

## EXPERIMENT III

### Alkalinity

**PURPOSE:** To determine the alkalinity of a water sample using a double - endpoint titration for determination of  $[\text{OH}^-]$  and  $[\text{CO}_3^{2-}]$ , and compare the results to those of a potentiometric titration.

## INTRODUCTION

Alkalinity is a parameter that is measured on almost all environmental samples -drinking water, natural waters, polluted waters, sewage, and industrial wastes. Alkalinity refers to the buffering capacity of water samples and to their ability to neutralize acidic pollution from rainfall or wastewater. For municipal sewage or industrial wastes, the amount of alkalinity is important in determining the type of treatment which should be employed.

In the Northeast, alkalinity is primarily caused by the presence of carbonate ( $\text{CO}_3^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) ions, although hydroxide ( $\text{OH}^-$ ) ions may also contribute, especially when there is industrial pollution. Living organisms, such as aquatic life, function best in a pH range of 5.0 to 9.0 and levels of 20 to 200 mg/L are typical alkalinity values for fresh water. When the pH is above 8.3, carbonate ( $\text{CO}_3^{2-}$ ) is the primary contributor to alkalinity; when the pH is below 8.3, bicarbonate ( $\text{HCO}_3^-$ ) becomes the dominating factor. The values of alkalinity are reported in units of "mg  $\text{CaCO}_3/\text{L}$ " because of its relationship to hardness, which is reported using the same unit.

Although large environmental labs perform alkalinity tests using automated methods (1 sample/minute), we will employ the traditional analyses of using an acid-base titration with two endpoints. To gain insight into the double-endpoint titration technique you will perform a potentiometric titration, pH vs. titrant volume of your water sample. These techniques are described in more detail below.

The alkalinity analysis consists of:

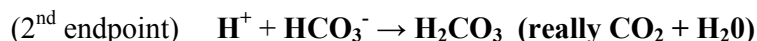
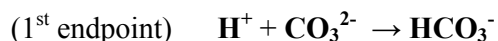
[A] Preparation and Standardization of a Titrant.

[B] Titration of a prepared unknown using the standardized titrant.

[C] Titration of a natural water sample (well, river or lake water) using the standardized titrant.

### Part 1: DETERMINATION OF ALKALINITY

A sample may contain any of the three anions (carbonate, bicarbonate, or hydroxide) or some combinations of them. Because these can all behave as bases, we will titrate with a strong acid. Hydrochloric acid (HCl) can be used, but we will be using sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Regardless of the source of the  $\text{H}^+$  the following reactions will occur:



The two pKa values for the carbonate system are  $\text{pK}_{\text{a}1} = 6.35$  and  $\text{pK}_{\text{a}2} = 10.33$ .

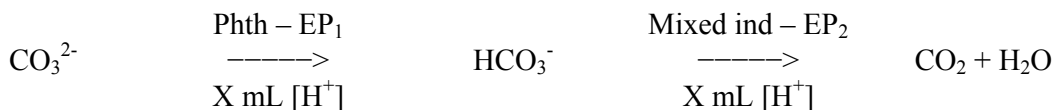
The unknown and your aqueous sample could contain any **one** of the following combinations of the anions responsible for alkalinity:

- [1] carbonate only. ( $\text{CO}_3^{2-}$ )
- [2] bicarbonate only ( $\text{HCO}_3^-$ )
- [3] hydroxide only, ( $\text{OH}^-$ )
- [4] carbonate and bicarbonate ( $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ )
- [5] carbonate and hydroxide ( $\text{CO}_3^{2-}$  and  $\text{OH}^-$ )

We need to consider each of these five situations separately to see how the ions will behave at the two different endpoints of the titration (using two different indicators). One of the indicators we will use is phenolphthalein (we will use the abbreviation "phth" from now on). It has a pinkish color at basic pH values and changes to colorless as we go below pH 8.3 (endpoint #1, EP<sub>1</sub>). The second indicator has traditionally been methyl orange, which changes from yellow to orange at a pH range of about 2-3; however, many people find this color change difficult to observe. We will, therefore, use a mixture of indicators (bromocresol green/methyl red), which gives a color change easier to see (from a blue-green to a very light pink, yellow, or colorless). This is endpoint #2 (EP<sub>2</sub>).

Let us now consider the five different possibilities for analyzing and detecting the amount of carbonate, bicarbonate, and hydroxide that is present in a sample.

**[1] CARBONATE ONLY ( $\text{CO}_3^{2-}$ )**

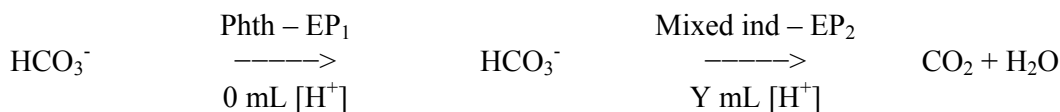


When carbonate ion is added to water the resulting pH falls in the range of 11-12. It can be titrated with acid to bicarbonate, the equivalence point occurring at a pH ≈ 8.3. Phenolphthalein (phth) will show a color change from pink to colorless in this pH range and it is ideal for detecting the first endpoint (EP<sub>1</sub>).

The bicarbonate ion can then accept another H<sup>+</sup> to become "carbonic acid", which is really carbon dioxide (*aq*) and water. The mixed indicator will change color in this pH range and will allow us to detect the second endpoint (EP<sub>2</sub>).

► Notice that if carbonate is the only original species, it should require equal amounts of H<sup>+</sup> for each endpoint.

**[2] BICARBONATE ONLY ( $\text{HCO}_3^-$ )**



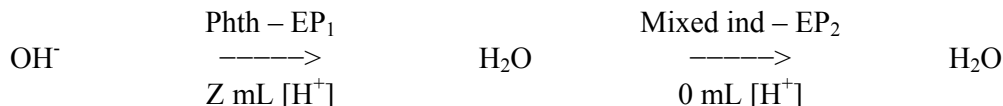
If bicarbonate is the only substance in the sample, what would happen when phenolphthalein is

added to detect the first endpoint? The indicator would immediately turn colorless because  $\text{HCO}_3^-$  would give a pH lower than the first endpoint. [Actually the indicator might appear as a very light pink color, but would require only a drop or two of acid to become colorless.]

In other words, the bicarbonate is ready to be titrated only to the second endpoint and would require some amount of acid ( $Y \text{ mL } [\text{H}^+]$ ).

- ▶ Notice that if bicarbonate is the only original species, it should require approximately 0 mL of  $[\text{H}^+]$  for the **first** endpoint.

### [3] HYDROXIDE ONLY ( $\text{OH}^-$ )

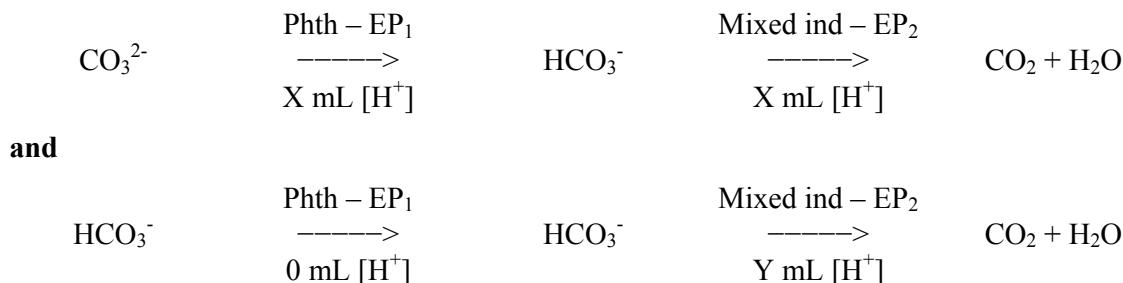


If hydroxide is the only substance in the sample, it is very basic and the phenolphthalein will turn a deep pink. Thus acid needs to be added until the color disappears. At that time, we know that all of the  $\text{OH}^-$  has been converted to water, which can no longer react with additional acid.

When we add the mixed indicator it should immediately change color (or it might require a drop or two of acid). This occurs because there isn't any base left to react with the acid.

- ▶ Notice that if hydroxide is the only original species, it should require approximately 0 mL of  $[\text{H}^+]$  for the **second** endpoint.

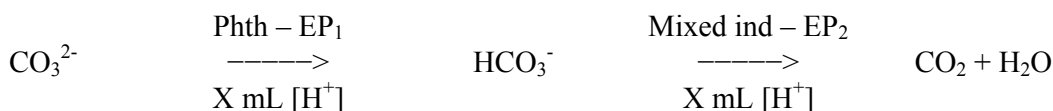
### [4] CARBONATE ( $\text{CO}_3^{2-}$ ) and BICARBONATE ( $\text{HCO}_3^-$ )



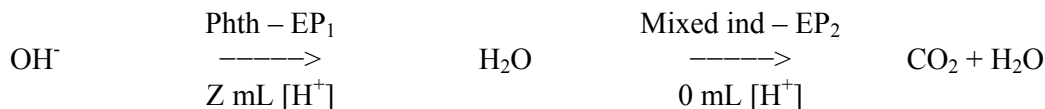
During the first titration, only the carbonate reacts, producing bicarbonate at the first endpoint. Then bicarbonate reacts with acid to reach the second endpoint, but we now have two sources of the  $\text{HCO}_3^-$ .

- ▶ bicarbonate that was originally in the sample
  - ▶ bicarbonate that was produced from the carbonate during the first titration.
- Essentially the results are identical to adding the two separate situations together.
- ▶ Notice that this means the **second endpoint** volume ( $X + Y$ ) will be larger than the first endpoint and neither endpoint requires zero mL of acid.

**[5] CARBONATE ONLY (CO<sub>3</sub><sup>2-</sup>) and HYDROXIDE (OH<sup>-</sup>)**



and



Again we can add the two individual results together to predict the relative volumes of the two endpoints. For the first titration, acid is needed to react with both the carbonate and the hydroxide ions, but when the first endpoint is reached, the hydroxide is finished, because it has all been converted to water.

Then the bicarbonate (produced from the carbonate) is left to react with the acid to reach the second endpoint.

- Notice that this means the first **endpoint** volume (X + Z) will be larger than **the second endpoint** volume (X) and neither endpoint is zero.

It would be a good idea to summarize our discussion in a table. By comparing the relative amounts of acid required for the first and second endpoints, we will be able to identify the components of our aqueous sample or unknown.

**TABLE III-1**

SAMPLE	EP <sub>1</sub> volume	EP <sub>2</sub> volume	Comparison
CO <sub>3</sub> <sup>2-</sup> ONLY	X mL [H <sup>+</sup> ]	X mL [H <sup>+</sup> ]	EP <sub>1</sub> = EP <sub>2</sub>
HCO <sub>3</sub> <sup>-</sup> ONLY	0 mL [H <sup>+</sup> ]	Y mL [H <sup>+</sup> ]	EP <sub>1</sub> ≈ 0
OH <sup>-</sup> ONLY	Z mL [H <sup>+</sup> ]	0 mL [H <sup>+</sup> ]	EP <sub>2</sub> ≈ 0
CO <sub>3</sub> <sup>2-</sup> and HCO <sub>3</sub> <sup>-</sup>	X mL [H <sup>+</sup> ]	(X + Y) mL [H <sup>+</sup> ]	EP <sub>1</sub> < EP <sub>2</sub> but EP <sub>1</sub> ≠ 0
CO <sub>3</sub> <sup>2-</sup> and OH <sup>-</sup>	(X + Z) mL [H <sup>+</sup> ]	X mL [H <sup>+</sup> ]	EP <sub>1</sub> > EP <sub>2</sub> but EP <sub>2</sub> ≠ 0

To use this table we only have to know how much acid was required to reach each endpoint and match it up with one of the five possibilities.

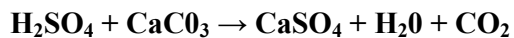
Question #1 (include in Results & Conclusion of report);

The combination HCO<sub>3</sub><sup>-</sup> & OH<sup>-</sup> was omitted from the possible combination of ions that could be identified in a sample. Why? Write an equation to support your answer.

**CALCULATIONS TO REPORT ALKALINITY VALUES**

Results from the alkalinity analysis are reported in units of "mg CaCO<sub>3</sub>/L sample". This is used because traditionally "water hardness" is also reported with the same unit.

We will have data from our experiment to represent the mL of acid required (A) and the molarity (M) of the sulfuric acid. Using the reaction below, we can convert these measurements to the desired unit of "mg CaCO<sub>3</sub>/L sample".



Because we will use 20.0 mL of sample, the conversion looks like this:

$$\frac{A \text{ ml H}_2\text{SO}_4}{20.0 \text{ mL sample}} \times \frac{M \text{ moles H}_2\text{SO}_4}{1 \text{ L H}_2\text{SO}_4} \times \frac{1 \text{ mole CaCO}_3}{1 \text{ mole H}_2\text{SO}_4} \times \frac{100. \text{ g CaCO}_3}{1 \text{ mole CaCO}_3} \times \frac{1 \text{ mg CaCO}_3}{1 \times 10^{-3} \text{ g CaCO}_3}$$

When all constants are collected and the units are cancelled, we get Equation (1):

$$\blacktriangleright \text{Alkalinity (in mg CaCO}_3\text{/L sample)} = \mathbf{A} \times \mathbf{M} \times (5.00 \times 10^3) \quad \text{Eq. 1}$$

The results from an alkalinity analysis are reported using five different parameters:

- ▶ total alkalinity - the result based on the total amount of acid used
- ▶ phenolphthalein alkalinity - the result based on the amount of acid required to reach the first endpoint
- ▶ carbonate alkalinity - the result due to the presence of CO<sub>3</sub><sup>2-</sup> in the sample
- ▶ bicarbonate alkalinity - the result due to the presence of HCO<sub>3</sub><sup>2-</sup> in the sample
- ▶ hydroxide alkalinity - the result due to the presence of OH<sup>-</sup> in the sample

To report these five values, we use the same Equation (1) to do every calculation. Only the value of A will be different {our molarity (M) is the same for the entire experiment}. It will be helpful to look at another table to determine the value of A. EP<sub>1</sub> and EP<sub>2</sub> refer to titrant volumes (H<sub>2</sub>SO<sub>4</sub>) at the two respective endpoints.

TABLE III-2

SAMPLE	Total ALK	phth ALK	CO <sub>3</sub> <sup>2-</sup> ALK	HCO <sub>3</sub> <sup>-</sup> ALK	OH <sup>-</sup> ALK
CO <sub>3</sub> <sup>2-</sup> ONLY	A=EP <sub>1</sub> + EP <sub>2</sub>	A=EP <sub>1</sub>	A=EP <sub>1</sub> + EP <sub>2</sub>	A=0	A=0
HCO <sub>3</sub> <sup>-</sup> ONLY	A=EP <sub>2</sub>	A=0	A=0	A=EP <sub>2</sub>	A=0
OH <sup>-</sup> ONLY	A=EP <sub>1</sub>	A=EP <sub>1</sub>	A=0	A=0	A=EP <sub>1</sub>
CO <sub>3</sub> <sup>2-</sup> and HCO <sub>3</sub> <sup>-</sup>	A = EP <sub>1</sub> + EP <sub>2</sub>	A=EP <sub>1</sub>	A = 2 X EP <sub>1</sub>	A = EP <sub>2</sub> - EP <sub>1</sub>	A=0
CO <sub>3</sub> <sup>2-</sup> and OH <sup>-</sup>	A=EP <sub>1</sub> + EP <sub>2</sub>	A=EP <sub>1</sub>	A = 2 X EP <sub>2</sub>	A=0	A = EP <sub>1</sub> - EP <sub>2</sub>

To use this table, we first have to identify what is in our sample by going through the analysis with Table III-1. Then, knowing what is in the sample, we come to Table III-2 and go to the line with that category. By following across the line, we know what value of A to substitute into Equation (1) for our different parameters.

### **LAB PRECAUTIONS (for all sessions)**

- ▶ You must wear safety goggles throughout this experiment.
- ▶ We will be working with dilute acids and bases, but you may want to consider washing your hands well if in contact with the solutions.
- ▶ You may wish to wear a lab coat or apron to protect your clothing.
- ▶ If you have any cuts or sores on your hands, you may wish to wear gloves.
- ▶ Clean any spills you may have with plentiful amounts of water.
- ▶ Do not rub your eyes unless your hands have been thoroughly rinsed.
- ▶ You must wash your hands before you leave this (and any lab).

### **PROCEDURE A. PREPARATION of H<sub>2</sub>SO<sub>4</sub> SOLUTION**

#### EQUIPMENT NEEDED:

- 100-mL graduated cylinder
- 1000-mL (1 L) storage bottle with cap

- [ 1 ] Using your 100-mL graduated cylinder, measure about 60 mL of 0.1 N (0.05 M) H<sub>2</sub>SO<sub>4</sub> into a 1000-mL storage bottle with cap.
- [ 2 ] Add distilled water to the bottle until it is about quarter-filled. Mix well. Add distilled water until the bottle is about half-filled and mix very well. (We are not measuring the amount of distilled water that we added because we will be determining the molarity of this solution later in the procedure.)

#### **Question #2** (to be included in your notebook before starting lab):

Assuming you made approximately 500 mL of solution, what do you expect its approximate molarity to be? (Recall the formula  $M_1V_1 = M_2V_2$ )

- [ 3 ] Label this solution. You may want to cover the cap with plastic film to minimize evaporation if you intend to use it next week.

▶ **SAVE THIS SOLUTION FOR THE ENTIRE EXPERIMENT!**

### **PROCEDURE B. PREPARATION of Na<sub>2</sub>CO<sub>3</sub> SOLUTION**

#### EQUIPMENT NEEDED:

- 1 500-mL volumetric flask with cap

- [ 1 ] Obtain a vial of dried Na<sub>2</sub>CO<sub>3</sub> (probably labeled as ALK-STD). Weigh the vial full (and record the weight to the fourth decimal place). Then transfer the contents of the vial into a clean 500-mL volumetric flask and weigh the empty vial. The difference in mass represents the grams of Na<sub>2</sub>CO<sub>3</sub> that are now in the volumetric flask. The amount should be close to 0.5 grams.
- [ 2 ] Add about 50 mL of distilled water to the 500-mL volumetric flask and swirl to dissolve. Add about 50 mL more of distilled water and swirl; continue until all of the sodium

carbonate has dissolved. Then fill to the line with distilled water, cap, and mix well.

[3] You have just prepared the "Standard Sodium Carbonate Solution" and you need to calculate its molarity and include the calculation in your lab report.

**EXAMPLE:** Suppose you added 0.5210 g Na<sub>2</sub>CO<sub>3</sub> STD (99.96% pure by weight) and diluted it to a final volume of 500.0 mL. What is the molarity of the solution?

$$M(\text{Na}_2\text{CO}_3) = \frac{0.5210 \text{ g STD}}{0.5000 \text{ L sol'n}} \times \frac{99.96 \text{ g Na}_2\text{CO}_3}{100.0 \text{ g STD}} \times \frac{1 \text{ mole Na}_2\text{CO}_3}{105.96 \text{ g Na}_2\text{CO}_3}$$

$$M(\text{Na}_2\text{CO}_3) = M(\text{CO}_3^{2-}) = 0.009830 \text{ M}$$

### **PROCEDURE C. STANDARDIZATION of H<sub>2</sub>SO<sub>4</sub> SOLUTION**

#### **EQUIPMENT NEEDED:**

- 1 50-mL buret and buret funnel
- 1 heating plate
- 3 250-mL Erlenmeyer flasks
- 1 10-mL volumetric pipet and pipet pump (or rubber bulb)

- [ 1] Pour about 5 mL of your sulfuric acid solution into your buret and swirl it around. Pour into sink and repeat. This is "conditioning" your buret, so that any liquid inside is now your solution and not water or something else. Put your buret in the clamp and, using your buret funnel, fill the buret to about the 0-mL line, making sure that the tip is filled and has no bubbles.
- [ 2] Using a 10.0 mL volumetric pipet and pipet pump (or rubber bulb), transfer two 10.0 mL portions of your "Standard Sodium Carbonate Solution" into a 250-mL Erlenmeyer flask. Using a graduated cylinder, add about 20 mL of distilled water. Then add 3-4 drops of phenolphthalein and swirl (the solution should be pink).

**Question #3** (to be included in your notebook before starting lab):

Estimate how many mL of your sulfuric acid solution will be required to titrate 20.0 mL of your "Standard Sodium Carbonate Solution" to the first endpoint (EP<sub>1</sub>)? The reaction is



**EXAMPLE:** Using 20.0 mL of the 0.009830 M STD (from above), we get

$$20.0 \text{ mL STD} \times \frac{0.009830 \text{ moles CO}_3^{2-}}{\text{L STD sol'n}} = 0.1966 \text{ mmoles CO}_3^{2-}$$

$$0.1966 \text{ mmoles CO}_3^{2-} \times \frac{1 \text{ mole H}^+}{1 \text{ mole CO}_3^{2-}} \times \frac{1 \text{ mole H}_2\text{SO}_4}{2 \text{ mole H}^+} = 0.09830 \text{ mmole H}_2\text{SO}_4$$

$$0.09830 \text{ mmole H}_2\text{SO}_4 \times \frac{1 \text{ L sol'n}}{0.01 \text{ moles H}_2\text{SO}_4} = 9.83 \text{ mL of H}_2\text{SO}_4 \text{ solution needed} \\ (\text{<estimated M from Procedure A})$$

[ 3] Record the initial buret reading (estimate the second decimal place; i.e., X.XX mL - you do not have to start at 0.00 mL!).

Titrate with a piece of white paper under your flask so that you can see the color change easier and have a flask of distilled water nearby so that you can compare your

endpoint color to it.

Quickly add about half of your estimated amount (using **your numbers** in the previous example), constantly swirling the flask to ensure mixing. Slow down and continue titrating until the pink color starts to disappear; then go drop-by-drop **until the color has completely disappeared** (keep comparing to the distilled water flask).

(WARNING: Your instructor will very quickly become weary of being asked, "Is this still pink?", etc.)

Record the final reading from the buret. The difference (final - initial readings) is the volume of acid for EP<sub>1</sub>.

[ 4 ] Refill your buret and record the initial reading. Add 3-4 drops of the "mixed indicator" to the same flask from step [3] above. The color should be blue-green.

**Question #4** (to be included in your notebook before starting this step):

How many mL of your sulfuric acid solution should be required to reach the second endpoint?

[ 5 ] Quickly add about 1 / 2 of your answer to Question #4 to your flask (should still have some blue-green-gray color), with constant swirling. Remove the flask and place on a heating plate; heat to just boiling - do not allow it to spatter. Using a double-folded paper towel or hand towel, take the flask to the sink and cool under running cold water until it doesn't feel too hot to touch. [Your instructor might also have dish pans of ice water available for this purpose.]

The color of your solution might have changed back to pink; if it did (or didn't), that's OK. Continue the titration (if it was pink, a drop or two of acid will make it turn back to blue-green). **The end-point is when all of the blue-green color is gone** (sometimes the endpoint appears yellowish, sometimes very pale pink, sometimes almost colorless: the important thing is that the blue-green is no longer there!).

Record the final reading from the buret. The difference (final - initial readings) is the volume of acid for EP<sub>2</sub>.

[ 6 ] Empty the contents of your flask into the sink with running water. Then repeat steps [1] through [5] for two more samples of your "Standard Sodium Carbonate Solution".

[ 7 ] Calculate the molarity of your sulfuric acid solution, using all six endpoint volumes. Calculate the average molarity, deviations, standard deviation (or average deviation) Include in report (Example below).

EXAMPLE: Continuing with values from the previous examples, suppose that EP<sub>1</sub> required 10.01 mL of H<sub>2</sub>SO<sub>4</sub> and EP<sub>2</sub> required 9.91 mL of H<sub>2</sub>SO<sub>4</sub>

$$\frac{20.0 \text{ mL STD sol'n}}{10.01 \text{ mL H}_2\text{SO}_4} \times \frac{0.009830 \text{ moles CO}_3^{2-}}{1 \text{ L STD sol'n}} \times \frac{1 \text{ mole H}^+}{1 \text{ mole CO}_3^{2-}} \times \frac{1 \text{ mole H}_2\text{SO}_4}{2 \text{ moles H}^+}$$
$$= 0.00982 \text{ M H}_2\text{SO}_4, \text{ from EP}_1$$

And

$$\frac{20.0 \text{ mL STD sol'n}}{9.91 \text{ mL H}_2\text{SO}_4} \times \frac{0.009830 \text{ moles CO}_3^{2-}}{1 \text{ L STD sol'n}} \times \frac{1 \text{ mole H}^+}{1 \text{ mole CO}_3^{2-}} \times \frac{1 \text{ mole H}_2\text{SO}_4}{2 \text{ moles H}^+}$$
$$= 0.00992 \text{ M H}_2\text{SO}_4, \text{ from EP}_2$$

## PROCEDURE D. TITRATION of UNKNOWN and AQUEOUS SAMPLE

### EQUIPMENT NEEDED:

- 1 50-mL buret and buret funnel
- 1 hot plate
- 3 250-mL Erlenmeyer flasks
- 1 10-mL volumetric pipet and pipet pump (or rubber bulb)

- [ 1] Use the same set-up as in Procedure (C). Transfer 20.0 mL of unknown  $\text{CO}_3^{2-}$  to each of three 250-mL Erlenmeyer flasks using the 10.0 mL volumetric pipet and pipet pump (or rubber bulb). Add about 20 mL of distilled water to each (using a graduated cylinder) and then 3-4 drops of phenolphthalein. Fill the buret with your sulfuric acid solution and record the initial reading.
- (a) If the color of the solution is very pale pink, slowly add 2 or 3 drops of  $\text{H}_2\text{SO}_4$ . If the color disappears, record  $\text{EP}_1$  as equal to zero. If the solution is colorless, do not add any  $\text{H}_2\text{SO}_4$ ; we will also record this endpoint as zero. Proceed to Step [2].
- (b) If the color of the solution is a definite pink, slowly add  $\text{H}_2\text{SO}_4$  with swirling until the solution becomes colorless (comparing to a flask containing distilled water as before. Record the final volume in the buret. The difference (final - initial readings) is the volume of acid for  $\text{EP}_1$ .
- [ 2] Refill the buret with your sulfuric acid solution and record the initial volume. To the same flask from Step [1], add 3-4 drops of **mixed indicator**.
- (a) If the color of the solution is not a bright blue-green, slowly add 2 or 3 drops of  $\text{H}_2\text{SO}_4$ . If the blue-green disappears, record  $\text{EP}_2$  as equal to zero. If the solution was yellowish, pale pink, or almost colorless when the indicator was added, also record this endpoint as zero.
- (b) If the color of the solution is blue-green, slowly titrate until the blue-green starts to fade, remove the sample and heat it on the hot plate to almost boiling, cool it, and continue titrating until the blue-green color disappears. Record the final volume from the buret. The difference (final - initial readings from this step) indicates the volume for  $\text{EP}_2$ .
- [ 3] After you have completed the first trial, you can titrate the next two much more quickly because you know the approximate volume of acid required for each endpoint. You could, therefore, add 1/2 or 2/3 of that amount very quickly and then slow down near the endpoint. You should also know what components are in your unknown.
- [4] Repeat the procedure, but use 20.0 mL of your natural water sample. Everything else remains the same.
- [ 5] Using Table III-1, you should be able to identify the components of your unknown and of your water sample. Then, using Table III-2 and Equation (1), calculate the five different alkalinities for each.

EXAMPLE: Suppose my unknown,  $\text{CO}_3^{2-}$  - EC, required 8.11 mL of 0.00987 M  $\text{H}_2\text{SO}_4$  to reach  $\text{EP}_1$  and an additional 2.95 mL to reach  $\text{EP}_2$ . This means that  $\text{EP}_1 > \text{EP}_2$  and from Table III-1, that tells me that my unknown contains  $\text{CO}_3^{2-}$  and  $\text{OH}^-$ . I now need to go to Table III-2 to find the values of A that should be substituted into Eq. (1):

► **Alkalinity** (in mg CaCO<sub>3</sub>/L sample) =  $A \times M \times (5.00 \times 10^3)$

(a) Total Alkalinity:  $A = EP_1 + EP_2 = 8.11 \text{ mL} + 2.95 \text{ mL} = \mathbf{11.06 \text{ mL}}$   
Total alkalinity =  $(11.06) \times (0.00987) \times (5.00 \times 10^3)$   
**Total alkalinity = 546 mg CaCO<sub>3</sub>/L**

(b) Phenolphthalein Alkalinity:  $A = EP_1 = \mathbf{8.11 \text{ mL}}$   
Phenolphthalein alkalinity =  $(8.11) \times (0.00987) \times (5.00 \times 10^3)$   
**Phenolphthalein alkalinity = 400. mg CaCO<sub>3</sub>/L**

(c) Carbonate alkalinity:  $A = 2 \times EP_2 = 2 \times 2.95 \text{ mL} = 5.90 \text{ mL}$   
Carbonate alkalinity =  $(5.90) \times (0.00987) \times (5.00 \times 10^3)$   
**Carbonate alkalinity = 291 mg CaCO<sub>3</sub>/L**

(d) **Bicarbonate alkalinity = 0 mg CaCO<sub>3</sub>/L** (because there isn't any in the unknown.  
Bicarbonate alkalinity cannot be negative)

(e) Hydroxide alkalinity:  $A = EP_1 - EP_2 = 8.11 \text{ mL} - 2.95 \text{ mL} = 5.16 \text{ mL}$   
Hydroxide alkalinity =  $(5.16) \times (0.00987) \times (5.00 \times 10^3)$   
**Hydroxide alkalinity = 255 mg CaCO<sub>3</sub>/L**

## PROCEDURE E. POTENTIOMETRIC TITRATION of UNKNOWN

### EQUIPMENT NEEDED:

- 1 50-mL buret and buret funnel
- 1 ring stand and buret clamp
- 1 pH meter and electrode
- 1 magnetic stirrer and stirring bar
- 1 100- or 250-mL beaker and squirt bottle
- 1 10-mL volumetric pipet and pipet pump (or rubber bulb)

[ 1 ] Calibrate the pH meter as you were taught in the previous experiment.

[ 2 ] Transfer 20.0 mL of your unknown to a 100-mL or 250-mL beaker (containing the magnetic stirring bar). Add enough distilled water to cover the tip of the electrode. Fill the buret with the sulfuric acid solution prepared in procedure A and record the initial reading. Slowly turn on the magnetic stirrer, making sure that the stirring rod is not hitting the electrode (which is very expensive!). Record the initial pH (i.e./ when 0 mL of sulfuric acid has been added).

There are two methods to do this titration because you already know the approximate amount of acid required to reach the first and second endpoints. (Some of you will have only one endpoint; it doesn't matter if it is the first or second endpoint/ you would stop after you have reached it.)

(a) You can add H<sub>2</sub>SO<sub>4</sub> in 0.5 mL increments/ recording the pH at each step (as shown in the example), until you are 1.0 mL beyond the last endpoint. (You know if you have one or two endpoints to reach from your indicator titration.)

**OR**

(b) You can add acid in larger amounts (i.e./ 2 mL) until you get close to the first endpoint/ then slow down and add in 0.5 mL increments until you are 1.0 mL beyond the first endpoint/ speed up again until you are close to the second

endpoint/ slow down in smaller increments until you are 1.0 mL beyond the last endpoint. (If you only have one endpoint/ you would have stopped 1.0 mL beyond it.)

- [ 3] Clean up your work space and return burets/ magnetic stirrers and stirring bars/ pH meters and electrodes to their proper places.
- [ 4] For the report/ you will need to construct a graph (as indicated in Figure III-1) with pH (y axis) vs mL sulfuric acid (x axis). On the same graph/ you will plot  $(-\Delta\text{pH}/\Delta\text{mL})$  on the y axis against mL sulfuric acid (x axis). The peaks in the  $-\Delta\text{pH}/\Delta\text{mL}$  curve help to pinpoint where the largest changes in slope occur and these indicate where EP<sub>1</sub> and EP<sub>2</sub> volumes are. (See example on next pages.)

**EXAMPLE:** To estimate the value of  $-\text{DpH}/\text{DmL}$  at 5.00 mL we use the points at 4.50 and 5.50 mL. From Table III-3, pH = 11.54 at 4.50 mL of H<sub>2</sub>SO<sub>4</sub> and pH = 10.95 at 5.50 mL of H<sub>2</sub>SO<sub>4</sub>.

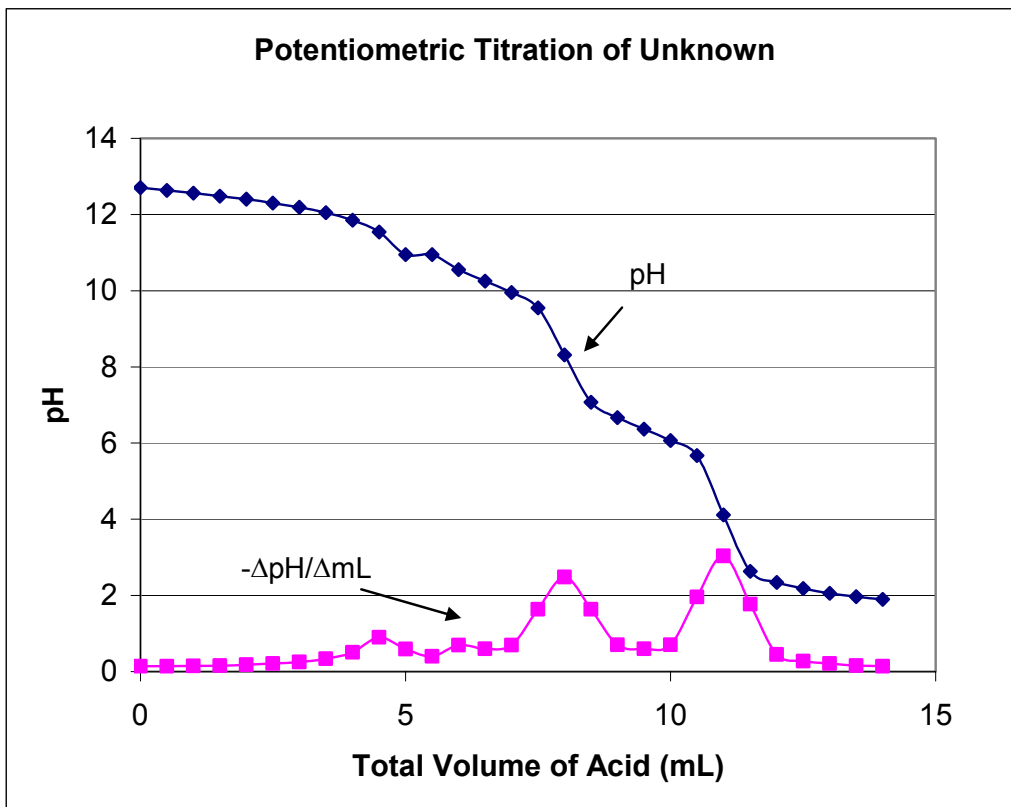
$$\frac{-\Delta\text{pH}}{\Delta\text{mL}} = \frac{-(11.54 - 10.95)}{(4.50 \text{ mL} - 5.50 \text{ mL})} = \frac{0.59}{1.00} = 0.59 \text{ mL}^{-1}$$

TABLE III-3

mL acid	pH	$-\Delta\text{pH}/\Delta\text{mL}$
0.00	12.70	0.14
0.50	12.63	0.14
1.00	12.56	0.15
1.50	12.48	0.16
2.00	12.40	0.18
2.50	12.30	0.21
3.00	12.19	0.25
3.50	12.05	0.34
4.00	11.85	0.51
4.50	11.54	0.90
5.00	10.95	0.59
5.50	10.95	0.40
6.00	10.55	0.70
6.50	10.25	0.60
7.00	9.95	0.70
7.50	9.55	1.64
8.00	8.31	2.48
8.50	7.07	1.64
9.00	6.67	0.70
9.50	6.37	0.60
10.00	6.07	0.70
10.50	5.67	1.96
11.00	4.11	3.04
11.50	2.63	1.77
12.00	2.34	0.45
12.50	2.18	0.28
13.00	2.06	0.21
13.50	1.97	0.16
14.00	1.90	0.14

[ 5] From your graph, obtain the volumes of acid for your endpoint(s) and calculate the five alkalinity values for your unknown as you did in Part D. These results may differ somewhat from Part D.

Figure III-1



## **REQUIREMENTS for your LAB REPORT**

### **Experiment #III: Alkalinity**

#### PURPOSE:

In **your words**, state the goals of this experiment.

#### PROCEDURE:

Do not repeat the directions given in the manual. Simply reference them. However, you should mention any changes that were made or any information that was unique to your analysis.

#### DATA:

Data Tables Required For:

- Standardization of sulfuric acid solution (molarity)
- Alkalinity determination for unknown CO<sub>3</sub> # \_\_\_\_\_
- Alkalinity determination for natural water sample
- Potentiometric Titration of unknown

Graph of potentiometric titration of unknown.

Data tables should contain all amounts used, and should be completed with a determination of the average for three trials and the standard deviation of this value.

#### SAMPLE CALCULATIONS:

You need to show sample calculations for one trial only for each:

- Molarity of standard sodium carbonate
- Molarity of sulfuric acid solution
- Alkalinities of unknown CO<sub>3</sub> # \_\_\_\_\_
- Alkalinities of natural water sample

#### RESULTS & CONCLUSIONS:

- Has the goal of the experiment been met?
- Summarize the results, including the answer to your unknown (with unknown number) and the natural water sample.
- Sources of possible or known errors and consequences of those errors (i.e., high results, low results, sporadic results, why?)
- Suggestions for improvements

#### OVERALL:

- Organization of report.
- Neatness and legibility
- Grammar and spelling