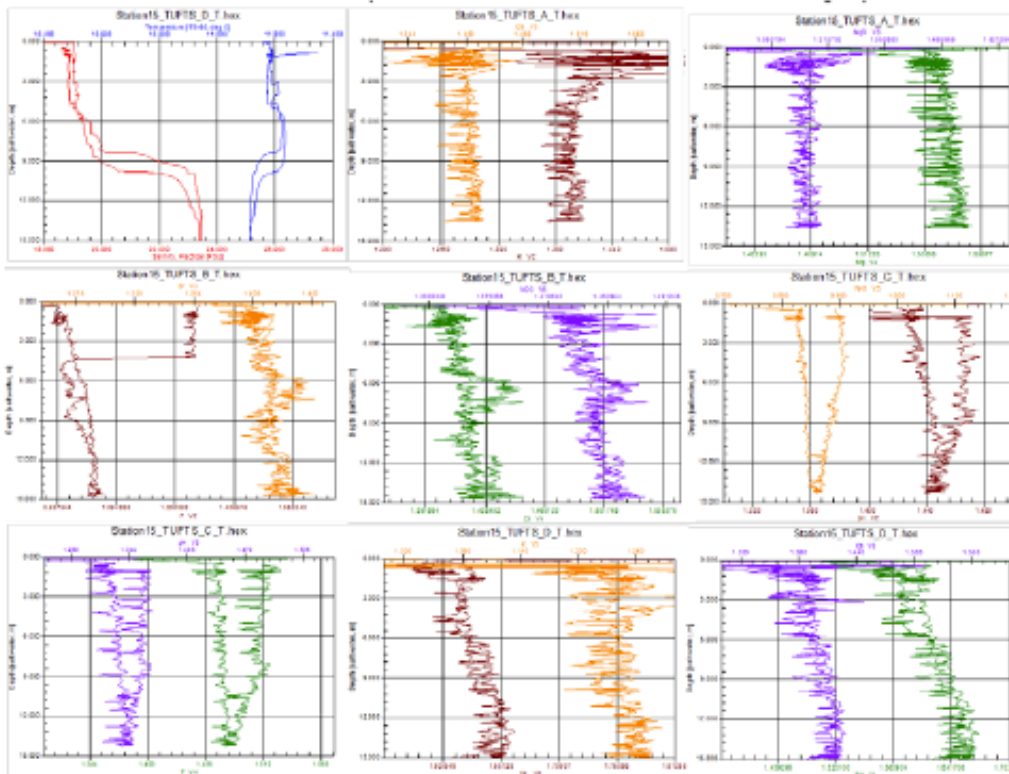


Figure 10. In-situ ISE sensor array data from Station 15 (100 km from Franklin Bridge)

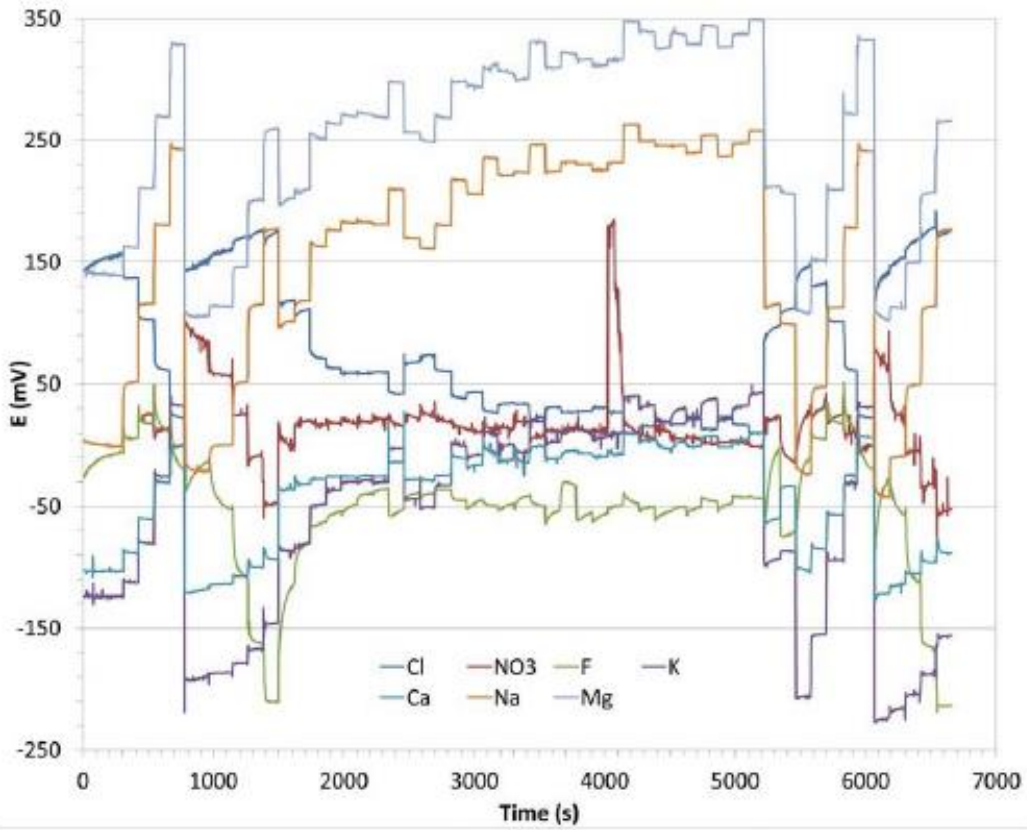


Figure 11. Raw calibration and sample data for sensor array showing response to ionic species.

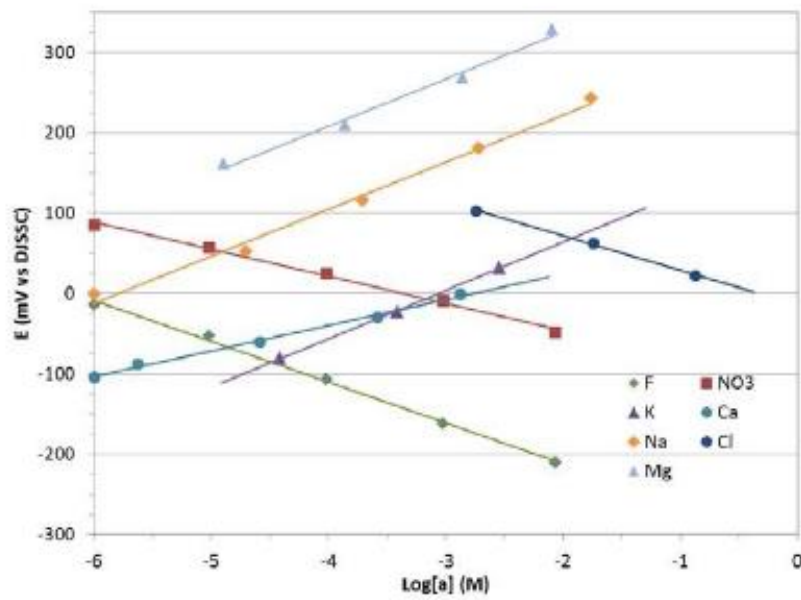


Figure 12. Calibration curves for the ISE sensors used to generate the relationships shown in Figure 13

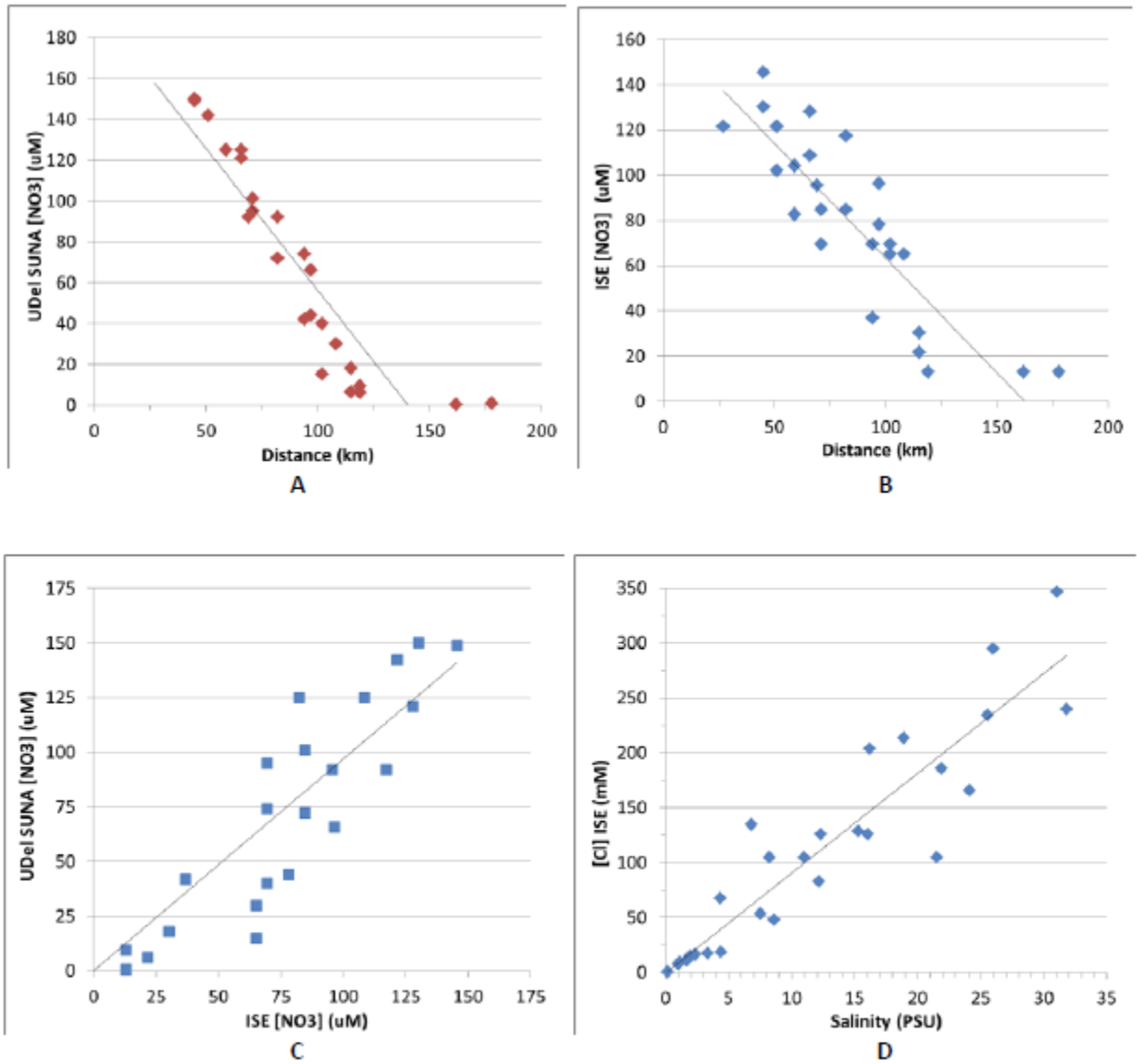


Figure 13. (A-C) Comparison of the nitrate analyses obtained with the UDel SUNA NO₃⁻ analyzer and the NO₃⁻ ISE sensor as a function of distance from the Franklin Bridge, and (D) Comparison of measurements taken with the chloride ISE sensor and CTD salinity unit.