AUTOMATED DETERMINATION OF ALKALINITY USING THE METROHM OMNIS INSTRUMENTATION

TABLE OF CONTENTS:

Page

1. SCOPE AND APPLICATION 2
2. SUMMARY OF THE METHOD 2
3. EQUIPMENT AND SUPPLIES 2
4. REAGENTS AND STANDARDS 3
5. SAMPLE ANALYSIS/QUANTITATION 6
6. TROUBLESHOOTING/MAINTENANCE 7
7. DATA ARCHIVAL 7
8. QUALITY CONTROL/DATA ASSESSMENT 9
9. SAFETY/HAZARDOUS WASTE MANAGEMENT 9
10. REFERENCES/DEFINITIONS 10

APPENDIX OF SIGNIFICANT CHANGES 10

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

1. SCOPE AND APPLICATION

1.1. The method is applicable to drinking, surface, ground, and saline waters as well as industrial and domestic waste. The method detection limit (MDL) is 0.70 mg $CaCO_3$/L and the practical quantitation limit (PQL) is 2.5 mg $CaCO_3$/L.

1.2. The test covered by this SOP is ALKALINITY.

2. SUMMARY OF THE METHOD

2.1. This method, based on Standard Methods 2320 B-2021, is used for determining the alkalinity of water samples with an automatic titration instrument – Metrohm OMNIS Robot.

2.2. A fully automatic titration procedure is employed to titrate aqueous samples electrometrically to an end point of 4.5 (or 4.5 and 4.2 for alkalinity samples below 20 mg $CaCO_3$/L). The alkalinities are then calculated from the amount of the titrant (0.02 N H_2SO_4) used in the titration.

2.3. Interferences – Substances such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements. Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.

2.4. Sample Preservation and Holding Time – Samples for alkalinity determination are stored at ≤ 6 °C (not frozen) and must be analyzed within 14 days of collection to avoid qualification.

3. EQUIPMENT AND SUPPLIES

3.1. Instrumentation: Metrohm OMNIS Robot.

3.2. Equipment:

Equipment	Manufacturer/Vendor[1]	Model/Catalog Number
pH Electrode	Metrohm	d-Aquatrode – 6.00202.300
Analytical Balance	Mettler Toledo	MS204TS/0
Adjustable Pipette, 10–100 µL	Eppendorf/Fisher	Research Plus, 3123000047
Adjustable Pipette, 100–1000 µL	Eppendorf/Fisher	Research Plus, 3123000063
Adjustable Pipette, 1–10 mL	Eppendorf/Fisher	Research Plus, 3123000080
Volumetric Flask, Class A, Assorted	Fisher (SR)	10-212B; 10-210-5D; 10-212E; 10-212-5L; 10-208M
Graduated Cylinder, Class A, Assorted	Fisher (SR)	08-553A; 08-548D
Glass Beaker, Assorted	Fisher (SR)	02-540E; 02-540G; 02-540K; 02-555-20E
Or Equivalent		
[1]**Note:** (SR) designates equipment is typically ordered through the in-house stockroom		

3.3. Consumables and frequently replaced supplies:

Supplies/Consumables	Vendor[1]	Catalog Number
Electrode filling solution	Metrohm	

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

Lithium Grease	Fisher	NC0484446
Centrifuge Tubes, Polypropylene, 50 mL	Fisher (SR)	05-538-68, 05-53855A
Pipette tips, Eppendorf, 200 µL	Fisher (SR)	05-403-41
Pipette tips, Eppendorf, 1000 µL	Fisher (SR)	05-403-43
Pipette tips, Eppendorf, 10 mL	Fisher (SR)	05-403-116
Sample Beakers, Polypropylene, Assorted	Fisher (SR)	08-732-119; 08-732-120; 08-732-122
Syringe, Polypropylene	Fisher (SR)	B303134
Syringe Filters, Polypropylene, 25mm (0.45 µm pore size)	Fisher (SR)	05-713-404A
Weigh Dish, Hexagonal, Assorted	Fisher (SR)	02-202-102; 02-202-100
Weigh Dish, Aluminum, 110 mm	Fisher (SR)	08-732-100
Pipet, Transfer, Polyethylene, 7mL	Fisher (SR)	13-711-7M
Parafilm	Fisher (SR)	13-374-12
Or Equivalent		
[1]**Note:** (SR) designates supply is typically ordered through the in-house stockroom		

4. REAGENTS AND STANDARDS (SEE DEP SOPS NU-041 and NU-042)

Note: Before preparing reagents or standards, or running samples, please read the safety notes in the safety/hazardous waste section of this SOP and the MSDS for the chemicals used in this analysis.

Note: Standard preparations must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each standard are generated in the module and documented in the reagent and standard logsheet (NU-RGTSTD) submitted with each analysis folder. The reagent and standard logsheet (NU-RGTSTD) template is located at \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\MetaData\Auto-T\Forms\. Follow preparation and labelling instructions in DEP SOP NU-042. A Certificate of Analysis (CoA) for each purchased reagent and standard is maintained in the CertificatesofAnalysis subfolder within the Auto-T folder on the Nutrients Drive. All containers holding standards or reagents must be labeled with their unique ID and expiration date.

Note: The volumes prepared for the reagents and standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard or reagent must not be changed.

4.1. Chemicals:

	Chemical	Alias	Manufacturer[1]	Catalog Number	Purity	Storage
4.1.1.	Sodium Carbonate Anhydrous	Na_2CO_3	Fisher Chemical	S263-500	ACS, ≥95%	Room Temp
4.1.2.	Sulfuric Acid (0.02N (N/50)/Certified)	H_2SO_4	Fisher Chemical	SA226-1	ACS, ≥99%	Room Temp
4.1.3.	Sulfuric Acid	H_2SO_4	Fisher Chemical (SR)	A300S-212	Concentrated, ACS Plus ≥95%	Room Temp
4.1.4.	Minerals QC CRM	ALTQC	NSI Lab Solutions	QCI-136	See CoA	Fridge after opening

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

4.1.5.	pH 4.00 Buffer	4 Buffer	Fisher Chemical (SR)	SB101-500	N/A	Room Temp
4.1.6.	pH 7.00 Buffer	7 Buffer	Fisher Chemical (SR)	SB107-500	N/A	Room Temp
4.1.7.	pH 10.00 Buffer	10 Buffer	Fisher Chemical (SR)	SB115-500	N/A	Room Temp
4.1.8.	DI Water	H_2O	In house	N/A	N/A	N/A
Or Equivalent [1]**Note:** (SR) designates chemical is typically ordered through the in-house stockroom						

Deionized water is replaced daily. All other purchased chemicals are given the expiration date from the CoA and/or chemical container. If there is not an expiration date listed, the expiration date is designated by following the protocol in SOPs NU-041 and NU-042.

4.2. Reagents:

4.2.1. 0.02 N Certified Sulfuric Acid Standard – purchased from Fisher Scientific (4.1.2.). Replace after one month of use. If unavailable, prepare and standardize the acid manually according to the instructions in 4.2.2 through 4.2.3.

4.2.2. 0.020 N Sodium Carbonate Solution (only used for standardization of prepared acid (4.2.3.)) –

Na_2CO_3 (4.1.1.)	1.0606 g
DI water (4.1.8.)	to 1000 mL

Add 1.0606 g (to the nearest +/- 0.05 mg) Na_2CO_3 (dried at 105 ºC overnight and cooled in a desiccator) to a 1 L volumetric flask and dilute to the mark with deionized (DI) water. Invert flask at least 8 times to mix.

Store refrigerated. Holding time, 30 days.

4.2.3. 0.02 N Prepared Sulfuric Acid Standard – If the certified standard is not available, use the following procedure:

H_2SO_4 (4.1.3)	555.6 µL
DI water (4.1.8)	to 1000 mL

To a 1L volumetric flask add approximately 500 mL DI water. Pipette 555.6 µL of conc. H_2SO_4 into the flask. Dilute to the mark. Invert flask at least 8 times to mix. Titrate against 0.020 N sodium carbonate solution (see 4.2.1.) to standardize.

Store at room temperature. Titrate against 0.020 N sodium carbonate solution (see 4.2.1.) to standardize after 1 month. For standardization procedure, reference 5.3.1 and Standard Methods 2320 B-2011 section 3*b*.

4.3. Calibration Standards and Quality Control Standards:

4.3.1. 0.20 N (10,000 mg $CaCO_3$/L) Sodium Carbonate Spiking Solution –

Na_2CO_3 (4.1.1.)	1.0606 g
DI water (4.1.8.)	to 100 mL

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

Add 1.0606 g (to the nearest +/- 0.05 mg) Na_2CO_3 (dried at 105 °C overnight and cooled in a desiccator) to a 100 mL volumetric flask and dilute to the mark with DI water. Invert flask at least 8 times to mix.

Molecular weight factor: 0.945

Store refrigerated. Holding time, 30 days.

4.3.2. A certified quality control sample – ALTQC (4.1.4.)

Prepared following the supplier's instructions, if needed. The standard can be stored at room temperature, but is generally stored in the refrigerator. The concentration is provided by the manufacturer. There is not a recommended holding time by the manufacturer, but standard is given a 28-day holding time upon opening.

4.3.3. Laboratory Fortified Blank (LFB) –

Na_2CO_3 Spiking Solution (4.3.1.)	200 µL
DI water (4.1.8.)	40 mL

Add 200 µL of the 10,000 mg $CaCO_3$/L Na_2CO_3 solution to a 40 mL aliquot of DI water for a 50 mg $CaCO_3$/L spike.

Prepared daily. (Spike code _N2.)

4.3.4. Continuing Calibration Verification (CCV):

4.3.4.1. CHCK1 (100 mg $CaCO_3$/L check standard) –

Na_2CO_3 Spiking Solution (4.3.1.)	400 µL
DI water (4.1.8.)	40 mL

Add 400 µL of 10,000 mg $CaCO_3$/L Na_2CO_3 solution to a 40 mL aliquot of DI water.

Prepared daily.

4.3.4.2. CHCK3 (50 mg $CaCO_3$/L check standard) –

Na_2CO_3 Spiking Solution (4.3.1.)	200 µL
DI water (4.1.8.)	40 mL

Add 200 µL of 10,000 mg $CaCO_3$/L Na_2CO_3 solution to a 40 mL aliquot of DI water.

Prepared daily.

4.3.5. Buffer solutions at pH 4.00, 7.00 and 10.00 (4.1.5., 4.1.6., 4.1.7.) are used as calibration standards.

Store at room temperature. The expiration date is provided by the manufacturer.

5. SAMPLE ANALYSIS/QUANTITATION (SEE DEP SOP NU-033)

Note: Allow the samples to come to room temperature prior to measuring the alkalinity.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

5.1. Calibration:

5.1.1. Pour approximately 50 mL of buffers 4.00, 7.00 and 10.00 (4.1.5., 4.1.6., 4.1.7.) into three separate glass tubes appropriately labeled.

5.1.2. A multi-level calibration with pH 4.00, 7.00, 10.00 buffers may be carried out either independently on a daily basis or together with samples in each run.

5.1.3. Following the calibration and before samples are analyzed, a repeat measurement of the three calibration standards is taken. This is used to evaluate the relative error of the calibration.

5.2. Analysis of samples:

5.2.1. Start-up of the Metrohm OMNIS Software – Choose the appropriate method (alkalinity alone or in combination with other tests). Set up the run sequence corresponding to the timetable of Metrohm OMNIS software.

5.2.2. Loading samples – Pour 50 mL of sample or standard into a glass sample tube. Load the sample tubes onto the autosampler in a sequence determined in section 5.2.1. It is recommended to run a tap water sample at the very beginning as a rinse to clean up the system and condition the probe.

Note: Samples are not to be filtered. If it is suspected that a sample with heavy particulate matter is causing matrix interference or instrumentation failure, the sample may be filtered and the data qualified and reported with a comment. Filtered samples will be indicated on the backlog or bench sheet with an F.

Example Run Sequence:

Rinse – Tap water
pH CAL – 4.00, 7.00, and 10.00 pH buffers (5.1.)
pH CAL Check – 10.00, 7.00, 4.00 pH buffers (reverse)
MDL – (blank - DI water)
ALTQC (4.3.2.)
CHCK1 or **CHCK 3** (4.3.4.)
Blank – DI water
MBLK – Method blank: DI water (one per batch)
LFB_N2 (one per batch, 4.3.3.)
Batched samples: one sample run in duplicate (sample ID_D) for each batch of max. 20 samples.
Blank – DI water (before every CHCK)
CHCK 3 or **CHCK1** – alternate CCV CHCK every 20 cups
Blank – DI water

Click on the START button to start the run.

5.3. Calculations:

5.3.1. Standardization/acid normality is given by (used if certified H_2SO_4 solution is unavailable) –

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

$$\frac{(\text{grams of } Na_2CO_3\text{/L solution}) \times (\text{mL of } Na_2CO_3 \text{ titrated})}{53.00 \times (\text{mL of acid used in standardization})}$$

5.3.2. Alkalinity of samples (performed by instrument software) –

$$\frac{(\text{Normality of acid}) \times (\text{mL of acid}) \times 50{,}000}{\text{Volume of sample (mL)}}$$

5.3.3. Alkalinity of low alkalinity samples (performed by instrument software) –

$$\frac{[(2A - B) \times \text{Normality of acid} \times 50{,}000]}{\text{Volume of sample (mL)}}$$

A = mL of acid to pH 4.5
B = mL of acid to pH 4.2

5.4. For general calculations see Sections 5.9 of the FDEP Quality Manual.

6. TROUBLESHOOTING/MAINTENANCE

6.1. Problems with calibration may be due to instrument failure. Consult troubleshooting section of instrument manual.

6.2. Always keep the probe in water or electrode storage solution when not in use. For further details on maintenance of the instrument and the probe, refer to related hardware manual.

7. DATA ARCHIVAL

7.1. All analytical results are automatically saved in the database of the instrument software.

7.2. The raw data is archived in the export file used for the LIMS QCM upload as well as the instrument software. A report folder is created for each analytical run. A folder may contain more than one analysis (e.g. Alkalinity, and/or Conductivity) in it if the analyses are part of the same analytical run. The folder is labeled with the test (e.g., ALK and/or W-COND), filename/s (YYMMDDN-O#), and initials of the analyst.

7.3. The export file is used to create a general results report. Follow these steps to create the general result report:

7.3.1. Create a delimited file from the instrument CSV. Open excel, go to file – open – browse – locate the run files folder for that year – set the file type to “All Files” – select the run file. A dialogue box should appear, select “Delimited” – Next – Uncheck “Tab” – Check “Semicolon” – Finish.

7.3.2. Format the delimited file as a table. Use “Ctrl+A” to select all the data in the file, go to the home tab in Excel and select “Format as Table”, ensure the proper data is selected and press “OK”.

7.3.3. Filter the table to show the data you need. Select the filter drop-down for the column header “Subsample name” and deselect “Subsample name”.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.3.4. In a new excel sheet, open the form NU-AUTOTSHEET-1. Record the File Name and copy and paste the results from the delimited table into the appropriate form columns. Print the form as a PDF. Sign the form in Adobe using a certificate.

7.4. Each report folder should contain the following items – general results report, calibration report(s), reagent and standard and pipette logsheet(s), and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

7.5. The report folders are on file with the nutrients and general chemistry supervisory personnel. Files are stored according to DEP SOP LB-006.

7.6. The analytical file can be authorized online if necessary by scanning the entire folder into the correct year on the Nutrients drive at \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\AnalysisFolders\Auto-T\. Once the authorizer has made comments and digitally signed all items of the pdf after reviewal, the QC report from QCM is saved as "YYMMDDN-O#_Authorization" and digitally signed as well. The signed analytical file and QC report is saved into a folder.

7.7. Method validation data is on file with the supervisor. Digital copy is also stored on the network, under an appropriate sub-folder in \\floridadep\data\labs\Lab5\Chemistry\Inorganic\Nutrient\Validations\Metrohm.

8. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES (SEE DEP SOP NU-038 AND NU-043)

8.1. A CCV standard (CHCK1 or CHCK3, 4.3.4.) and a QC standard (ALTQC, 4.3.2.) must be analyzed prior to every analytical run. Recoveries must be 90 to 110% for the CCV standards. Recovery for the ALTQC standard must be within the manufacturer's certified limit but not exceed 85 to 115%.

8.2. Analyze a blank and a CCV (CHCK1 or CHCK3) standard every 20 cups tested and at the end of the analyses.

8.3. Each sample batch begins with an MBLK and one LFB (4.3.3). One randomly selected sample is run in duplicate for every batch of 20 samples. Acceptance limits for the blanks and MBLKs are < 0.70 and > -0.70 mg $CaCO_3$/L.

8.4. Acceptance limits for the LFBs are 90 – 110%. The upper and lower control limits (UCL and LCL) are calculated in the QC Statistics module in LIMS. The limits are evaluated regularly and documented at least annually. The QC Statistics Calculation Reports are archived annually with the PC-Titrate instrument validation data on the Chemistry drive: \\floridadep\data\labs\Lab5\Chemistry\Inorganic\Nutrient\Validations\PC Titrate\QC Stats Limits\. These reports are used to monitor ongoing instrument performance and show that the assigned limits are achievable.

8.5. The sample RPD must be less than 10% for results above the PQL.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

8.6. For general method performance and acceptance criteria for QC measures and corrective action for out-of-control data and contingencies for handling out-of-control or unacceptable data, refer to DEP SOPs NU-038 and SOP NU-043.

8.7. Calibration – The calibration standards (4.3.5.) are 4.00, 7.00, and 10.00 pH buffers. Every day samples are analyzed a new calibration is performed at the beginning of the analysis. Per the manufacturer's recommendation, the calibration is acceptable if the slope value is between 0.95 and 1.03.

8.8. Following the calibration and before samples are analyzed, a repeat measurement of the three calibration standards is taken. The measured values must be within 0.05 pH units of the buffer solution value. This will be used to evaluate the relative error of the calibration.

8.9. Annual MDL verification is performed using the LIMS statistics tracker module, (see DEP SOP NU-043). Method blank (MBLK) data is collected and utilized for the ongoing MDL verification.

9. SAFETY/HAZARDOUS WASTE MANAGEMENT

9.1. Review the laboratory Health and Safety Plan (accessible at https://floridadep.sharepoint.com/dear/SitePages/Lab%20Health%20and%20Safety.aspx).

9.2. Safety glasses, gloves and lab coats should be worn at all times whilst handling samples and reagents.

9.3. Read the MSDS information for safe reagent and sample handling.

9.4. Buffers and leftover samples with a pH value of > 2 or < 12.5 units may be flushed down the sink with water.

10. REFERENCES/DEFINITIONS

For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time of use.

10.1. Standard Methods Online, 2320 B-2021.

10.2. Metrohm OMNIS Instrument Operations Manual.

10.3. DEP SOP NU-033, Summary of Sample Analysis Procedures for the General Chemistry and Nutrients Workgroups.

10.4. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

10.5. DEP SOP NU-041, Reagent Preparation Procedure.

10.6. DEP SOP NU-042, Standard Preparation Procedure.

10.7. DEP SOP NU-043, Nutrients and General Chemistry Quality Assurance and Data Authorization Guidelines.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

10.8. Laboratory Health and Safety Plan.

10.9. DEP SOP LB-006, Standard Operating Procedure for Records Maintenance and Storage.

10.10. OMNIS Software 4.4.1.

10.11. Quality Manual, Bureau of Laboratories, FDEP.

Appendix of Significant Changes

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.