Autotitrator pH/Alkalinity: Quick Start Guide

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_2CO_3). Although total alkalinity is equal to the stoichiometric sum of all bases in solution, not just carbonates, ~97% of alkalinity in typical seawater is due to carbonates.

Note that this method should only be used on interstitial water (IW) squeezed from the core material by the titanium squeezers. The RHIZON samplers alter the pH and alkalinity of the IW samples and should not be analyzed for alkalinity or pH.

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.

$$H^+ + CO_3^{2-} = HCO_3^-$$

$$H^+ + HCO_3^- = H_2CO_3$$

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.

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 ~2.325 mM)
- Potassium chloride (KCl)
- Borax ($Na_2B_4O_7 \cdot 10H_2O$)
- Sodium bicarbonate ($NaHCO_3$)
- Sodium carbonate (Na_2CO_3)

Reagent solutions

- 0.1 M HCl solution (premade from Fisher, AMS# CH5009)
- 3 M KCl solution (224 g KCl in 1 l reagent water)

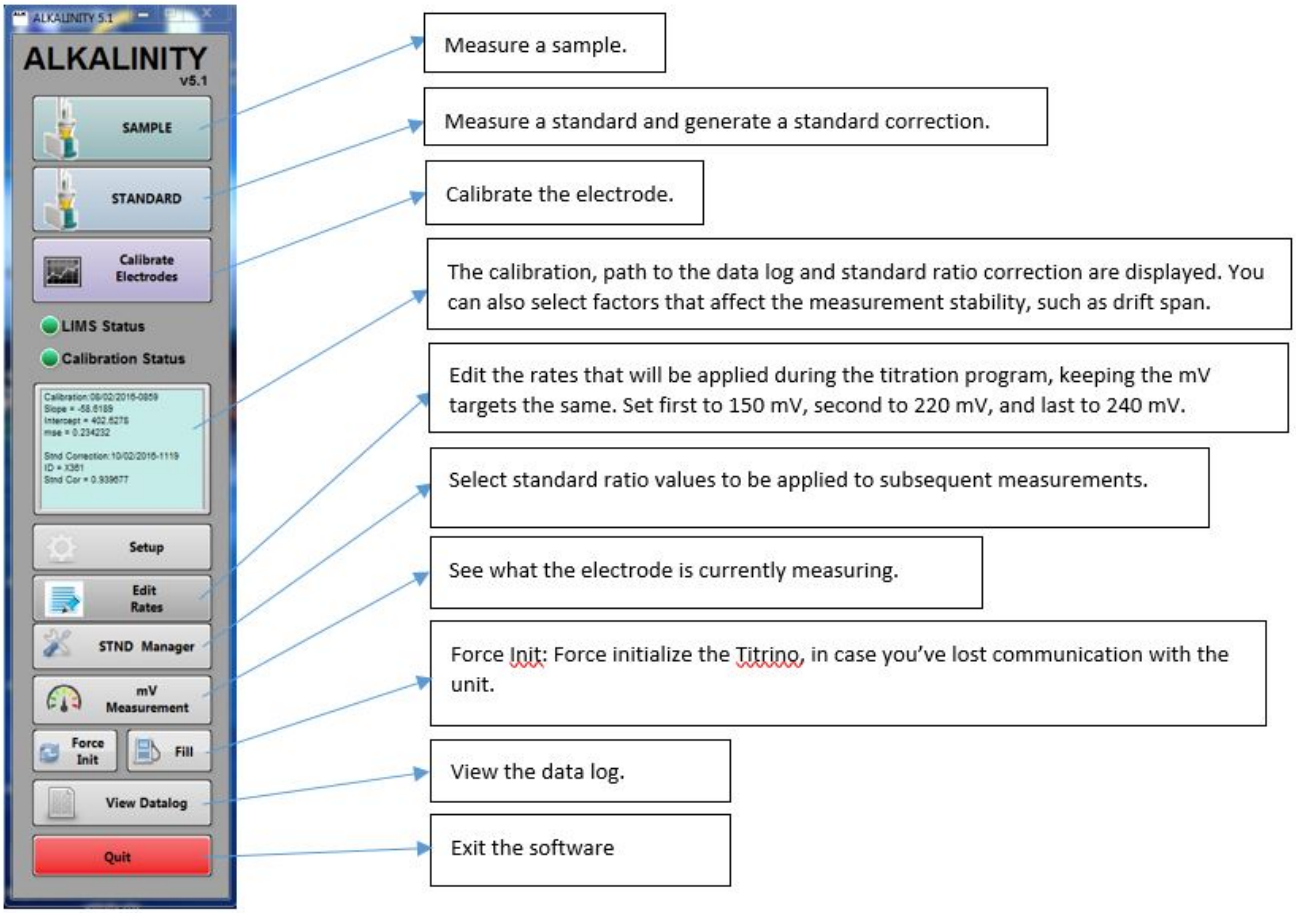
Stock standard solutions (1 l)

- 0.1 M borax solution (38.1 g borax in 1 l reagent water)
- 0.5 M $NaHCO_3$ (42 g sodium bicarbonate in 1 l reagent water)
- 0.1 M Na_2CO_3 (10.6 g sodium carbonate in 1 l reagent water)
- 0.5 M Na_2CO_3 (53.0 g sodium carbonate in 1 l reagent water)

Standard solutions (100 ml)

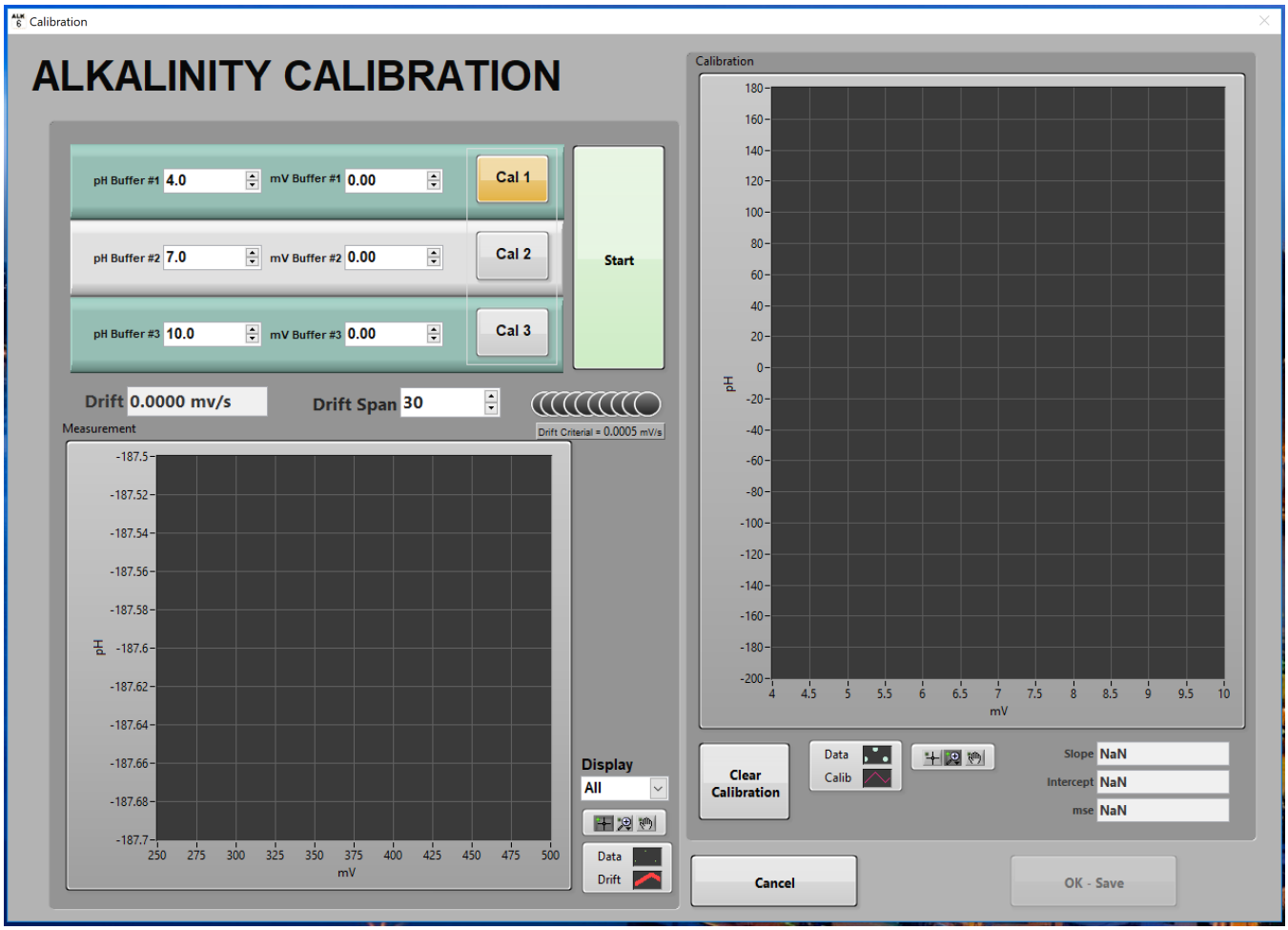
- 5 mM alkalinity (pipet 2.5 ml 0.1 M Na_2CO_3 into 97.5 ml 0.7 M KCl)
- 20 mM alkalinity (pipet 10 ml 0.1 M Na_2CO_3 into 90 ml 0.7 M KCl)
- 40 mM alkalinity (pipet 20 ml 0.1 M Na_2CO_3 into 80 ml 0.7 M KCl)
- 50 mM alkalinity (pipet 10 ml 0.5 M $NaHCO_3$ into 90 ml 0.7 M KCl)
- 100 mM alkalinity (pipet 10 ml 0.5 M Na_2CO_3 into 90 ml 0.7 M KCl)

Main instrument panel



Calibrating the electrode

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



1. Make sure the water bath temperature is set to 25°C. Ensure no air bubbles are present in the acid dispensing line. Press **DOS** on the body of the titrator to push acid through the line to remove potential air bubbles. Select **Calibrate Electrodes** from the Main instrument panel.
2. Enter your range of buffers (4, 7, 10).
3. Select your Drift Span. The default drift span is 30.
4. Place 3 mL of the first buffer solution in the vessel. Add stir bar. Remove the electrode from the storage solution, rinse with DI water, and blot dry with a Kimwipe. Do not rub the electrode, as this can cause a static charge. Insert the electrode tip into the titration vessel (not touching the bottom of the cup or the stir bar). Confirm that the frit is in the solution.
5. Select **Cal 1** and then **Start**. Measure until the drift gets close to 0.0. Usually approximately 500 seconds will be adequate. Select **Stop** when satisfied with measurement.
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, the slope value of the regression curve should be close to –59 pH/mV. Select **OK-Save** to save the calibration.

Dispensing rate

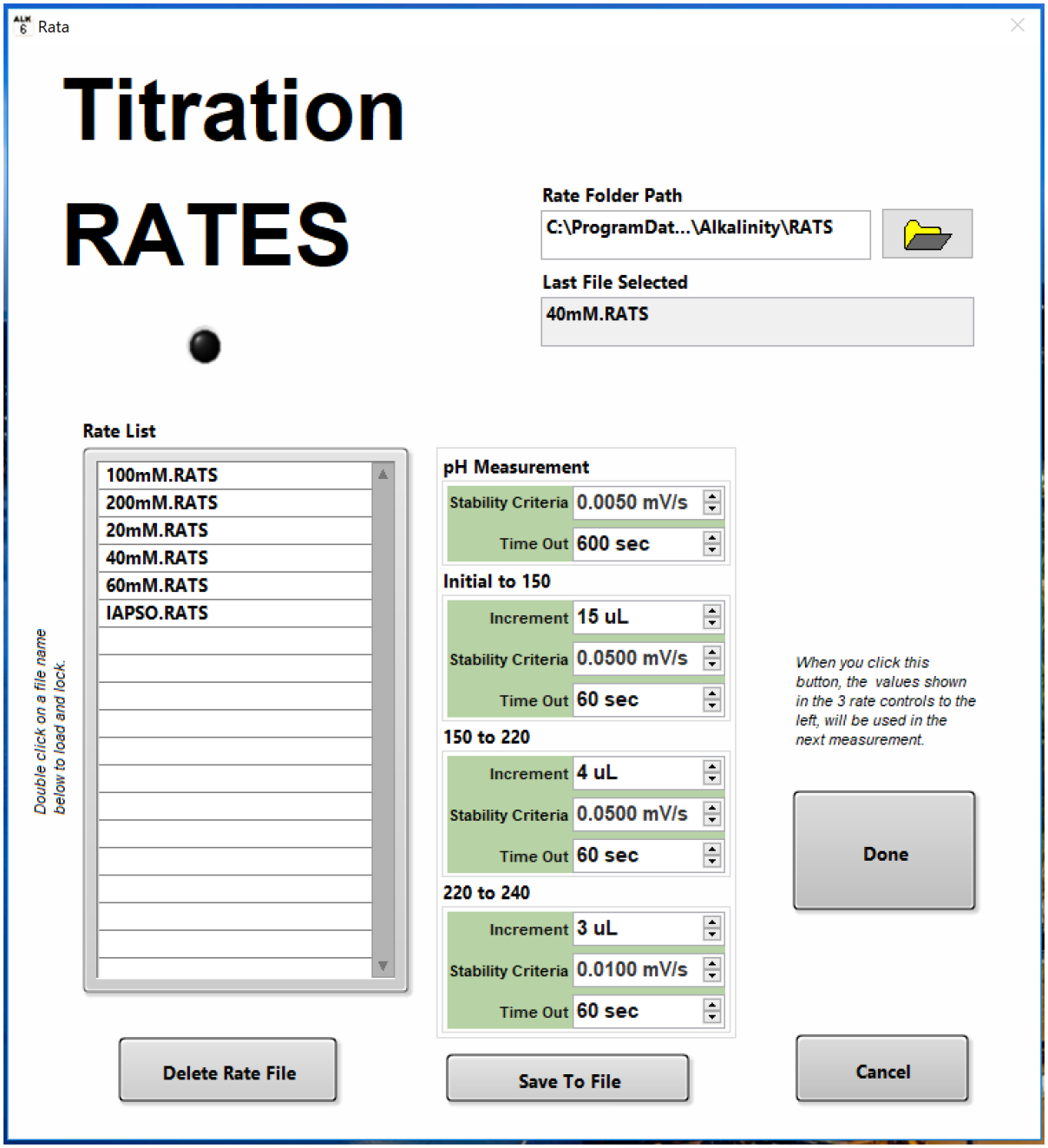
The rate at which the titrator dispenses acid into the sample can be adjusted according to the expected alkalinity value. Higher alkalinities may require faster dispensing rates. The dispensing rate can be selected from a list of predetermined programs or a new dispensing rate program can be created.

Select **Edit Rates** from the Main instrument panel.

To create a new rate program:

1. Set your **Stability Criteria** for each step of the program: Measurement continues until Stability Criteria (mV/s) is satisfied.
2. Select your **Increment** for each mV level (initial to 150, 150 to 220 and 220 to 240): How much acid is added in each increment.
3. Set the **Time Out** for each step of the program: Seconds until rate program times out if Stability Criteria is not satisfied.

4. **Save To File**.



Standard ratio correction

Calculating the standard ratio correction (estimated vs. actual alkalinity) for the anticipated range of alkalinity values accounts for measurement error in acid strength. Standard ratio correction 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). It is good practice to have IAPSO, 20 mM and 40 mM standard ratio corrections calculated before arriving at the first site. This prepares you for alkalinities up to 40 mM.

The measurement is repeated until at least 3 consistent values are obtained within 5% of actual value for each standard:

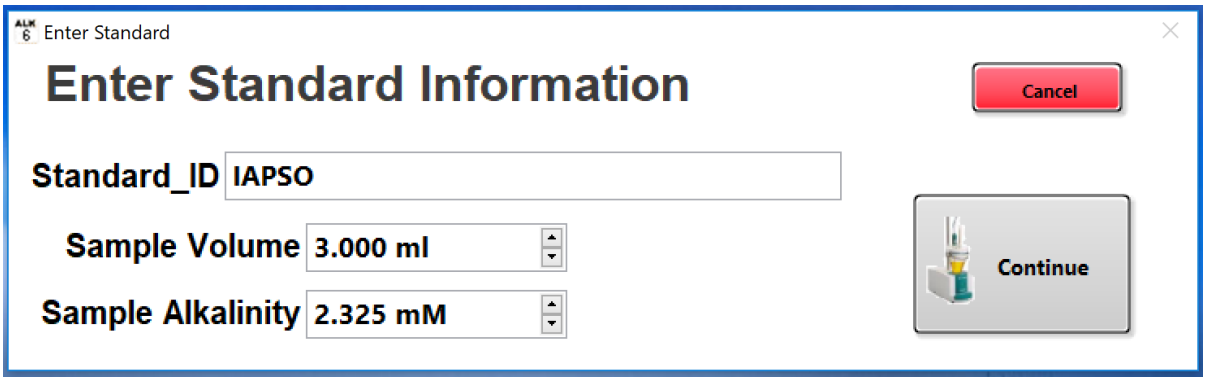
- IAPSO = 2.21–2.44 mM

- 20 mM standard = 19–21 mM
- 40 mM standard = 38–42 mM

Make sure to select a correct dispensing rate program for the standard in question. You can access the rates by selecting **Edit Rates** from the Main instrument panel.

Before any measurement, press the red STOP/FILL button on the titrator itself. This will fill the syringe pump and ensure you will not run out of acid during the titration.

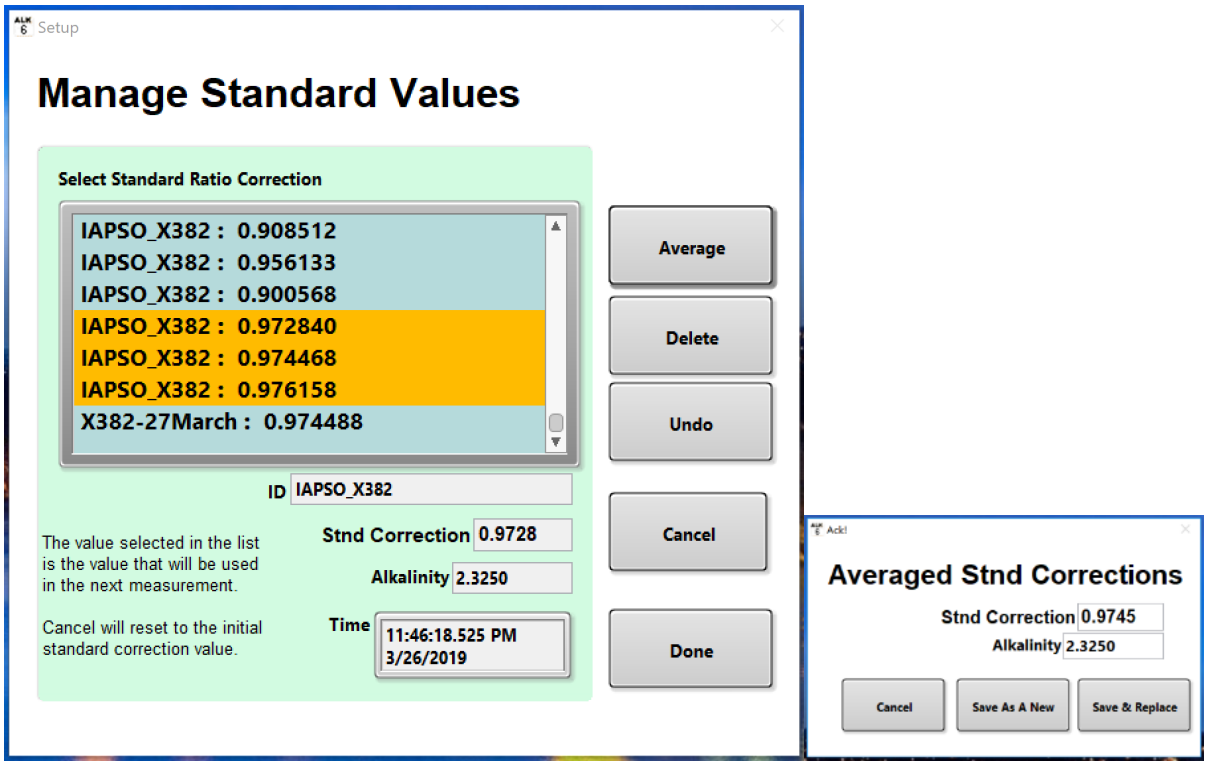
To start creating a standard ratio correction, select **STANDARDS** from the Main instrument panel.



1. Place 3 ml of standard in vessel. Add stir bar and immerse electrode in vessel. Confirm that the frit is in the solution.

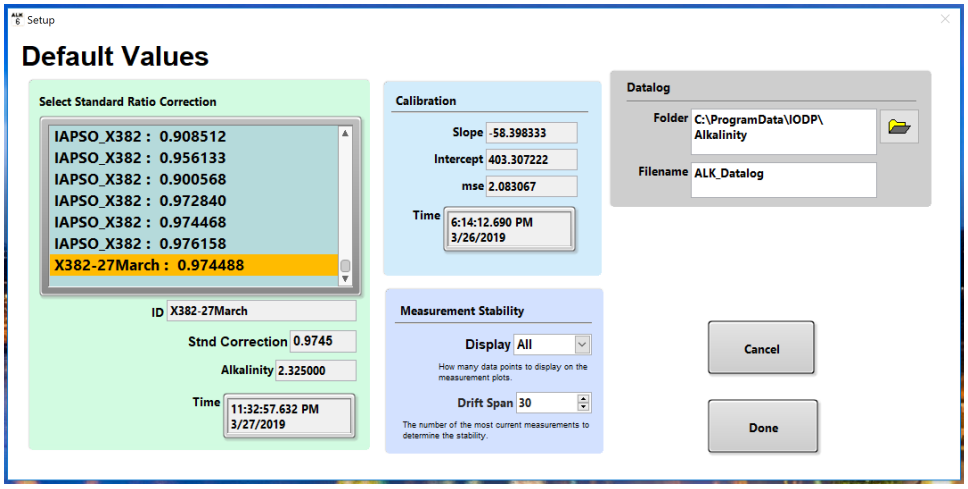
2. Select **Continue**.
3. Click **START**.
4. Insert the acid dispensing probe when prompted.
5. When finished, clean vessel and electrode. Repeat steps 1–4 until you have at least three consistent measurements per standard.

Now go to the **STND Manager**, selected from the Main instrument panel.



1. Select the three measurements you want to average and click **Average**.
2. The window to the right shows the next step in which you can save the new standard ratio correction or replace an old one. Usually we save as a new ratio (e.g. 371_13august). *The window showing the name creation is not shown.*
3. Click **Done**.

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



This window also shows the electrode calibration values, the path to the datalog file, the default setting for the Drift Span and where to select the standard ratio correction.

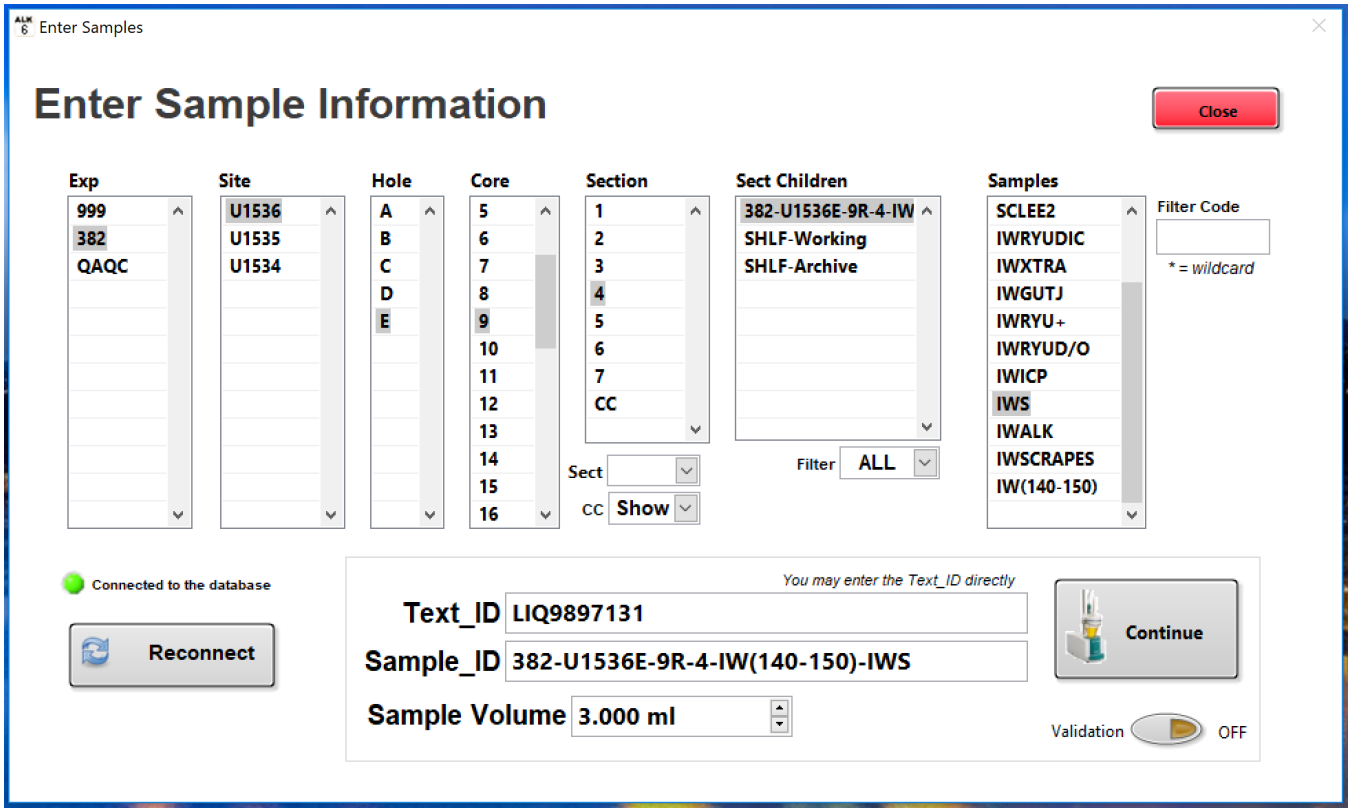
To select a saved standard ratio correction double-click it.

Measuring samples

The system is now calibrated, dispensing rate and standard ratio correction selected. Generally, start with the slowest dispensing rate, assuming the alkalinity will be around the value of IAPSO. Same with the standard ratio correction, start with the IAPSO standard ratio correction and adjust according to what is measured in the samples.

Before any measurement, press the red STOP/FILL button on the titrator itself. This will fill the syringe pump and ensure you will not run out of acid during the titration.

Select **SAMPLE** from the Main instrument panel.

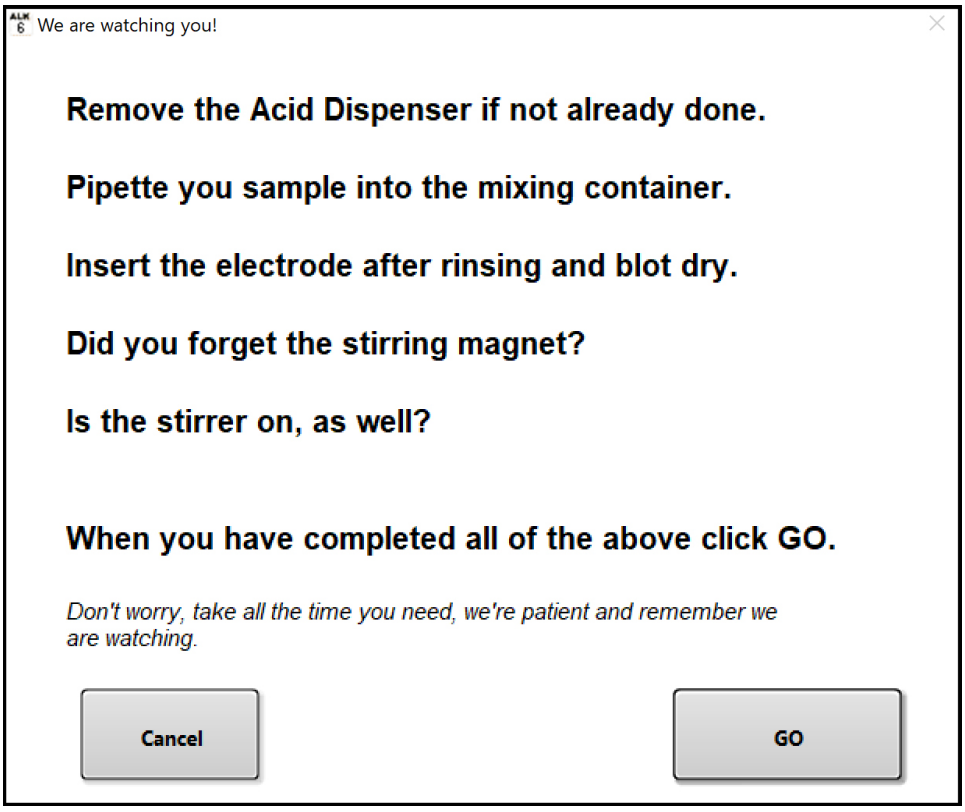


Select the sample (IWS) from LIMS tree. Alternatively, type or scan in a Text_ID. If you use a **Filter Code** IWS, the software will only bring up the IWS sample, which can be handy if your IW has a lot of children.

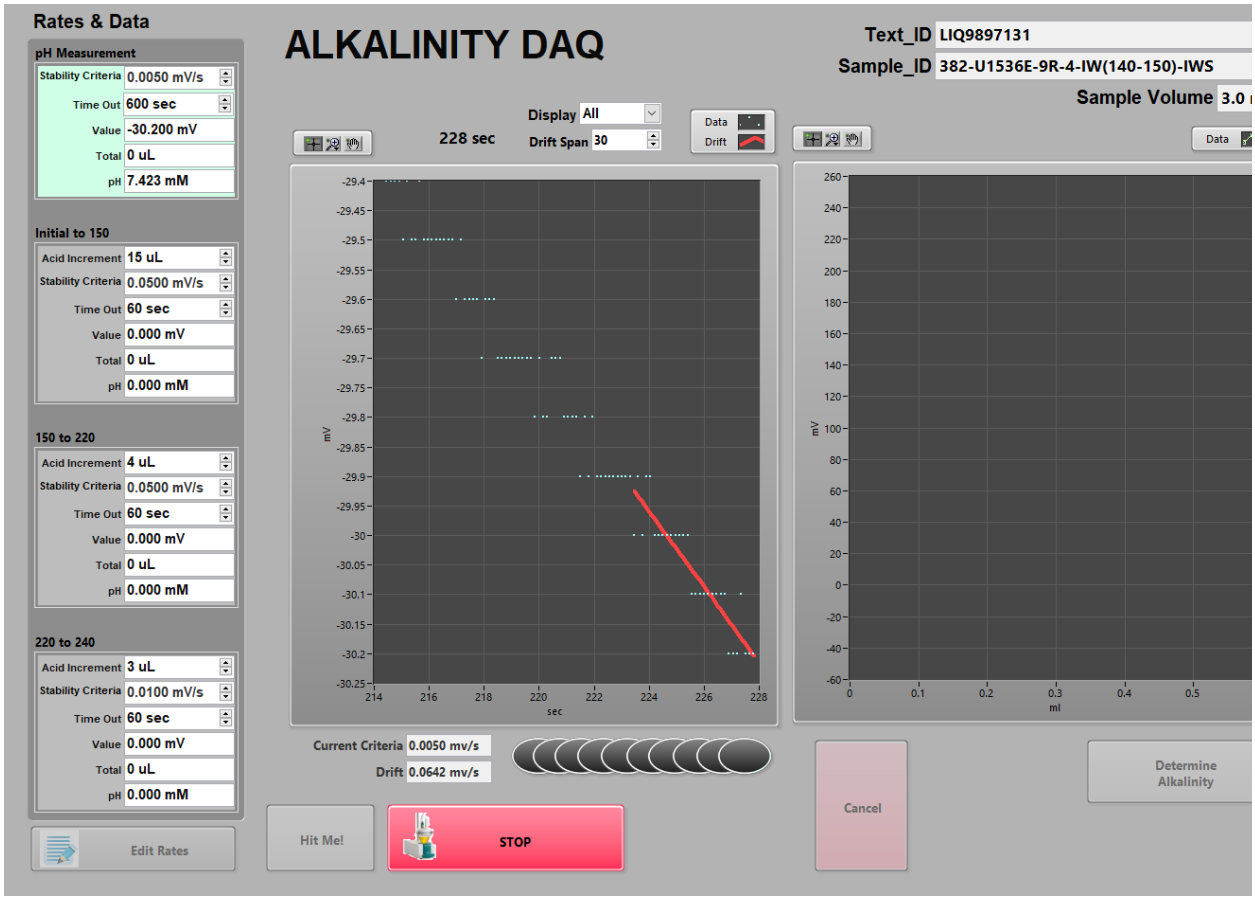
Place 3 ml of the sample in the vessel. Add stir bar. Remove the electrode from the storage solution, rinse with DI water and blot dry with a Kimwipe. Do not rub the electrode, as this can cause a static charge. Insert the electrode tip into the titration vessel (not touching the bottom of the cup or stir bar). Confirm that the frit is in the solution.

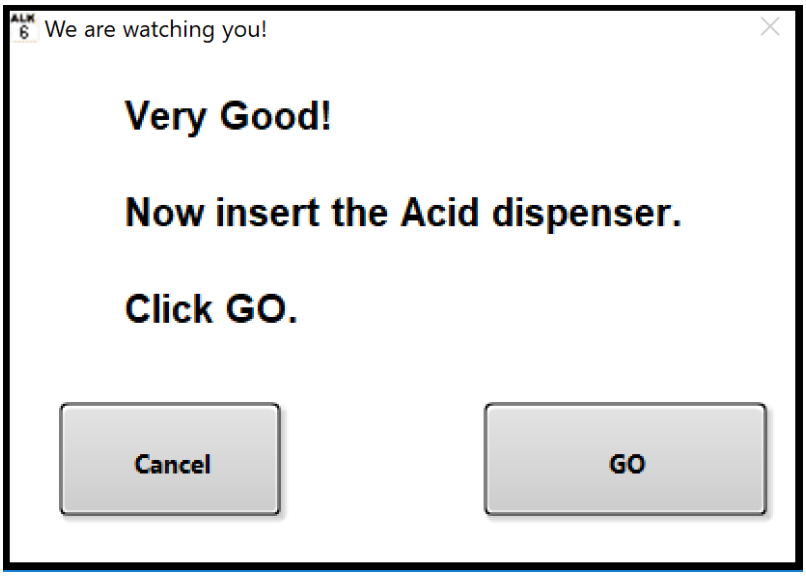
Select **Continue**.

Click **START**. The software will guide you through.

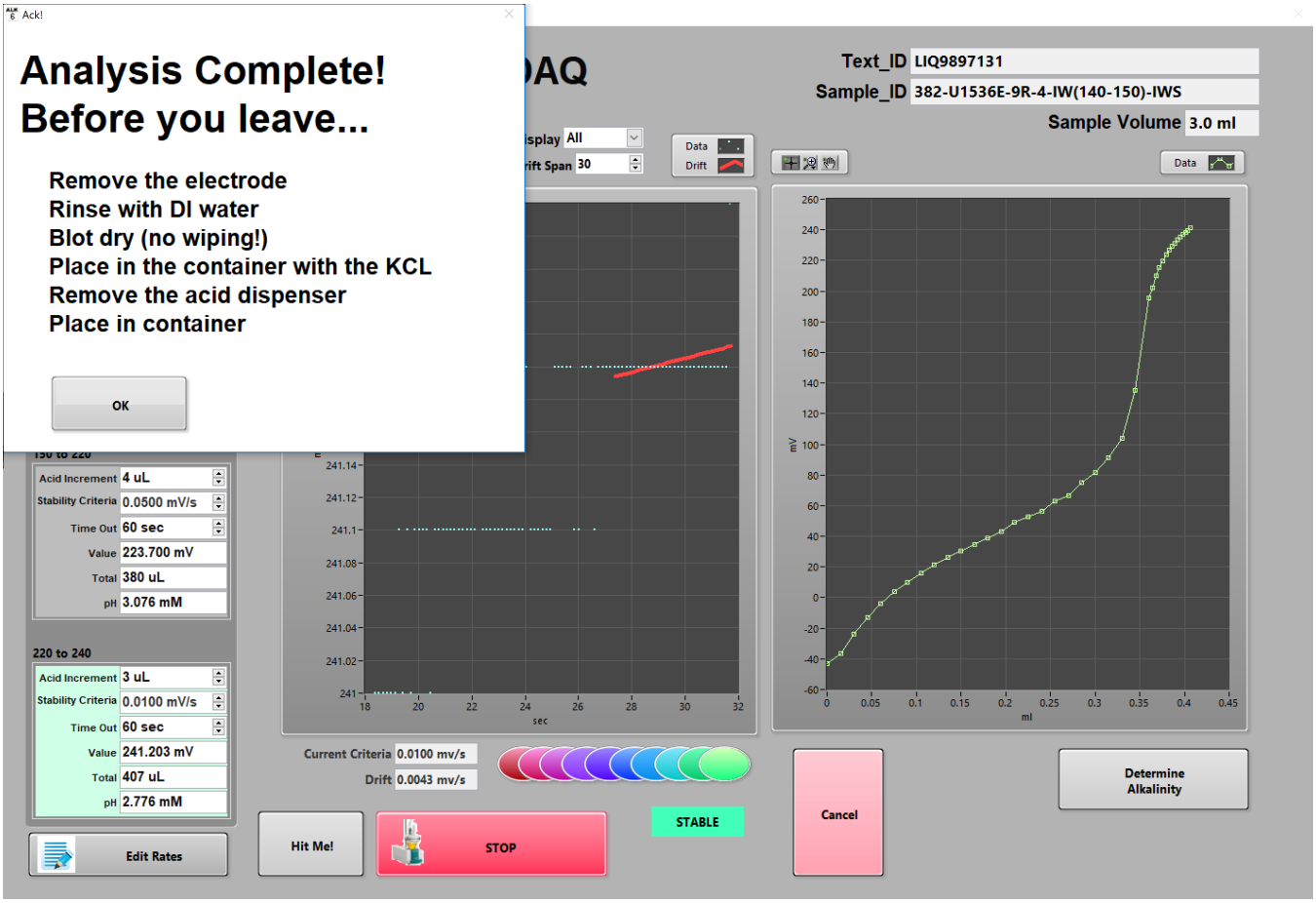


After completing all the steps in the "We are watching you!" box, click **GO**. The pH measurement will commence.

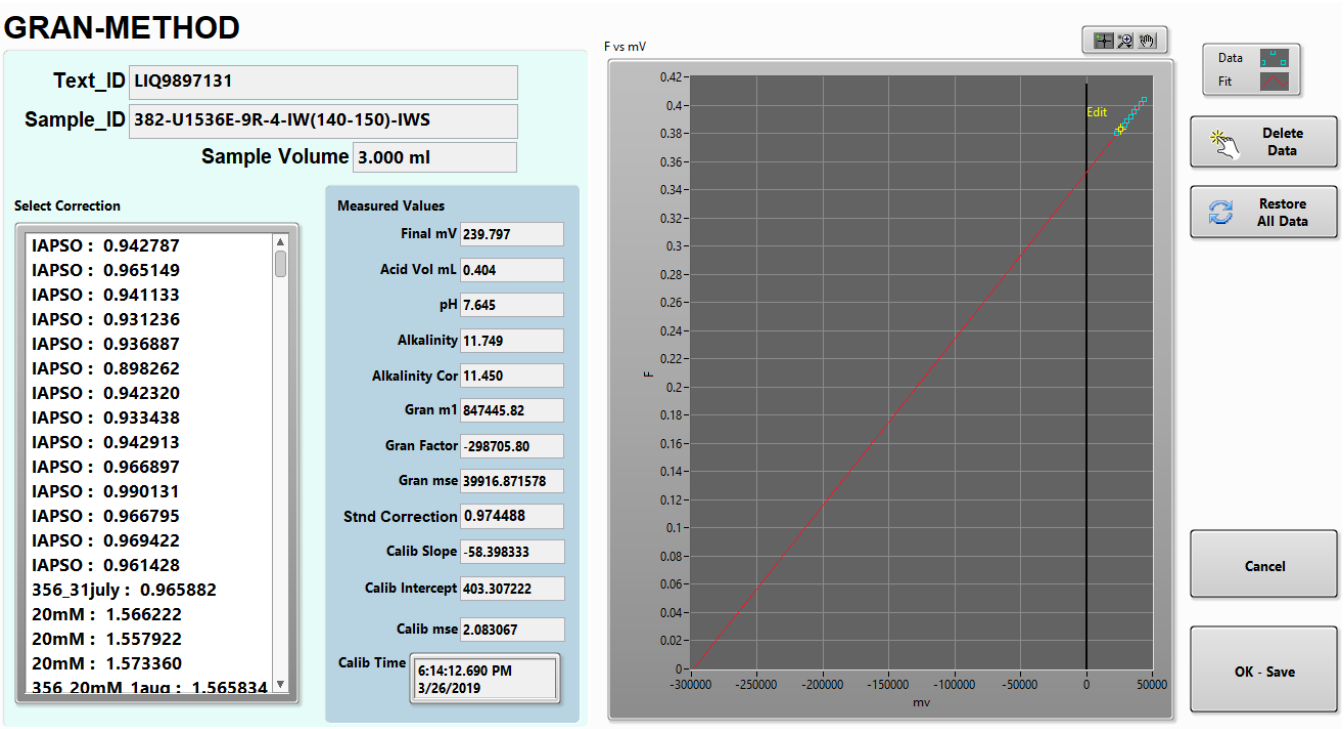

Rates & Data
ALKALINITY DAQ
Text_ID LIQ9897131
Sample_ID 382-U1536E-9R-4-IW(140-150)-IWS
Sample Volume 3.0
pH Measurement
Stability Criteria 0.0050 mV/s
Time Out 600 sec
Value -30.200 mV
Total 0 uL
pH 7.423 mM
Initial to 150
Acid Increment 15 uL
Stability Criteria 0.0500 mV/s
Time Out 60 sec
Value 0.000 mV
Total 0 uL
pH 0.000 mM
150 to 220
Acid Increment 4 uL
Stability Criteria 0.0500 mV/s
Time Out 60 sec
Value 0.000 mV
Total 0 uL
pH 0.000 mM
220 to 240
Acid Increment 3 uL
Stability Criteria 0.0100 mV/s
Time Out 60 sec
Value 0.000 mV
Total 0 uL
pH 0.000 mM
Edit Rates
228 sec
Display All
Drift Span 30
Data
Drift
mV
sec
ml
Current Criteria 0.0050 mv/s
Drift 0.0642 mv/s
Hit Me!
STOP
Cancel
Determine Alkalinity


We are watching you!
Very Good!
Now insert the Acid dispenser.
Click GO.
Cancel
GO

Insert the acid dispenser probe when prompted. Click **GO**. The alkalinity measurement will commence.



Analysis is complete. Click **OK**. This will take you to the Gran-method window.



The Gran-Method window appears with the results of the titration. Write the **pH** and the **Alkalinity Cor** value in the blue book. This is the result with the standard ratio correction applied to it. Click **Ok/Save**. This will upload the result to LIMS assuming the MUT uploader is active.

When finished, transfer the residue into a 5 ml cryo vial. Clean the vessel, the electrode and the acid dispensing probe.