

# OpenAlk User Guide

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# **Acknowledgements**

This project was originally developed by Dr. Eyal Wurgaft during his time at Woods Hole Oceanographic Institute as a postdoc in 2018. This system used a digital syringe pump common to oceanographic automation and a standard Orion pH meter to perform semi-automatic, open-cell Gran titration of seawater for total alkalinity analysis. The system was coded in Matlab and included a second channel for NaOH titration to allow for non-carbonate organic alkalinity titration, such that it was referred to as the 'NCA titrator' in the lab, based on the procedure reported in Cai et al. (1998). This setup was used to analyze samples from several studies (Song et al., 2020; Ringham, 2022).

The plans and Matlab code were used at various labs within WHOI, including working with Mallory Ringham and Aleck Wang.

Mallory went on to pursue a postdoc at Stony Brook University, where she worked under Matt Eisaman. Mallory and Matt worked with SBU undergraduate students Katherine Hillis and Yu Han Huang to port the Matlab code to Python and integrate the pump with a Raspberry Pi. The students named the project CAPT'n (CO2 and Alkalinity by Precise Titration).

Mallory is now lead oceanographer at Ebb Carbon, a company engaged in marine-based Carbon Dioxide Removal. Ebb was co-founded by Matt Eisaman. Mallory and Anthony Canalungo, software engineer at Ebb, worked to further enhance the project and develop it into a product that could be easily used and readily reproduced by the chemical oceanography community. Mallory and Anthony want to offer their thanks to others at Ebb who contributed ideas and testing and helped with code reviews.

All involved hope that in addition to providing good ocean chemistry measurements, the project can serve as a learning tool, offering opportunities for learning chemical oceanography and modern software development practices, as well as a chance to develop some skills around electronics and hardware engineering.

Tragically, Eyal passed away in 2022. We dedicate this version of the project to him.

# **Quick Start**

- 1. Buy whatever materials you don't have from the **BOM**.
- 2. Follow the setup & assembly instructions laid out in the <a href="Setup & Assembly">Setup & Assembly</a> section.
- 3. Mix the acid titrant following the Acid Titrant SOP.
- 4. Ensure your pH probe is properly calibrated, follow the Calibration SOP if needed.
- 5. Take salinity measurements of your seawater using your preferred method, follow the <u>Salinity Measurement SOP</u> if using the refractometer suggested in the BOM.
- 6. After doing all the above, follow the main Alkalinity Measurement SOP.

# **Bill of Materials (BOM)**

#### PC & Communication

- For Windows: PC with Windows 10 or later
- For Linux: 64-Bit Mini PC (<u>link</u>) and 16GB flash drive (<u>link</u>), or PC of your choosing with Ubuntu 20.04 LTS or later
- Monitor, keyboard, and mouse of your choosing
- USB-MiniUSB Cable (<u>link</u>), this is for the pH meter connection and is just listed here as an alternative in case you don't receive one with the meter
- USB-RS232 Serial wire-end cable (link), this is for the pump connection
- Single-Pole 22AWG Dupont Connectors (<u>link</u>), these must be 22AWG for power transmission purposes
- Wago 221 Inline Connectors (<u>link</u>)
- Wire strippers, cutters, and phillips-head screwdriver of your choosing

#### Syringe Pump

- Norgren Kloehn Versa Pump V6 (link)
- Norgren 2.5 mL Syringe (link)
- Norgren 3-Way Non-Distribution Rotary Valve (<u>link</u>)
- Card edge connector (link), recommended by Norgren
- 1/4-28 to 1/16 in. Barb Adapter (link), need at least 2 of these
- 1/16 in. OD PEEK tubing (link)
- 1/16 in. ID Tygon tubing (link)
- 24V DC power supply, with DC female connector (<u>link</u>)

# pH Meter

- Thermo Fisher Orion Star A211 pH meter and electrode (link)
- Orion pH buffer kit (<u>link</u>)
- Orion pH electrode filling solution (<u>link</u>)

# Salinity Meter

 Misco Palm Abbe PA203 digital refractometer (<u>link</u>), or whatever method you prefer to generate salinity measurements in PSU

#### **Acid Titrant**

- Hydrochloric Acid 37% (12.1M), liquid, reagent grade (link)
- Sodium Chloride, powder, reagent grade (<u>link</u>)

# Certified Reference Material (CRM)

Dickson CRM Seawater (<u>co2crms@ucsd.edu</u>)

# General Lab Supplies

- Ring stand with clamp (link)
- Magnetic stir plate (<u>link</u>)
- Small stir bars, 10mm x 3mm (link)
- Kimwipes (<u>link</u>)
- 1-10 mL pipette and tips (link)
- Volumetric flask with stopper, 500 mL (link)
- Pyrex reagent bottle, 500 mL (link)
- 250ml glass beakers (<u>link</u>)
- Borosilicate glass vials, 25mL (<u>link</u>)
- DI water, from source of your choosing
- DI water wash bottles (<u>link</u>)
- Plastic tub for glassware soaking (link)
- Alconox detergent (<u>link</u>)
- Transfer pipettes (<u>link</u>)
- Weigh boats (<u>link</u>)
- Mass balance, .001g readability (link)
- Parafilm (<u>link</u>)

# **Setup & Assembly**

PC Setup and Software Install: Windows

Download the latest **stable release** of <u>Python</u> (currently 3.11.9) by choosing the "Windows installer (64-bit)" option, and running the installer after it downloads. **On the first installer screen, check "add python.exe to PATH"** and then select "Install Now."

Download <u>Git for Windows</u> and follow the on-screen install instructions. We recommend installing the default selection of components on the first screen, and choosing the following settings on the screens that follow:

- Nano or Visual Studio Code as the default editor rather than Vim.
- Override the default branch name to be "main."
- Under "adjusting your PATH environment," choose the recommended option of "Git from the command line and also from 3rd party software" to allow using git on the windows command line.
- Under "choosing the SSH executable," select the bundled OpenSSH option.
- Under "choosing HTTPS transport backend," select the OpenSSL library.
- Under "configuring the line ending conversions," choose "Checkout Windows-style, commit Unix-style line endings" to ensure compatibility between Windows and Unix.
- Use MinTTY if installing Git Bash (not necessary).
- Git pull default behavior should be "fast-forward or merge."
- Credential helper should be Git Credential Manager.
- Under "Configuring extra options," choose enable file system caching.
- Under "Configuring experimental options," leave all options unselected.

Open the command prompt by typing "cmd" into the search bar and choosing "Command Prompt." Then download the software package from our public <u>GitHub repository</u> using the following command:

```
Unset
git clone https://github.com/ebbcarbon/openalk.git
```

You should now have a folder in your home directory called "openalk." In the Command Prompt, run the following commands one at a time:

```
Unset cd openalk
```

```
pip3 install -r requirements.txt
```

You may need to wait a minute for the packages to be installed; you should see a terminal message saying "Successfully installed:" with a bunch of packages listed if everything went smoothly.

In the File Explorer, search for the project directory (openalk) and find the run.py file in the root directory of the project. Right-click on the file and select "Create shortcut," then drag and drop the shortcut onto the desktop. You can rename the shortcut whatever you like; optionally and to make the shortcut more recognizable, you can right-click on the shortcut and under Properties, choose "Change Icon," and select the icon file from the project's "install" directory.

You should now be able to open the application using only the desktop shortcut.

PC Setup and Software Install: Linux

If using the mini PC, follow the <u>Ubuntu Desktop installation guide</u>. We recommend installing the latest LTS version of Ubuntu, 22.04 LTS. If using your own machine, we recommend having at least Ubuntu 20.04 and Python 3.8 installed.

Once in the Ubuntu installation, open a terminal window and enter the command:

```
Unset sudo apt install -y git
```

The software package can be downloaded from our public <u>GitHub repository</u> using the following command:

```
Unset
git clone https://github.com/ebbcarbon/openalk.git
```

Make sure to run the above command in whichever directory you want to install the package.

When you've done the above, navigate to the project's root directory and run the following command:

Unset make install

The remaining install steps should be done by the Makefile automatically.

#### Wiring and USB-Serial Connections

Preparing the power cable: the power supply should come with a DC female connector that has green screw terminals for the DC positive and negative. Open the 22AWG Dupont connector package and take out a red and black cable. Press-fit the female ends of the cables into a Dupont connector housing (the black plastic housing also in the package) until you hear a small click and the cable can no longer be removed, then cut off the male connector on the other side of the cable. Using the wire strippers, strip a small amount of the insulation off (~5mm) where the male end used to be, and install the red cable (the bare wire end) into the positive terminal of the DC female connector and the black cable (the bare wire end) into the negative terminal of the DC female connector, ensuring no conductor remains exposed. It may help to twist the bare wire strands together before installing to prevent fraying. Then use a phillips head screwdriver to fasten the terminals until they are tight and the cables cannot be removed.

Preparing the RS232 cable: the RS232 cable comes with six wires (see connection diagram below). You will only need the Orange, Yellow, and Black wires, which correspond to serial transmit, receive, and ground; you can either cut the others back to the jacket so they don't interfere, or just wrap them in electrical tape. Regardless of what you do, at least use some wire cutters to cut off the tinned ends of the other wires so they don't accidentally make contact with any of the other wires or pins. Open the 22AWG Dupont connector package and take out a blue, yellow, and black cable. Press-fit the female ends of the cables into a Dupont connector housing (the black plastic housing also in the package) until you hear a small click and the cable can no longer be removed, then cut off the male connector on the other side of the cable. Using the wire strippers, strip a fair amount of the insulation off (~10mm) where the male end used to be, following the guide on the Wago connectors. Using the Wago connectors, connect the blue, yellow, and black cables you just made to the orange, yellow, and black wires, respectively, on the RS232 cable.

#### 5.1 USB-RS232-WE-PWR Connections and Mechanical Details

The following Figure 5.1 shows the cable signals and the wire colours for the signals on the USB-RS232-WE cable.

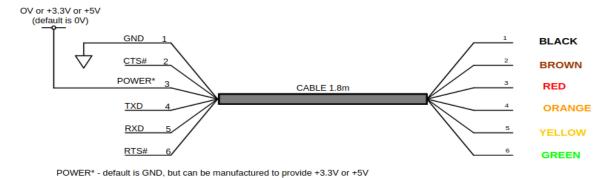


Figure 3-6 Drive Interface

Figure 5.1 USB-RS232-WE Connections

The pump's card edge connector (the green plastic piece with pins) press-fits onto the circuit board and has 36 pins arranged in alternating order from left to right, as shown here:

Make sure the connector is pressed all the way down into the circuit board and fasten the bolts tightly on the top and bottom to ensure a good connection.

PC Board PC Board Back Side Bock Side Front Side COM Setup SIO Output SIO Input SIO Clock SIO Strobe SIO Ground RS232 TX COM Ground RS485 "B" RS485 "A" RS232 RX N/A RS485 "B" RS485 "A" Error + 13 Error User Out 3 180 User Input 3 User Input 2 User Input 1 User Out 2 User Out 1 200 **19** I/O Ground Reset Input I/O Ground Reset Ground DVM Ground DVM Input Address 8 Address 2 29 31 300 Address 4 Address 1 Pwr Input +Pwr Input Address Switch Rear Edge of Right Side Plote

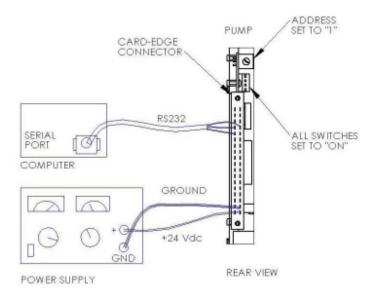
(back to top)

Use a small flathead screwdriver to set the address dial on the back of the drive to "1" and ensure all four of the COM switches are in the "ON" position (to the left).

Connect the 24V positive/red and negative/black to pins 35 and 33, respectively, as shown here.

Using the RS232 converter cable, connect the orange/blue, yellow, and black wires to pins 7,8, and 10, respectively, as shown below.

Figure 3-7 Pump Connections with Card Edge Connector



#### Example of proper pin connections:

The Dupont connectors should press-fit onto the pins with a snug connection, and remain intact even while moving the apparatus. Don't be afraid to use a little extra force, just be careful not to snap the pins off.



After you've done the above, you need to check which serial ports the devices are connected to on your system, as this will be a necessary input to the user interface. Follow the instructions below depending on your operating system.

**Windows:** type "Device Manager" into the search bar and select it from the list. After plugging the MiniUSB end of the USB-MiniUSB cable into the port on the back of the pH meter, plug the USB end into one of the PC's USB ports. It should show up in Device Manager under the "Ports" heading – click into the menu and you should see the COM port it connected to (e.g. COM5). Then, do the same for the RS232 converter cable, plugging the USB end into the PC and noticing the port it connects to (it may take a moment to install the drivers for the cable if you've never used one before). Make note of the port addresses before proceeding.

**Linux:** in a terminal, run the following command to monitor dmesg output:

```
Unset sudo dmesg --follow
```

After plugging the MiniUSB end of the USB-MiniUSB cable into the port on the back of the pH meter, plug the USB end into one of the PC's USB ports. You should see the dmesg output triggered by the connection, and a message saying something like "connected to ttyUSB0." Then, do the same for the RS232 converter cable, plugging the USB end into the PC and noticing the port it connects to. Make note of the port addresses before proceeding.

# Laboratory Set up

A lab bench suitable for handling chemical reagents should be set up and equipped with the items listed under general laboratory supplies.

Refer to supplier specific Safety Data Sheets (SDS) for proper handling and disposal instructions of all solutions, reagents, and chemicals.

# **SOP: Salinity Refractometer Calibration**

# Scope

Calibration of the Misco refractometer with DI water for precise measurement of salinity in seawater samples. The instrument should be calibrated daily to ensure accurate readings.

# Safety

- Lab coat
- Eye protection
- Nitrile gloves

#### **Materials**

- Refractometer
- DI water
- Transfer pipette
- Waste beaker
- Kimwipes

#### Procedure

- 1. With the device off, open the sample cover and wipe the sample well and measuring surface dry with a kimwipe.
- 2. Pipette ~3 drops of DI water onto the measuring surface (or until the surface is fully covered with DI) and close the sample cover. For best accuracy, wait at least thirty seconds for the temperature of the liquid to equalize to that of the instrument.
- 3. Press the "GO" button to power up the refractometer.
- 4. Press the "MENU" button until the display reads "SET ZERO? (GO) TO SET".
- 5. Press "GO" to automatically calibrate the refractometer. A successful calibration will read "READY". If you get an error while calibrating, repeat steps 1-5.
- 6. Open the sample cover and wipe away the DI water with a kimwipe until the measuring surface is dry. The instrument is now ready to take salinity readings.

# **SOP: Salinity Measurement**

#### Scope

Measurement of seawater salinity (PSU) using the Misco refractometer.

#### Safety

- Lab coat
- Eye protection
- Nitrile gloves

#### Materials

- Refractometer
- Seawater sample
- Transfer pipette
- Waste beaker
- Kimwipes

#### Procedure

- 1. Ensure the refractometer is properly calibrated according to the <u>SOP</u> before taking any measurements on actual seawater samples.
- 2. With the device off, open the sample cover and wipe the sample well and measuring surface dry with a kimwipe.
- 3. Pipette ~3 drops of seawater sample onto the measuring surface (or until the surface is fully covered with sample) and close the sample cover. For best accuracy, wait at least thirty seconds for the temperature of the liquid to equalize to that of the instrument.
- 4. Press the "GO" button to power up the refractometer.
- 5. Press the "MENU" button until the display reads "Seawater PSU".
- 6. Press "GO", the screen will say "Ready".
- 7. Press "GO" to take the measurement. The screen will say "Reading" and the measurement should take around five seconds, after which it will display the reading in PSU (e.g., "32"). If you get an error, repeat steps 2-6.
- 8. Open the sample cover and wipe away the seawater with a kimwipe until the measuring surface is dry.
- 9. To take another measurement, repeat steps 2-6.
- 10. To turn the instrument off, press and hold the "GO" button for five seconds.

#### Related Documents

Misco Palm Abbe Digital Refractometer PA203 Manual: <a href="https://misco.com/wp-content/uploads/2011/03/MISCO-MAN-PA20X-1.pdf">https://misco.com/wp-content/uploads/2011/03/MISCO-MAN-PA20X-1.pdf</a>

# **SOP: pH Probe Calibration & Care**

#### Scope

Calibration of the Orion pH probe with calibration buffers for precise measurement of pH in seawater samples. The instrument should be calibrated daily to ensure accurate readings.

#### Safety

- Lab coat
- Eye protection
- Nitrile gloves

#### **Materials**

- Orion Star A211 pH meter
- ROSS electrode pH probe
- ROSS storage solution
- ROSS electrode reference fill solution
- pH 4.01 buffer (red)
- pH 7.00 buffer (yellow)
- pH 10.01 buffer (blue)
- DI water
- Waste beaker
- Kimwipes

#### Procedure

- 1. Check that the pH meter is on and that all electrical connections are clean, dry, and in good working order.
- 2. Remove the pH probe from the storage container and visually inspect the probe. Pay close attention to the glass bulb making sure that it is clean and free from any cracks.
- 3. Remove any salt deposits as necessary.
- 4. If the internal reference fill solution is low, add more until you are about a half inch from the bottom of the fill port.
- 5. Use DI water to rinse the pH probe and blot the glass electrode dry using a kim wipe.
- 6. Press **CAL(F1)** on the pH meter to begin the calibration. If using the A215 meter dual channel, use the **up/down arrows** to select the pH calibration if needed.
- 7. Place the probe in the pH 4.01 buffer solution, press **START(F3)**, and wait for the reading to stabilize.
- 8. Once the pH value stops blinking, press **ACCEPT(F2)** > **NEXT(F2)** for the next calibration point.
- 9. Remove the pH probe from the pH 4.01 buffer, DI water rinse, and blot dry.
- 10. Place the pH probe in the pH 7.00 buffer.
- 11. Repeat steps 7 8.

- 12. Remove the pH probe from the 7.00 buffer, DI water rinse, and dry.
- 13. Place the pH probe in the pH 10.01 buffer.
- 14. Repeat steps 7 8.
- 15. Once the pH value has stabilized, press **ACCEPT(F2)**, **CAL DONE(F3)** to confirm calibration.
- 16. Remove the pH probe from the 10.01 buffer, DI water rinse, and dry.
- 17. After confirming the calibration, the screen will show the calibration slope. This should read between 98 and 102% for a successful calibration.
- 18. The pH probe is now ready for measurements. Store the pH probe wet in the storage container until ready for use. Add storage solution to the storage container as needed.

# **SOP: Acid Titrant Mixing**

#### Scope

Preparation of the acid titrant for alkalinity measurements, 0.1M HCl in 0.6M NaCl solution.

#### Safety

- Lab coat
- Eye protection
- Nitrile gloves

#### Materials

- DI water
- 12.1M (37%) Hydrochloric Acid solution
- Sodium Chloride (solid)
- 500mL volumetric flask with stopper
- 1-10mL pipette with tips
- 500mL Pyrex glass reagent bottle
- Mass balance and weigh boat
- Funnel (if needed)
- Waste beaker
- Kimwipes

#### Procedure

- 1. Rinse all glassware 3 times with DI water.
- Fill the volumetric flask about <sup>2</sup>/<sub>3</sub> of the way with DI water.
- 3. Weigh out 17.532g NaCl for a 500mL solution (35.064g for a 1L solution).
- 4. Add the NaCl to the volumetric flask, using a funnel if needed, and mix (swirl and invert) until solid is completely dissolved.
- 5. In a fume hood using the pipette, draw 4.13mL of 12.1M HCl for a 500mL solution (8.26mL for a 1L solution).
- 6. Dispense HCl from the pipette into the volumetric flask, cap the flask, and mix (swirl and invert) until completely dispersed.
- 7. Add remaining DI water to the volumetric flask until you reach the fill line, cap the flask, and mix (swirl and invert) until completely dispersed.
- 8. Transfer the solution from the volumetric flask into the Pyrex reagent bottle.
- 9. Label the reagent bottle with "0.1M HCl in 0.6M NaCl" and the date the solution was prepared.
- 10. Rinse all glassware 3 times with tap water and then DI water, and leave out to dry.
- 11. Wipe down scale, counter, fume hood, and any other work surfaces.

```
Calculations for 500mL solution:
       NaCl:
```

0.6M0.5L=x(g)58.44 g mol-1

x=17.532g

HCI:

0.1M0.5L=12.1Mx x=0.00413L x=4.13mL

#### Calculations for 1L solution:

NaCl:

(0.6M)(1L)=x/(58.44 g mol-1), where x is in g

x=35.064g

HCI:

(0.1M)(1L)=(12.1M)(x) x=0.00826L

x=8.26mL

# SOP: Calibration with Certified Reference Material (CRM) or other reference solution

#### Scope

Running the alkalinity measurement system against a known reference solution to calculate the exact acid titrant concentration. Batches of secondary standard solution can be produced from sterile preserved seawater where the alkalinity has been measured multiple times with a system calibrated to the CRM. Secondary standards must be carefully stored so that they are not affected by evaporation or biological activity.

# Safety

- Lab coat
- Eye protection
- Nitrile gloves

#### **Materials**

- Alkalinity titrator setup
- Certified Reference Material (CRM) seawater or other secondary standard
- Mass balance
- Sample vials
- DI water
- Waste beaker
- Kimwipes

#### **Procedure**

- 1. Using the mass balance, weigh out 4 samples of CRM (or secondary standard) in individual sample vials of around 16-22g each.
- 2. Titrate the samples (according to the titration section of the <u>alkalinity SOP</u>) until the measured TA agrees with the reference within ± 1 µmol kg<sup>-1</sup>.
- 3. The acid concentration is calculated by the following formula:

$$[C]_{HCl} = [C]_{HCl}^* \frac{TA_{CRM}}{TA_{measured}}$$

Where  $[C]_{HCI}$  is the acid concentration,  $[C]_{HCI}^*$  is the initial assumed concentration used for the titration,  $TA_{CRM}$  is the certified TA value, and  $TA_{measured}$  is the measured TA of the CRM (mean of the two precise results). Record the old and new TA value, and the new imputed acid concentration.

- After the [HCl] is recorded, you'll be ready to move on to measuring samples. Plan to titrate at least 2 duplicates, and be ready to run a third if values do not converge within ± 2 μmol kg<sup>-1</sup>.
- 5. At the end of the day, repeat this process and record the change in acid concentration.

# **SOP: Alkalinity Measurement**

#### Scope

Running the alkalinity measurement system with seawater samples of unknown alkalinity.

#### Safety

- Lab coat
- Eye protection
- Nitrile gloves

#### Materials

- Alkalinity titrator setup
- Certified Reference Material (CRM) seawater
- Sample seawater
- Mass balance
- Sample vials
- DI water
- Waste beaker
- Kimwipes

#### Procedure

#### Setup/Overview

- 1. Check that the power is connected to both the pump and pH meter. For the pH meter, the display will turn on; for the pump, you should hear its motor buzz for a moment. Then ensure the serial cables to the pump/pH meter are plugged into the computer's USB ports.
- 2. Remove the blue rubber stopper from the electrode. Check the level of the solution inside the electrode and fill it if necessary. Clean off any residual salt.
- 3. Open the titrator interface by double-clicking on the desktop icon or selecting it from the applications menu.
- 4. Open the acid titrant bottle and put the acid input tube (the leftmost tube leaving the pump) into the bottle after wiping it with a Kimwipe. Cover with parafilm. Put the outlet tube into a waste beaker.
- 5. On the interface under "Serial Ports," enter the port addresses corresponding to the pump and pH meter press the "Connect Devices" button to establish the serial connection to the pump and pH meter. You should hear the pump's motor buzz for a moment and see a popup on the screen saying "Device connection successful." If there was an error and you see a message saying "Connection failed," re-check that the serial cables are connected properly to each device and plugged into the computer's USB ports. Then try connecting again.

- 6. On the interface, press the "wash" button, making sure to minimize bubbles in tubes by pinching them out. This will rinse the syringe with acid 3x.
- 7. Connect the outlet tube to the pH electrode with a narrow strip of parafilm, ensuring that the tube tip is level with the bulb at the bottom of the electrode.
- 8. Run a few junk seawater samples until the system stabilizes to within ±2 µmol/kg.
- 9. Run CRM (or secondary standards) according to the <u>SOP</u> and recalculate the acid titrant concentration.
- 10. Begin measuring sample TA. Start with the "Weighing Samples" section, then proceed to the "Titration" section.
- 11. At the end of the day, rerun CRM (or secondary standards) and record the new acid titrant concentration.
- 12. When finished, proceed to the "Shutdown" section to ensure the system is shut down properly for the next day.

#### **Weighing Samples**

- 1. Pour or add seawater with a syringe (approximately 18 g) into a tared titration vial, ensuring that no droplets of water are stuck to the top or sides of the vial. Record the mass of seawater added to the nearest milligram (0.001g). (Target range ~16-22g)
- **2.** Add a small stir bar to the vial, taking care not to splash the seawater and cause droplets of water to stick to the sides of the vial.
- 3. Weigh out as many samples as you like and think you can get through—evaporation should not impact the TA. Make sure they are labeled and massed correctly. We usually run triplicates, or duplicates if TA values agree within +/- 2µmol/kg.

#### **Titration**

- 1. Lift electrode/outlet tubing out of the previous sample and rinse well with DI water. For pH buffer readings, the probe must be carefully dried with a Kimwipe (although the Kimwipe should not touch the actual probe tip). For total alkalinity measurements, this is unnecessary—just rinse it and don't worry about drying it.
- 2. If the acid outlet tubing has been removed due to calibration, replace it, affixing with a strip of parafilm. Be careful not to flick acid around when moving it.
- 3. Lower the electrode into the new sample and turn on the stir bar fast enough that the sample is well-mixed, but not so much that it pulls air bubbles into the solution.
- 4. Enter the sample mass, salinity, and acid concentration, then click "Start." The box labeled "System Status" will give you updates about what the system is doing at any given time.
- 5. When the titration is finished, the results will be saved automatically to the directory where you installed the repository, in CSV format.
- 6. Turn off the stir plate, remove the electrode and stir bar from the sample, and remove the sample from the stir plate.
- 7. Wash the electrode with DI water in-between samples.
- 8. Repeat steps 1-7 as necessary. If done before calibration, junk water titrations should be performed until results agree to ±2 μmol/kg.

#### Shutdown

- 1. Turn off the stir plate, remove the electrode, and place the outlet tubing into an acid waste beaker.
- 2. Rinse the electrode briefly and replace it in the storage solution.
- 3. On the interface, press the "empty" button to empty the syringe of any remaining acid.
- 4. Remove inlet tubing from the acid bottle and place in a DI water beaker.
- 5. On the interface, press the "wash" button to wash the syringe 3x with DI water.
- 6. Remove the inlet tubing and leave the tubing hanging from something to prevent it from touching the lab bench.
- 7. Close the interface and (if you prefer) disconnect the power from the pump and pH meter.

# References

Cai W. J., Wang Y. and Hodson R. E. (1998) Acid-base properties of dissolved organic matter in the estuarine waters of Georgia, USA. Geochim. Cosmochim. Acta 62, 473–483.

Song, S., Wang, Z.A., Gonneea, M.E., Jroeger, K.D., Chu, S.N., Li, D., and Liang, H., 2020. An important biogeochemical link between organic and inorganic carbon cycling: Effects of organic alkalinity on carbonate chemistry in coastal waters influenced by intertidal salt marshes. Geochimica et Cosmochimica Acta, v. 275, pp. 123-139.

Lu, X., Ringham, M., Hirtle, N., Hillis, K., Shaw, C., Herndon, J., Carter, B. and Eisaman, M., 2022. Characterization of an Electrochemical Approach to Ocean Alkalinity Enhancement. AGU Fall Meeting Abstracts, GC31C-01.