Arikaree Environmental Laboratory
Revision 2
Date: Feb. 11, 2020

TITLE: Acid Neutralization Capacity (ANC) SOP

ANALYTES: Acid Neutralization Capacity

1) Applicable Matrices

a) This method is applicable to ground, surface and waste waters.

2) Scope and Application

a) Acid Neutralization Capacity (ANC) measures a sample's ability to neutralize strong acids due to dissolved species able to accept protons. This method determines ANC via titration with 0.1 N Hydrochloric acid within the range of pH 4.5 and pH 3.5 at which contributions of hydroxide, carbonate, and bicarbonate are neutralized.

3) Interferences

a) Soaps, oily matter, or precipitates may coat the pH electrode. This generally should not be a problem with the types of samples analyzed in the Arikaree Lab.

4) Equipment and Supplies

a) Analytical balance capable of measuring to 0.0001g.

b) Glass beaker with ground glass stopper.

c) ThermoScientific Orion star A211 pH meter with combined pH electrode and temperature probe.

d) Gilmont micrometer buret.

e) Stir plate

f) Stir bar

g) 50mL class A graduated cylinder

h) 100mL plastic beaker

i) Aries Gemini High Purity water system for preparation of ASTM Type I water AKA "ultrapure."

j) Squirt bottle containing ultrapure water.

k) Kim® Wipes

5) Reagents and Standards

a) Standard pH 4.01, 7.00 buffers for pH meter calibration.

b) Standardized 0.1N Hydrochloric acid

c) **0.01639N Na_2CO_3 Stock Standard Solution**

(1) Weigh ~1g of Na_2CO_3 in glass beaker with ground glass stopper. Dry in oven at 150°C for 2 hours.

(2) Remove from oven, and place in a desiccator to cool.

(3) Clean a class A 1,000mL volumetric flask. Fill half-full with ultrapure water.

(4) Weigh out precisely 0.8686g Na_2CO_3, on the analytical balance, in a weigh boat or on weigh paper. Quantatively transfer Na_2CO_3 to volumetric flask and swirl flask to dissolve.

(5) Once the carbonate has dissolved, dilute with ultrapure water to the mark on the flask. Invert the flask to mix its contents.

(6) Transfer flask contents to a clean, properly labeled 1L Nalgene bottle.

(7) Dilute this solution 1:100 to make the working Lab Fortified Blank (LFB)

6) Sample Collection, Preservation, Shipment, and Storage

a) Samples shall be collected in a way ensuring they represent environmental concentrations at the time of collection.

b) The samples shall be filtered through a 0.45µm membrane filter, either in the field or when they arrive in the lab.

c) Store the samples in the freezer frozen, or in a fridge from 0-6°C.

d) The samples should be on ice in a cooler during transport.

7) Quality Control

a) 0.1N HCl must be standardized daily when samples are being analyzed using the sodium bicarbonate standard solution (LFB). If the standard titrates at >±5% of the known value, redo the standardization. If after a second attempt the standard is still out of control, replace the acid titrant.

b) A blank sample must also be analyzed daily using 35mL of ultrapure water. Result must be between 0-10 uEq/L. If not, recalibrate pH meter and reanalyze.

c) The pH meter must be calibrated daily when samples are being analyzed. The slope obtained from the calibration must be within the specs stated for the pH electrode (92-102%).

d) A duplicate analysis must be performed at least once during analysis if less than 20 samples are analyzed. Otherwise, one duplicate every 20 samples, or 5% of the samples must be duplicated. Duplicate data will be collected and analyzed to determine control limits.

8) Calibration

a) **pH Meter Calibration Procedure**

(1) Turn on pH meter

(2) Remove Plug on electrode

(3) Remove the electrode from the storage solution, and rinse it with ultrapure water. Blot dry with a Kim® Wipe.

(4) Press the button beneath the word "Cal" on the screen.

(5) Fill a small cup with pH 7 buffer.

(6) Place electrode into cup so it is fully submerged in buffer.

(7) Press the button beneath the word "Start"

(8) Allow the meter to stabilize. Once stabilized, make sure the calibrated reading is correct. If not, press the button beneath "Edit" and change the value to 7.00.

(9) Press the button beneath "Accept."

(10) Rinse the electrode with ultrapure water and blot dry with a Kim® Wipe.

(11) Press the button beneath "Next."

(12) Fill a cup with pH 4.01 buffer.

(13) Follow step 8 but change the pH value to 4.01 if needed.

(14) Fill a cup with pH 10.01 buffer.

(15) Follow step 8 but change the pH value to 10.01 if needed.

(16) pH 10.01 buffer is the last buffer. Press the button beneath "End Cal." The slope of the calibration will be displayed. Be sure it is between 92 and 102%. If it is outside this range, recalibrate. If after recalibration, the slope is still out of range, be sure the electrode is filled with electrode filling solution. If it is low, fill the electrode to just below the opening where the plug was.

9) Procedure

a) **Titration Procedure**

(1) Turn on pH meter and calibrate (see calibration procedure above).

(2) Obtain an ANC benchsheet from the top drawer to the right of the ANC station.

(3) Fill in the top fields of the first sample table. Record the sample name and volume of sample. For the first sample, it will be "Titrant Standard," and "35mL."

(4) Rinse an ~1 in. stir bar with ultrapure water. Dry the stir bar with a kim wipe Drop into a 100mL plastic beaker.

(5) In the class A 50mL graduated cylinder, precisely measure 35mL of 0.01639N Na_2CO_3 Standard solution. Pour solution into a clean, dry, 100mL plastic beaker.

(6) Start sample stirring on stir plate. Rinse the pH electrode and temperature probe(if applicable) with ultrapure water, and blot dry with a kim wipe. Place pH electrode and temperature probe (if applicable), into sample. Be sure pH electrode is not being struck by the stir bar, as this could damage the electrode.

(7) Press measure on pH meter and allow meter to measure the sample. "Stabilizing AR" will flash on the display if the auto-read function is active. If for some reason, the auto-read function is off, press "set-up," > "channel">"mode and settings." Select "Read Type" and select "auto."

(8) While the pH meter is stabilizing, fill the micrometer buret with 2.0mL of 0.1N HCl titrant.

(9) Once the pH meter has stabilized, record the initial pH of the sample on the benchsheet.

(10) Begin adding titrant from the micrometer buret until the pH of the sample gets to pH 4.50. Record the volume of titrant used to get to that pH.

(11) Keep titrating, stopping every 0.2 pH units to record the total amount of titrant used. Don't just record the amount of titrant used to get from one pH point to another, but the total amount of titrant used so far. Titrate until a pH of 3.50 is reached. You should have 7 data points.

(12) Go to the Data Calculation Procedure below if analyzing the carbonate standard solution. If analyzing samples, repeat procedure for next sample and calculate when finished analyzing samples

b) **Data Calculation Procedure**

(1) Open the ANC_calculation.xlsx excel spreadsheet located in the Kiowa shared folder.

(2) S Vol (sample volume) should stay the same with each sample (35mL) except if there is less sample used.

(3) Vi is the amount of titrant used per step in pH. Input these volumes with their corresponding pH.

(4) Click on the data tab, and scroll down and select "Regression".

(5) For the Y-range select the Vi column and for the X-range select the Gran F column.

(6) Look down to the output options, and click the tick box for output range and select K2. Click OK.

(7) It will say "Output will overwrite existing data." Allow it by clicking OK.

(8) Correlation coefficient (r^2) should be a minimum of 0.9990.

(9) Record ANC value on benchsheet.

10) Corrective Action for Out-of-Control Results

a) In the event of an out of control QC sample (duplicate, LFB, blank), the sample will be reanalyzed or a different sample will be used for QC(duplicate).

b) If the reanalyzed QC sample is still out of control, the pH meter will be recalibrated and QC sample reanalyzed.

c) If recalibration of pH meter still does not correct the problem, troubleshoot the meter to find the problem. Check the micrometer buret for volume accuracy. Check anything that could be causing bad results.

11) Waste Management

a) Any waste generated during this analysis, as long as it is above pH 2.5, can be disposed of down the drain.

12) References

a) "Alkalinity and Acid Neutralizing Capacity," U.S. Geological Survey TWRI Book9, Chapter 26, Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo, version 4.0, 2012.

b) Val's notes.