Laboratory Manager Approval: Kristy E. Hrehor / 08/19/2021

QA Manager Approval: Jeffrey Moore / 08/19/2021

SM2320B – Alkalinity: Titration Method

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1. Scope and Application

1.1 This method covers the determination of alkalinity in drinking, surface, and saline waters and industrial wastes. Alkalinity is the measure of a sample's acid –neutralizing capacity. It is the sum of all titratable bases. Because the alkalinity of many surface waters is primarily the function of carbonate, bicarbonate and hydroxide content, it is taken as an indication of contributions from borates, phosphates, silicates and other bases.

1.2 Restricted Procedure

1.2.1 This procedure is restricted to use by an analyst experienced in the operation of a pH meter and digital burette. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2. Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Plan (see SOP reference 13.6) for Quality Control Definitions.

2.2 Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3 Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4 Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The

ICV is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.5 Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration.

2.6 LCS (Laboratory Control Sample) and LCSD (Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision.

3. Interferences

3.1 Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally.

4. Safety

4.1 Refer to the EPD Laboratory Safety/Chemical Hygiene Plan and Fire Safety Plan, online revision.

5. Apparatus and Equipment

5.1 Sample Container: plastic half-gallon container

5.2 150 ml glass beakers

5.3 Approved pH meter with pH electrode and reference electrode with automatic temperature compensation.

5.3.1 Glass electrode

5.3.2 Reference electrode- a silver-silver chloride or other reference electrode with automatic temperature compensation. Note: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

5.4 Stir plate and stir bar

5.5 Class A graduated cylinders and pipettes

5.6 Thermometer and/or temperature sensor for automatic compensation.

5.7 Digital Burette

6.1 Reagent Water:

Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest. (Deionized, HPLC, Milli-Q water or equivalent. Milli-Q water has a resistivity of 18.2[MΩ·cm]@ 25ºC and a TOC of 50 ug/L or less).

6.2 Acid Titrant (.02N H_2SO_4):

6.2.1 Certified and commercially prepared solution purchased from JT Baker Catalog No: 5693-03 Sulfuric Acid, 0.02N or equivalent.

6.2.2 This solution is stable until expiration date on box or within 1 year of opening date, whichever is sooner.

6.3 High Level LCS Stock Standard (1000 mg/L $CaCO_3$):

6.3.1 A certified and commercially prepared solution purchased from AccuStandard, Inc. Catalog No: WC-ALK-10X-1, or equivalent.

6.3.2 This solution is stable until expiration date on bottle or 6 months of opening date, whichever is sooner.

6.3.1 LCS/LCSD Standard (30 mg/L $CaCO_3$):
Pipette 60 ml of High Level LCS Stock Standard Solution (Section 6.3) into a 2000 mL volumetric flask and dilute to volume with reagent water (Section 6.1). Prepare fresh every 3 months.

6.4 Low Level LCS Stock Standard (1000 mg/L CaCO3):
A certified and commercially prepared solution, purchased from Sigma Aldrich Catalog No: ALK-1000-500ml, or equivalent. This solution is stable until expiration date on bottle or 6 months of opening date, whichever is sooner. Store in refrigerator.

6.4.1 Low Level LCS/LCSD Check Standard (15 mg/L $CaCO_3$):
Pipette 30 ml of LCS Stock Solution (Section 6.5) into a 2000 mL volumetric flask and dilute to volume with reagent water (Section 6.1). Prepare fresh every 3 months.

6.5 Reference Filling Solution:

6.5.1 Thermo Scientific™ Orion™ pH Electrode Filling Solution Thermo Scientific™ 900011, Fisher Catalog# 13-641-686 or equivalent.

6.6 pH Buffers:

6.6.1 pH Buffer 4.00- VWR catalog # BDH5022-4L or equivalent.

6.6.2 pH Buffer 7.0.- VWR catalog # BDH5050-4L or equivalent.

6.6.3 pH Buffer 10.0- VWR catalog # BDH5076-4L or equivalent.

6.6.4 pH Buffer 12.0 - VWR catalog # BDH5022-4L or equivalent.

6.6.5 ICV pH Buffer 7.00 – VWR catalog # BDH5054-4L or equivalent.

7. Sample Collection

7.1 Samples are collected in a half-gallon plastic container.
7.2 The samples are stored at 0 - 6º C (not frozen).
7.3 Sample holding time is 14 days.
7.4 Samples are refrigerated at 0 - 6º C (not frozen) until analysis.
7.5 No chemical preservation is required.

8. Calibration

8.1 Calibration Standards

8.1.1 The pH meter calibration standards are discussed in the pH standard operating procedure SOP 3-003, SOP reference 13.2.

8.2 Calibration Curve

8.2.1 The pH meter is calibrated daily according to the pH standard operating procedure SOP 3-003, SOP Reference 13.2. and section 10.1. of this SOP.

8.3 Calibration Verification:

8.3.1 Laboratory Control Standard (LCS) - The acid titrant is verified using a second source standard > 20 mg/l and is recorded as an LCS for control charting purposes. The LCS and LCSD (Laboratory Control Standard Duplicate) values must be within 10% of the true value. The LCS/LCSD pair is analyzed once per analytical batch.

8.3.2 Low level check standard – The acid titrant is verified using a second source standard < 20 mg/l. The Low level check standard is analyzed once daily prior to sample analysis.

9. Quality Control

9.1 The default control limits for SM2320B are 90 - 110% recovery for Alkalinity for LCS recoveries. The EPD Laboratory applies LCS recovery limits to LCDs. Note, unless specified by method, the EPD Laboratory does not validate batch quality based on LCSD recoveries.

9.2 By default, the EPD Laboratory sets LCS/LCSD precision limits for this method to be 0 - 15% RPD.

9.3 LCS/LCSD recovery and precision limits are static (i.e. not adjusted by control chart results).

9.4 The Low Level Alkalinity Check control limits are static at 75 -125% recovery for Alkalinity.

9.5 10% of all routine samples over time must be analyzed in duplicate. This is accomplished per section 9.8.

9.6 By default, the EPD Laboratory sets default sample precision control limits to be 0 – 15% RPD. These limits are static.

9.7 Batch samples in groups of 17.

9.8 For batches of 1 to 10 routine samples, one sample/sample duplicate pair must be analyzed. For batches of 11 to 17 routine samples, two sample/sample duplicate pairs must be analyzed using different samples for each pair. When choosing two samples for duplicate analyses, the first duplicate should be chosen from within the first 10 samples in the batch and the second duplicate should be chosen from the remaining samples in the batch.

9.9 Refer to Table 14.1 for Reporting Limits (RLs), Table 14.2 for Quality Control Acceptance Criteria and Table 14.3 for Quality Control Procedures associated with this method and Standard Operating Procedures for Control Charts and Control Limits.

9.10 The control limits are static and appear in Table 14.2. Control charts must still be performed even though limits are static.

9.11 The temperature compensation probe must be verified at least quarterly using a NIST traceable thermometer. The allowable temperature deviation of the pH meter temperature sensor compared to a NIST traceable thermometer is ± 2° C. This verification must be recorded in the pH, Conductivity, Turbidity, and Alkalinity Maintenance Logs.

9.12 The titrator should be calibrated every 6 months using an outside vendor service.

10. Procedure

10.1 Remove sample bottles from the cold storage and allow equilibration to room temperature prior to sample preparation and/or analysis. The samples should be at the same temperature as the buffers used for calibration.

10.2 Remove the pH electrode from the pH ICV storage solution.

10.2.1 Inspect the electrode and the level of the reference electrode filling solution.

10.2.2 Rinse probe well with reagent water.

10.2.3 If filling solution is below the filling hole by more than ¼ inch, add filling solution (See Section 6.5).

10.2.4 If reference chamber has layers of KCl crystals, empty chamber by gently pressing air in chamber with disposable pipette while holding probe upside down.

10.2.5 Refill with reagent water and shake several times to dissolve crystals. Empty chamber and repeat again with reagent water. Empty chamber and refill with Reference filling solution (See Section 6.5) to the top of the chamber hole.

10.2.6 Allow one hour for probe readings to stabilize after replacing filling solution.

10.2.7 Record in maintenance log.

10.3 Rinse the probe well with reagent water and gently blot dry.

10.4 Press the POWER button on the meter and wait for the pH numbers to appear and the meter to warm up. Important: Always ensure that the reference electrode with the automatic temperature compensation is plugged in securely to the rear of the meter and check the temperature adjustment when monitoring samples. Note: If the temperature is staying at 25ºC then the temperature compensation is not working.

10.5 Pour up fresh 4.0, 7.0, and 10 buffer solutions daily into 3 separate 50 ml beakers containing stir bars. Keep buffer solutions covered with parafilm when not in use.

10.6 Calibrate pH meter

10.6.1 Press calibrate button.

10.6.2 When 'CAL 1' appears on screen, place the beaker with the 4.0 buffer on stir plate under the probe, turn stirrer on to stir gently. Immerse electrode into the 4.0 buffer solution. Allow the reading to stabilize. When the pH symbol stops blinking, the meter is stable.

10.6.3 Before removing the 4.00 buffer solution, press the calibrate button and turn off the stirrer. When 'CAL 2' appears, raise electrode out of the 4.00 buffer solution, rinse well with reagent water, and blot excess water from the electrode with a tissue.

10.6.4 Place the beaker containing the 7.0 buffer solution on the stir plate, turn on the stirrer to stir gently, immerse the pH probe into the 7.0 buffer solution and wait for the meter to stabilize and the pH symbol to stop blinking.

10.6.5 Press the calibrate button on the pH meter and wait for "CAL 3" to appear, turn off the stirrer, raise the probe out of the 7.0 buffer solution, rinse well with reagent water and blot excess water off of the probe with a tissue.

10.6.6 Place the beaker containing the 10.0 buffer on the stir plate, turn on the stirrer to gently stir and immerse the probe into the 10.0 buffer solution.

10.6.7 Allow the meter to stabilize, wait for pH symbol to stop blinking.

10.6.8 Press the measure/save/print button to save the calibration curve and the "SLOPE' reading will appear on the screen. Make sure to record the "SLOPE" reading on the sample bench sheet.

10.6.9 The slope should be between 92% - 102%. If not, clean the electrode according to manufacturer's instructions and calibrate the meter again following the instructions above.

10.6.10 Read the 4.0, 7.0 and 10.0 buffers and record the results on the worksheet. Results must be within ± 0.1 pH units of true value.

10.6.11 Verify the calibration by checking a second source standard (ICV). Record the result on the bench sheet.

10.7 Perform a backlog of pending samples. Batch samples in groups of 17. For each batch choose a QC sample and analyze a sample duplicate for a minimum of 10% of the samples.

10.8 Procedure for using the Titrator (Digital Burette)

10.8.1 To power on the instrument, press the **ON/Off** key (located under the digital display window and to the left). **Note: Do not rotate the hand wheels when the valve is set to 'Titrate' and the titrating tube is closed with the screw cap.**

10.8.2 Fill digital burette smoothly up to the upper position by turning the hand wheels gently towards the back or clockwise. Make sure the digital burette has been calibrated. It must be calibrated professionally every six months.

10.8.3 Press the CLEAR key (located on top of instrument) once briefly in order to set the display value to zero.

10.8.4 Place the beaker of the sample to be titrated on a stirring plate under the opening of the titrating tube. Turning the hand wheels towards you or counter-clockwise, delivers liquid up to the titration end point according to the parameter analysis SOP. The ml titrated will appear in the display window.

10.8.5 **Note: (If the volume is insufficient for the entire titration, press the Pause key (located to the right of the power button), then refill by gently turning back the hand wheels to the upper position (the displayed value remains unchanged during this process). Press the Pause key again and continue with the titration. This can also be done if air bubbles appear during titration because the titrator was not completely primed. The liquid can be dispensed into another receptacle for priming without the display value being changed. If the displayed value is inadvertently deleted, it can be restored by pressing the CLEAR key again.**

10.9 Procedure for Alkalinity Values of 20 mg/l or Greater

10.9.1 After the pH meter has been calibrated, transfer 100 ml sample into beaker and place on stir plate and start stirrer.

10.9.2 Lower probes into sample and press the pH key.

10.9.3 Wait for pH to stabilize and start titration.

10.9.4 Titrate with 0.02N H_2SO_4 solution to a pH of 4.5. Do not over titrate.

10.9.5 Record the burette reading on worksheet and use equation in section 11.1 to obtain the alkalinity result. Note: when using 0.02N acid and 100 ml of sample, the equation condenses to: Alkalinity, mg $CaCO_3$/L = A x 10.

10.9.6 Rinse the probe well with reagent water and blot the excess water off of the probe with a tissue between samples.

Note: If more than 15 ml's of titration solution is required to reach a pH of 4.5, stop titrating, and report a result of > 150 mg/l on the worksheet and in Labworks.

10.10 Procedure for Low Level Alkalinity of 20 mg/l or Less

10.10.1 Follow procedure in section 10.9, but stop the titration at a pH of 4.5. Record the volume of titrant used and exact pH.

10.10.2 Next, carefully add additional titrant to reduce the pH exactly 0.3 pH units to pH of 4.2 and again record the volume of titrant used.

10.10.3 Use calculation from section 11.2. to obtain alkalinity result. Note: when using 0.02N acid and 100 ml of sample, the equation condenses to: Alkalinity, mg $CaCO_3$/L = (2B-C) x 10.

10.10.4 Rinse the probe well with reagent water and blot the excess water off of the probe with a tissue between samples.

11. Calculations

11.1 Potentiometric titration to end point pH:

$$\text{Alkalinity, mg } {}^{\text{CaCO}_3}/_{\text{L}} = \frac{(A * N * 50{,}000)}{\text{ml}_{\text{Sample}}}$$

11.1.1 Where:

A = ml of titrant
N = Normality of acid standard

11.2 Potentiometric titration of low alkalinity:

$$\text{Total Alkalinity, mg } {}^{\text{CaCO}_3}/_{\text{L}} = \frac{\left((2B - C) * N * 50{,}000\right)}{\text{ml}_{\text{Sample}}}$$

11.2.1 Where:

B = ml titrant to first recorded pH
C = total ml of titrant to achieve pH 0.3 units lower than B
N = Normality of acid standard

11.3 Percent Recovery:

11.3.1 LCS/LCSD:

$$\%\mathrm{Recovery} = \frac{\mathrm{Conc_{spiked}}}{\mathrm{Conc_{expected}}} * 100$$

11.3.1.1 Where:

$\mathrm{Conc_{spiked}}$ = Concentration found in the spiked sample

$\mathrm{Conc_{expected}}$ = Expected concentration

11.4 Relative Percent Difference (%RPD or RPD):

$$\%\mathrm{RPD} = \frac{|\mathrm{X_1} - \mathrm{X_2}|}{\frac{(\mathrm{X_1} + \mathrm{X_2})}{2}} * 100$$

11.4.1 Where:

$|\mathrm{X_1} - \mathrm{X_2}|$ = Absolute difference between two values

$\frac{(\mathrm{X_1} + \mathrm{X_2})}{2}$ = Average of two values

12. Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, SOP Reference 13.5.

13. References

13.1 Standard Methods SM2320B - Alkalinity: Titration Method, 1997.

13.2 GA EPD Laboratory SOP - SM4500-H+B - pH SOP 3-003, online revision.

13.3 GA EPD Laboratory SOP’s – Initial Demonstration of Capability SOP 6-001, online revision, or Continuing Demonstration of Capability SOP 6-002, online revision.

13.4 GA EPD Laboratory SOP - EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.

13.5 GA EPD Laboratory SOP - EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.6 GA EPD Laboratory – Laboratory Quality Assurance Plan, online revision.

13.7 GA EPD Laboratory SOP - Laboratory Safety/ Chemical Hygiene Plan & Fire Safety Plan, online revision.

13.8 Manual for the Certification of Laboratories Analyzing Drinking Water, EPA/815-R-05-004, January 2005.

14. Reporting Limits RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 14. 1 RLs for Method SM 2320B

Parameters/Method	Analyte	Matrix (aqueous) RL	Matrix (aqueous) Units
SM 2320B	Alkalinity	1.0	mg/L

Table 14. 2 Acceptance Criteria for Method SM 2320B

QC Type	Analyte	Accuracy (%R) LCL	-	Accuracy (%R) UCL	Precision (%RPD)
LCS/LCSD	Alkalinity	90	-	110	15
Low Level Check	Alkalinity	75	-	125	NA
Sample Duplicate	Alkalinity	NA	-	NA	15
All control limits are static.					

Table 14. 3 Summary of Calibration and QC Procedures for Method SM 2320B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
SM 2320B	Alkalinity	Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, a method blank and a blind sample. In addition, the analyst must prepare one standard.	Once per analyst	QC Acceptance Criteria Table 14.2 and Initial Demonstration SOP (Reference 13.3)	Recalculate results: locate and correct problem with system and rerun demonstration for those analytes that did not meet criteria	
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria Table 14.2 and Continuing Demonstration of Capability SOP (Reference 13.3)		
		Laboratory Control Sample (LCS/LCSD)	One LCS/LCSD per analytical batch	QC Acceptance Criteria Table 14.2	Correct problem and reanalyze the LCS/LCSD and all samples in the affected batch	If unable to reanalyze, flag with a "J"

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
SM 2320B	Alkalinity	Low level check	Once per day prior to sample analysis	QC Acceptance Criteria Table 14.2	Correct problem and reanalyze the Low level check	If unable to reanalyze, flag with a "J"
		Sample Duplicate	10% of all samples analyzed over time	QC Acceptance Criteria Table 14.2	Evaluate out of control event and reanalyze sample	
		Temperature Compensation Probe check	At least quarterly	± 2° C	Correct problem or replace probe	

Updates to Previous Version:
Updates made for online version.
Section 2
Section 6
Section 9
Section 10