Autotitrator pH/Alkalinity User Guide

User Guide: Autotitrator pH/Alkalinity

Manual information

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Origination date:	2/14/08
Approved:	Version 2.0 (June 2013)
Revision:	IODP-II V3.0 (J. Suhonen, X382, May 2019)
Domain:	Chemistry
System:	Titration and Refractometry
Keywords:	Titration, pH, Alkalinity

User Guide contents

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 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 approximately at pH = 4.2.

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

$$H^+ + HCO_3^- = H_2CO_3$$
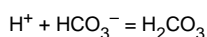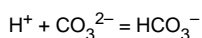
The alkalinity determination in this method (Gran titration) relies on a mathematical evaluation of the second equivalence point of carbonate titration in seawater using the most stable part of the titration curve (i.e., the part beyond the equivalence point on the low pH side). In essence, the Gran 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

$$H^+ + SO_4^{2-} = HSO_4^-$$
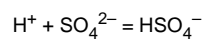
plays an important role in establishing the pH of the solution through a buffering effect. This change in slope, however, has no effect on the Gran extrapolation intercept with the y-axis and is not accurate enough to estimate sulfate concentrations.

Apparatus, supplies and reagents

Laboratory apparatus

Hardware and software

-	Metrohm Titrino 794 autotitrator
-	LabVIEW *Alkalinity* program v6.5
-	Laboratory oven
-	Desiccator
-	Water bath
-	Analytical balance system

Figure 1. Metrohm Autotitrator (Note: dispenses 0.1 M HCl).

Supplies

-	Pipettes, Class A: 0.5, 2, 3, 5, 8, 10, and 20 ml
-	Adjustable pipettor, 100–5000 μl
-	Volumetric flasks, Class A: 100 ml, 1 l

-	Combination electrode (Metrohm, combined pH glass electrode, model 6.0234.100)
-	pH paper, to bracket pH 7 (pH 1–12 paper)
-	5 ml snap-cap vials
-	Magnetic stir bars

Laboratory reagents

Dry reagents

-	Hydrochloric acid (HCl), ultrapure
-	Potassium chloride (KCl), certified ACS
-	Borax ($Na_2B_4O_7 \cdot 10H_2O$)
-	Sodium bicarbonate ($NaHCO_3$), certified ACS
-	Sodium carbonate (Na_2CO_3), certified ACS

Reagent solutions

-	0.1 N 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 g sodium carbonate in 1 l reagent water)

Standard solutions (100 ml)

-	5 mM Na_2CO_3 alkalinity (pipet 2.5 ml 0.1 M Na_2CO_3 into 97.5 ml 0.7 M KCl)
-	20 mM Na_2CO_3 alkalinity (pipet 10 ml 0.1 M Na_2CO_3 into 90 ml 0.7 M KCl)
-	40 mM Na_2CO_3 alkalinity (pipet 20 ml 0.1 M Na_2CO_3 into 80 ml 0.7 M KCl)
-	50 mM $NaHCO_3$ alkalinity (pipet 10 ml 0.5 M $NaHCO_3$ into 90 ml 0.7 M KCl)
-	100 mM $Na2CO_3$ alkalinity (pipet 10 ml 0.5 M $Na2CO_3$ into 90 ml 0.7 M KCl)
-	IAPSO standard seawater (alkalinity ~2.325 mM)

Reagent water

18.2 M millipore deionized water

Buffer solutions

NBS buffers: commercially obtained low ionic strength solutions at pH 4.00, 700, and 10.00 (stable indefinitely; store in the chem lab refrigerator when not in use).
Tris buffer: tris(hydroxymethyl)amino methane or 2-amino-2-(hydroxymethyl)-1,3-propanediol
Bis buffer: bis(hydroxymethyl)methylamino methane or 2-amino-2-methyl-1,3-propanediol (not commercially available because of its highly hygroscopic nature; prepare as follows):

1. Heat reagent water in a glass beaker while adding *Bis* and stirring.
2. When precipitation is observed (saturation), add HCl until pH = 7 as tested with pH paper.
3. Cool solution (a gel forms in the beaker), then decant the water and place in a warm oven until dry.
4. Scrape dry remains from the bottom of the beaker and place in a vacuum desiccator to cool.
5. Take first weight quickly upon removal from desiccator when making up the buffer. See *ODP Tech Note 15* for complete instructions on making up the powdered buffer.
6. Redry in oven and cool in desiccator each time prior to weighing.
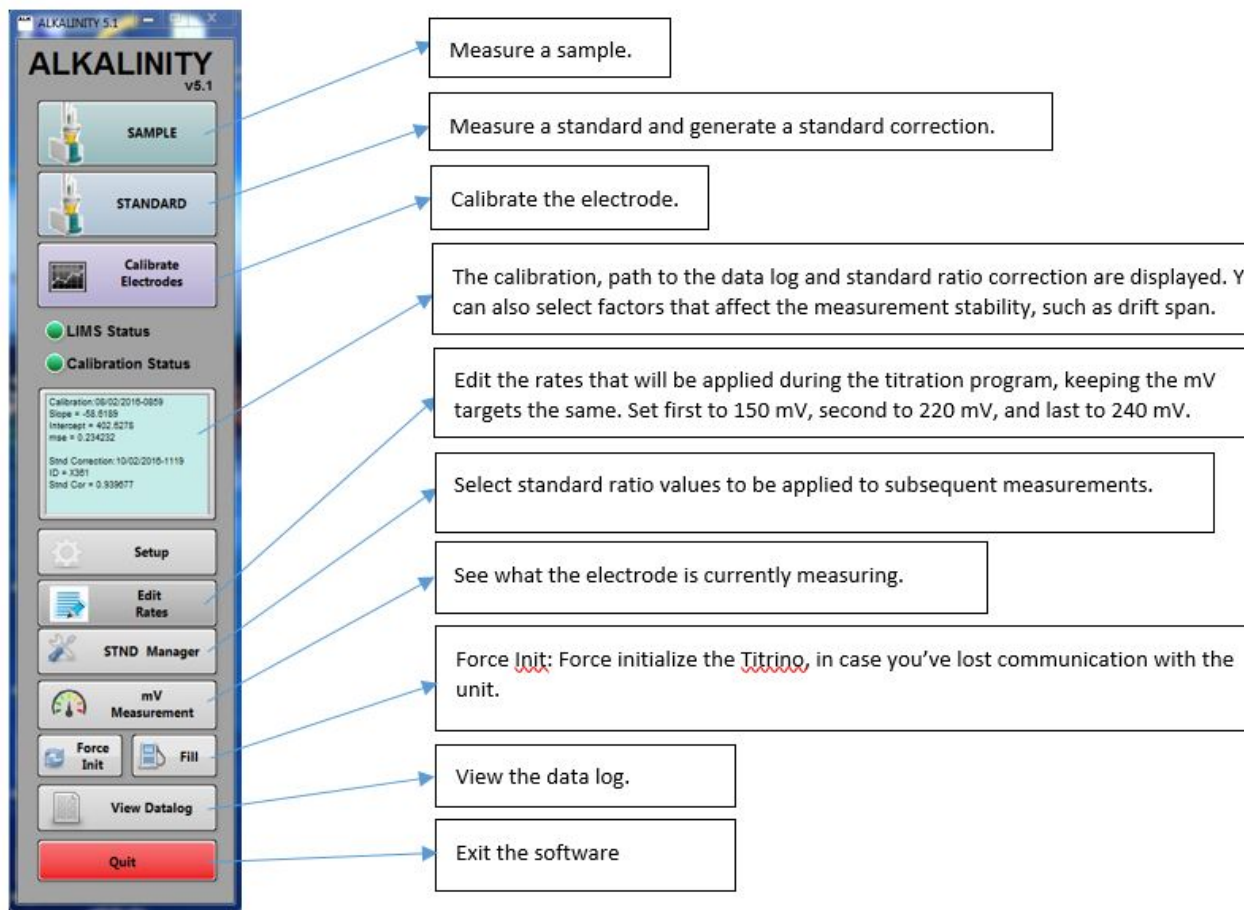7. Make new *Bis* buffer at the beginning of each expedition.

Main instrument panel

Figure 2. 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.
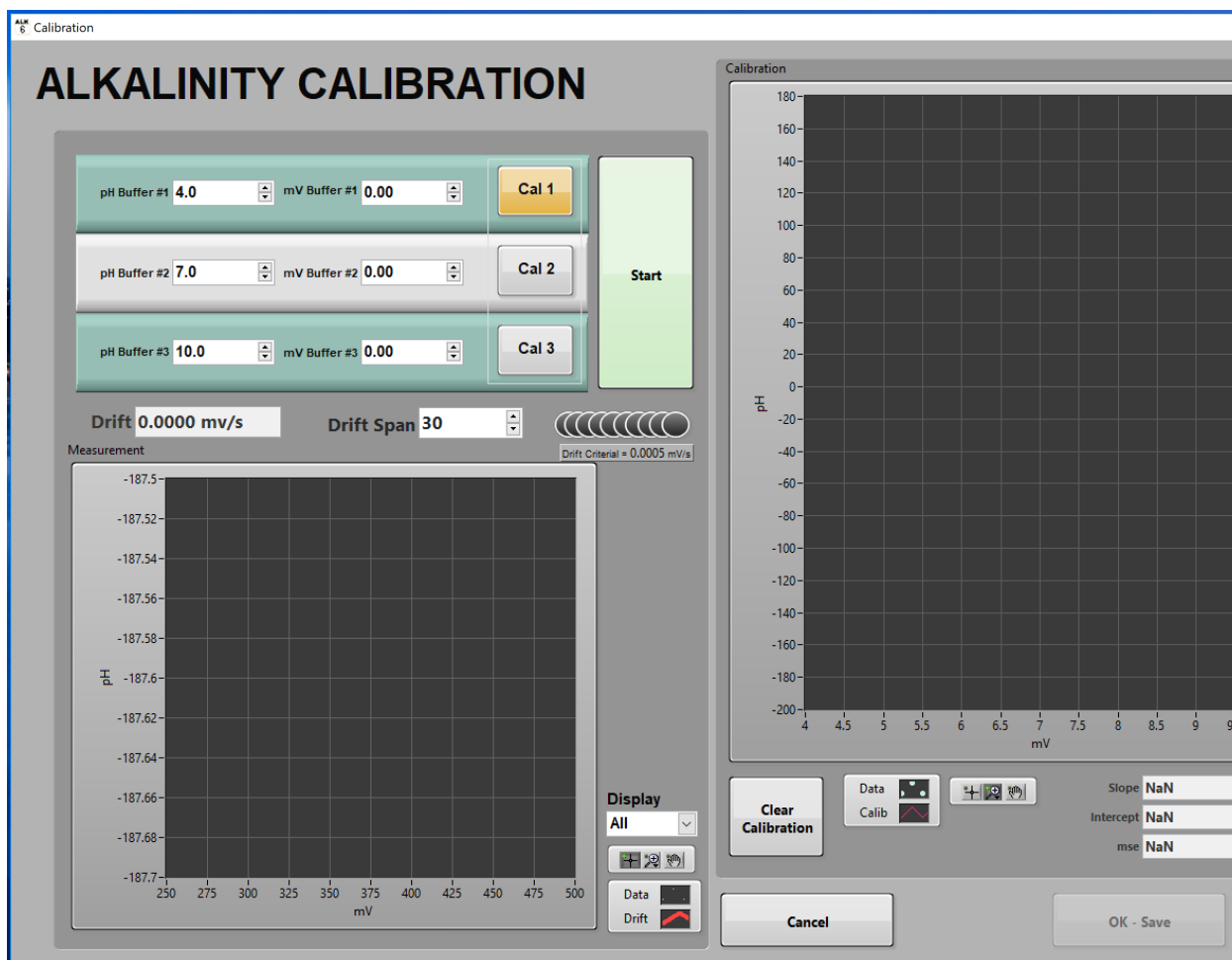
Figure 3. Electrode calibration.

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.

Selecting a dispensing rate

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

To select a dispensing rate, double-click on the desired rate on the **Rate List**. Click **Done**.

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.
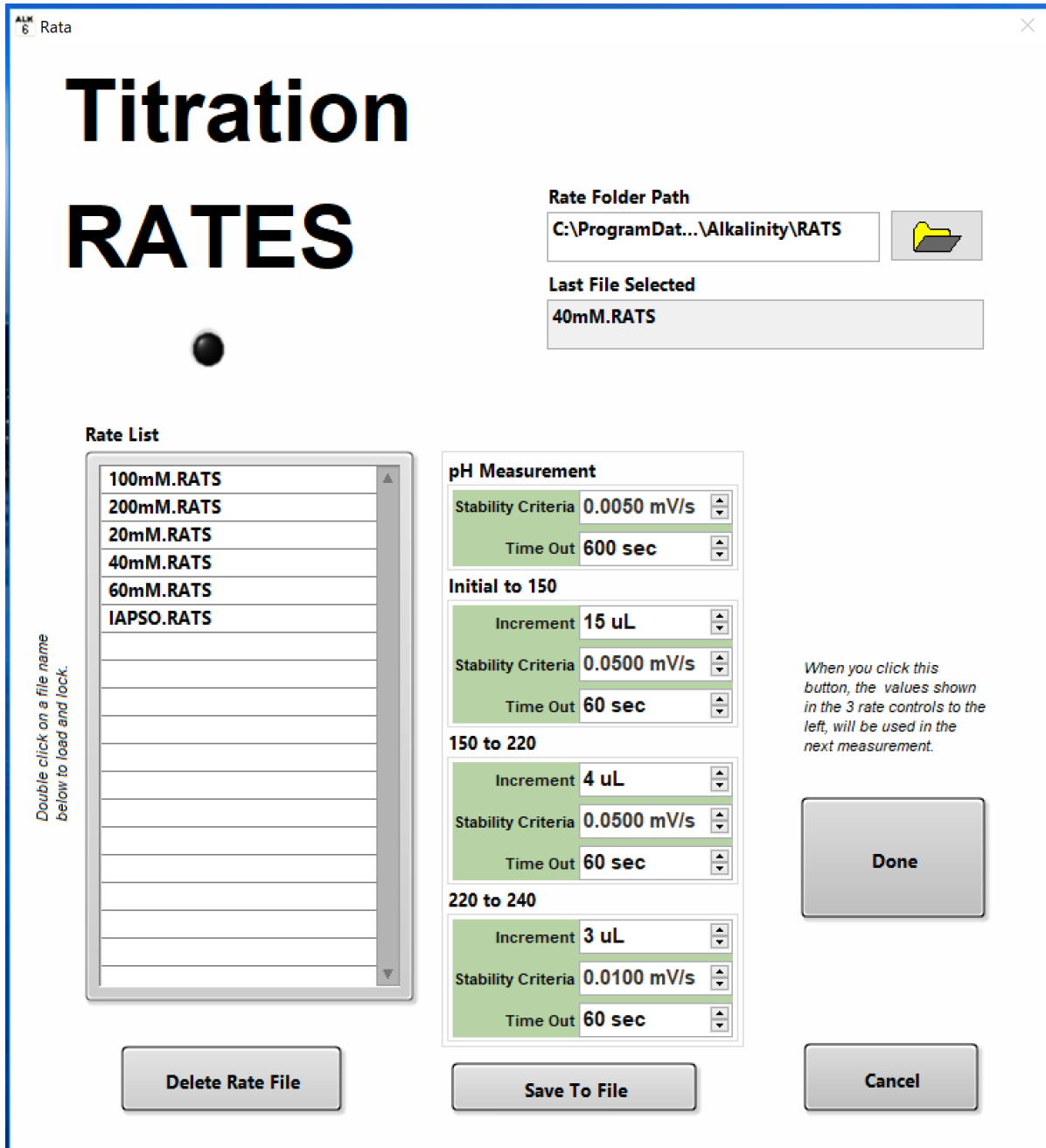4. **Save To File**.

Figure 4. Selecting a dispensing rate.

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

Generating standard values

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 (*Figure 1*). 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 and enter the information for the standard in question.

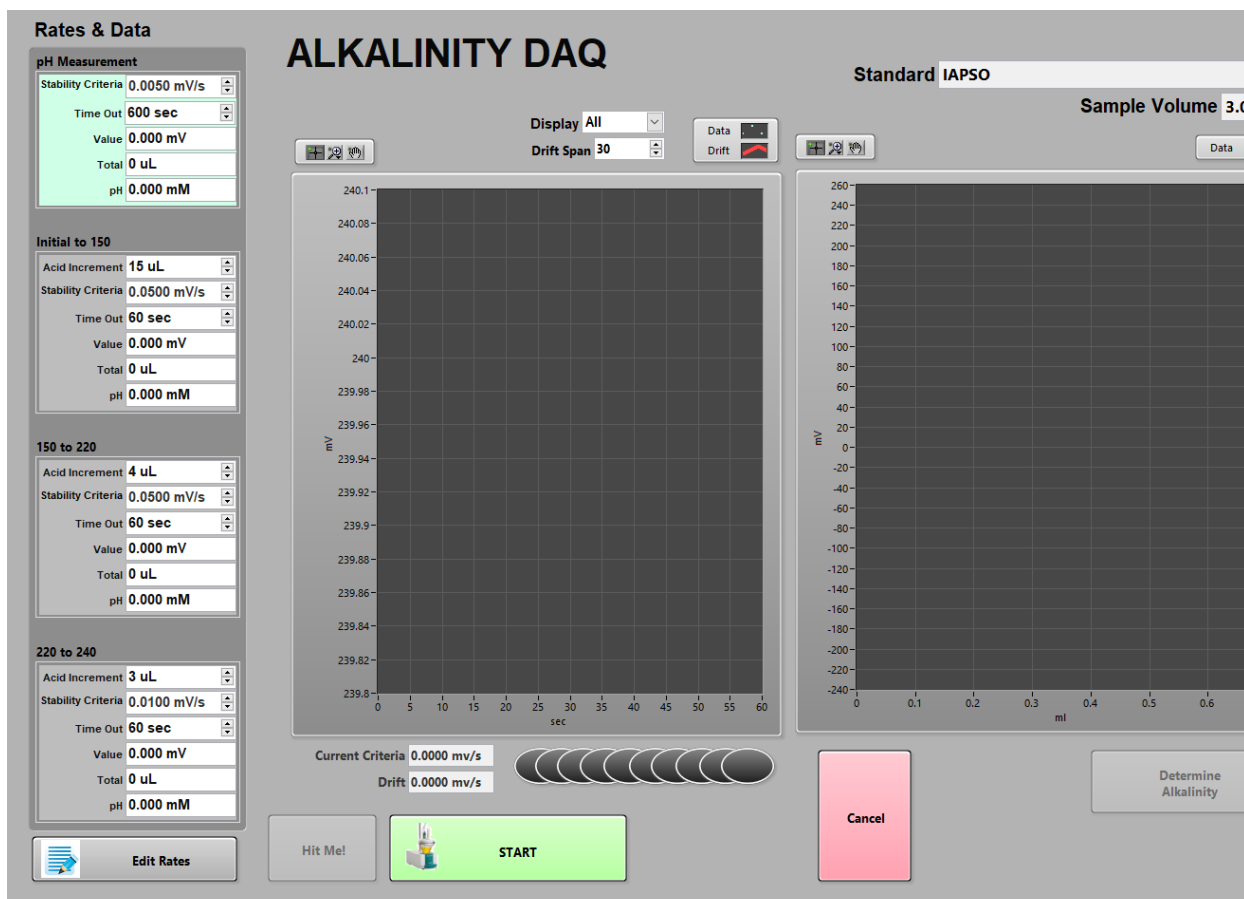**Figure 5. Entering standard information.**

Figure 6. Measuring a standard for standard ratio correction.

1. Place 3 ml of standard in vessel. Add stir bar and immerse electrode in vessel. Confirm that the frit is in the solution. Check that your **Drift Span** is 30.
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.

Managing standard values
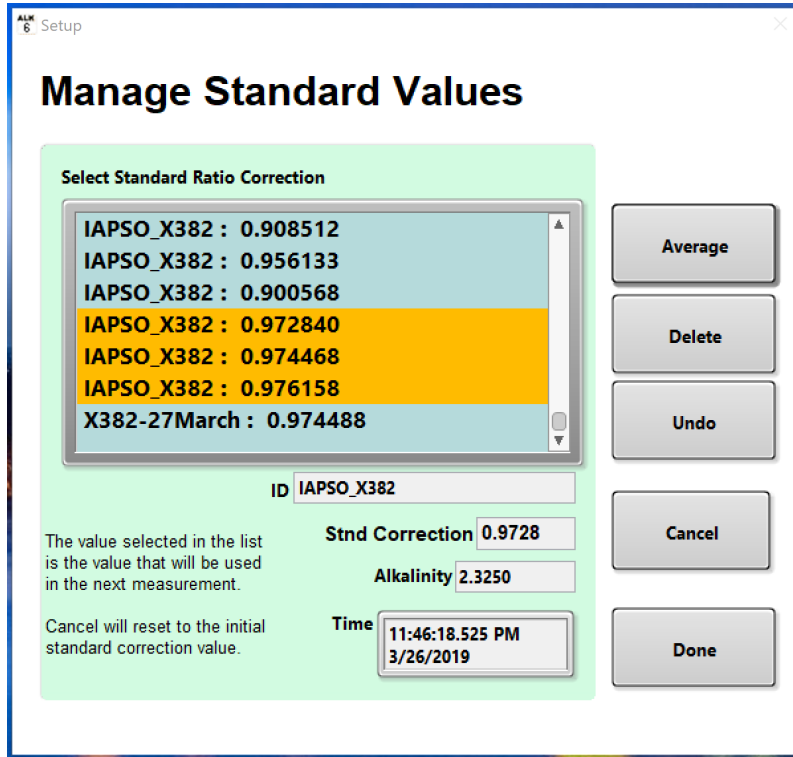
Select **STND Manager** from the Main instrument panel.

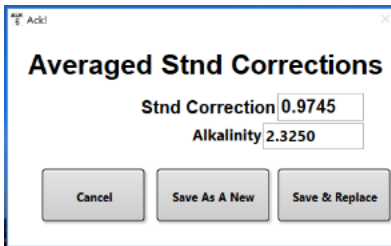**Figure 7. Averaging standard measurements.**

Figure 8. Saving the averaged standard correction.

1. Select the three measurements you want to average and click **Average**.
2. The small window 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).

To select a standard ratio correction for subsequent measurements go to **Setup** in the Main alkalinity interface.
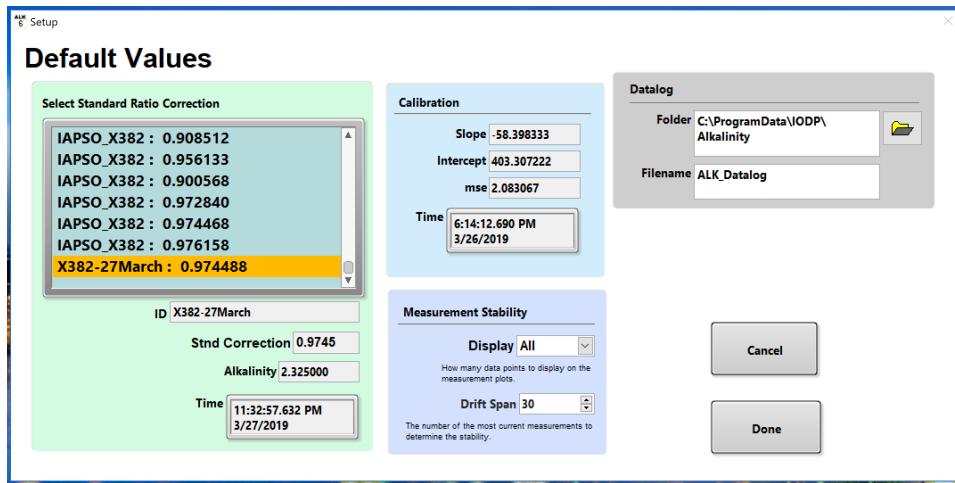
Figure 9. Selecting the standard ratio correction file to use.

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.

Drift span

A drift span of 30 (default) indicates that a minimum of 30 measurements will be taken after each addition of titrant (acid). The difference between the first and last measurements is compared to the stability criteria specified in the dispensing rate program. Stability criteria acts as follows:

If the difference between the first and the last measurement is smaller than the stability criteria, the next increment of acid will be dispensed.

If the difference between the first and the last measurement is larger than the stability criteria, measurement will continue at that increment until the stability criteria is satisfied.
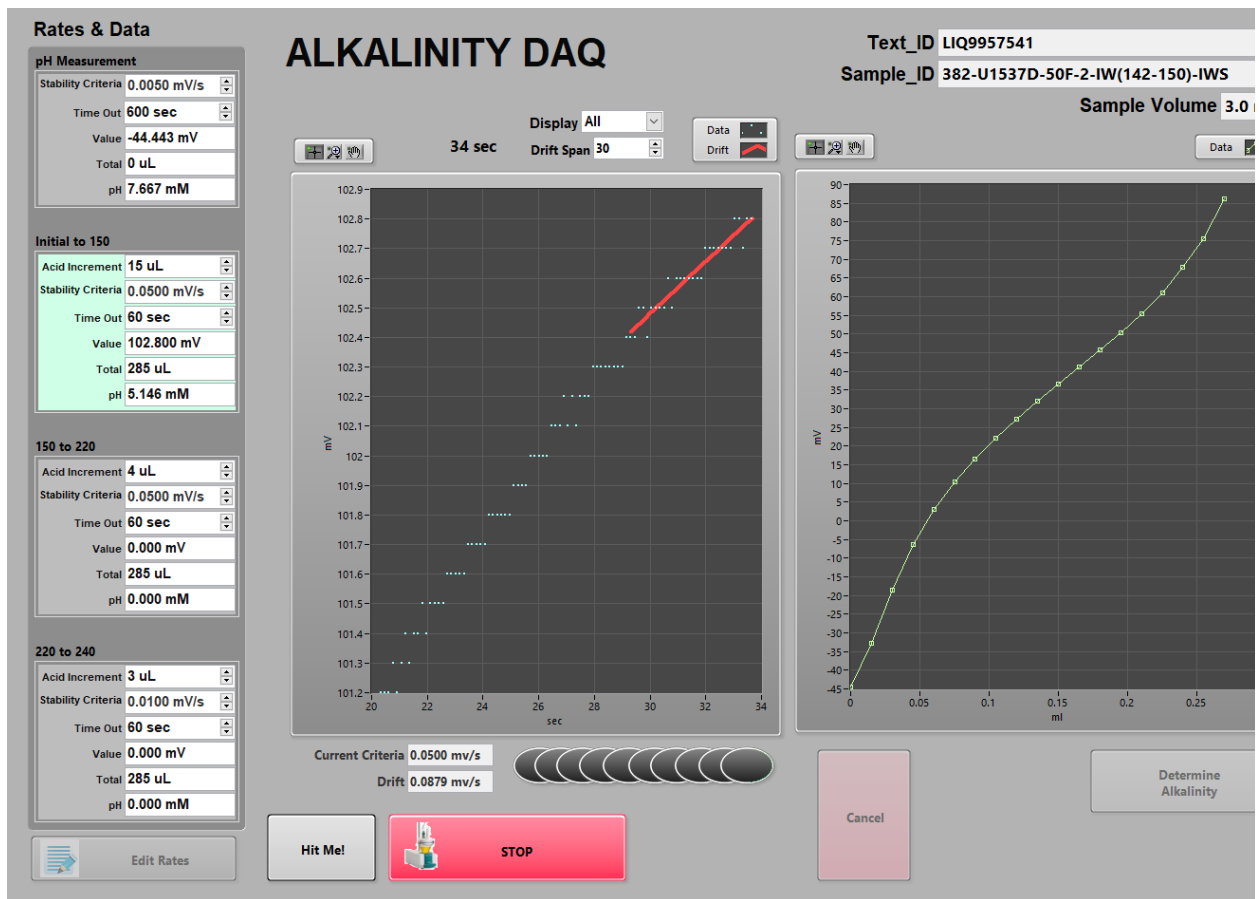
Figure 10. Drift Span.

Sample preparation and analysis

Sample storage and preservation

Use 3 ml of interstitial water sample (usually pipetted from the IWS vial). Store residual sample in a 5 ml snap cap tube for additional shipboard analysis.

Sample preparation and analysis

The laboratory technician receives a whole-round sample at the catwalk to squeeze for interstitial water, which is passed through a 0.45 µm filter before analyzing pH and alkalinity. Note that RHIZON samples will produce incorrect pH and alkalinity values and should not be analyzed.

The general procedure for analyzing pH and alkalinity on interstitial water samples is as follows:

1. Pipette a 3 mL sample into the titration vessel and add stir bar.
2. Take an initial pH reading.
3. Titrate to determine total equivalent alkalinity value.
4. Upload data to LIMS.
5. Store titrated sample in a sealed cryo vial.

Entering sample information

The system should now be calibrated and dispensing rate as well as the 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 (*Figure 1*). 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.

Figure 11. Entering sample information.

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 useful 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**.
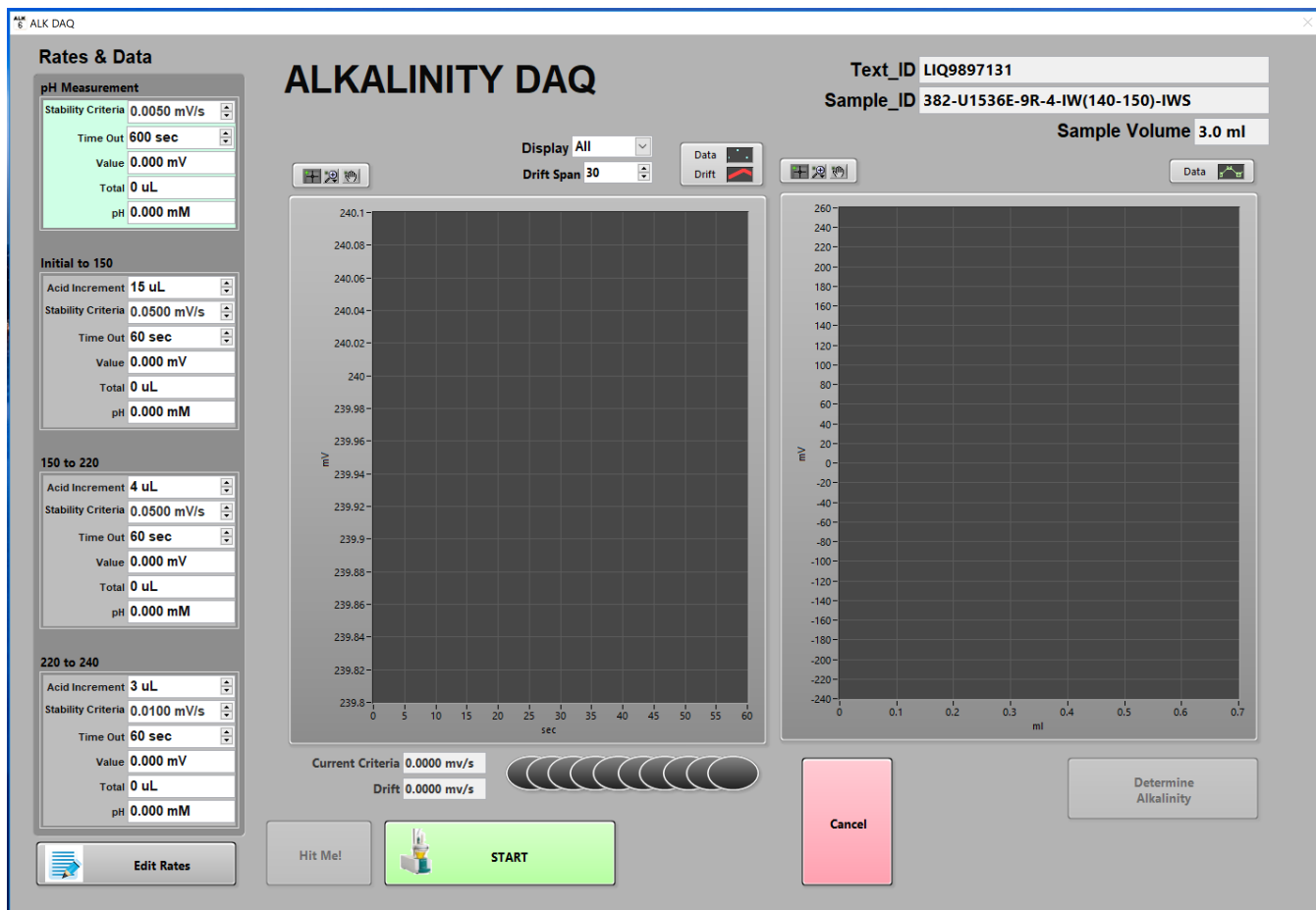
Figure 12. Alkalinity data acquisition window.

Click **START**. The software will guide you through.
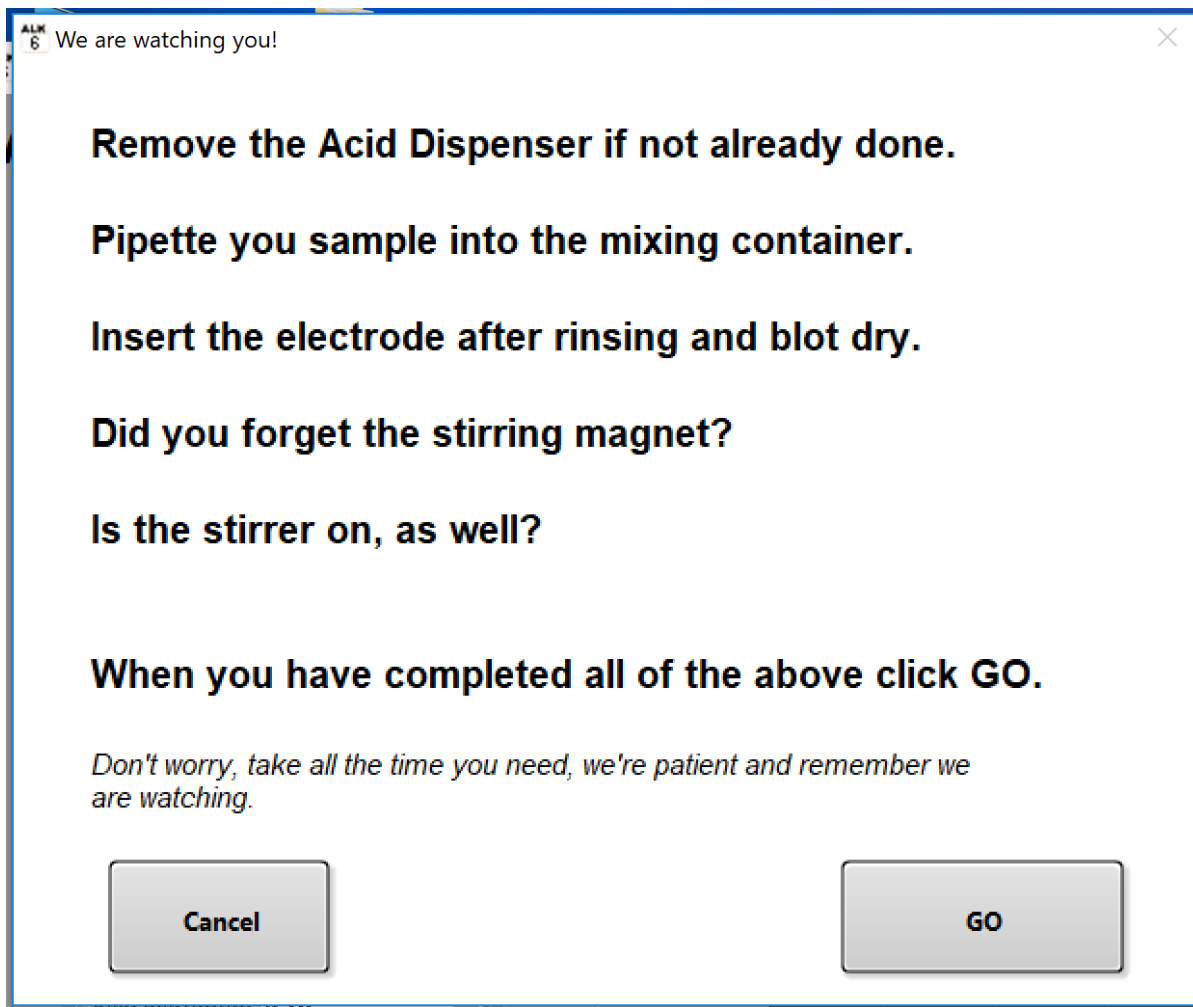
Figure 13. Reminders before starting the pH measurement.

After completing all the steps in the guide window, click **GO**. The pH measurement will commence.

Measuring pH

The titrator measures and records the pH value for each sample before titration for alkalinity begins.

Figure 14. Measuring pH.

Once the pH measurement is complete, you will be reminded about the acid dispenser.

Figure 15. Acid dispenser reminder prior to starting the alkalinity measurement.

Insert acid dispenser probe when prompted. Click **GO**.

Measuring alkalinity

The alkalinity titration is automatic once you have inserted the acid dispenser probe and clicked **GO**. The plot on the left side displays the 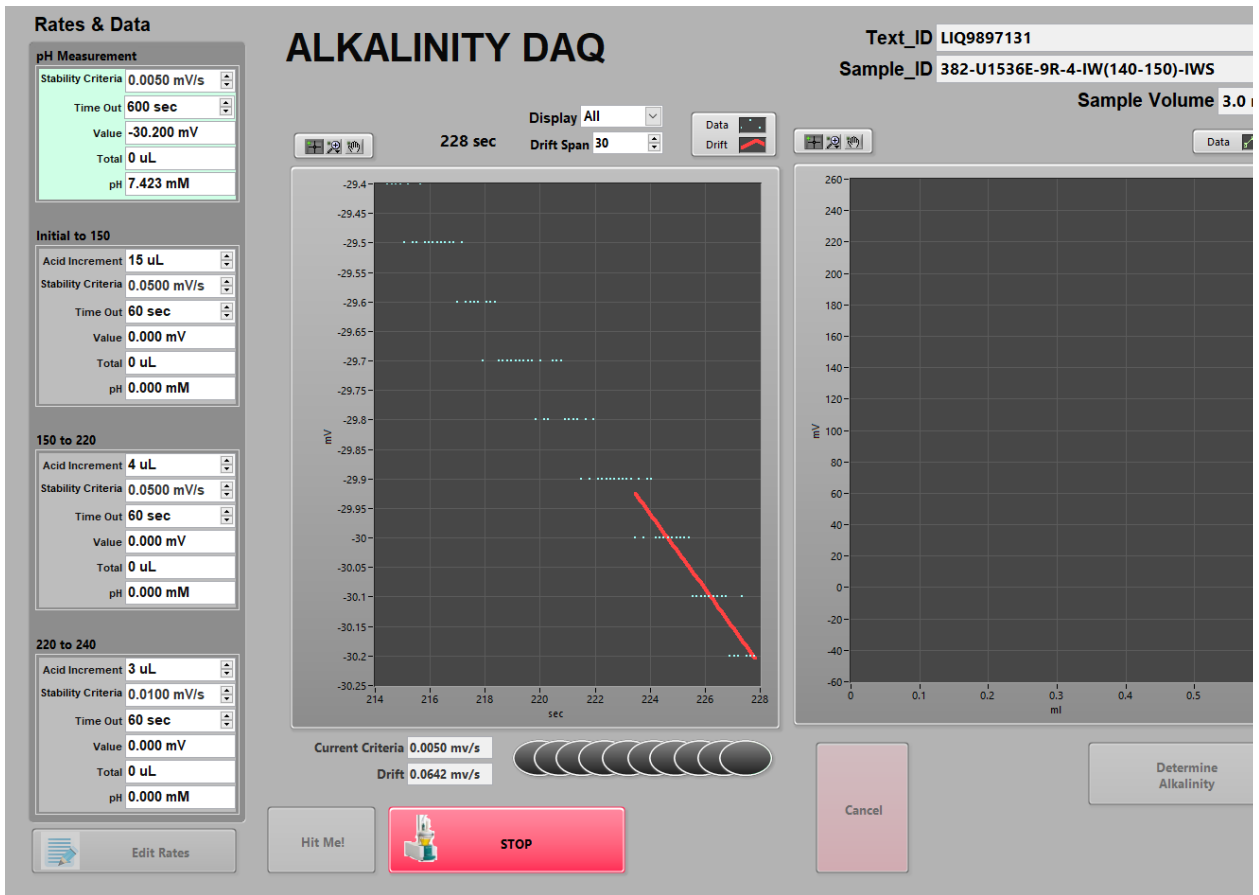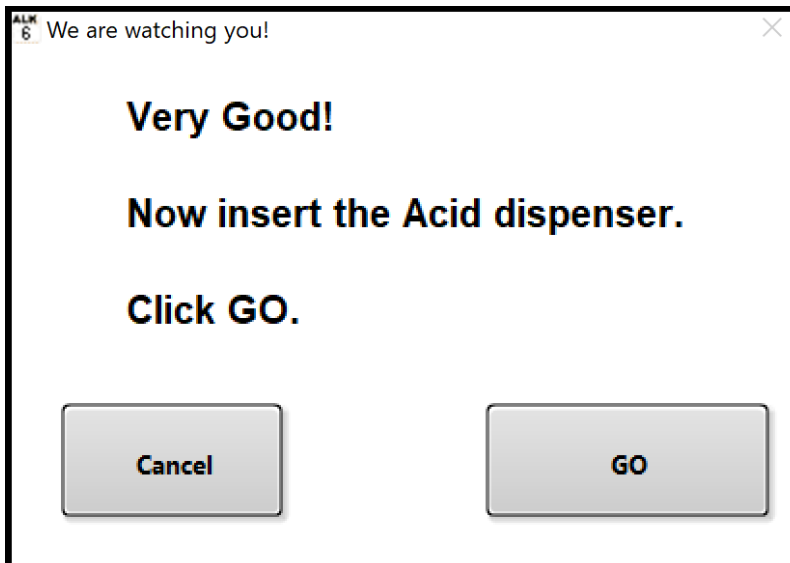signal coming directly from the electrode in real time. The y-axis is the mV reading, and the x-axis is time in seconds. The readings will continue until the stability criteria is satisfied, which provides a final mV reading. The green trend on the plot right side of the figure is the trend of mV readings vs. acid additions in ml. The mV readings come from the final value reached upon satisfying the stability criteria.
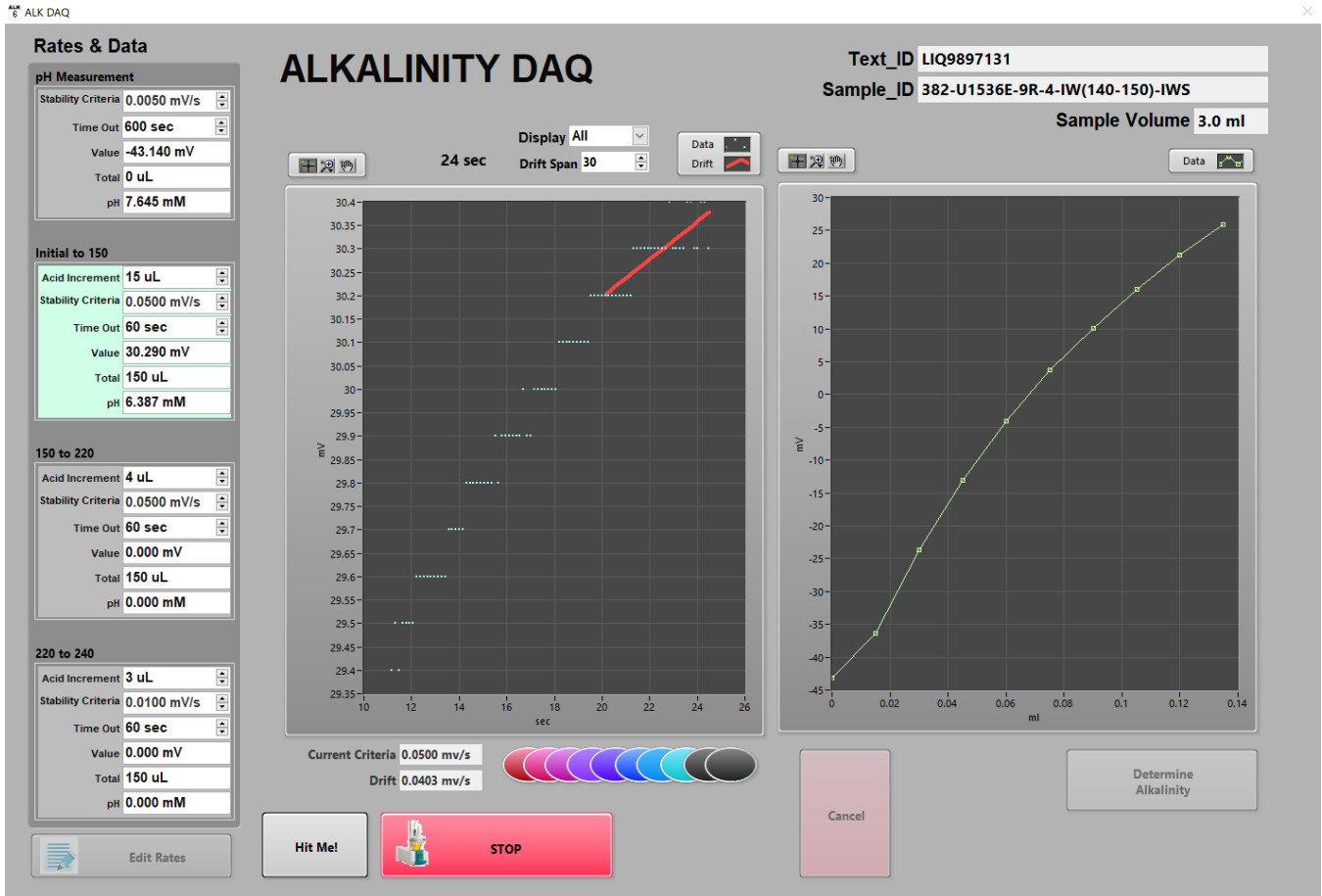

Figure 16. Measuring Alkalinity.

The alkalinity titration will continue through the three stages of the dispensing rate program. The software will let you know once the analysis is complete.

Figure 17. Analysis complete.

Analysis is complete. Click **OK**. This will take you to the Gran-method window.
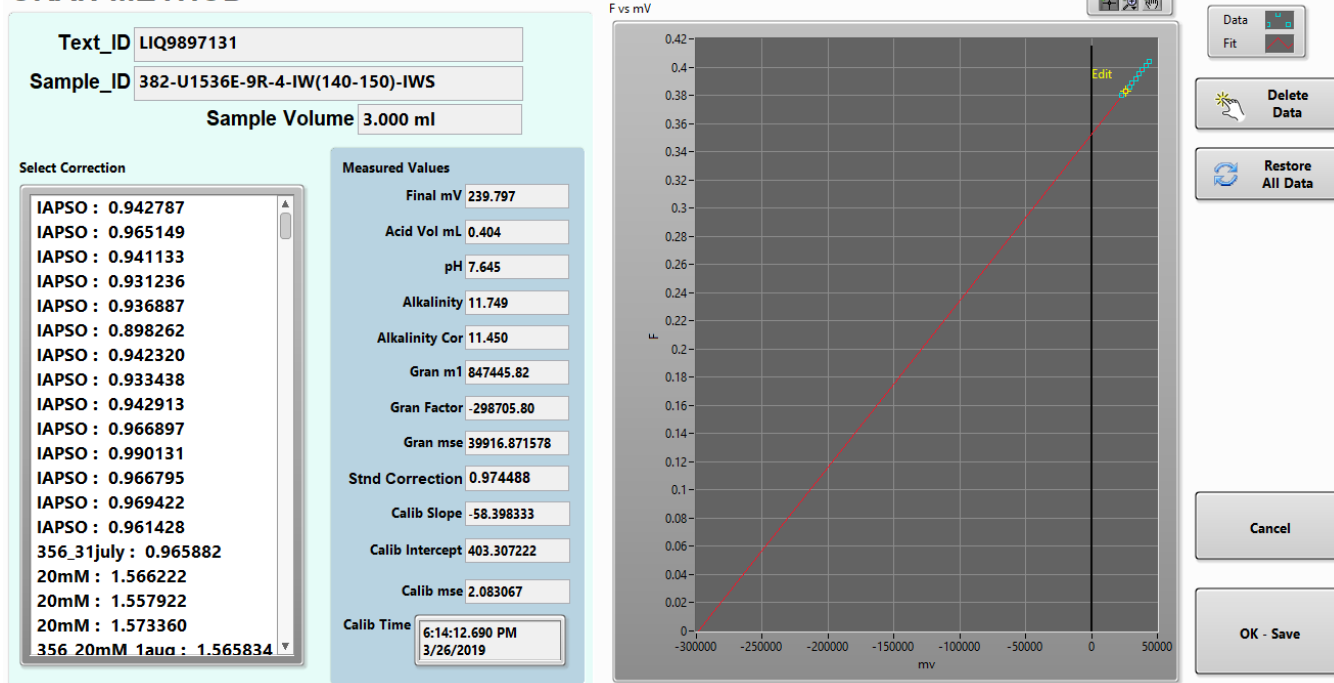
Figure 18. Gran-method window.

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

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

Cleaning up after measurement

1. Remove electrode from cup.
2. Rinse electrode with DI water in squeeze bottle.
3. Blot the electrode dry with a Kimwipe. Do not rub the electrode, which could cause static charge buildup.
4. Place the electrode in a storage container containing 3 M KCl.
5. Rinse and dry the acid dispensing tip and stir bar.
6. Pipette or pour the titrated alkalinity IW sample into a container to ship to repository or scientist.
7. Write on label how much HCl was added during titration.
8. Rinse the titration vessel cup with DI water and dry.

Data handling

Editing Gran factor points

Outlier Gran factor points can be deleted from the linear portion of the curve to improve the accuracy of sample results as follows:

1. When the titration is complete, the **Calculations** window opens.
2. Zoom in on the Gran factor points.
3. Select the point to be deleted.
4. Click **Delete Data**. This will only delete the selected point. Click **Ok - Save** when finished.
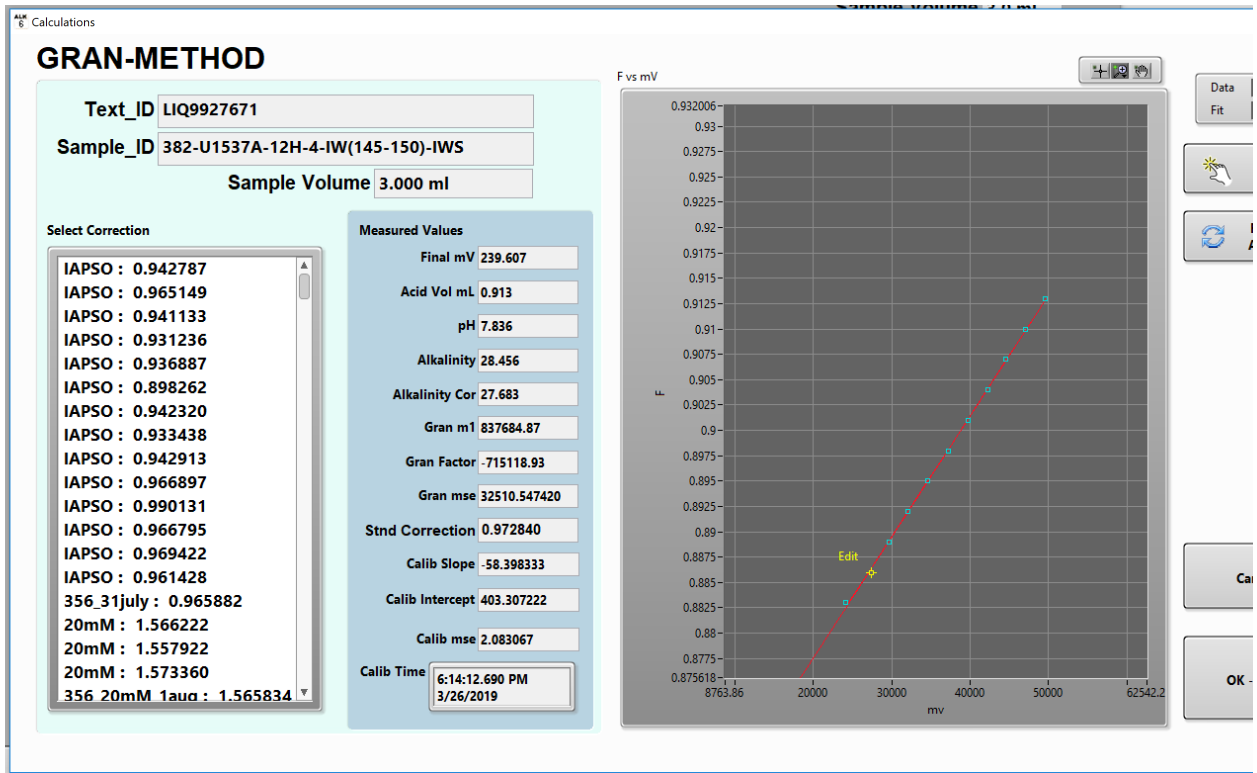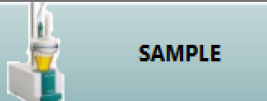
Figure 19. Editing Gran factor points.

Data reports

Data reports are not available at the instrument, but data can be viewed by selecting **View Datalog** (*Figure 20*) from the Main instrument panel. Also, the software appends the alkalinity results to the DAT file *C:\ProgramData\ODP\Alkalinity.* The best way to view the alkalinity values is via LIMS Reports. It is also highly recommended to record the alkalinity and pH values in the blue laboratory notebook to protect against inadvertent data loss.
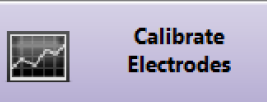
ALKALINITY
v6.5

SAMPLE

STANDARD

Calibrate
Electrodes

◯ LIMS Status

◯ Calibration Status

```
Calibration:26/03/2019-1814
Slope = -58.3983
Intercept = 403.3072
mse = 2.083067

Stnd Correction:27/03/2019-2332
ID = X382-27March
Stnd Cor = 0.974488
```

Setup

Edit
Rates

STND Manager

mV
Measurement

Force
Init

Fill

View Datalog

Quit

Datalog Entries

Type	Text_ID	Sample_ID		Top	Btm	Date - Time		
Sample	LIQ9898121	382-U1536E-12R-3-IW(141-151)-		440.09	440.19	19-04-19 20:02:093 UTC		
	ALK	ALK Cor	pH	Sample Vol	Acid Vol	CAL Date		
	0.0000	0.0000	0.00	3.00	0.00	19-03-26 18:14:123 UTC		
Status		STND Cor	STND Name		STND Alk	CAL M0	CAL M1	CAL MSE
Aborted		0.000000	X382-27March		2.3250	403.307222	-58.398333	2.083067

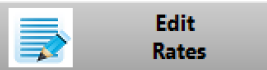| Type	Text_ID	Sample_ID		Top	Btm	Date - Time		
Sample	LIQ9898121	382-U1536E-12R-3-IW(141-151)-		440.09	440.19	19-04-19 20:44:233 UTC		
	ALK	ALK Cor	pH	Sample Vol	Acid Vol	CAL Date		
	10.0231	9.7674	7.80	3.00	0.35	19-03-26 18:14:123 UTC		
Status		STND Cor	STND Name		STND Alk	CAL M0	CAL M1	CAL MSE
Saved		0.974488	X382-27March		2.3250	403.307222	-58.398333	2.083067

Type	Text_ID	Sample_ID		Top	Btm	Date - Time		
Sample	LIQ9899271	382-U1536E-15R-3-IW(144-151)-		466.17	466.24	19-04-20 02:05:393 UTC		
	ALK	ALK Cor	pH	Sample Vol	Acid Vol	CAL Date		
	9.5958	9.3510	7.85	3.00	0.34	19-03-26 18:14:123 UTC		
Status		STND Cor	STND Name		STND Alk	CAL M0	CAL M1	CAL MSE
Saved		0.974488	X382-27March		2.3250	403.307222	-58.398333	2.083067

Type	Text_ID	Sample_ID		Top	Btm	Date - Time		
Sample	LIQ9900981	382-U1536E-19R-3-IW(140-150)-		505.80	505.90	19-04-20 11:12:443 UTC		
	ALK	ALK Cor	pH	Sample Vol	Acid Vol	CAL Date		
	7.3725	7.1844	7.83	3.00	0.27	19-03-26 18:14:123 UTC		
Status		STND Cor	STND Name		STND Alk	CAL M0	CAL M1	CAL MSE
Saved		0.974488	X382-27March		2.3250	403.307222	-58.398333	2.083067

Type	Text_ID	Sample_ID		Top	Btm	Date - Time		
Sample	LIQ9901821	382-U1536E-21R-2-IW(141-151)-		523.51	523.61	19-04-20 14:03:083 UTC		
	ALK	ALK Cor	pH	Sample Vol	Acid Vol	CAL Date		
	6.3477	6.1857	7.76	3.00	0.24	19-03-26 18:14:123 UTC		
Status		STND Cor	STND Name		STND Alk	CAL M0	CAL M1	CAL MSE
Saved		0.974488	X382-27March		2.3250	403.307222	-58.398333	2.083067

Type	Text_ID	Sample_ID		Top	Btm	Date - Time		
Sample	LIQ9902871	382-U1536E-24R-1-IW(138-148)-		550.78	550.88	19-04-20 19:45:023 UTC		
	ALK	ALK Cor	pH	Sample Vol	Acid Vol	CAL Date		
	5.4845	5.3446	8.09	3.00	0.21	19-03-26 18:14:123 UTC		
Status		STND Cor	STND Name		STND Alk	CAL M0	CAL M1	CAL MSE
Saved		0.974488	X382-27March		2.3250	403.307222	-58.398333	2.083067

Figure 20. Datalog.

Quality assurance/quality control

Overview

A quality assurance/quality control (QA/QC) program ensures that a measurement system is performing within control limits and therefore provides high-quality data. The QA/QC program for this system includes instrument calibration, calibration verification, and accuracy and precision monitoring.

Instrument calibration

The instrument is calibrated by the onboard laboratory specialist at the beginning of the expedition. Calibration is verified routinely during operation.

Analytical batch

An analytical batch is a group of samples run together in one sequence, sharing a calibration curve, blanks, reference materials, and verification samples. The alkalinity batch size is 10 samples. Each batch of 10 unknown samples contains a sample to verify precision and a sample to verify accuracy.

Blanks

Blanks are not run for this method because DI water has no buffering capacity and would therefore fail the slope program. Thus, blanks are not applicable to this chemistry.

Calibration/calibration verification

–	The electrode is calibrated against pH buffers at the beginning of each expedition.
–	Borax/IAPSO standard ratio corrections at generated at the beginning of each expedition.
–	Recalibration is performed when precision or accuracy is not within ±5%.

Precision

Precision is the degree to which further measurements will show the same or similar results.

–	Duplicates are not run on samples because that would require using 6–10 mL of the interstitial water, which is usually too large a sample amount to justify. Instead, duplicate calibration verification samples (e.g., duplicate IAPSO standard measurements) are compared to calculate precision. Select a standard close to the alkalinity value of the IW samples being analyzed if possible.
–	Precision is measured with every batch of 10 samples.
–	Precision control limit allows a difference of ±5%.
–	If the precision control limit is exceeded, the system must be recalibrated and all samples run since the previous in-control precision measurement must be repeated.

Accuracy

Accuracy is the degree of closeness of a measured value to the actual (true) value.

–	Standards are run with every batch of 10 samples. Select a standard close to the alkalinity value of the IW samples being analyzed if possible.
–	Accuracy control limit allows a difference of ±5% from true standard value.
–	If the accuracy control limit is exceeded, the system must be recalibrated and all samples run since the previous in-control accuracy measurement must be repeated.

Limits of detection and quantitation

–	Samples are not reported as less than the detection limit for alkalinity. The only way a sample could not be analyzed is if its initial pH (before acid addition) is <4.2, which is rare.
–	Results are reported to three decimal places.
–	The titration uncertainty is ±0.003 ml. When carried through the alkalinity calculation, this uncertainty results in the alkalinity difference being 50 µM, though it is also dependent on the starting pH.

Software dataflow

Two primary data types are generated by this system: pH and alkalinity. The alkalinity measurement depends on a series of pH measurements, thus the pH value of the sample is determined before the alkalinity titration begins.

pH dataflow

Calibration

User-configurable variables include the following (*Figure 21*). Refer to drift span for more information about these values:

$mVSpan: drift span; number of samples to determine the slope (default = 30); the slope calculation is

$$N\text{current sample} – N[(\text{current sample}) – \$mVSpan]$$

$mVthreshold: slope threshold; maximum calculated value for the reading to be considered stable; also stability criteria.
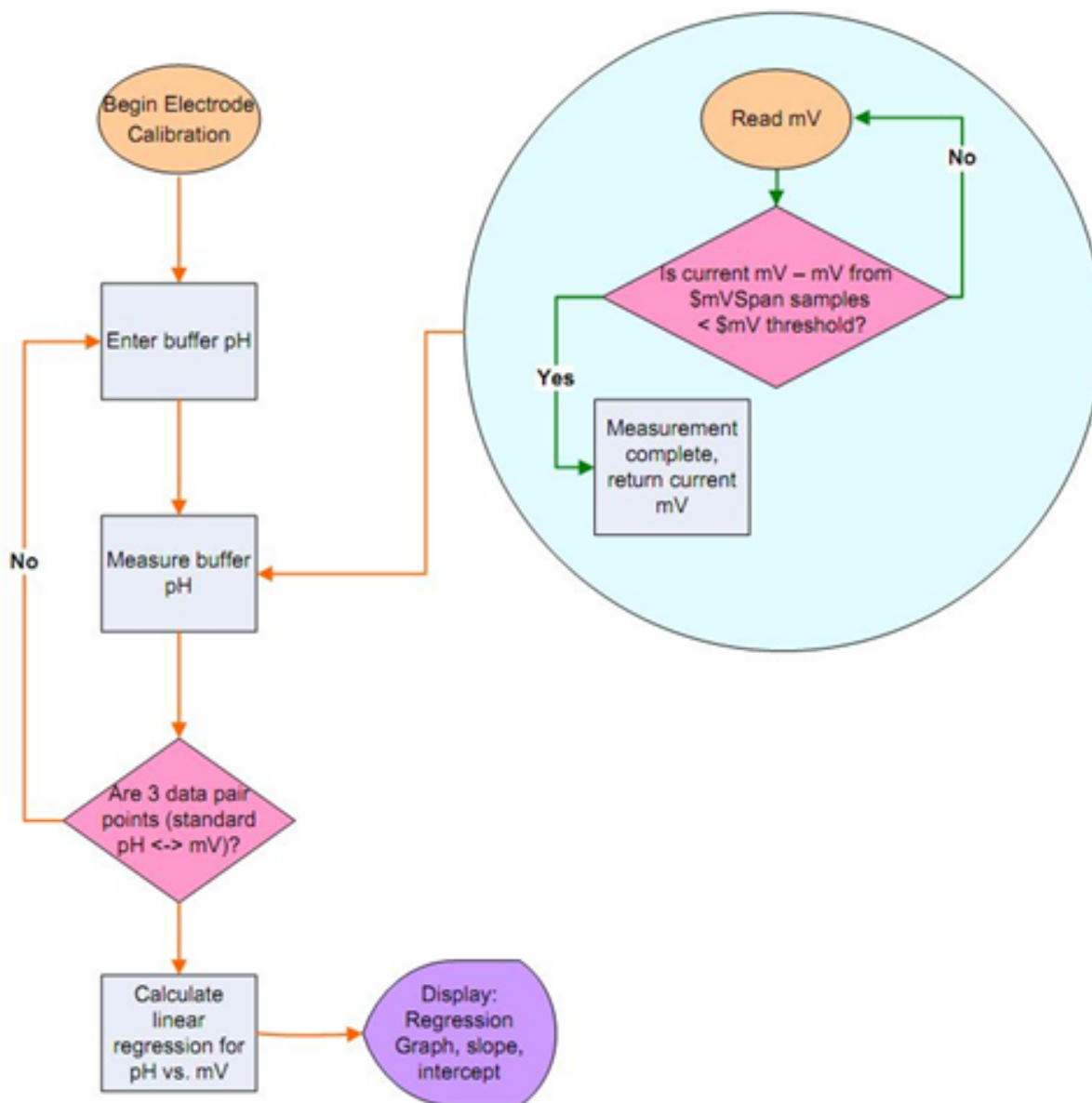
Figure 21. Alkalinity electrode calibration dataflow.

Alkalinity dataflow

User-defined variables (*Figure 13*), with values from the example given in the Dispensing rate section:
$MV1: rate 1 mV threshold (150 mV)
$MV2: rate 2 mV threshold (220 mV)
$MV3: rate 3 mV threshold (240 mV)
$Rate1: rate for first mV threshold (15 µl)
$Rate2: rate for second mV threshold (4 µl)
$Rate3: rate for third mV threshold (3 µl)
$SlopeSpan: number of samples used to calculate the slope (default = 30)
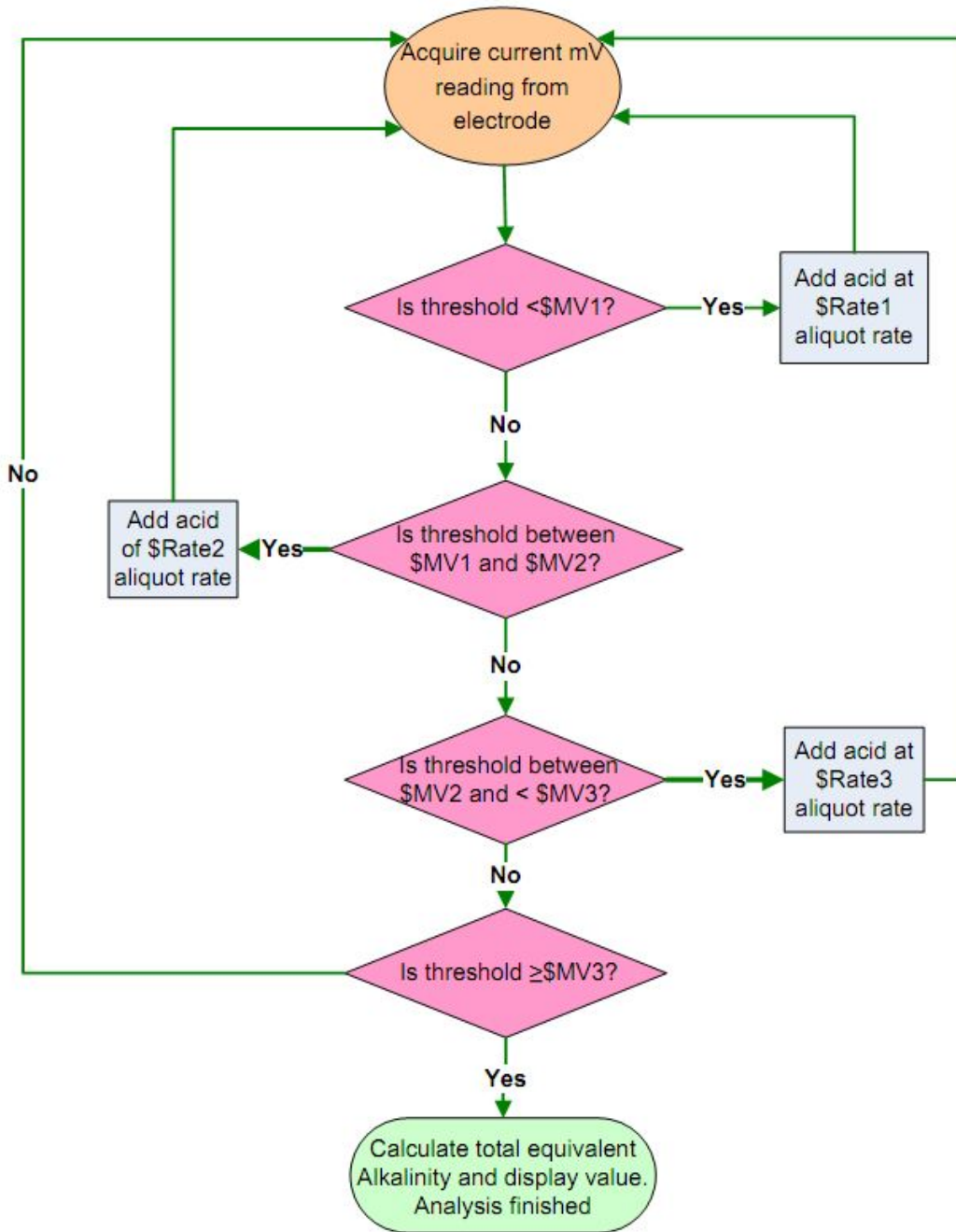**$StabilityThreshold:** maximum slope value to ensure a stable reading (also referred to as stability criteria)

Figure 22. Alkalinity measurement data flow.

LIMS integration

In LIMS terminology, we perform two types of alkalinity analyses: ALKALINITY and ALK_QAQC:
ALKALINITY analyses include pH and alkalinity tests performed on interstitial water samples.
ALK_QAQC includes the same physical tests performed on a calibration standard or standard sample.
ALK_QAQC analysis has three different variations:
CALIBRATE: tests done to calibrate the autotitrator
STANDARD: standard analyses
REPLICATE: duplicate sample analyzed to check precision and/or accuracy

LIMS stores several components of each analysis, which are detailed in the chart below.

Analysis	Component	Unit	Description
ALKALINITY	alkalinity	mM	Ability of a solution to neutralize acid to the equivalence point of carbonate
	pH	NA	Acidity or basicity of a solution ($-\log[H+]$)
	acid_quantity	µl	Amount of 0.1 M HCl added to the sample during titration
	correction_factor	—	Correction factor for non-ideal behavior of samples to adjust calibration
ALK_QAQC	alkalinity	mM	Ability of a solution to neutralize acid to the equivalence point of carbonate
	pH	NA	Acidity or basicity of a solution ($-\log[H+]$)
	acid_quantity	µl	Amount of 0.1 M HCl added to the sample during titration
	correction_factor	—	Correction factor for non-ideal behavior of samples to adjust calibration
	slope	—	Slope of the calibration equation
	intercept	—	Intercept value of the calibration equation
	corr	Rho	Correlation coefficient of the calibration

Uploading data to LIMS

When the alkalinity titration finishes, the GRAN-METHOD window shows the slope information, correction factors, and the final alkalinity value (*Figure 18*). Edit outlier Gran factor points, if necessary. When satisfied with the results, click **Ok**/**Save** to load the values into LIMS.

Health, safety and environment

Safety

Wear personal protective equipment including close-toed shoes, lab coat, gloves and safety glasses when working with acids of any strength.
Use a fume hood when making solutions from concentrated acids.

Pollution prevention

Make reagent and standard solutions in quantities no larger than needed to complete sample analysis.

Waste management

Neutralize acid solutions before disposal.

Maintenance/Troubleshooting

–	Make sure the probe storage container is filled with 3 M KCl solution and the reservoir is filled with 0.1 M HCl solution.
–	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 and remove air bubbles.
–	Change out the Drierite trap when ~50% of the color turns from blue to pink.
–	In case of a bubbling noise, top up your temperature-controlled water bath. Use tap water. Check titration vessel for air space and eliminate if present.

Consumables

Electrode: Metrohm 6.0234.100 or equivalent.
0.1   M HCl, Fisher CH5009
Microvalve buret tip, Metrohm 020683244, CM5129