Introduction

Method overview
Alkalinity is the measure of how much acid it takes to lower the pH of a water sample enough to convert all bicarbonate (HCO$_3^-$) and carbonate (CO$_3^{2-}$) to carbonic acid (H$_2$CO$_3$). Although total alkalinity is equal to the stoichiometric sum of all bases in solution, ~97% of alkalinity in seawater is due to carbonates.

Method theory
To measure alkalinity, a pore water sample is titrated with an acid to an endpoint at which carbonate is converted to bicarbonate and bicarbonate is converted to carbonic acid. In seawater, this endpoint occurs at about pH = 4.2.

\[
\begin{align*}
H^+ + CO_3^{2-} &\rightarrow HCO_3^- \\
H^+ + HCO_3^- &\rightarrow H_2CO_3
\end{align*}
\]

The alkalinity determination in this method (Gran titration) relies on a mathematical evaluation of the second equivalence point of carbonate titration in seawater using the most stable part of the titration curve (i.e., the part beyond the equivalence point on the low pH side). In essence, the Gran method linearizes the titration curve by means of a simple function:

\[
F = (v + V_0) \times 10^E/A,
\]

where:
- \(F\) = Gran factor,
- \(v\) = volume of acid added to the solution in the titration vessel,
- \(V_0\) = original volume of the sample,
- \(E\) = EMF (millivolts) at \(v\), and
- \(A\) = slope of electrode determined on the basis of the electrode calibration.

Generally, the slope is ~59 mV at 25°C. Slope is determined during calibration (see Calibrating the electrode)

The function \(F\), when plotted as a function of the volume of acid added (\(v\)), is linear when sufficiently removed from the equivalence point. We measure mV instead of pH to determine the endpoint because this method offers better precision. The optimum range of millivolts for linearity is 220–240 mV. The value of \(v\) at \(F = 0\) is the equivalence point from which the alkalinity is evaluated.

The slope of the \(F\) vs. \(v\) plot changes with variations in the sulfate content of the samples. This is because at lower pH values the following reaction

\[
H^+ + SO_4^{2-} = HSO_4^- 
\]

plays an important role in establishing the pH of the solution through a buffering effect. This change in slope, however, has no effect on the Gran extrapolation intercept with the \(y\)-axis and is not accurate enough to estimate sulfate concentrations.

Reagents
- IAPSO standard seawater (alkalinity ~20.325 mM)
- Potassium chloride (KCl)
- Borax (Na$_2$B$_4$O$_7$·10H$_2$O)
- Sodium bicarbonate (NaHCO$_3$)
- Sodium carbonate (Na$_2$CO$_3$)
Reagent solutions
- M HCl solution (premade from Fisher, AMS# CH5009)
- 0.7 M KCl solution (52 g KCl in 1 L reagent water)

Stock standard solutions (1 L)
- M borax solution (38.1 g borax in 1 L reagent water)
- 0.5 M NaHCO₃ (42 g sodium bicarbonate in 1 L reagent water)
- M Na₂CO₃ (10.6 g sodium carbonate in 1 L reagent water)
- 0.5 M Na₂CO₃ (53 g sodium carbonate in 1 L reagent water)

Standard solutions (100 mL)
- 5 mM Na₂CO₃ (pipet 2.5 mL 0.1 M Na₂CO₃ into 97.5 mL 0.7 M KCl)
- 20 mM Na₂CO₃ (pipet 10 mL 0.1 M Na₂CO₃ into 90 mL 0.7 M KCl)
- 40 mM Na₂CO₃ (pipet 20 mL 0.1 M Na₂CO₃ into 80 mL 0.7 M KCl)
- 50 mM NaHCO₃ (pipet 10 mL 0.5 M NaHCO₃ into 90 mL 0.7 M KCl)
- 100 mM Na₂CO₃ (pipet 10 mL 0.5 M Na₂CO₃ into 90 mL 0.7 M KCl)

Main instrument panel

- Measure a sample.
- Measure a standard and generate a standard correction.
- Calibrate the electrode.
- The calibration, path to the data log and standard ratio correction are displayed. You can also select factors that affect the measurement stability, such as drift span.
- Edit the rates that will be applied during the titration program, keeping the mV targets the same. Set first to 150 mV, second to 220 mV, and last to 240 mV.
- Select standard ratio values to be applied to subsequent measurements.
- See what the electrode is currently measuring.
- Force Init: Force initialize the Titrino, in case you’ve lost comms with the unit.
- Fill: Fill the buret.
- View the data log.
- Exit the software.
Instrument calibration

To ensure accuracy of sample measurements, the titrator settings must be optimized. Calibration of the system includes calibrating the electrode, selecting a dispensing rate program, and calculating a standard ratio.

Calibrating the electrode

Before the titrator can be used to measure samples, the electrode must be calibrated against pH buffers in the same range expected in samples. Generally, calibration at pH 4, 7, and 10 covers the necessary range.

1. Select **Calibrate Electrodes** from the main Alkalinity interface.
2. Enter your range of buffers (4, 7, 10).
3. Select your Drift Span. A drift span of 30 (default) indicates that a min of 30 measurements will be taken after each addition of titrant (acid). The difference between the first and last measurement is compared to the drift tolerance specified in the rate program.
4. Place 3 mL of first buffer solution in vessel. Add stir bar and immerse electrode in vessel.
5. Select **Cal 1** and then **Start**.
6. When finished, clean vessel and the electrode.
7. Repeat steps 4–6 with each calibration buffer, selecting **Cal2** and **Cal3** when appropriate.
8. When all three buffers have been run, select **OK-Save** to save the calibration.

Dispensing rate

The rate at which the titrator dispenses the acid into the sample can be adjusted according to the expected alkalinity value. Higher alkalinitities may require faster dispensing rates. The dispensing rate can be selected from a list of predetermined programs, or a new dispensing rate program can be created.

Select **Edit Rates** from the main alkalinity interface.
Calculating the standard ratio (estimated vs. actual alkalinity, “fudge factor”) for the anticipated range of alkalinity values accounts for measurement error in acid strength. Standard ratio can be calculated using borax solution, sodium bicarbonate solution, or IAPSO standard seawater, as necessary, to most closely match alkalinity values (within 5 mM, to preserve the first-order transfer function) of the unknown samples. Generally, IAPSO standard seawater is used to establish this ratio, and additional calibration standards are used if samples deviate >5 mM from the alkalinity of IAPSO (~2.325 mM). The measurement is repeated until at least 3 consistent measurements are obtained within 5% of actual value for each standard:

- IAPSO = 2.21–2.44 mM
- 20 mM standard = 19–21 mM
- 40 mM standard = 38–42 mM

To start creating a standard ratio, select **STANDARDS** from the main alkalinity interface.
1. Place 3 mL of standard in vessel. Add stir bar and immerse electrode in vessel.
2. Select **Continue**.

3. Click **START**.
4. Insert the acid dispensing probe when prompted.
5. When finished, clean vessel and electrode.
6. Repeat steps 1–4 until you have at least three consistent measurements per standard.

Now go to the **STND Manager**, selected from the main alkalinity interface.
1. Select the three measurements (or however many were done in the prior step) and click **Average**.
2. The window to the right shows the next step to which you can save the new ratio to a new name or replace a prior name. Usually we save as a new ratio (e.g. 361P_13april). *The window showing the name creation is not shown.*
3. Click **Done**.

To select a standard ratio for subsequence measurements go to **Setup** in the main alkalinity interface.

### Measuring samples

The system is now calibrated, dispensing rates selected (generally start with the slowest rate, assuming that alkalinity will be around the value of IAPSO) and standard ratio selected (again, generally start with the IAPSO standard ratio and adjust accordingly to what is measured in the samples).

Select **SAMPLE** from the main alkalinity interface.
Select the sample (IWS) from the LIMS database. Use the tree or type in the Text_ID in the appropriate field. There’s currently a minor ‘glich’ in the tree method if you don’t use the filter = “IWS.” So without explaining the entire issue, just remember to put “IWS” in the filter field. Good to go...SCIENCE!!

1. Place 3 mL of standard in vessel. Add stir bar and immerse electrode in vessel.
2. Select Continue.

3. Click START.
4. The first measurement that the system measures, is sample pH. Record the value in the blue book (just in case…).
5. Insert the acid dispensing probe when prompted.
6. When the titration is complete, a window appears showing the results.
Click **Done/Save** to save the results to the LIMS database. The value saved to the db, and the value you need to note in the blue book (just for completeness, in case...) is the “Corrected Alkalinity” value. This is the value with the standard ratio applied to it.

When finished, clean vessel and the electrode.