Hydrogeochemistry – Fall 2018

Lab Exercise #2

Alkalinity and pH

**Background**

Alkalinity is a measure of the capacity of an aqueous solution to neutralize acids. Alkaline compounds in the water, such as bicarbonate, carbonate, and hydroxide, combine with H+ to make new compounds, thereby removing H+ ions from solution and decreasing acidity (which means increasing pH). Without this acid-neutralizing capacity, any acid added to a stream would cause an immediate drop in stream pH. Measuring alkalinity is important for determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. It's one of the best measures of the sensitivity of the stream to acid inputs.

Alkalinity in streams is influenced by rocks and soils, salts, certain plant activities, and certain industrial wastewater discharges.

Total alkalinity is quantified as the amount of acid (e.g., sulfuric acid) that is needed to lower the pH of a water sample to 4.2. At this pH, all the alkaline compounds in the sample are "used up.” Alkalinity is often reported as milligrams per liter of calcium carbonate (mg/L CaCO3), because carbonate is a common alkaline compound in natural waters.

*Adapted from EPA.gov* *(5.10 Total Alkalinity)*

**Objectives**

* Learn to record pH using a pH meter
* Generate a titration curve by monitoring changes in pH during acid titration
* Calculate alkalinity for a standard solution and a natural water sample

**Materials**

* pH meter
* pH buffer solutions
* electrical conductivity meter
* syringe/syringe filters
* beaker
* stir plate
* stir bar
* titrant cartridges containing strong acid (1.6 N H2SO4) and weak acid (0.16 N H2SO4)
* digital titrator
* ring stand
* standard solution (5.5 mM Na2CO3 + 34.5 mM NaHCO3)
* unknown samples

**Methods**

During this lab, you will generate titration curves for a sodium carbonate-bicarbonate buffer solution and for unknown solutions. These measurements will enable you to determine the alkalinity (buffering capacity) of natural waters. Each group will titrate at least three samples.

**Titrations:**

1. Set up your lab notebook with the following columns: clicks, pH
2. The pH meter should be calibrated. Check the calibration by measuring the pH of buffer solutions (pH 4.0, 7.0, and 10.0)
3. For the standard solution, measure out 40 mL in a graduated cylinder and pour into the beaker. No filtration is required.
4. For each unknown sample, pull 40 mL of a sample into a syringe. Record the exact volume within 1 mL. Attach a syringe filter (0.45 µm nylon) and filter the solution into a 100 ml beaker. The standard does not need to be filtered. Note: titration of an unfiltered sample yields *acid neutralizing capacity* rather than *alkalinity*.
5. Record the electrical conductivity (µS/cm) of the standard solution and of your samples.
6. Place a stir bar magnet into the solution, and put the beaker on the magnetic stirrer at slow speed.
7. Measure the initial pH of the solution before adding any sulfuric acid.
8. Insert the cartridge into the digital titrator and turn the dial until a drop of acid emerges from the delivery tube. Use the strong acid (1.6 N) for the standard. Use the weak acid (0.16 N) for your samples. Wipe away the acid with a Kimwipe and do not let it fall into your sample. Reset the number of clicks to zero.
9. Secure the titrator to the ring stand.
10. Add titrant and record the number of clicks and the pH measured after each number of clicks. Note that the pH will change rapidly at some points and more slowly at others. If the pH is changing rapidly, add very few drops at a time before recording pH. Each click of the digital titrator corresponds to 1/800 mL of acid.
11. Record the number of clicks required to bring the solution to pH 4.2.
12. Wash glassware with deionized water between samples.

**Alkalinity calculation:**

1. Calculate the alkalinities of the standard and each unknown sample using the following equation:

Alkalinity (mg/L CaCO3) = (B x N x 50,000)/V

B = the volume of acid (mL) to reach pH 4.2

N = the normality of the acid (*N* units are equal to mole equivalents per L);

V = volume of sample (mL)

50,000 = factor that converts eq/L of neutralized acid to mg/L CaCO3; each mole of CaCO3 can neutralize two H+ by converting CO32- to HCO3- then HCO3- to H2CO3. The molecular mass of CaCO3 is 100.09 g/mol.

**Report (due on Blackboard)**

1. *Total Dissolved Solids* (TDS) is a value that indicates the total mass of solutes in solution. Since these solutes are typically charged ions, TDS is proportional to electrical conductivity (EC), a measure of the solutions ability to conduct electrical current. Use the EC value (µS/cm) to estimate TDS (ppm) for the standard solution and one sample using the relationship:

TDS (mg/L) = 0.64 x EC (µS/cm)

1. Make a separate graph for each titration **your group** completed. Plot amount of acid added (in ml) on the x-axis versus pH on the y-axis. Mark the inflection point(s) on the titration curve. What is the significance of the inflection point? Write a couple sentences explaining why there is variation in the rate of pH change per addition of acid.

1. Use the Henderson-Hasselbach equation to determine the concentration of bicarbonate (HCO3-) at the final equivalence point of the titration of the standard solution.
2. Write a few sentences describing how the titration curve of the unknown samples compare to the standard. Use information such as the initial pH, slope, inflection points, etc. for the comparison.
3. Calculate alkalinity (units of mg CaCO3/L) for the standard and each sample that your group titrated. This calculation assumes that all alkalinity is derived from carbonate and bicarbonate ions. Show your calculations.
4. Compare alkalinity values to the values obtained for TDS. What percent of TDS does alkalinity comprise? How did alkalinity and TDS vary amongst the standard and samples analyzed? If differences are observed, what environmental factors might explain those differences?
5. How would you determine whether your water samples are oversaturated or undersaturated with respect to carbonate minerals (e.g. calcite)?
6. Turn in your report electronically by uploading it to Blackboard.