

# Autotitrator pH/Alkalinity User Guide

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## Introduction

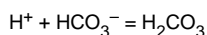
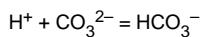
### Method overview

Alkalinity is the measure of how much acid it takes to lower the pH of a water sample enough to convert all bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) to carbonic acid ( $\text{H}_2\text{CO}_3$ ). 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.



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:

$$F = (v + V_0) \times 10^{E/A}$$

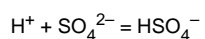
where:

- 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  $25^\circ\text{C}$ . 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



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





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

## Equipment

- Metrohm 794 Basic Titrino autotitrator
- Metrohm 728 Stirrer
- Haake P5 water bath
- Combination electrode (Metrohm, combined pH glass electrode, model 6.0234.100)
- LabVIEW Alkalinity program v6.

## Reagents

- 0.1 M HCl solution (premade from Fisher, AMS# CH5009)
  - Used as titrant. Fills titration reservoir.
- 3 M KCl solution (224 g KCl in 1 l reagent water)
  - Electrode solution
- NBS buffers: commercially obtained low ionic strength solutions at pH 4.00, 7.00, and 10.00 (stable indefinitely; store in the chem lab refrigerator when not in use)
  - Used to calibrate the electrode

## Standards

- IAPSO standard seawater (alkalinity ~2.325 mM)
- Higher alkalinity standards:
  - Stock standard solutions (1 l)
    - 0.5 M NaHCO<sub>3</sub> (42 g sodium bicarbonate in 1 l reagent water)
    - 0.5 M Na<sub>2</sub>CO<sub>3</sub> (53.0 g sodium carbonate in 1 l reagent water)
    - 0.1 M Na<sub>2</sub>CO<sub>3</sub> (10.6 g sodium carbonate in 1 l reagent water)
  - Standard solutions (100 ml)
    - 100 mM alkalinity (pipet 10 ml 0.5 M Na<sub>2</sub>CO<sub>3</sub> into 90 ml 0.7 M KCl)
    - 50 mM alkalinity (pipet 10 ml 0.5 M NaHCO<sub>3</sub> into 90 ml 0.7 M KCl)
    - 40 mM alkalinity (pipet 20 ml 0.1 M Na<sub>2</sub>CO<sub>3</sub> into 80 ml 0.7 M KCl)
    - 20 mM alkalinity (pipet 10 ml 0.1 M Na<sub>2</sub>CO<sub>3</sub> into 90 ml 0.7 M KCl)

## Instrument Setup and Calibration

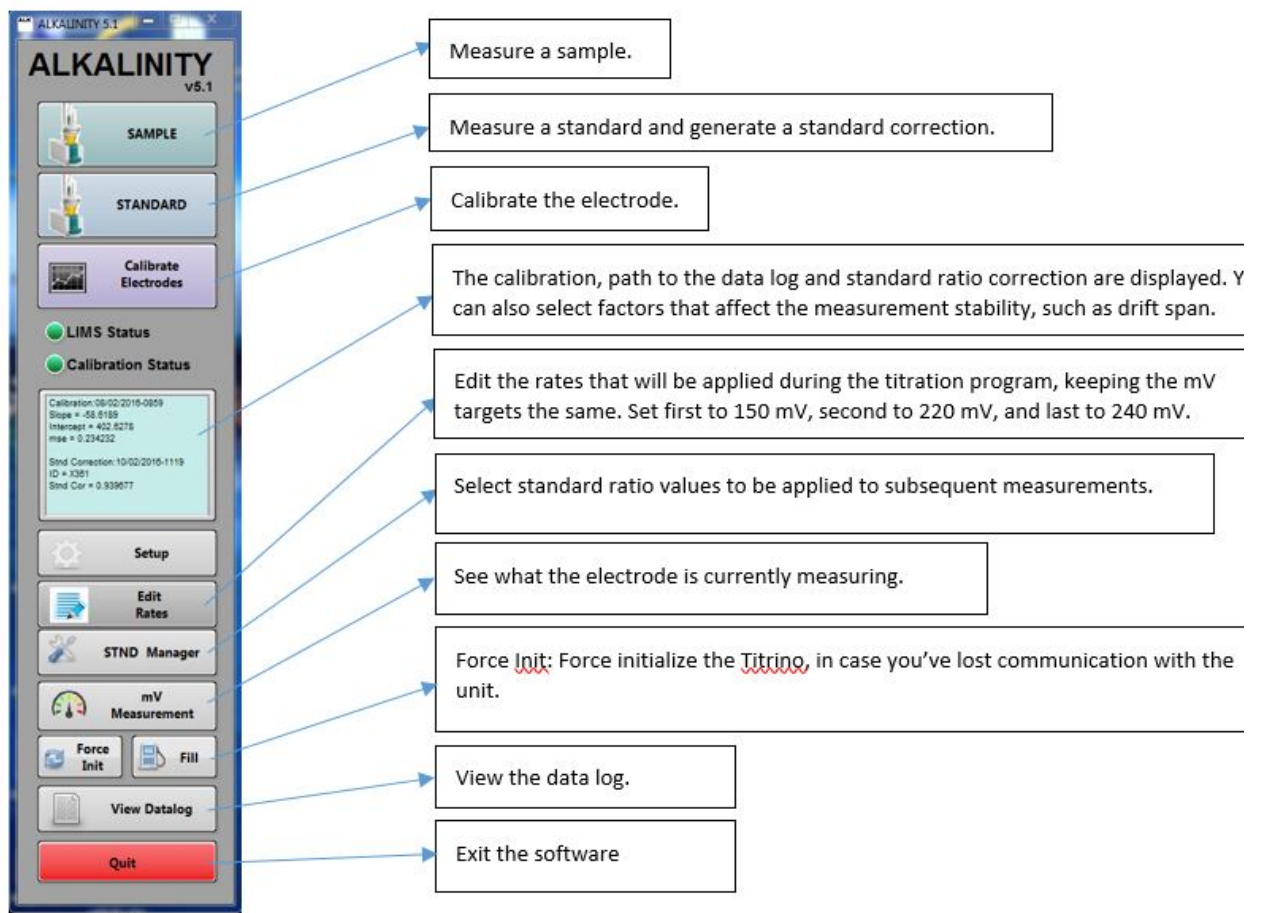


Figure 2. Main instrument panel.

## 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. Make sure the gray side-hole plug for the electrode is unplugged before starting a measurement.

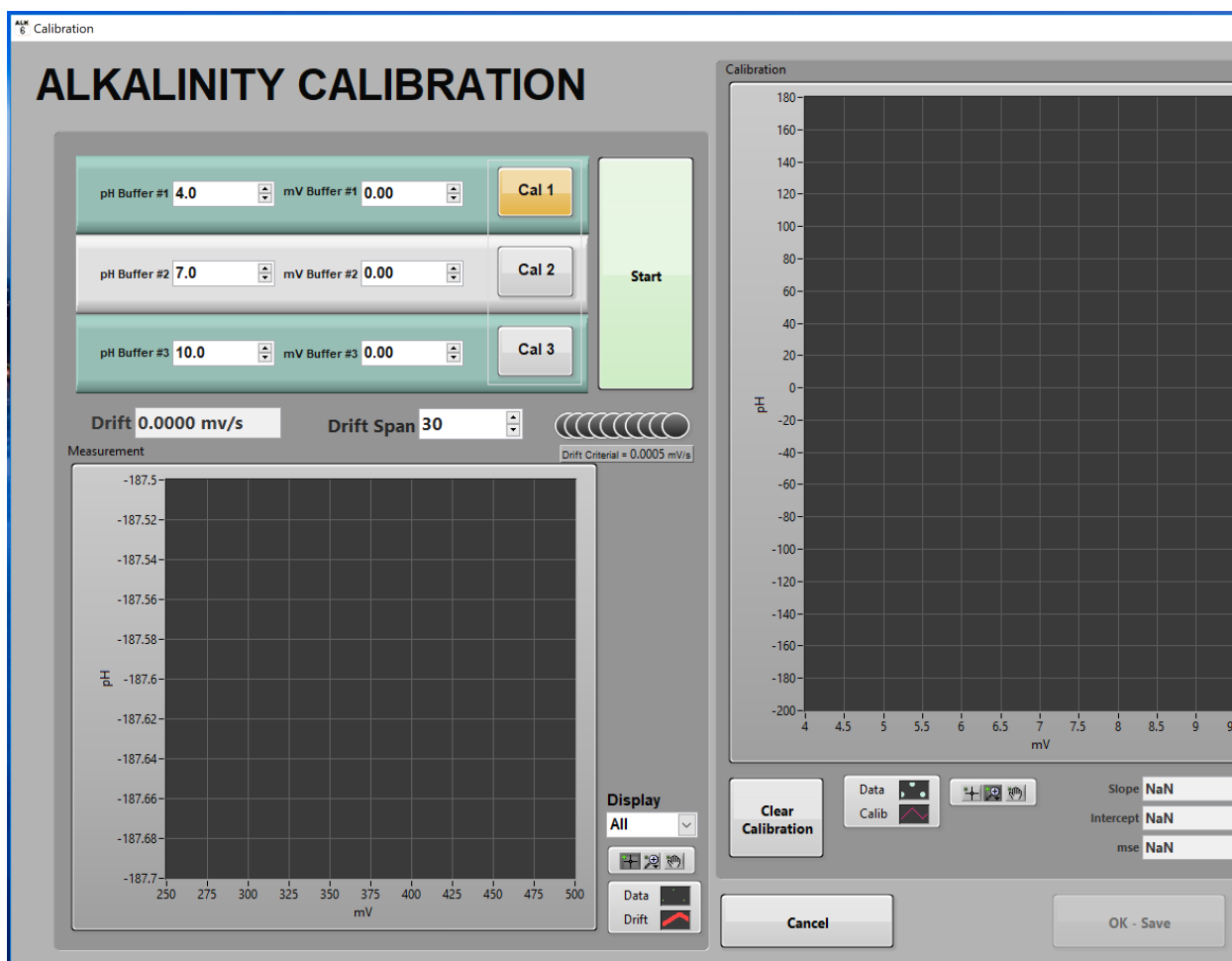
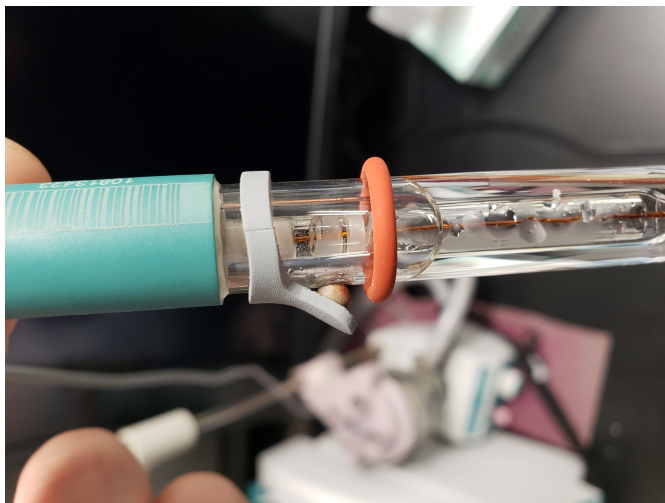


Figure 3. Electrode calibration.

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.

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**.

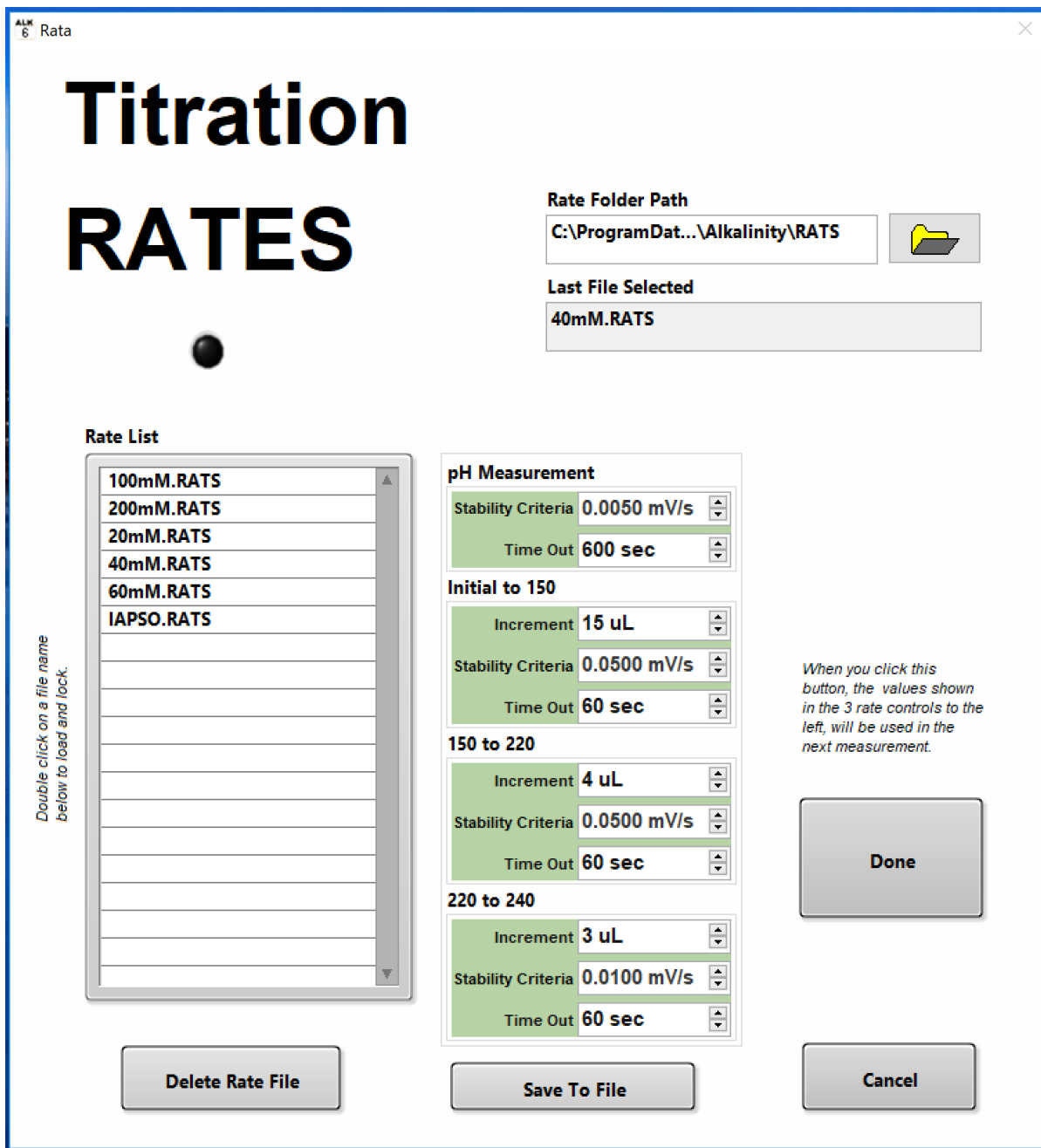


Figure 4. Selecting a dispensing rate.

## 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

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.

ALM 6 Enter Standard

## Enter Standard Information

Standard\_ID IAPSO

Sample Volume 3.000 ml

Sample Alkalinity 2.325 mM

Cancel

Continue

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 turn stirrer on
2. Rinse and dry the electrode and then immerse the electrode in the vessel. Confirm that the frit is in the solution. Check that your **Drift Span** is 30.
3. Select **Continue**.
4. Click **START**.
5. Insert the acid dispensing probe when prompted.
6. 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](#).

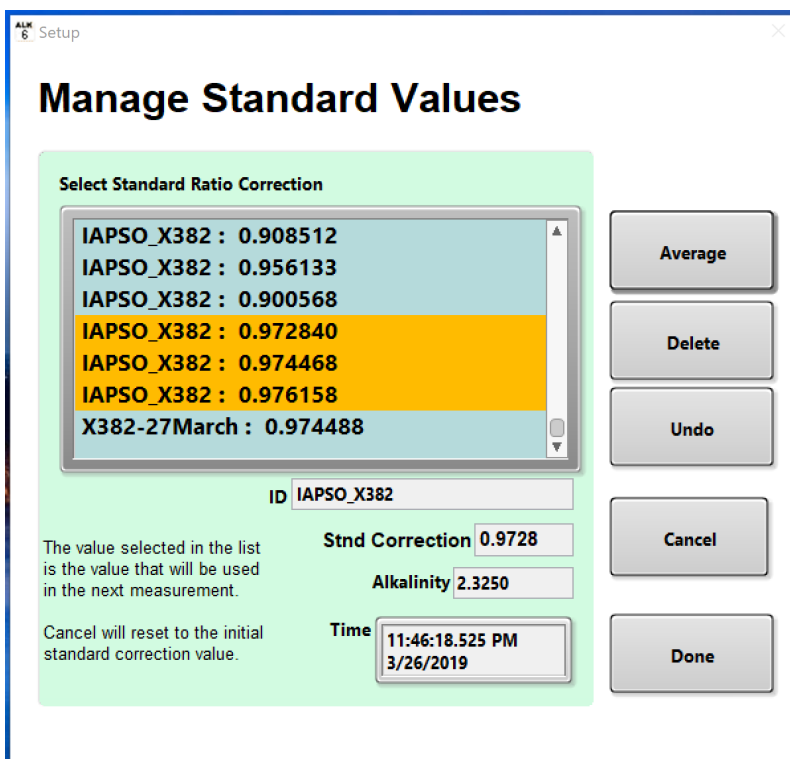


Figure 7. Averaging standard measurements.

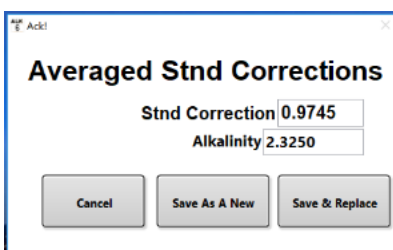


Figure 8. Saving the averaged standard correction.

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](#).

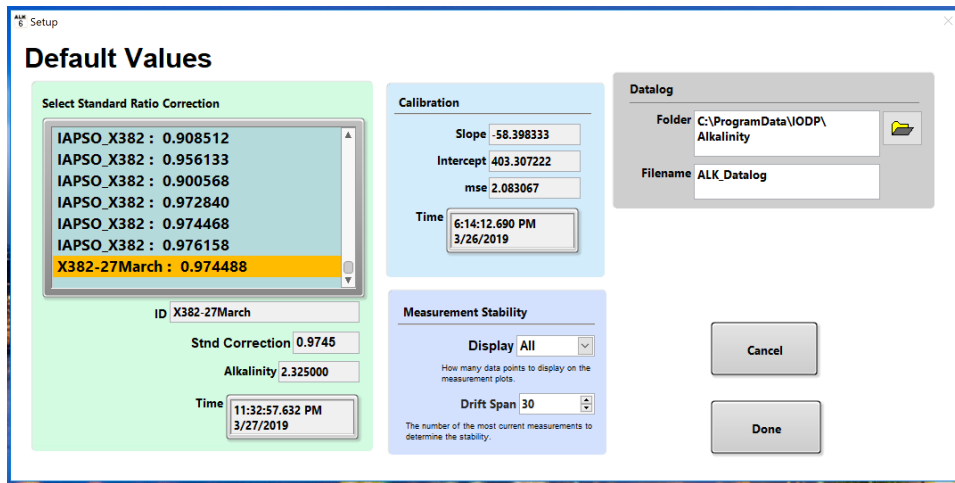


Figure 9. Selecting the standard ratio correction file to use.

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.



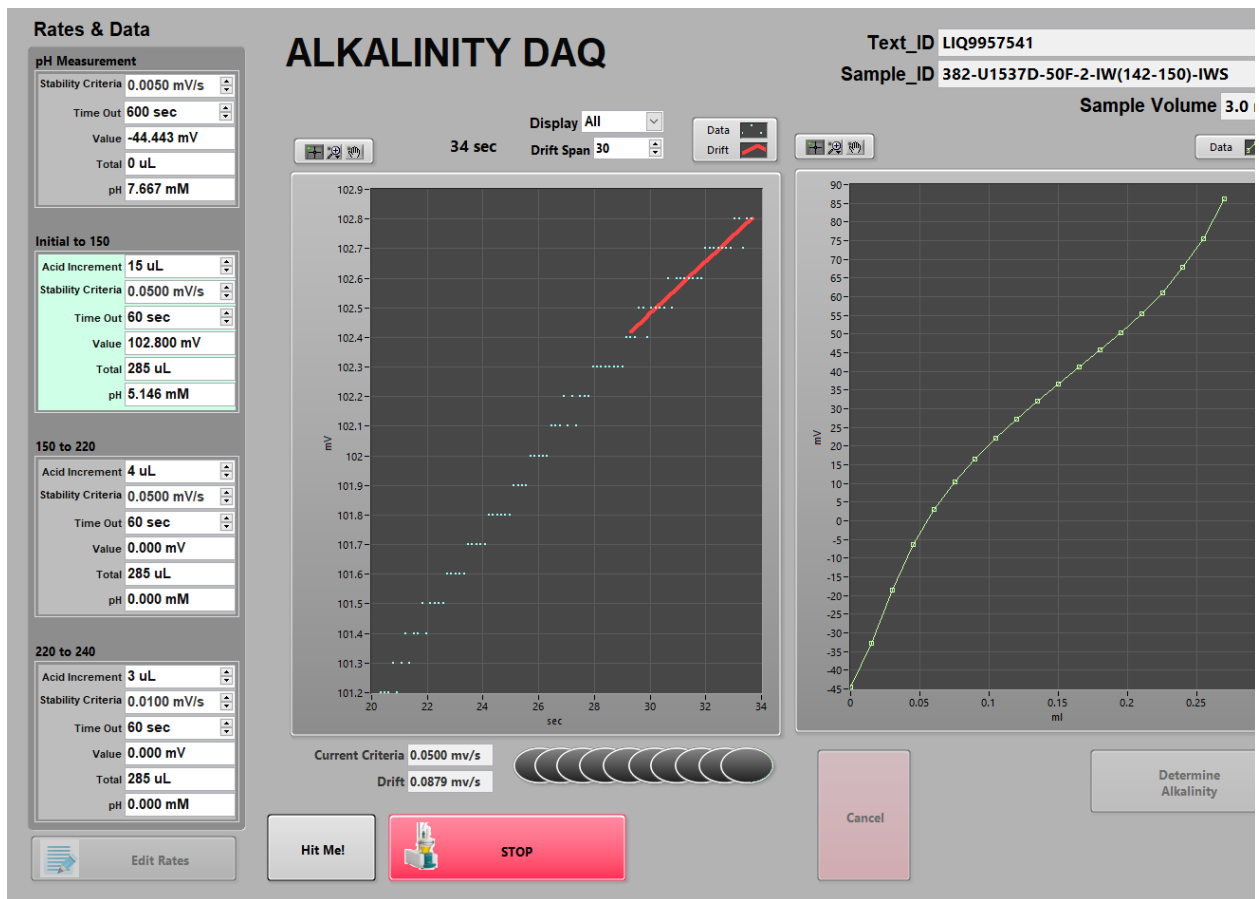


Figure 10. Drift Span.

## Instrument Operation

### 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  $\mu\text{m}$  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](#).

ALM 6 Enter Samples ✕

## Enter Sample Information

Close

Exp	Site	Hole	Core	Section	Sect Children	Samples	Filter Code
999	U1536	A	5	1	382-U1536E-9R-4-IW	SCLEE2	<input type="text"/>
382	U1535	B	6	2	SHLF-Working	IWRYUDIC	* = wildcard
QAQC	U1534	C	7	3	SHLF-Archive	IWXTRA	
		D	8	4		IWGUTJ	
		E	9	5		IWRYU+	
			10	6		IWRYUD/O	
			11	7		IWICP	
			12	CC		IWS	
			13			IWALK	
			14			IWSCRAPES	
			15			IW(140-150)	
			16				

● Connected to the database
 You may enter the Text\_ID directly

Reconnect

Continue

Validation  OFF

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**.

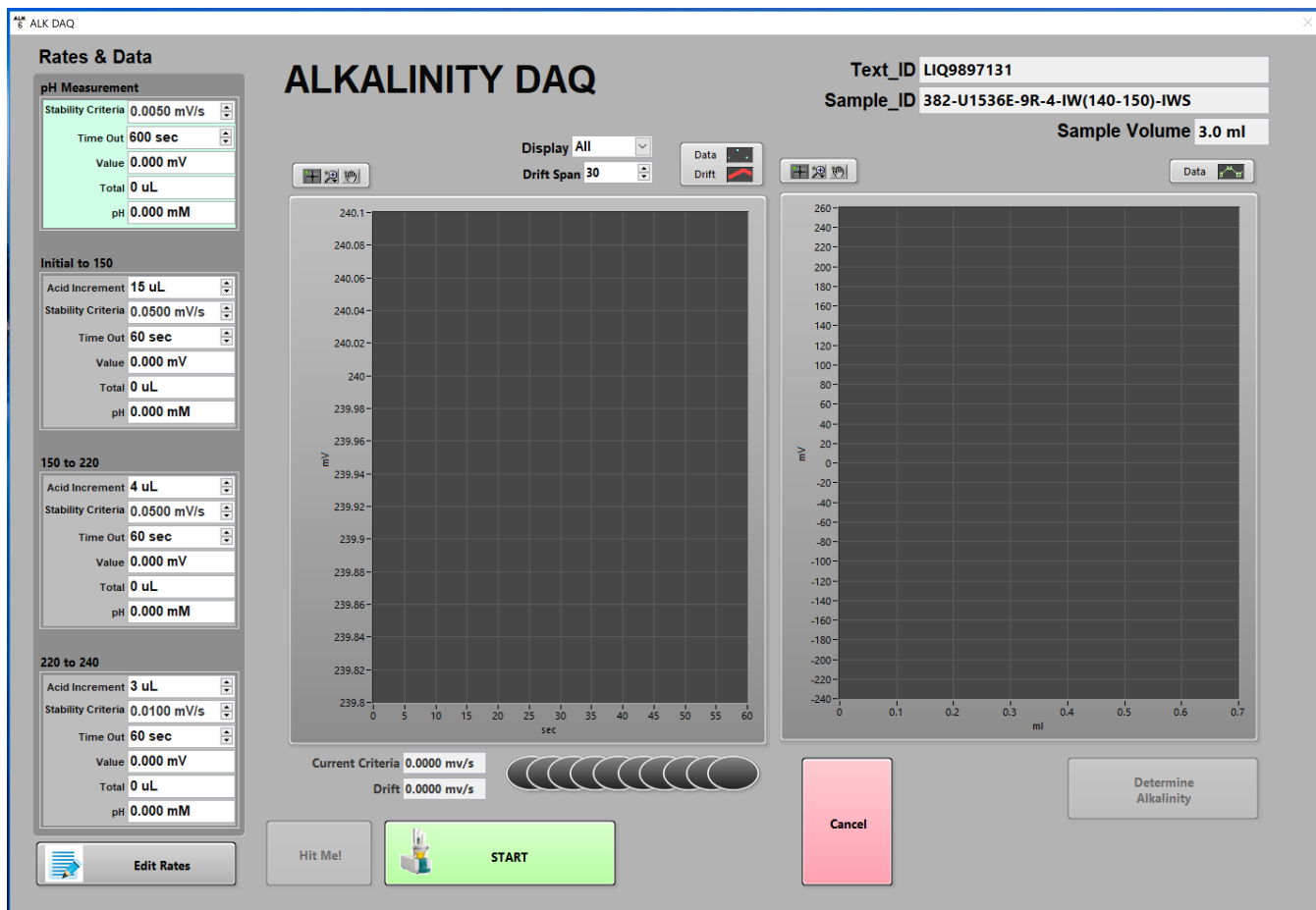


Figure 12. Alkalinity data acquisition window.

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

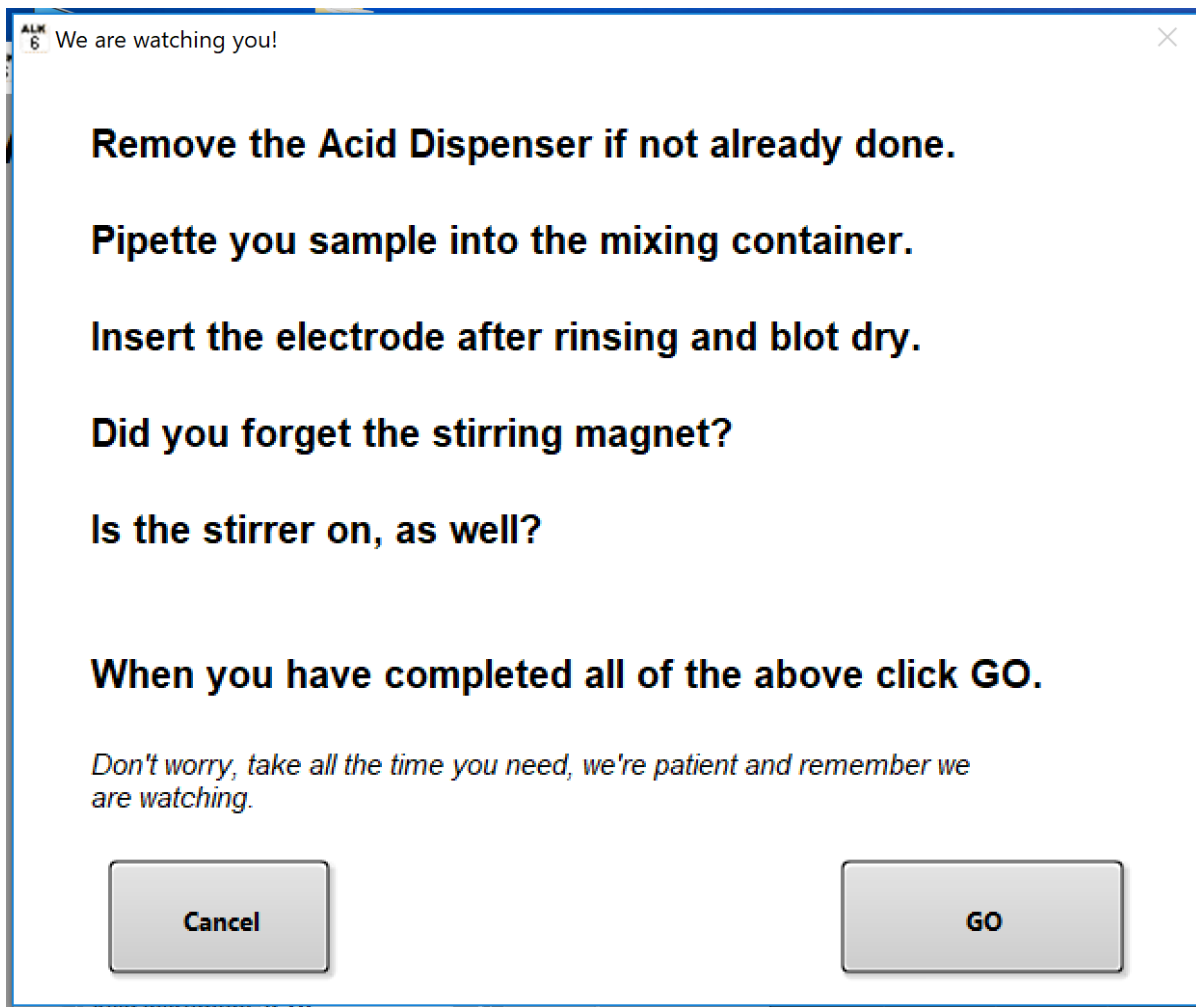


Figure 13. Reminders before starting the pH measurement.

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.

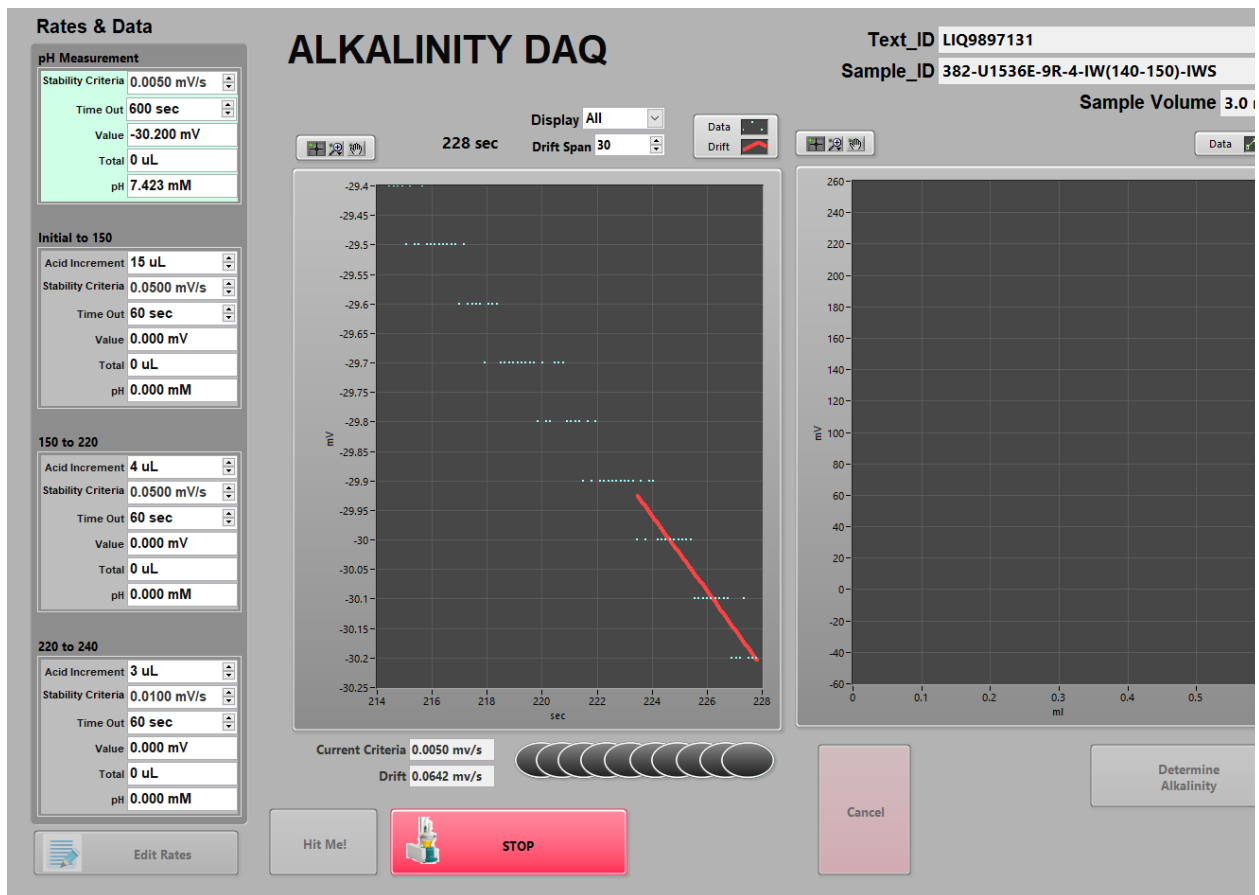


Figure 14. Measuring pH.

Once the pH measurement is complete, insert the acid dispenser probe when prompted. Click **GO**. The alkalinity measurement will commence.

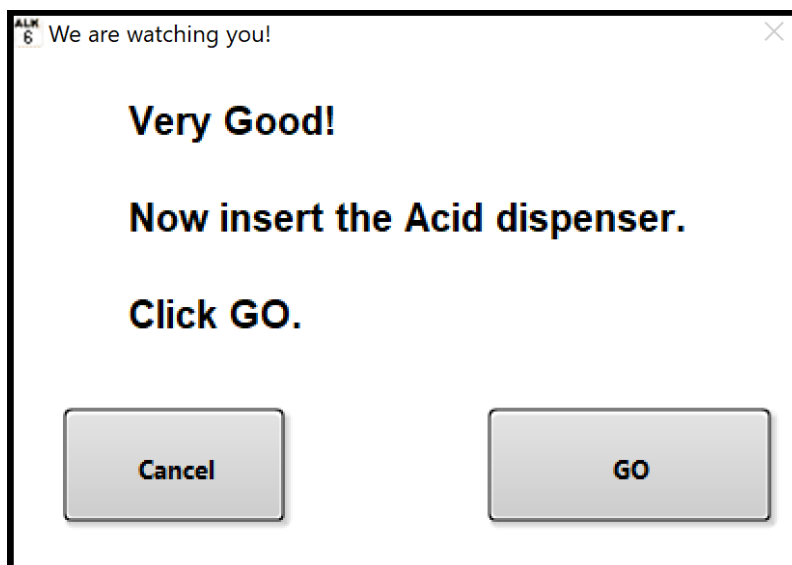


Figure 15. Acid dispenser reminder prior to starting the alkalinity measurement.

## 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](#).

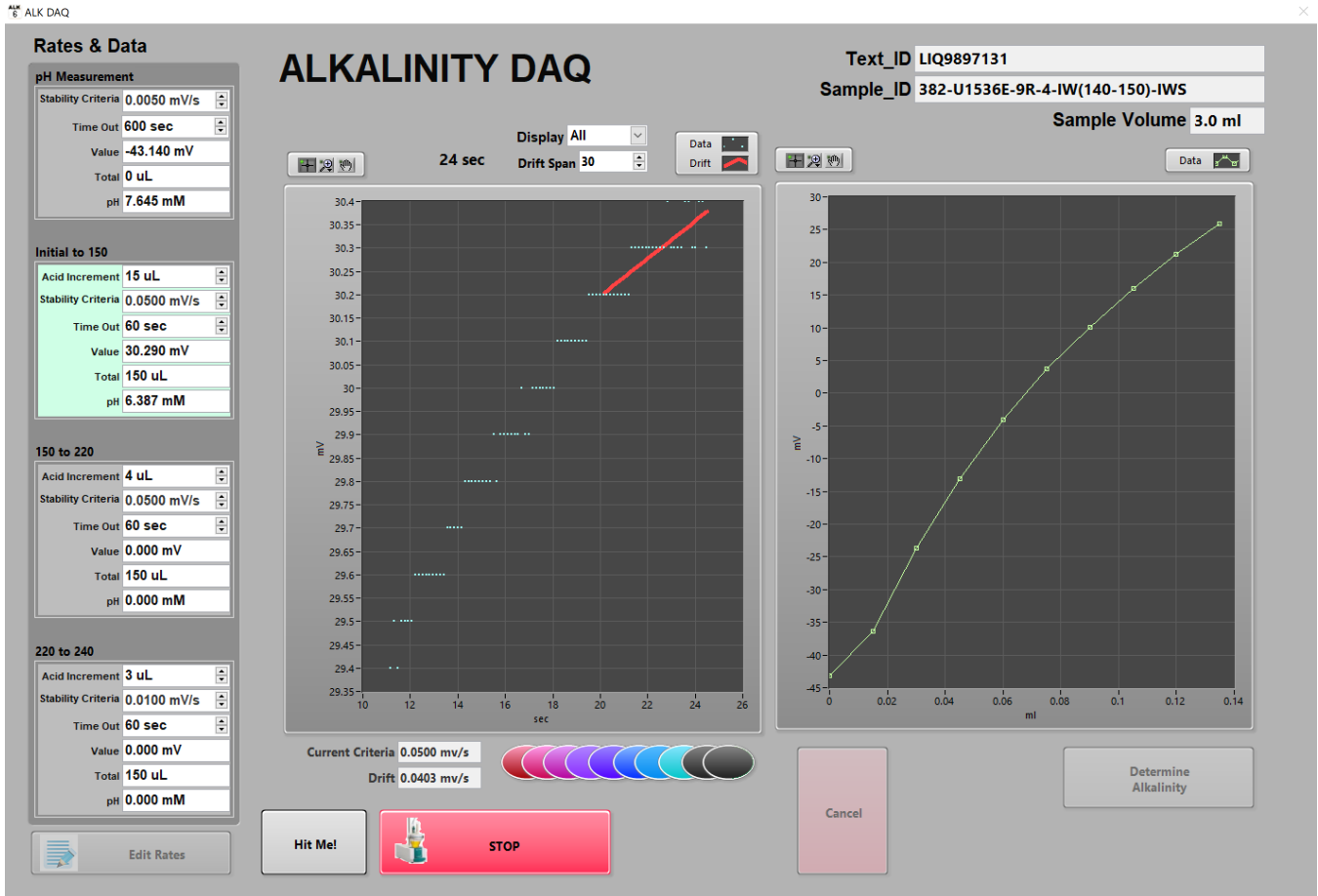


Figure 16. Measuring Alkalinity.

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.

## Analysis Complete! Before you leave...

Remove the electrode  
Rinse with DI water  
Blot dry (no wiping!)  
Place in the container with the KCL  
Remove the acid dispenser  
Place in container

Text\_ID LIQ9897131  
Sample\_ID 382-U1536E-9R-4-IW(140-150)-IWS  
Sample Volume 3.0 ml

Display All    Data    Drift

150 to 220

Acid Increment 4 uL  
Stability Criteria 0.0500 mV/s  
Time Out 60 sec  
Value 223.700 mV  
Total 380 uL  
pH 3.076 mM

220 to 240

Acid Increment 3 uL  
Stability Criteria 0.0100 mV/s  
Time Out 60 sec  
Value 241.203 mV  
Total 407 uL  
pH 2.776 mM

Current Criteria 0.0100 mv/s    Drift 0.0043 mv/s

Hit Me!
STOP
STABLE
Cancel
Determine Alkalinity

Figure 17. Analysis complete.

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

## GRAN-METHOD

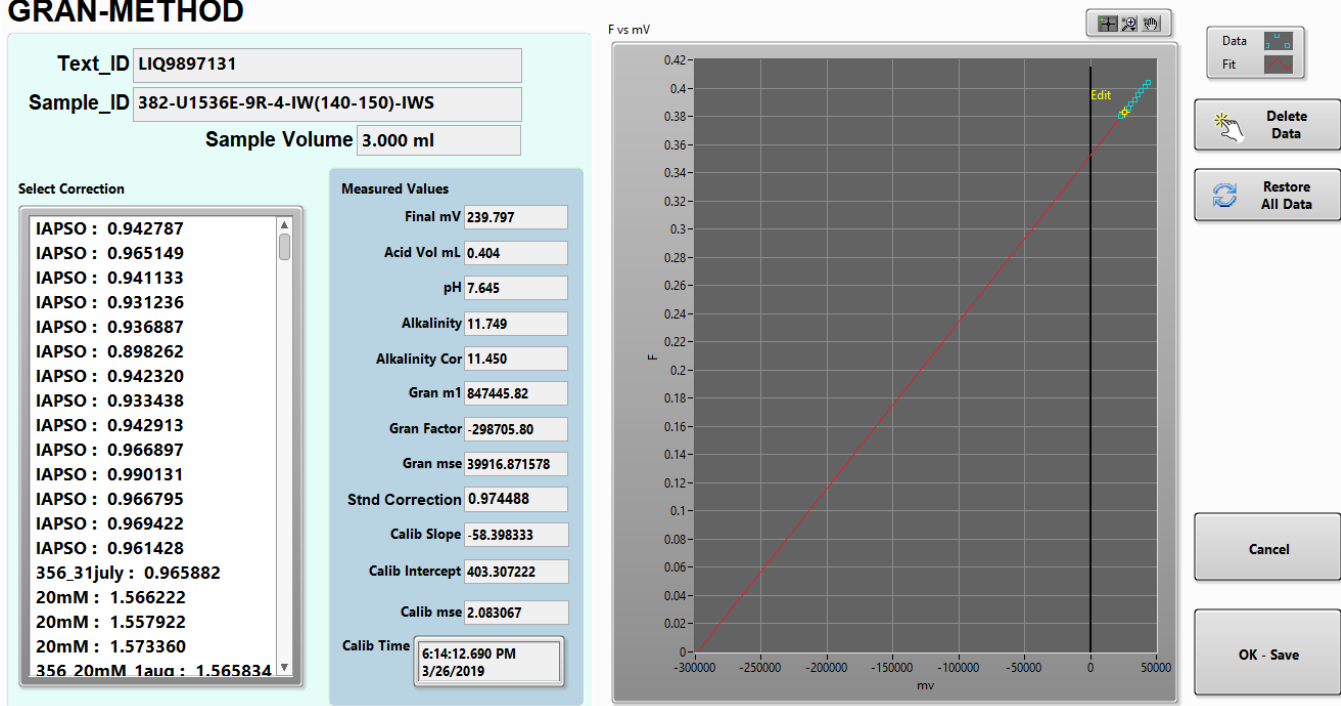


Figure 18. Gran-method window.

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.

## Instrument Clean Up

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 and Upload

### 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.



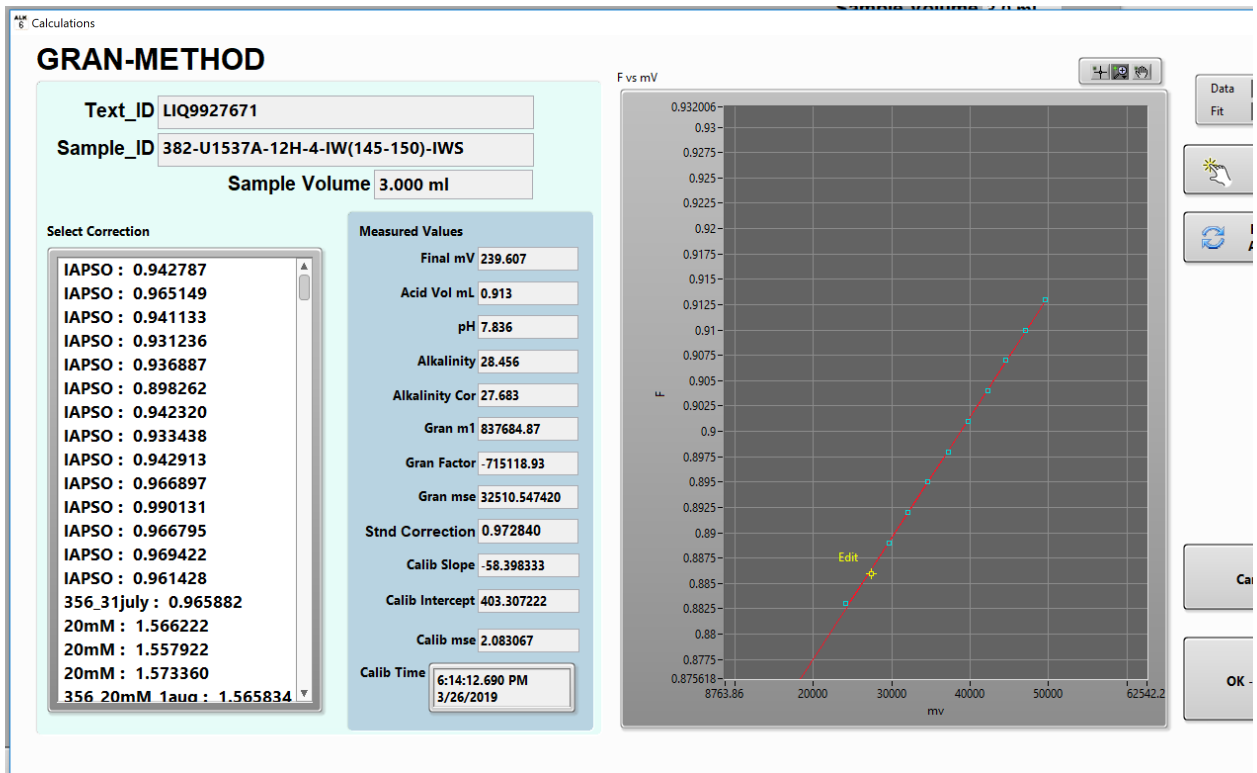


Figure 19. Editing Gran factor points.

## Uploading data to LIMS

Data is uploaded to LIMS using MUT uploader. Make sure MUT uploader is open, set to the correct expedition, and set to automatic upload.

Click **OK - Save** in the **Calculations** window.

A text file will be created and placed in the MUT upload directory with the sample data. MUT uploader then uploads the data to LIMS.

## 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**

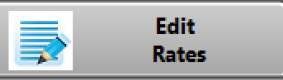
**LIMS Status**

**Calibration Status**

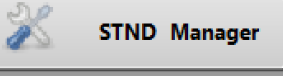
Calibration:26/03/2019-1814  
Slope = -58.3983  
Intercept = 403.3072  
mse = 2.083067  
  
Std. Correction:27/03/2019-2332  
ID = X382-27March  
Std Cor = 0.974488



**Setup**



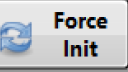
**Edit Rates**



**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.

IAPSO/Na<sub>2</sub>CO<sub>3</sub> standard ratio corrections are generated at the beginning of each expedition.

Recalibration is performed when precision or accuracy is not within  $\pm 5\%$ .

## 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  $\pm 5\%$ .

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  $\pm 5\%$  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  $\pm 0.003$  ml. When carried through the alkalinity calculation, this uncertainty results in the alkalinity difference being 50  $\mu\text{M}$ , 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

$$N_{\text{current sample}} - N[(\text{current sample}) - \$mV\text{Span}]$$

**\$mVthreshold:** slope threshold; maximum calculated value for the reading to be considered stable; also stability criteria.

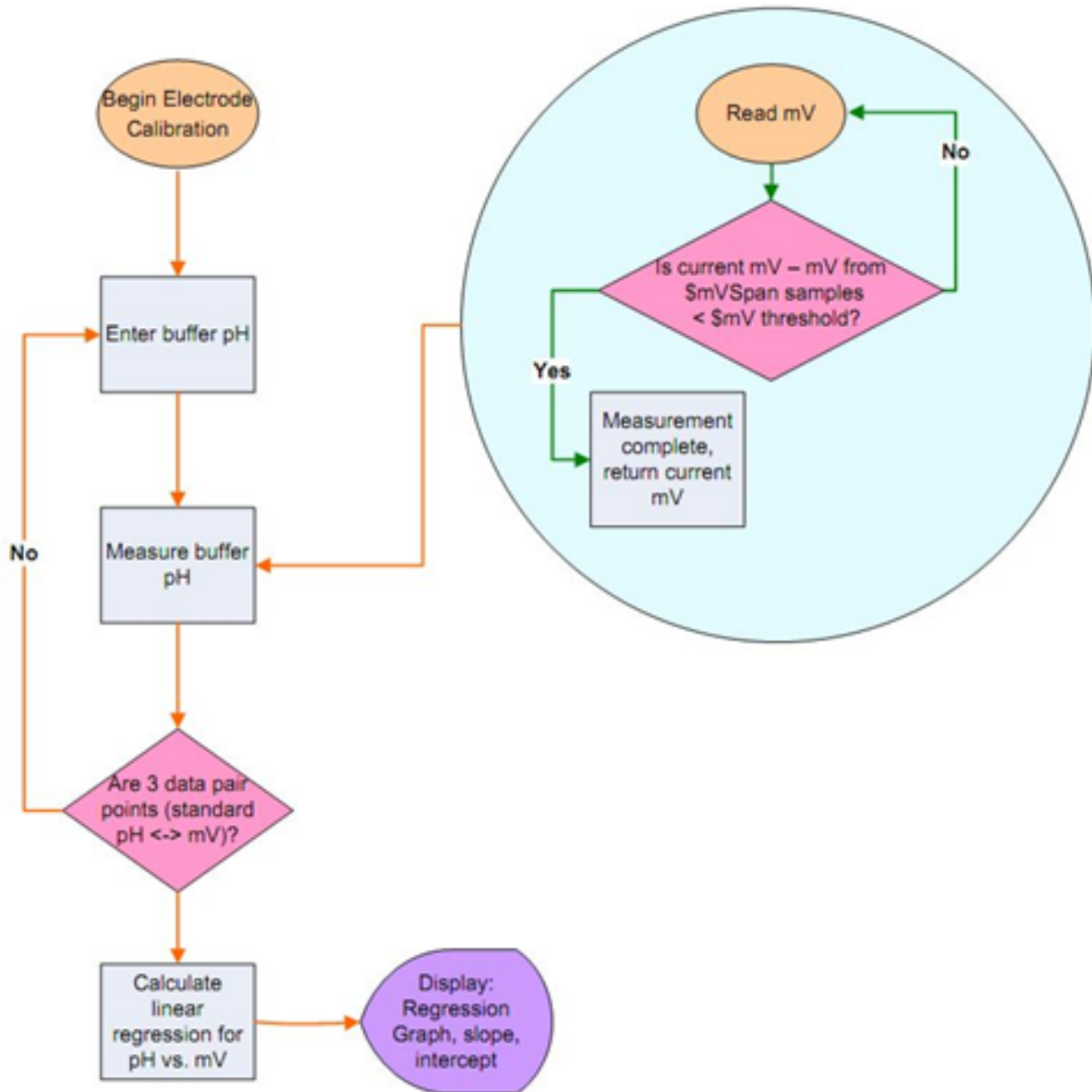


Figure 21. Alkalinity electrode calibration dataflow.

## 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)

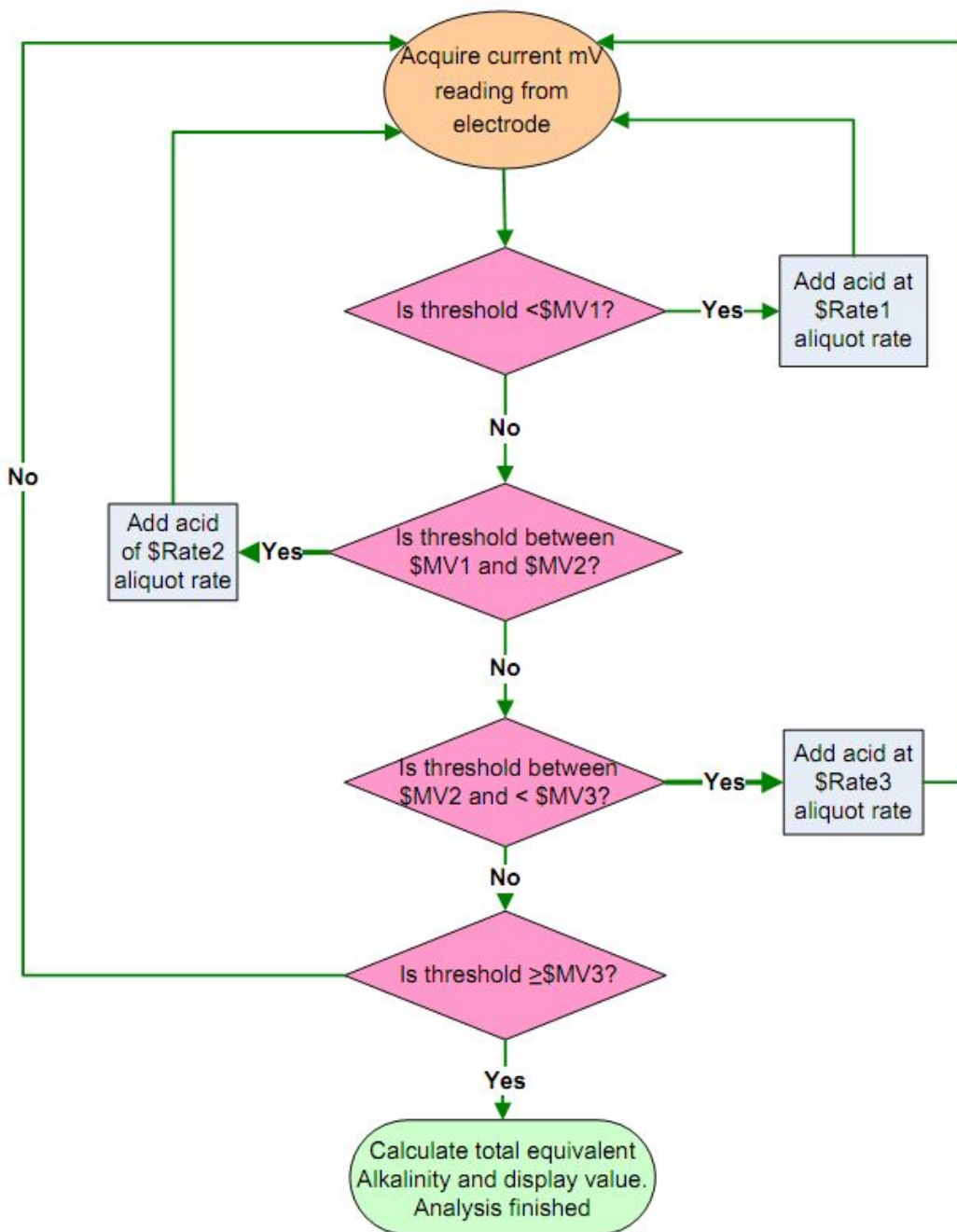


Figure 22. Alkalinity measurement data flow.

## Data Available in LORE

### Interstitial Waters Standard Report

- **Exp:** expedition number
- **Site:** site number
- **Hole:** hole number
- **Core:** core number
- **Type:** type indicates the coring tool used to recover the core (typical types are F, H, R, X).
- **Sect:** section number

- **A/W:** archive (A) or working (W) section half.
- **Top offset on section (cm):** position of the upper edge of the sample, measured relative to the top of the section.
- **Bottom offset on section (cm):** position of the lower edge of the sample, measured relative to the top of the section.
- **Top depth CSF-A (m):** position of observation expressed relative to the top of the hole.
- **Top depth [other] (m):** position of observation expressed relative to the top of the hole. The location is presented in a scale selected by the science party or the report user.
- **Sampling tool:** tool used to collect sample
- **Data columns:** header lists parameter measured and concentration units, followed by wavelength (for ICP-AES) and then analysis method.

## Expanded ALKALINITY Report

- **Exp:** expedition number
- **Site:** site number
- **Hole:** hole number
- **Core:** core number
- **Type:** type indicates the coring tool used to recover the core (typical types are F, H, R, X).
- **Sect:** section number
- **A/W:** archive (A) or working (W) section half.
- **text\_id:** full text ID of sample
- **sample\_number:** sample number of sample. text ID with sample type prefix removed.
- **label\_id:** id combining exp, site, hole, core, type, sect, A/W, parent sample name (if any), sample name
- **sample\_name:** name of sample
- **x\_sample\_state:**
- **x\_project:** expedition project the sample is uploaded under. typically the same as Exp.
- **x\_capt\_loc:** not used
- **location:** location sample was taken
- **x\_sampling\_tool:** tool used to collect sample
- **changed\_by:** name of person who uploaded sample
- **changed\_on:** date and time sample was uploaded
- **sample\_type:** type of sample. typically LIQ, for liquid.
- **x\_offset:** top offset of parent sample where sample was taken in m
- **x\_offset\_cm:** top offset of parent sample where sample was taken in cm
- **x\_bottom\_offset\_cm:** bottom offset of parent sample where sample was taken in cm
- **x\_diameter:** not used
- **x\_idmp:** not used
- **x\_orig\_len:** not used
- **x\_length:** length of sample in m
- **x\_length\_cm:** length of sample in cm
- **status:**
- **old\_status:**
- **original\_sample:**
- **parent\_sample:**
- **standard:**
- **login\_by:** name of person logged into LIMS application used for this test
- **sampled\_date:**
- **legacy:**
- **test changed\_on:** date of last edit of analysis
- **test date\_started:** date analysis was started
- **test group\_name:**
- **test status:**
- **test old\_status:**
- **test test\_number:** number assigned to performed analysis on sample
- **test date\_received:** date analysis was uploaded to LIMS
- **test instrument:** instrument used to perform analysis
- **test analysis:** analysis type
- **test x\_project:** project test was assigned to
- **test version:**
- **test order\_number:**
- **test replicate\_test:**
- **rest sample\_number:** sample number for sample the analysis was performed on
- **Top depth CSF-A (m):** position of observation expressed relative to the top of the hole.
- **Bottom depth CSF-A (m):** position of observation expressed relative to the top of the hole.
- **Top depth CSF-B (m):**
- **Bottom depth CSF-B (m):**
- **alkalinity (mM):** measured alkalinity value in mM, Ability of a solution to neutralize acid to the equivalence point of carbonate
- **correction\_factor:** Correction factor for non-ideal behavior of samples to adjust calibration
- **pH:** measured pH value, Acidity or basicity of a solution (-log[H+])
- **sample description:** description/comment of sample
- **test test\_comment:** comment added for performed analysis
- **result comments:** comment added for analysis results

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	$\mu\text{l}$	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	$\mu\text{l}$	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.

Black  $\text{Ag}_2\text{S}$  may precipitate in the diaphragm of the electrode from sulfide containing samples. You will most likely notice a decline in the electrode's performance, and the diaphragm that has turned black. Treat the diaphragm with freshly prepared 7% Thiourea solution in 0.1 mol/l HCl.

## Consumables

Electrode: Metrohm 6.0234.100 or equivalent.

0.1 M HCl, Fisher CH5009

Microvalve buret tip, Metrohm 020683244, CM5129

## LIMS component table

The following tables contain all of the LIMS components for the entire ALKALINITY (and pH) process.



ANALYSIS	TABLE	NAME	ABOUT TEXT
ALKALINITY	SAMPLE	Exp	Exp: expedition number
ALKALINITY	SAMPLE	Site	Site: site number
ALKALINITY	SAMPLE	Hole	Hole: hole number
ALKALINITY	SAMPLE	Core	Core: core number
ALKALINITY	SAMPLE	Type	Type: type indicates the coring tool used to recover the core (typical types are F, H, R, X).
ALKALINITY	SAMPLE	Sect	Sect: section number
ALKALINITY	SAMPLE	A/W	A/W: archive (A) or working (W) section half.
ALKALINITY	SAMPLE	text_id	Text_ID: automatically generated database identifier for a sample, also carried on the printed labels. This identifier is guaranteed to be unique across all samples.
ALKALINITY	SAMPLE	sample_number	Sample Number: automatically generated database identifier for a sample. This is the primary key of the SAMPLE table.
ALKALINITY	SAMPLE	label_id	Label identifier: automatically generated, human readable name for a sample that is printed on labels. This name is not guaranteed unique across all samples.
ALKALINITY	SAMPLE	sample_name	Sample name: short name that may be specified for a sample. You can use an advanced filter to narrow your search by this parameter.
ALKALINITY	SAMPLE	x_sample_state	Sample state: Single-character identifier always set to "W" for samples; standards can vary.
ALKALINITY	SAMPLE	x_project	Project: similar in scope to the expedition number, the difference being that the project is the current cruise, whereas expedition could refer to material/results obtained on previous cruises
ALKALINITY	SAMPLE	x_capt_loc	Captured location: "captured location," this field is usually null and is unnecessary because any sample captured on the JR has a sample_number ending in 1, and GCR ending in 2
ALKALINITY	SAMPLE	location	Location: location that sample was taken; this field is usually null and is unnecessary because any sample captured on the JR has a sample_number ending in 1, and GCR ending in 2
ALKALINITY	SAMPLE	x_sampling_tool	Sampling tool: sampling tool used to take the sample (e.g., syringe, spatula)
ALKALINITY	SAMPLE	changed_by	Changed by: username of account used to make a change to a sample record
ALKALINITY	SAMPLE	changed_on	Changed on: date/time stamp for change made to a sample record
ALKALINITY	SAMPLE	sample_type	Sample type: type of sample from a predefined list (e.g., HOLE, CORE, LIQ)
ALKALINITY	SAMPLE	x_offset	Offset (m): top offset of sample from top of parent sample, expressed in meters.
ALKALINITY	SAMPLE	x_offset_cm	Offset (cm): top offset of sample from top of parent sample, expressed in centimeters. This is a calculated field (offset, converted to cm)
ALKALINITY	SAMPLE	x_bottom_offset_cm	Bottom offset (cm): bottom offset of sample from top of parent sample, expressed in centimeters. This is a calculated field (offset + length, converted to cm)
ALKALINITY	SAMPLE	x_diameter	Diameter (cm): diameter of sample, usually applied only to CORE, SECT, SHLF, and WRND samples; however this field is null on both Exp. 390 and 393, so it is no longer populated by Sample Master
ALKALINITY	SAMPLE	x_orig_len	Original length (m): field for the original length of a sample; not always (or reliably) populated
ALKALINITY	SAMPLE	x_length	Length (m): field for the length of a sample [as entered upon creation]
ALKALINITY	SAMPLE	x_length_cm	Length (cm): field for the length of a sample. This is a calculated field (length, converted to cm).
ALKALINITY	SAMPLE	status	Status: single-character code for the current status of a sample (e.g., active, canceled)
ALKALINITY	SAMPLE	old_status	Old status: single-character code for the previous status of a sample; used by the LIME program to restore a canceled sample
ALKALINITY	SAMPLE	original_sample	Original sample: field tying a sample below the CORE level to its parent HOLE sample

ALKALINITY	SAMPLE	parent_sample	Parent sample: the sample from which this sample was taken (e.g., for PWDR samples, this might be a SHLF or possibly another PWDR)
ALKALINITY	SAMPLE	standard	Standard: T/F field to differentiate between samples (standard=F) and QAQC standards (standard=T)
ALKALINITY	SAMPLE	login_by	Login by: username of account used to create the sample (can be the LIMS itself [e.g., SHLFs created when a SECT is created])
ALKALINITY	SAMPLE	login_date	Login date: creation date of the sample
ALKALINITY	SAMPLE	legacy	Legacy flag: T/F indicator for when a sample is from a previous expedition and is locked/uneditable on this expedition
ALKALINITY	TEST	test_changed_on	TEST changed on: date/time stamp for a change to a test record.
ALKALINITY	TEST	test_status	TEST status: single-character code for the current status of a test (e.g., active, in process, canceled)
ALKALINITY	TEST	test_old_status	TEST old status: single-character code for the previous status of a test; used by the LIME program to restore a canceled test
ALKALINITY	TEST	test_test_number	TEST test number: automatically generated database identifier for a test record. This is the primary key of the TEST table.
ALKALINITY	TEST	test_date_received	TEST date received: date/time stamp for the creation of the test record.
ALKALINITY	TEST	test_instrument	TEST instrument [instrument group]: field that describes the instrument group (most often this applies to loggers with multiple sensors); often obscure (e.g., user_input)
ALKALINITY	TEST	test_analysis	TEST analysis: analysis code associated with this test (foreign key to the ANALYSIS table)
ALKALINITY	TEST	test_x_project	TEST project: similar in scope to the expedition number, the difference being that the project is the current cruise, whereas expedition could refer to material/results obtained on previous cruises
ALKALINITY	TEST	test_sample_number	TEST sample number: the sample_number of the sample to which this test record is attached; a foreign key to the SAMPLE table
ALKALINITY	CALCULATED	Top depth CSF-A (m)	Top depth CSF-A (m): position of observation expressed relative to the top of the hole.
ALKALINITY	CALCULATED	Bottom depth CSF-A (m)	Bottom depth CSF-A (m): position of observation expressed relative to the top of the hole.
ALKALINITY	CALCULATED	Top depth [other] (m) CSF-B (m)	Top depth [other] (m): position of observation expressed relative to the top of the hole. The location is presented in a scale selected by the science party or the report user.
ALKALINITY	CALCULATED	Bottom depth [other] (m) CSF-B (m)	Bottom depth [other] (m): position of observation expressed relative to the top of the hole. The location is presented in a scale selected by the science party or the report user.
ALKALINITY	RESULT	acid_quantity	RESULT acid quantity (mL): amount of acid titrant added to the sample during the alkalinity measurement.
ALKALINITY	RESULT	alkalinity (mM)	RESULT alkalinity (mM): alkalinity expressed in millimoles of carbonate per liter of sample
ALKALINITY	RESULT	alkalinity-calib_asman_id	RESULT alkalinity calibration ASMAN_ID: serial number of ASMAN record containing the alkalinity calibration file
ALKALINITY	RESULT	alkalinity-calib_filename	RESULT alkalinity calibration filename: file name of the alkalinity calibration file
ALKALINITY	RESULT	configuration_asman_id	RESULT configuration ASMAN_ID: serial number of ASMAN record containing the alkalinity instrument configuration file
ALKALINITY	RESULT	configuration_filename	RESULT configuration filename: file name of the alkalinity instrument configuration file
ALKALINITY	RESULT	correction_factor	RESULT correction factor: Gran titration correction factor determined for the instrument's specific setup and reagents
ALKALINITY	RESULT	pH	RESULT pH (unitless): pH of the sample prior to acid titration
ALKALINITY	RESULT	run_asman_id	RESULT run ASMAN_ID: serial number of ASMAN record containing the run file
ALKALINITY	RESULT	run_filename	RESULT run filename: file name of the run file
ALKALINITY	SAMPLE	sample_description	SAMPLE comment: contents of the SAMPLE.description field, usually shown on reports as "Sample comments"
ALKALINITY	TEST	test_test_comment	TEST comment: contents of the TEST.comment field, usually shown on reports as "Test comments"

ALKALINITY	RESULT	result comments	RESULT comment: contents of a result parameter with name = "comment," usually shown on reports as "Result comments"
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## Archive Version

[LMUG-pH\\_Alkalinity Autotitrator\\_UG-230220-1718-112.pdf](#)