

# STANDARD OPERATING PROCEDURE

## For

### Determination of Total Alkalinity

### by Standard Methods SM 2320 B (SM 23<sup>rd</sup> Edition)

SOP #: SM 2320 B

REVISION #: 3.1

DATE: March 2024

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## LIST OF REVISIONS

Rev. #	Date	Description of Revision	Section #
0	April 1999	None	
1.0	December 2000	Sections were revised Assorted minor typos, etc., were corrected	14 & 15 Throughout document
1.1	January 2002	New Table 1 was added Tables 2-5 were updated	18 18
1.2	November 2003	Instrumentation changed from ORION Model 410 A to Accumet AB15. Tables 3-5 were updated.	6.1 18
1.3	November 2006	Changed equipment. Specified QC elements. Updated Tables 3-5	6.0 9.3 18
1.4	March 2016	Instrument changed to a TitraLab® autotitrator Section added. Tables 2-4 deleted.	Throughout document 6 18
2.0	March 2022	Updated document for a new instrument – Metrohm 855 Robotic Titrosampler	Throughout document
3.0	January 2023	Changed Revision Table citations from Page # to Section # Updated section. Updated quality control section. Revised extensively the procedure section. Revised extensively the maintenance section. Updated the reference list. Updated Table 1.	List of Revisions 6.1 9.1 11 14 17 18
3.1	March 2024	Updated Standard and Reagent Preparation Form Revision Counting samples between ongoing calibration verification checks Definition of Analytical Batch Added Updated Tray Protocol for Figure 1 and Figure 2	11.8 3.3, 3.4, & 3.5 3.8 11.8.1 & 11.8.2



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## 1.0 SCOPE AND APPLICATION

- 1.1 This standard operating procedure describes the method used to determine total alkalinity of potable and non-potable waters using auto-titration. Alkalinity of water is its acid neutralizing capacity. It is the sum of all titratable bases. This method is intended to be used by experienced or trained analysts and should not be attempted without reading all user manuals and receiving bench training.
- 1.2 When sulfuric acid is added to a sample containing alkalis such as hydroxide, carbonate and bicarbonate, the hydrogen ions from the acid react with the hydroxyl ions of alkalis to produce salt, carbon dioxide, and water. At pH 4.5, all alkalis have been consumed and a sample's alkalinity can be determined, expressed as milligrams of calcium carbonate per liter (mg/L  $\text{CaCO}_3$ ).

## 2.0 SUMMARY

A 100 mL volume of sample is added to a titration vessel and placed in an automated sample changer. After starting the software program, the workstation starts adding sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to the sample until the sample reaches a pH of 4.5. The program calculates alkalinity from the amount of acid delivered to bring the sample's pH down to 4.5. This is a one endpoint titration and is used for samples having an alkalinity greater than or equal to 20 mg  $\text{CaCO}_3$ /L. A low alkalinity, two endpoint titration (4.5 and 4.2 endpoints) method is used for samples having an alkalinity less than 20 mg  $\text{CaCO}_3$ /L. <sup>(17.1)</sup>

## 3.0 DEFINITIONS

- 3.1 Quality Control Sample (QCS) – A solution of method analytes of known concentrations. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.
- 3.2 Method Blank (Reagent Blank) – Consists of reagent water and all reagents (including preservatives) that normally are in contact with a sample during the entire analytical procedure. It is used as an Initial Calibration Blank (ICB) and as Continuing Calibration Blanks (CCB). For this method, the ICB and CCB are equivalent to the LRB.
- 3.3 Laboratory Reagent Blank (LRB) – An aliquot of the method blank that is treated and processed exactly as a sample. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus. The LRB is counted as a sample and is included in the 10-count towards ongoing calibration verification.
- 3.4 Laboratory Duplicates (DUP) – Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures. The DUP is counted as a sample and is included in the 10-count towards ongoing calibration verification.
- 3.5 Laboratory Fortified Blank (LFB) – An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurement. The LFB is counted as a sample and is included in the 10-count towards ongoing calibration verification.



- 3.6 Stock Standard Solution – A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.7 Instrument Performance Check (IPC) Standard - A solution of the method's analyte, of known concentration, used to evaluate the performance of the instrument. Depending on when it is run following instrument calibration, it may also be called an Initial Calibration Verification (ICV) or a Continuing Calibration Verification (CCV). For this method, the IPC and LFB are equivalent.
- 3.8 Analysis Batch – A group of no more than 20 field samples. Field sample analyses include only those samples derived from a field sample matrix. These include the initial and duplicate field samples as well as all Laboratory Fortified Sample Matrices.

#### **4.0 INTERFERENCES**

- 4.1 Substances that can coat the pH electrode, such as oils, precipitates and suspended matter can cause poor response time. If a poor response time occurs, stop the analysis, and gently rinse the electrode several times with reagent water.
- 4.2 Minimize air exposure as much as possible, especially with wastewater samples, as a loss or gain of carbon dioxide (CO<sub>2</sub>) can occur. Samples containing high bacteria levels can also affect CO<sub>2</sub> levels.
- 4.3 When running the auto-titrator, do not close out or log out of the program or try logging in under a different user during a run batch as data will be lost and the run batch will need to be analyzed again from the beginning.

#### **5.0 SAFETY**

- 5.1 Standard laboratory protective clothing and eye covering is required.

#### **6.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE**

- 6.1 Collect samples in polyethylene or borosilicate glass bottles. Fill bottle completely and cap tightly. Transport to lab in a cooler containing ice. This method requires a 100-mL sample for each analysis. Additional sample volume is required for duplicates or if the low alkalinity test must be performed after the regular alkalinity test. A sample collection bottle size of 500 mL is required.
- 6.2 Store samples at 4°C for up to 14 days.
- 6.3 Analyze samples suspected of containing high levels of bacteria (see Section 4.2) as soon as possible or within a day.

#### **7.0 EQUIPMENT AND SUPPLIES**

- 7.1 Tiamo Light software, Version 3.0, build 122 with an HP LaserJet P1005 printer.
- 7.2 Metrohm 855 Robotic Titrosampler Workstation (WS) with a 16-position sample tray and sample changer, 5-mL and 20-mL dosino, 772 Peristaltic Pump, 1-L dosino vessels, and a Metrohm 802 stirrer.
- 7.3 Titration Vessels (vessels): 150-mL plastic; reusable



- 7.4 Combination pH electrode with temperature sensor, Metrohm 6.00257.000
- 7.5 Volumetric flasks: 50-mL, 100-mL, Class A
- 7.6 Air displaced Brandtech Transferpettes: 0.2-mL, 0.4-mL, 0.5-mL, 0.6-mL, 0.8 mL, 1.0-mL, 2.0-mL, 4.0-mL and 10.0-mL. Transferpettes are tested on the balance each day when used to achieve Class A measurements.
- 7.7 Graduated cylinder: 100-mL, Class A
- 7.8 Auto-pipettor
- 7.9 Pipettes: 50-mL, plastic and disposable
- 7.10 Parafilm
- 7.11 Laboratory tape or labels
- 7.12 Marker pens

## 8.0 REAGENTS AND STANDARDS

**Reagents and Standards Preparation Bench Sheets for this method are standalone documents found in Sharepoint\DEP Wall Experiment Station – DELS\DELS-QAP\Bench Data Forms\Active Bench Data Forms\Section 1 – EICL-Active\Metrohm Alkalinity Standard & Reagent Prep 3.1.docx**

- 8.1 Sodium Carbonate Stock Standard ( $\text{Na}_2\text{CO}_3$ ): 0.05 N = 2500 mg  $\text{CaCO}_3/\text{L}$ ; certified; purchased commercially. Store at room temperature until manufacturer's expiration date.
- 8.2 QCS Sodium Carbonate Stock Standard ( $\text{Na}_2\text{CO}_3$ ): 0.05 N = 2500 mg  $\text{CaCO}_3/\text{L}$ ; certified; purchased commercially from a different vendor than in section 8.1. Store at room temperature until manufacturer's expiration date.
- 8.3 Sulfuric Acid Stock Standard ( $\text{H}_2\text{SO}_4$ ): 0.02 N; certified; purchased commercially. Store at room temperature until manufacturer's expiration date.
- 8.4 pH Buffers: 4.00, 7.00, and 10.00.
- 8.5 QCS pH Buffer 4.00 (different manufacturer than the pH buffers in 8.4).
- 8.6 ASTM Type I Reagent Water

## 9.0 QUALITY CONTROL

- 9.1 System Purge: Purge the system of any trapped air bubble by first running reagent water through both dosing units by going to the Manual Button on the lower left of the screen. Then change from the reagent water bottles under the dosing units to the sulfuric acid titrant (0.02-N  $\text{H}_2\text{SO}_4$ ). Prepare the dosing units again to fill lines with titrant and purge air bubbles. See Procedure in Section 11.0.
- 9.2 Method Blank (MB): All method blanks in this method are prepared the same way, whether the blank is used as an Initial Calibration Blank (ICB), LRB or a Continuing Calibration Blank (CCB). Method blanks test for instrument and method contamination.



9.3 Laboratory Fortified Blank (LFB): Other than concentration, an LFB is prepared no differently than any IPC (Instrument Performance Check), which could include the Initial Calibration Verification standard (ICV) or the Continuing Calibration Verification standards (CCV). Nomenclature for calibration verification can use IPC terminology, or these standards can all be called LFBs. The LFB counts as a sample. Varying concentrations can be used for calibration verification if samples are higher in concentration. See Standard & Reagent Preparation bench sheet for Alkalinity by SM 2320 B.

9.4 Quality Control Standard (QCS): Run a QCS at the beginning of every run when a new calibration is performed. The QCS verifies the pH probe is calibrated properly and also serves as a second source check of the primary sodium carbonate standard. See Standard & Reagent Preparation bench sheet for Alkalinity by SM 2320B. Other concentrations can be used if samples are higher in concentration.

*Note: The  $\text{Na}_2\text{CO}_3$  used for the QCS must be purchased from a different vendor than the  $\text{Na}_2\text{CO}_3$  used for the LFB.*

9.5 Run a duplicate sample for every 10 samples in a batch.

9.6 All QC elements and acceptance limits are summarized in Table 1.

9.7 Position 16 is a dedicated position for the burette preparation procedure only.

9.8 Run a sample and its duplicate within a bracket of 10 samples.

## 10.0 CALIBRATION AND STANDARDIZATION

**10.1 pH Electrode: Calibration for the pH electrode is incorporated into the run table using a method specific for pH calibration and is included in the procedure section below. Cups 1-3 are used for calibration and Cup 4 is used for calibration verification using a second source pH 4 buffer.**

## 11.0 PROCEDURE

11.1 Turn on computer (button on lower right of the screen). Once it is warmed up, click on Tiamo to open the instruments software and enter your name to log in as the operator. The log in process tracks the operator and documents this information on sample/calibration reports. Let the sampler go through its pre-run set-up. The tower will lift the probe, stirrer, and washing unit out of the storage solution at slot 16. The tray will advance to slot 1, then go back to slot 16 but it will not lower back into the storage solution. Lower the probe back to special position 16 so the probe does not dry out.

- Click the **Manual** icon
- Select **Tower 1**
- Select **Move** tab.

This screen controls the rack position and lift position. At the lift position, use the drop-down list at the target position to select **special position**. Then press the green start button to lower the probe.

11.2 Check that the rinse container is full of reagent water and that the waste container is empty. These containers are located on the floor under the titrator in secondary containment bins. Be sure the labeled hoses are inserted into the correct containers and are all the way to the bottom of the container. Clear tubing is waste, opaque tubing is reagent rinse water. The waste can be emptied into the hazardous waste drum in the hazardous waste room.





- 11.3 Tighten down the tubing on the peristaltic pump found to the left of the tower (772 Pump unit). Adjust the tension on the tubing if necessary. Check this before purging the dosinos by first removing the Ross storage solution in position 16 and replacing it with a cup of reagent water.

- Navigate to **Manual** control icon
- Select **Tower 1**
- Select the **Move** tab
- Use the drop-down menu in the Lift position to select **Work position**. The probe will be raised.
- Replace the Ross storage solution with a cup of water
- Lower the probe by selecting **Special position** in the Lift position drop-down menu.
- Select the **Pump** tab
- Click the **Start** button for Pump 2

Make sure the pump is able to empty the contents of a sample cup. Adjust the tension on the peristaltic tubing if necessary.

- 11.4 Make sure the plug on the pH probe has been unplugged before the run starts.

- 11.5 Run reagent water through the 20 mL and 5 mL dosing units to check that the dosinos are rotating smoothly. Clear round 1000-mL bottles, containing reagent water, are attached below the dosing units.

- Press the **Manual** icon button on the lower left of the screen
- Select **Dosing Device 1**
- Select the **Prepare** tab
- Press the **Start** button
- Repeat the process for **Dosing Device 2**

If the dosing units are working properly, then change out the dosino round-clear reagent water bottles to the brown-square bottles containing the sulfuric acid (H<sub>2</sub>SO<sub>4</sub>): 0.02N. Prep both dosinos as above so the lines are filled with acid and no bubbles are present. Program reminds you to have a sample vessel in place during the preparation procedure. There is also a dosino preparation procedure as part of the run list prior to pH calibration.

- 11.6 Build the sample table by selecting the Workplace icon in the upper left corner of the screen.

- Select the **Determination Series** tab in the Run window
- Press the **Sample Table** drop down menu
- Load the appropriate alkalinity sequence table. For example, **Alk Template** or the **Low Alk Template**
- Press the **Load** button

Once loaded, the sequence table appears in the display with the appropriate methods already selected for each function performed in the run list: burette preparation, pH calibration, and alkalinity analysis. Any line in the run list can be edited by double clicking inside of a line. Drop-down menus allow the user to edit the method, sample position, sample ID, WinLIMS ID, Batch, sample size and volume units. The run list provides instructions to first run a method to prepare or purge the burets (dosinos), followed by running a method to calibrate the pH meter, and lastly instructions to run samples using one of two alkalinity methods. Once the information is entered,



save the table using the **Sample table** drop down menu. To do another run using the same sample table, reactivate or refresh the table by clicking on the blue arrow over the red dot. This icon is located at the top of the template under the **Sample data** header. Change what needs to be changed for the next run and save.

- 11.7 **Tray set up for pH Calibration** - Add 60 mL of pH buffer 4.0 to a sample vessel and place in the tray at slot #1. Add 60 mL of pH buffer 7.0 to a sample vessel and place in the tray at slot #2. Add 60 mL of pH buffer 10.0 to a sample vessel and place in the tray at slot #3. Add 60 mL of QCS pH Buffer 4.0 to a sample vessel and place in slot #4. Sample size is listed as 60 mL for pH buffers, slots 1 to 4. This is done for both the low curve determinations and for regular alkalinity determinations.
- 11.8 **Tray set up for standards** - Add 100 mL of Type 1 reagent water to a sample vessel and place in slot 5. This is done for both the low and the regular alkalinity curve runs. Sample size entered is 100 mL for all standards and samples. Standard and sample volume must always remain at 100 mL, otherwise the instrument method must be modified to properly calculate alkalinity.

The following tray set ups are used for the regular and low alkalinity template. The Standard & Reagent Bench Sheet can be found under [mass.gov.sharepoint.com/sites/DEP-WallExperimentStation-DELS/EICL/Standard & Reagent Prep Forms/ Active Forms/ Alkalinity/ Metrohm Alkalinity Standard & Reagent Prep 3.1.docx](https://mass.gov.sharepoint.com/sites/DEP-WallExperimentStation-DELS/EICL/Standard%20&%20Reagent%20Prep%20Forms/Active%20Forms/Alkalinity/Metrohm%20Alkalinity%20Standard%20&%20Reagent%20Prep%203.1.docx)

Also kept at: **DEP Wall Experiment Station - DELS\DELS-QAP\Bench Data Forms\Active Bench Data Forms\Section 1 - Inorganic Chemistry-Active.**



Run

Single determination    **Determination series**

**Start** **Stop** **Hold** **Pause**

**Determination parameters**

User: Peter Piro

Remark:

Autostart: 0 of Sample table

**Sample data**

	Method	Sample position	Sample ID	WinLIMS ID	Batch	Sample size	Sample size unit
1	Buret preparation	16				1.0	mL
2	855 pH Calibration Manual	1				60	mL
3	855, Manual Sample Addition, Alk	5	ICB		YYYYMMDD	100	mL
4	855, Manual Sample Addition, Alk	6	QCS 50 mg/L		YYYYMMDD	100	mL
5	855, Manual Sample Addition, Alk	7	LRB		YYYYMMDD	100	mL
6	855, Manual Sample Addition, Alk	8	MRL 20 mg/L		YYYYMMDD	100	mL
7	855, Manual Sample Addition, Alk	9	ICV/LFB 50 mg/L		YYYYMMDD	100	mL
8	855, Manual Sample Addition, Alk	10	Sample 1		YYYYMMDD	100	mL
9	855, Manual Sample Addition, Alk	11	Sample 2		YYYYMMDD	100	mL
10	855, Manual Sample Addition, Alk	12	Sample 3		YYYYMMDD	100	mL
11	855, Manual Sample Addition, Alk	13	Sample 4		YYYYMMDD	100	mL
12	855, Manual Sample Addition, Alk	14	Sample 5		YYYYMMDD	100	mL
13	855, Manual Sample Addition, Alk	15	Sample 6		YYYYMMDD	100	mL
14	855, Manual Sample Addition, Alk	16	Sample 7		YYYYMMDD	100	mL
15	855, Manual Sample Addition, Alk	17	DUP		YYYYMMDD	100	mL
16	855, Manual Sample Addition, Alk	18	CCV 100 mg/L		YYYYMMDD	100	mL
17	855, Manual Sample Addition, Alk	19	CCB		YYYYMMDD	100	mL
*							

Edit    Sample table    Loaded    SOP Alk Template

FIGURE 1

#### 11.8.1 Alkalinity Method for Samples $\geq 20$ mg/L

Prepare all the standards needed for the regular alkalinity method as listed on the Standard Preparation Bench Sheet. Place the standards into the correct position as listed on the sample run list as shown in Figure 1. Selection of CCV levels should be representative of field sample concentrations. If additional sets of 10 field samples are being analyzed, run CCVs at two levels to end the bracket: 50 mg/L and 100 mg/L.



Run

Single determination    **Determination series**

▶ Start    ■ Stop    || Hold    || Pause

**Determination parameters**

User: Peter Piro

Remark:

Autostart: 0 of Sample table ▼

**Sample data**

	Method	Sample position	Sample ID	WinLIMS ID	Batch	Sample size	Sample size unit
1	Buret preparation	16				1.0	mL
2	855 pH Calibration Manual	1				60	mL
3	855, Manual Sample Addition, Low Alk	5	ICB		YYYYMMDD	100	mL
4	855, Manual Sample Addition, Low Alk	6	QCS 12.5 mg/L		YYYYMMDD	100	mL
5	855, Manual Sample Addition, Low Alk	7	LRB		YYYYMMDD	100	mL
6	855, Manual Sample Addition, Low Alk	8	MRL 2 mg/L		YYYYMMDD	100	mL
7	855, Manual Sample Addition, Low Alk	9	ICV/LFB 12.5 mg/L		YYYYMMDD	100	mL
8	855, Manual Sample Addition, Low Alk	10	Sample 1		YYYYMMDD	100	mL
9	855, Manual Sample Addition, Low Alk	11	Sample 2		YYYYMMDD	100	mL
10	855, Manual Sample Addition, Low Alk	12	Sample 3		YYYYMMDD	100	mL
11	855, Manual Sample Addition, Low Alk	13	Sample 4		YYYYMMDD	100	mL
12	855, Manual Sample Addition, Low Alk	14	Sample 5		YYYYMMDD	100	mL
13	855, Manual Sample Addition, Low Alk	15	Sample 6		YYYYMMDD	100	mL
14	855, Manual Sample Addition, Low Alk	16	Sample 7		YYYYMMDD	100	mL
▶ 15	855, Manual Sample Addition, Low Alk	17	DUP		YYYYMMDD	100	mL
16	855, Manual Sample Addition, Low Alk	18	CCV 19.5 mg/L		YYYYMMDD	100	mL
17	855, Manual Sample Addition, Low Alk	19	CCB		YYYYMMDD	100	mL
*							

Edit ▼    Sample table ▼    Loaded    SOP Low Alk Template

FIGURE 2

### 11.8.2 Low Alkalinity Method

For the low alkalinity method, use the standards and tray set up as shown in Figure 2. For an additional set(s) of 10 samples, verify the calibration with a mid-level CCV equivalent to 12.5 mg/L of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).

11.9 Once the sample table is filled, print out the Sample table.

- Using the **Sample Table** drop down list



- Select **Print PDF**
- Select **Portrait** and click **Ok**
- Select the **print icon** in the PDF viewer
- Click **Print**

11.10 Once the autosampler tray is setup, click the Start button in the run window to start the sequence. The analysis will start with the burette preparation method and then proceed to pH calibration. The electrode will undergo a rinse between buffers, samples, and QC types. After the calibration buffers are done, remove sample vessels and add the rest of the samples to the tray, as needed. Remove and replace completed determinations if additional autosampler slots are needed.

11.11 Once the run is completed, print out the reports for the run.

- Select the **Database** icon
- Highlight the determinations to be printed in the Determination Overview screen
- Select **File**
- Select **Print**
- Select to print either **Determination Overview** or **Report**. A determination overview prints the run table with the time/date the determination started, the samples' starting pH, alkalinity results, the user's name, remarks, and batch date. A **Print determination overview (PDF)** screen opens. First select **Selected Determinations** and **Portrait**, and then selecting **OK**. This opens a PDF viewer and printing occurs inside the viewer. If printing a report is chosen, a **Report output** screen appears. Select only **Selected determination(s)** and select **Report template**. Then choose either a **WES Calibration report** template for the pH calibration report or the **WES 1 page Alkalinity report** template to print samples determinations. The output target is directly spooled to the HP LaserJet P1005 printer.

11.12 Sign and date every different report type of the printout and retain with the batch folder. Enter results into LIMS.

11.13 Remove sample vessels and pour into the hazardous waste container.

11.14 Wash vessels in dishwasher on "Cycle 1" (see user's manual located in drawer next to dishwasher) or hand wash with mild soap, rinsing at least 3 times with reagent water. Allow to air dry before stacking for reuse. Wipe down the tower and sample tray table, if necessary, with a damp Kim wipe.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The Tiamo software automatically calculates alkalinity, in milligrams of  $\text{CaCO}_3$  per liter using the following equations:

1 point titration: Alkalinity, mg  $\text{CaCO}_3/\text{L} = (\text{A} \times \text{N} \times 50,000) / \text{mL of sample}$

A = mL of acid used

N = normality of acid

2-point titration: Total alkalinity, mg  $\text{CaCO}_3/\text{L} = [(2 \text{ B}-\text{C}) \times \text{N} \times 50,000] / \text{mL of sample}$

B = mL of acid used to reach first pH

C = total mL acid used to reach 0.3 pH units lower



N = Normality of acid

These equations can also be viewed in the calculation section of the sample report.

### 13.0 METHOD PERFORMANCE

- 13.1 *Standard Methods for the Examination of Water and Wastewater* citation: Sodium carbonate solutions equivalent to 80 and 65 mg CaCO<sub>3</sub>/L were analyzed by 12 laboratories; standard deviations of 8 and 5 mg CaCO<sub>3</sub>/L, respectively, were reported with negligible bias.

The IDC for this method consisted of developing a low alkalinity method for samples less than 20 mg/L CaCO<sub>3</sub> and another method for samples greater than or equal to 20 mg/L CaCO<sub>3</sub>.

The method for the alkalinity starting at 20 mg/L CaCO<sub>3</sub> had three runs on separate days with a total of 7 MRLs equivalent to 20 mg/L CaCO<sub>3</sub> samples. The mean was 21.50 mg/L CaCO<sub>3</sub>. The percent recovery was 107.49% and the RSD was 0.81%. A total of 7 LFBs equivalent to 50 mg/L CaCO<sub>3</sub> were run: Mean 51.17 mg/L CaCO<sub>3</sub>, Recovery 102.34%, RSD 0.54%. Seven QCS samples equivalent to 50 mg/L CaCO<sub>3</sub> were also run: Mean 51.69 mg/L CaCO<sub>3</sub>, Recovery 103.38%, RSD 0.35%.

The method for low alkalinity tested an LFB equivalent to 12.5 mg/L CaCO<sub>3</sub>. In three runs on separate days a total of 7 replicates were analyzed. The mean was 12.35 mg/L CaCO<sub>3</sub>, Recovery 98.80% and RSD was 0.67%. Seven MRL standards equivalent to 2.0 mg/L CaCO<sub>3</sub> were run – mean 2.15 mg/L CaCO<sub>3</sub>, recovery 107.39%, RSD 1.11%. Seven QCS standards equivalent to 12.5 mg/L CaCO<sub>3</sub> standards were run yielding a mean of 12.51 mg/L CaCO<sub>3</sub>, Recovery of 100.04% and RSD of 1.14%.

### 14.0 MAINTENANCE

- 14.1 Wipe down the turntable and robotic arm with reagent water and paper towels after each use. Never use solvents or cleaners.
- 14.2 Ensure that there is always the proper amount of Ross reference electrode filling solution in the pH electrode (refer to the Combined pH Electrode User's Guide located on shelf above computer). Always store electrode in Ross storage solution recommended by the manufacture. There is a small plug on the pH electrode that must be closed when the electrode is not in use and open when the electrode is in use.
- 14.3 Periodically inspect all connections. Replace hoses, tubing, and connections if there is any sign of deterioration. Especially check the connections in the back of the tower.
- 14.4 Always change out the brown acid bottles below the dosinos for the clear reagent type 1 water bottles after a run and run a few preparation sequences for each dosino to displace the acid with type 1 water in the tubing and dosino.
- Go to the Manual icon
  - Select **Dosing Device 1 or 2**
  - Select the **Prepare** tab
  - Click **Start**.

Failure to do so will cause moving parts in the dosino to chemically fuse together and dosino failure. Put parafilm between the brown bottle opening and cap before tightening the orange cap.





- 14.5 If the Titrosampler is not being used daily or weekly, prior to a new analysis, run a manual dosino preparation sequence to make sure that the dosinos do not stick.

- Go to the Manual icon-
- Select **Dosing Device 1 or 2**
- Go to the **Prepare** tab
- Click **Start**

Make sure the Titrosampler has an empty cup to collect the purging waste. See sections 11.1-11.4. If the dosino sticks, go to the 807 Dosing Unit Manual page 31, Handling and Maintenance. The bottom of the dosino will need to be soaked in warm water to separate the fused parts. If the bottom of the buret becomes separated from the base, the buret will need to be replaced.

- 14.6 Make sure the cup sensor on the tower is clean. If a cup fault continues after the sensor has been cleaned, report the fault to the company and mark it in the maintenance book. The sensor may be faulty and need to be replaced.

## 15.0 POLLUTION PREVENTION

- 15.1 Refer to the WES Environmental Management System (EMS) policy and SOPs regarding pollution prevention.

- 15.2 The quantity of chemicals purchased should be based on expected usage during its shelf life. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

## 16.0 WASTE MANAGEMENT

- 16.1 WES laboratories fully comply with all applicable federal, state, and local environmental regulations. WES is also committed to protecting the air, water, and land by minimizing and controlling all chemical releases from fume hoods, biological safety cabinets, and bench operations. Refer to the WES EMS policy and SOPs regarding waste management.

- 16.2 All waste solvents are collected in sealed waste containers. Once the waste containers reach capacity, they are transferred to the WES hazardous waste storage room where they are emptied into a waste solvent drum. Within 180-days of waste accumulation, the waste solvent drum is transported off the premises by a licensed hazardous waste management contractor. Under the WES EMS, a chemical inventory database has been developed to track purchases and use of solvents and other hazardous materials, and the waste generated using these chemicals.

## 17.0 REFERENCES

- 17.1 *Standard Methods for the Examination of Water and Wastewater*, 23<sup>rd</sup> Edition, 2017. American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, DC.
- 17.2 855 Robotic Titrosampler Manual, 8.855.8001EN/2020-02-29 Metrohm AG, CH-9101 Herisau/Switzerland [www.metrohm.com](http://www.metrohm.com),
- 17.3 807 Dosing Unit Manual, 8.807.8002ML Metrohm AG CH09101 Herisau/Switzerland, [www.metrohm.com](http://www.metrohm.com)
- 17.4 Tiamo Tutorial, 8.101.8003EN, Metrohm International Headquarters, CH-9101 Herisau/Switzerland, [info@metrohm.com](mailto:info@metrohm.com) [www.metrohm.com](http://www.metrohm.com)



## 18.0 TABLES

**TABLE 1. Quality Control Elements and Acceptance Limits for the Analysis of Alkalinity by SM2320 B**

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per batch of 20 or fewer samples	$< \frac{1}{2}$ method MRL	Repeat using fresh reagent water. If failure continues, check dosing and rinsing functions are working properly and recalibrate.
Laboratory fortified blank (LFB)	One per sample batch of 20 or fewer samples	90 – 110% Recovery	Repeat with new standard. If failure continues, check dosing and rinsing functions are working properly and recalibrate.
Quality control sample (QCS) from an external source	One per sample batch	90 – 110% Recovery	Repeat with new QCS. If failure continues, check <i>dosing and rinsing functions are working properly and recalibrate.</i>
Laboratory duplicates	One per sample batch of 10 or fewer samples	Relative percent difference (RPD) $\leq 20\%$	Repeat using fresh sample. If failure continues, check dosing and rinsing functions are working properly and recalibrate.
Method Reporting Level (MRL)	One per sample batch	85 – 115% Recovery	Repeat using fresh sample. If failure continues, check dosing and rinsing functions are working properly and recalibrate.