Standard Operating Procedure (SOP) 3.2.1.1

Measuring Alkalinity

Although not always the case, alkalinity usually reflects the activity of calcium carbonate. The result is reported as milligrams per liter of calcium carbonate (mg/l $CaCO_3$).

Choosing a Sampling Method

For total alkalinity, a double endpoint titration using a pH meter and a digital titrator is recommended. This can be done in the field or in the lab. If you plan to analyze alkalinity in the field, it is recommended that you use a digital titrator. Another method for analyzing alkalinity uses a buret. For volunteer programs, using a digital titrator is recommended over the buret, because digital titrators are portable, economical, take less time, and have easy-to-read endpoints (results).

Digital Titrator

This method involves **titration**, the addition of small, precise quantities of sulfuric acid (the reagent) to the sample until the sample reaches a certain pH (the **endpoint**). The amount of acid used corresponds to the total alkalinity of the sample.

Digital titrators have counters that display numbers. A plunger is forced into a cartridge containing the reagent by turning a knob on the titrator. As the knob turns, the counter changes in proportion to the amount of reagent used. Alkalinity is then calculated based on the amount used. Digital titrators cost approximately $100; the reagents (chemicals) to conduct total alkalinity tests cost about $36. Additionally, alkalinity standards are needed for accuracy checks.

How to Measure Alkalinity

General procedures for measuring alkalinity are presented in this section for guidance only; they do not apply to all sampling methods.

The alkalinity method described below (using a digital titrator) was developed by the Acid Rain Monitoring Project of the University of Massachusetts Water Resources Research Center (River Watch Network, 1992).

STEP 1: Check equipment.

The volunteer should bring the following items to the site for each sampling session:

- Digital titrator;
- 100-ml graduated cylinder;
- 250-ml beaker;
- pH meter with built-in temperature sensor;
- reagent (sulfuric acid titration cartridge, 0.16 N);
- standard alkalinity ampoules, 0.500 N, for accuracy check; and
- bottle with deionized water to rinse pH meter electrode.

STEP 2: Collect the sample.

If you plan to analyze a water sample in the lab for alkalinity, then follow these collection and storage steps:

- Use 100 ml plastic or glass bottles.
- Label the bottle with site name, date, time, data collector, and analysis to be performed.
- Wearing gloves, plunge the bottle into the water. Fill the bottle completely and cap tightly.
- Avoid excessive agitation and prolonged exposure to air.
- Place the bottle in the cooler. Samples should be analyzed as soon as possible, but can be stored at least 24 hours by cooling to 4° C (39° F) or below. NOTE: Samples should be warmed to room temperature before analyzing (Hach, 1997).

STEP 3: Measure total alkalinity.

Alkalinity is usually measured using sulfuric acid with a digital titrator. Follow the steps below in the field or lab. Remember to wear latex or rubber gloves.

Add sulfuric acid to the water sample in measured amounts until the three main alkaline compounds (bicarbonate, carbonate, and hydroxide) are converted to carbonic acid. At pH 10, hydroxide (if present) reacts to form water. At pH 8.3, carbonate is converted to bicarbonate. At pH 4.5, all carbonate and bicarbonate are converted to carbonic acid. Below this pH, the water is unable to neutralize the sulfuric acid and there is a linear relationship between the amount of sulfuric acid added to the sample and the change in the pH of the sample. So, more

sulfuric acid is added to the sample to reduce the pH by exactly 0.3 pH units (which corresponds to an exact doubling of the pH) to a pH of 4.2. However, the exact pH at which the conversion of these bases might have happened, or total alkalinity, is still unknown.

Arriving at total alkalinity requires an equation (given below) to extrapolate back to the amount of sulfuric acid that was added to actually convert all the bases to carbonic acid. A multiplier (0.1) then converts this to total alkalinity as mg/l of calcium carbonate (CaCO3). To determine the alkalinity of your sample, follow these steps:

- Samples should be warmed to room temperature before analyzing..
- Insert a clean delivery tube into the 0.16N sulfuric acid titration cartridge and attach the cartridge to the titrator body.
- Hold the titrator, with the cartridge tip pointing up, over a sink or waste bottle. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to 0 and wipe the tip.
- Measure the pH of the sample using a pH meter. If it is less than 4.5, skip the next five steps.
- Insert the delivery tube into the beaker containing the sample. Turn the delivery knob while magnetically stirring the beaker until the pH meter reads 4.5. Record the number of digits used to achieve this pH. Do not reset the counter.
- Continue titrating to a pH of 4.2 and record the number of digits.
- Apply the following equation:

Alkalinity (as mg/l CaCO3) = (2a - b) x 0.1

Where:

a = digits of titrant to reach pH 4.5
b = digits of titrant to reach pH 4.2 (including digits required to get to pH 4.5)
0.1 = digit multiplier for a 0.16 titration cartridge and a 100-ml sample

Example:

Initial pH of sample is 6.5.
It takes 108 turns to get to a pH of 4.5.
It takes another 5 turns to get to pH 4.2, for a total of 113 turns.

Alkalinity = [(2 x 108) - 113] x 0.1 = 10.3 mg/l

- Record alkalinity as mg/l $CaCO_3$ on the data sheet.
- Rinse the beaker with distilled water before the next sample.

- Perform an accuracy check on the first field sample, halfway through the run, and after analysis of the last sample as described in Step 4, below.
- *If the pH of your water sample, prior to titration, is less than 4.5, proceed as follows:*

Insert the delivery tube into the beaker containing the sample.
Turn the delivery knob while swirling the beaker until the pH meter reads exactly 0.3 pH units less than the initial pH of the sample.
Record the number of digits used to achieve this pH.
Apply the equation as before, but a = 0 and b = the number of digits required to reduce the initial pH exactly 0.3 pH units.

Example:

Initial pH of sample is 4.3.
Enter "0" in the 4.5 column on the data sheet.
Titrate to a pH of 0.3 units less than the initial pH; in this case, 4.0.
It takes 10 digits to get to 4.0.
Enter this in the 4.2 column on the data sheet and note that the pH endpoint is 4.0.
Alkalinity = (0 - 10) x 0.1 = -1.0

- Record alkalinity as mg/l $CaCO_3$ on the data sheet**.**
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Tip: Alkalinity Calibration Standards
You will need to do an accuracy check on your alkalinity test equipment before the first field sample is titrated, again about halfway through the field samples, and at the final field sample. For this, you will need an alkalinity standard. Often, these come in pre-measured glass ampules. To use, break off the tip of the glass ampule and pour the liquid into a beaker. Then, follow the directions found under "Step 4: Perform an accuracy check." The price for the alkalinity standards is about $23 for 20 2-ml ampules

STEP 4: Perform an accuracy check.

This accuracy check should be performed on the first field sample titrated, again about halfway through the field samples, and at the final field sample. Check the pH meter against pH 7.0 and 4.0 buffers after every 10 samples.

- Snap the neck off an alkalinity ampule standard, 0.500 N; or, if using a standard solution from a bottle, pour a few milliliters of the standard into a clean beaker.
- Pipet 0.1 ml of the standard to the titrated sample (see above). Resume titration back to the pH 4.2 endpoint. Record the number of digits needed.
- Repeat using two more additions of 0.1 ml of standard. Titrate to the pH 4.2 after each addition. Each 0.1-ml addition of standard should require 250 additional digits of 0.16 N titrant.

STEP 5: Return the field data sheets and/or samples to the lab.

Volunteers should thoroughly clean all equipment and transport the samples to the designated lab. Alkalinity samples must be analyzed within 24 hours of their collection. If the samples cannot be analyzed in the field, keep the samples on ice and take them to the lab or drop-off point as soon as possible.

Make sure that the data sheets are complete, legible, and accurate, and that they account for all samples. Volunteers should make a copy of the completed data sheets before sending them to the designated person or agency in case the original data sheet becomes lost.

References and Further Reading

Portions of this chapter were excerpted and adapted from:

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Other references:

American Public Health Association (APHA), American Water Works Association, and Water Environment Federation. 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th ed. L.S. Clesceri, A.E. Greenberg, A.D. Eaton (eds). Washington, DC.

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http://www.epa.gov/owow/estuaries/monitor/chptr11.html#alkalinity