Standard Operating Procedure for the Determination of Alkalinity

1.0 Scope and Applicability:
This method is used to determine alkalinity in water. The alkalinity of water is its quantitative capacity to neutralize a strong acid to a designated pH. The measured value may vary significantly with the end point pH used in the determination . Alkalinity is a measure of a gross property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

2.0 Summary of Method:
A 50 mL aliquot of sample is measured for initial pH, then titrated to endpoints of pH 8.3 and pH 4.5 using 0.04 N H_2SO_4 The LIMS software calculates the total alkalinity in terms of $CaCO_3$.

3.0 Definitions:

ppm	parts per million
mL	milliliter
EPA	Environmental Protection Agency
LFB	Laboratory Fortified Blank

4.0 Interferences:
Soaps, oily matter, suspended solids or precipitates may coat the glass electrode and cause a sluggish response. Clean electrodes occasionally.

5.0 Safety:
Use safety precautions when transporting concentrated acid from a different room. Dispense concentrated acid in a fume hood and wear appropriate personal protection while doing so. This method does not address all safety issues associated with its use. The laboratory and it's Director are responsible for maintaining a safe work environment and current awareness of the file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS's) should be available to all personnel involved in this analysis.

6.0 Equipment and Supplies:
Note: Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 Mettler 50 mL disposable beakers

6.2 Mettler DLWIN software

6.3 Mettler DL53 titrator

6.4 Mettler ST20 sample changer

6.5 Mettler Methods Manuals

7.0 Reagents and Standards

7.1 Standard sulfuric acid (0.04 N). Dilute 27.8 mL of concentrated H_2SO_4 to 25 liters with reagent water.

7.2 Sodium carbonate solution (approx. 0.05 N): Dry several grams of primary standard at 103ºC for 1 hour and cool in a desiccator. Weigh approximately 2.5 grams and record the weight exactly. Transfer to a 1 liter volumetric flask, and fill to the mark with reagent water.

7.3 Alkalinity Spiking Solution

7.3.1 Dry the $NaHCO_3$ 1-2 hours at 103ºC. Dissolve 13.7 g of $NaHCO_3$ in reagent water and dilute to 200 mL.

100 ul = 82 ppm Total Alkalinity

= 100 ppm HCO_3

7.3.2 Determine the total alkalinity by multiplying number of mL of titrant used x 40.

7.3.3 Divide that number by 82.

7.3.4 Round off to nearest whole number. Take this number x 100 to find the total number of ul of spiking solution to add. Multiply the rounded off whole number by 82. This is the concentration (ppm) of the spike.

8.0 Sample Collection, Preservation and Storage:
Samples may be submitted in plastic or glass containers preserved by cooling to 4^0 C.with a maximum holding time of 14 days.

9.0 Quality Control
Each run consists of 10 or fewer samples, and a spike and duplicate. The instrument has

a pH calibration performed once per day. The acceptable recovery range for spiked samples is 90 to 110 %. The slope of the calibration curve must be between -56.6 to -58.6. Values outside of this range will require a pH recalibration and/or cleaning or replacement of the electrodes. The first run for the day should include a blank of 50 mL of reagent water and an LFB (50 mL of reagent water and a spike of 400 uL - section 7.3).

10.0 Calibration and Standardization

10.1 Acid Standardization

10.1.1 Place newly made acid in the brown dispenser bottle and flush the system by clicking on the burette icon, choose 20 mL under burette volume and type in 60 mL under dispense volume, click OK.

10.1.2 Place a wash beaker in front of the acid filled beaker and mark with red marker.

10.1.3 Press icon to rotate the turntable.

10.1.4 Choose forward direction and press OK.

10.1.5 Choose icon for change lift position, pick top, and press OK.

10.1.6 Pipet 15 mL of Na_2CO_3 into 3 beakers with a marked wash beaker after them.

10.1.7 Press sample icon and select new sample data and method # 3, press OK.

10.1.8 Type something into series ID and choose 3 samples, press OK.

10.1.9 Press modify, tab up to sample ID, type in 1, enter the weight of the Na_2,CO_3, press next arrow, and repeat this process for the other 2 beakers, press OK.

10.1.10 Press run, press online data icon.

10.1.11 Press system window when the titrator is finished, press record, press select, choose last data entry with method # 3, and press on line data icon.

10.1.12 Press print. Save this sheet in the worksheet storage book.

10.1.13 Multiply the titer by 0.04 to calculate the normality of the newly made acid and label bottles, as this normality will be entered into the LIMS for calculations.

10.1.14 The normality is determined by the titrator using the following formula:

$$\text{Normality} = \frac{(A \times B)}{(53 \times C)}$$

where: A = grams of Na_2CO_3 used
B = volume of Na_2CO_3 used (15)
C = Amount of H_2SO_4 titrate used (+15 mL of predose)

10.1.15 Label titrant bottle and storage container with new H_2SO_4 normality.

10.1.16 Enter the normality when filling the worklist on the LIM system.

10.2 pH Calibration is performed daily and is in order in the procedure.

11.0 Procedure

11.1 Set up

11.1.1 Double click on DLWIN

11.1.2 Click on set up and open.

11.1.3 Double click on titrator.stp

11.1.4 Click on auxiliary functions, changing burette volume to 20 mL and type 30 mL under dispense volume, and click OK.

11.1.5 Place a wash beaker about 1/3 full of reagent water in front of acid filled beaker and mark with red marker.

11.1.6 Press icon to rotate turntable

11.1.7 Choose forward direction, and press OK.

11.1.8 Choose icon for change lift position, pick top, and press OK.

11.2 pH Calibration

11.2.1 Place beakers with pH 4 and pH 7 buffers on the sample changer with a wash beaker after them marked with a red marker.

11.2.2 Press sample icon.

11.2.3 Select new sample data and method # 2, press OK.

11.2.4 Type something in series ID, choose 2 samples, and press OK (type in user if desired).

11.2.5 Press run, press on line data icon.

11.2.6 When titrator is finished, press system window, press record, press select, choose the last entry for method # 2 and press on line data icon.

11.2.7 Record slope and zero point, with the date, on the calibration record in the drawer below the computer.

11.3 Analyzing Samples

11.3.1 Press titrator window.

11.3.2 Pour 50 mL of each sample into a beaker, with up to 10 samples, a duplicate and spike for each batch. Use 400 uL of the spike which = 328 ppm. Place the beakers on the sample changer with a marked wash beaker at the end.

11.3.3 Press sample icon, choose new sample data, method ID is 1 for alkalinity, and OK.

11.3.4 Type something in series ID, type in # of samples, and user ID if desired, press OK.

11.3.5 Press modify, tab up to sample ID and type in the full log #, press

next arrow, and repeat the process for the total batch of samples, press OK.

11.3.6 Press run, press on line data icon and online curve icon.

11.3.7 When the batch is finished, press system window, press record, press select, choose last entry with method # 1 and press on line data icon.

11.3.8 Press print, OK. Daily, save the print outs of each batch for the LIMS record books.

11.3.9 The next morning (after the samples are logged in) minimize the DLWIN software, double click on the LIMS icon.

11.3.10 Choose #1, enter, type analyst #, enter, type I for instrument, enter, type I for import, enter, type N for new, enter, type alk, enter. The LIMS will ask for the first and last batch extension #. (Example 014). Continue as for any LIMS data entry.

11.3.11 If beaker overflows:

11.3.11.1 Use original titrator value for the pH, or measure the pH manually.

11.3.11.2 For mL to pH 8.3 use original titrator value.

11.3.11.3 For mL to pH 4.5, pipet 50 mL of sample into a beaker, add 2 to 7 mL of .4 N H2SO4 as a predose, run as a regular sample, add 10 x the mL of predose to mL used by the titrator for total mL, subtract mL to 8.3 from total mL for the mL to 4.5.

11.4 Operating the DL 53

11.4.1 Press data transfer on the DL53, press remote control, OK, toggle status off and on by pressing modify, OK. If remote control can't be turned back on, press sample and delete samples listed, press data transfer, and repeat remote control series.

11.4.2 To set up or modify a method, press method, use the arrow keys

and modify. Printed copies of all methods are kept in the drawer under the computer. The computer may download methods to the DL53 if they are lost by pressing titrator window, backup, send backup, memory copy, and OK.

11.4.3 Methods are printed by pressing backup, press get listing, press method listing, type in the method #, press print, and OK.

12.0 Data Analysis and Calculations

Note: LIMS System calculates total alkalinity, HCO_3, CO_3 and OH ion concentrations

Equivalent weights	Approx. Atomic Weights
1 eq wt of $CaCO_3$ =100/2 = 50	H = 1
1 eq wt of CO_3 = 60/2 = 30	Ca = 40
1 eq wt of HCO_3 = 61	C = 12
1 eq wt of OH = 17	O = 16

12.1 Converting from $CaCO_3$ to:

CO_3 : multiply by: 30/50 = 0.6

HCO_3 : multiply by: 61/50 = 1.22

OH : multiply by: 17/50 = 0.34

12.2 If the pH is less than or equal to 8.3:

Total Alkalinity x 1.22 = mL acid x N-acid x 50 mL sample

HCO_3 = total alkalinity x 1.22

CO_3 = 0

OH = 0

12.3 If the pH is greater than 8.3:

12.3.1 The following calculations are based on a sample volume of 50 mL and acid concentration of 0.04 N H_2SO_4. When plugged into the total alkalinity equation this becomes the constant 40. Adjust this constant to meet your situation.

12.3.2 If (mL to 8.3) < 1/2 total mL used:

Total alkalinity = total mL x 40

HCO_3 = [total mL - 2 (ml to 8.3)] 1.22 x 40

CO_3 = 2 (mL to 8.3) x 0.6 x 40

OH = 0

12.3.3 If the mL to 8.3 = 1/2 total mL used:

Total alkalinity = total mL x 40

HCO_3 = 0

CO_3 = 2 (mL to 8.3) x 0.6 x 40

OH = 0

12.3.4 If the mL to 8.3 > 1/2 total mL used:

Total alkalinity = total mL x 40

HCO_3 = 0

CO_3 = 2 [total mL - mL to 8.3] x 0.6 x 40

OH = [(2 x mL to 8.3) - total mL] x 0.34 x 40

12.3.5 If mL to 8.3 = total mL:

Total alkalinity = total mL x 40

HCO_3 = 0

$CO_3 = 0$

OH = total alkalinity x 0.34

13.0 Method Performance

A set of 7 low level spikes in reagent water are used to determine the Method Detection Level for alkalinity. The MDL was found to be .53. The bias is - 5 % at this level.

14.0 Pollution Prevention

This method uses only dilute sulfuric acid which when discarded with the sample is diluted further in the sink by tap water.

15.0 Waste Management

There is no waste associated with this method other than the plastic disposable beakers. For further information on waste management consult the Waste Management Manual for Laboratory Personnel and Less is Better: Laboratory Chemical Management for Waste Reduction, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W. , Washington D.C.,20036.

16.0 References

Method 2320B, *Standard Methods for the Examination of Water and Wastewater* 19th edition.

17.0 Tables, Diagrams, Flowcharts, Validation Data and Additional Information Documentation and Records

All records and print outs are kept in the alkalinity parameter book in the bookcase in room 306.