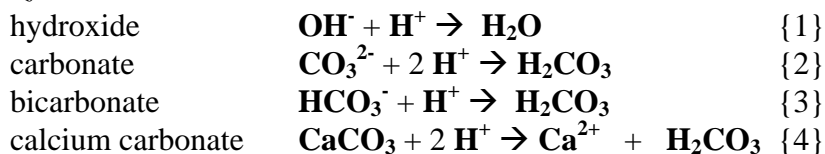


## ALKALINITY OF GROUNDWATER SAMPLES

### INTRODUCTION

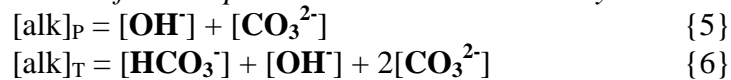
**Alkalinity** is a measure of the ability of a water sample to neutralize acids. It is an aggregate property that is derived from the sum of the neutralising capabilities of all bases present in a water sample. Alkalinity is measured by volumetric analysis using a standardized acid titrant. The endpoint is signalled by a colour change of a pH indicator, such as phenolphthalein or methyl orange or by using a pH meter. Alkalinity is a general water chemistry parameter and can be used to predict photosynthetic productivity and the buffering capacity of a lake against acid deposition. Note that alkalinity is not the same as pH (or if you like pOH). Alkalinity is a measure of a capacity factor, whereas the pOH ( $-\log [\text{OH}^-]$ ) is an intensity factor. The common ions that contribute to alkalinity in natural waters are hydroxide ( $\text{OH}^-$ ), carbonate ( $\text{CO}_3^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ , aka hydrogen carbonate). The bicarbonate ion is usually the dominant anion and the largest contributor to the alkalinity.

#### *Neutralization Reactions*



In some waters/wastewaters, other species such as ammonia, borates, phosphates and silicates may contribute to the alkalinity. Alkalinity can be measured as either the ‘phenolphthalein’ alkalinity (neutralization to a pH ~ 8.3) or as the ‘total’ alkalinity (pH ~ 4.2). The phenolphthalein alkalinity, written as  $[\text{alk}]_P$  when expressed as the number of moles of  $\text{H}^+$  neutralized per litre, is equal to the sum of the molar concentrations of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  (see equation below). Since the  $[\text{OH}^-]$  can be readily determined from the sample pH, the  $[\text{CO}_3^{2-}]$  can be calculated from the phenolphthalein alkalinity. If the initial pH of the sample is less than 8.3 to begin with, the phenolphthalein alkalinity is zero and  $[\text{OH}^-]$  and  $[\text{CO}_3^{2-}] \sim 0$ . The total alkalinity,  $[\text{alk}]_T$ , is a measure of all contributing ions (see equation below).

#### *Chemical Definitions of Phenolphthalein and Total Alkalinity*



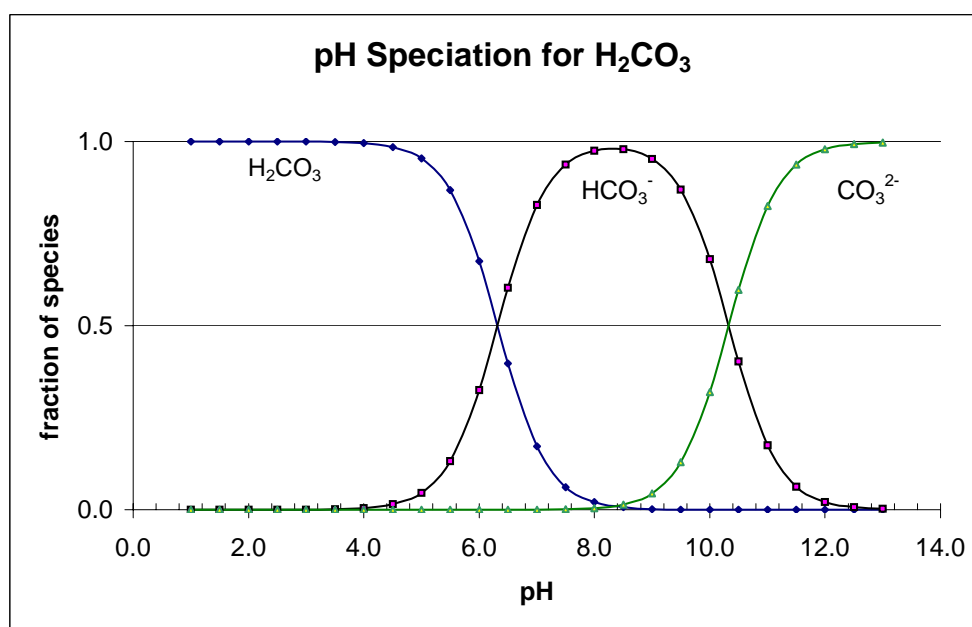
Note that the carbonate ion concentration is multiplied by a factor of two since each  $\text{CO}_3^{2-}$  ion will neutralize two protons when titrated to pH 4.2. To determine the concentration of the hydroxide, bicarbonate and carbonate ion, one needs to know the initial pH of the original sample and either the phenolphthalein alkalinity or the total alkalinity. Although, alkalinity is measured and used in stoichiometric calculations expressed as mol/L  $\text{H}^+$ , it is normally reported as mg/L  $\text{CaCO}_3$  (i.e., as having the same neutralizing ability as a certain concentration of  $\text{CaCO}_3$ ). For example, a water sample that has a total alkalinity reported as  $T_{\text{alk}} = 45 \text{ mg/L}$   $\text{CaCO}_3$  has the same neutralising capacity as a solution which contains 45 mg/L of  $\text{CaCO}_3$  (i.e.,  $9.0 \times 10^{-4} \text{ mol H}^+/\text{L}$ ), even though the sample may not contain any  $\text{CaCO}_3$  (see calculation below).

Since the neutralization of calcium carbonate requires 2 mols of  $\text{H}^+$  as in Eqn {4}, the conversion from mass of  $\text{CaCO}_3$  in mg to mols of  $\text{H}^+$  neutralized is given by,

$$[\text{H}^+] = \frac{45 \text{ mg CaCO}_3}{\text{L}} \times \frac{1 \text{ mol CaCO}_3}{100,000 \text{ mg CaCO}_3} \times \frac{2 \text{ mol H}^+}{1 \text{ mol CaCO}_3} = 9.0 \times 10^{-4} \text{ mol/L H}^+$$

Where the first term represents the reported alkalinity in mg/L  $\text{CaCO}_3$ , the second term is the formula weight of  $\text{CaCO}_3$  and the third term is the mole ratio from the neutralization reaction, Eqn. {4}.

The speciation diagram shown below can be easily derived from the acid dissociation constants ( $K_a$ 's) and can be used to show the relative portions of the various carbonate species ( $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) as a function of pH. The crossover points occur at the  $\text{pK}_a$  values of  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$ , respectively. At no pH is there a high concentration of all three forms of inorganic carbon. As can be seen from the diagram, at pH's between 6 and 10, the bicarbonate ion is the dominant form of inorganic carbon.



At pH < 6:



At pH > 11:



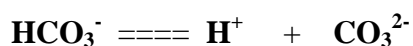
At 10 > pH > 7:



#### Acid Dissociation Reactions and Equilibrium Expressions



$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.8 \times 10^{-7}$$



$$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11}$$

**Example calculation converting titration data to mg/L CaCO<sub>3</sub>:**

If it takes 8.20 mL of 0.0190 N HCl to reach the phenolphthalein end-point using an 80.0 mL sample, then the phenolphthalein alkalinity is calculated as follows:

$$\begin{aligned} \text{equivalents of acid added} &= 8.20 \text{ mL} \times \frac{0.0190 \text{ equiv.}}{1 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \\ &= 1.56 \times 10^{-4} \text{ equiv.} \\ &= 1.56 \times 10^{-4} \text{ mol H}^+, \text{ since } K = \frac{1 \text{ equiv}}{1 \text{ mol}} \text{ for HCl} \end{aligned}$$

$$[\text{alk}]_P = \frac{1.56 \times 10^{-4} \text{ mol H}^+}{80.00 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1.95 \times 10^{-3} \text{ mol H}^+/\text{L}$$

It is customary to use square brackets to indicate the molar concentration. Thus,  $[\text{alk}]_P$  expresses the alkalinity to the phenolphthalein end-point in units of mol H<sup>+</sup>/L or M. However, it is common to report alkalinities as an equivalent amount of CaCO<sub>3</sub> in mg/L that would give rise to the same neutralizing capacity. Therefore, the equivalents of CaCO<sub>3</sub> having the same neutralising capacity as this 80.0 mL sample is  $1.56 \times 10^{-4}$ . The equivalent weight of CaCO<sub>3</sub> is 50 g/equiv (i.e., ½ of the molecular weight), since each mole of CO<sub>3</sub><sup>2-</sup> reacts with two moles of H<sup>+</sup>.

$$\begin{aligned} \text{weight of CaCO}_3 &= 1.56 \times 10^{-4} \text{ equiv.} \times \frac{50.0 \text{ g CaCO}_3}{1 \text{ equiv}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 7.79 \text{ mg CaCO}_3 \\ (\text{i.e. } 80.0 \text{ mL of sample has a neutralising capability of } 7.79 \text{ mg CaCO}_3) \end{aligned}$$

Converting this to a concentration by dividing by the sample volume, the phenolphthalein alkalinity ( $P_{\text{alk}}$ ) is reported as:

$$P_{\text{alk}} = \frac{7.79 \text{ mg CaCO}_3}{80.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 97.3 \text{ mg CaCO}_3/\text{L}$$

Similar calculations can be applied to total alkalinity values.

**Calculating the [OH<sup>-</sup>], [HCO<sub>3</sub><sup>-</sup>] and [CO<sub>3</sub><sup>2-</sup>] from pH, [alk]<sub>P</sub> and/or [alk]<sub>T</sub>**

$$[\text{OH}^-] = 10^{-\text{pOH}} \text{ where, } \text{pOH} = \text{pK}_w - \text{pH} \text{ and } \text{pK}_w = 14.00 \text{ at } 25^\circ\text{C}$$

Rearranging Eqn {5}

$$[\text{CO}_3^{2-}] = [\text{alk}]_P - [\text{OH}^-]$$

Rearranging Eqn {6}

$$[\text{HCO}_3^-] = [\text{alk}]_T - [\text{OH}^-] - 2[\text{CO}_3^{2-}]$$

If  $[\text{alk}]_P = 0$ , then rearrange  $K_{a2}$  expression and substitute into {6} to solve for  $[\text{CO}_3^{2-}]$

$$[\text{alk}]_T = \{[\text{H}^+][\text{CO}_3^{2-}]/K_{a2} + [\text{OH}^-] + 2[\text{CO}_3^{2-}]\}$$

and then use the  $K_{a2}$  expression to solve for

$$[\text{HCO}_3^-] = \{[\text{H}^+][\text{CO}_3^{2-}]/K_{a2}\}$$

## EXPERIMENTAL PROCEDURE for Alkalinity Measurements

*Sampling collection and handling:* Collect sample into glass or plastic bottles. Samples must be analyzed within 24 hours.

*Method No. 2320* (Standard Methods, 18<sup>th</sup> edition)

### *Operating Instructions for pH meters*

See individual operating instructions that accompany each instrument. Handle pH electrodes with care, the thin glass membrane is very fragile. Always rinse electrode thoroughly with distilled water between samples and blot dry.

### *Calibration with pH buffers*

Following the general operating instructions outlined with individual instruments.

### *pH Colour Indicators*

Colour indicators can also be used to determine the endpoint in total alkalinity determinations.

Methyl orange undergoes a colour change from yellow to orange between pH 4.5-4.2.

Alternatively, a mixture of bromocresol and methyl red can be used, which undergoes a blueish green to faint pink transition.

### *Standardization of the HCl stock*

1. Obtain ~200 mL of the stock ~0.1 N **HCl** solution and rinse a buret (including the tip) with three small portions. Check to clear all air bubbles from the stopcock and tip. Fill the buret.
2. Obtain ~0.5 g of dried **Na<sub>2</sub>CO<sub>3</sub>** (certified primary standard grade) and weigh exactly about 0.1 g into each of three 125 mL Erlenmeyer flasks. Label the flasks and record the exact mass of sodium carbonate in your notebook.
3. Dissolve the **Na<sub>2</sub>CO<sub>3</sub>** in about 75 mL of deionized water and titrate to pH 4.2 (or appropriate colour change).

### *Preparation of dilute HCl titrant*

1. Accurately prepare a solution of hydrochloric acid that is about 0.02 N by pipetting 50.0 mL of the supplied (approximately 0.1 N) stock **HCl** into a 250 mL volumetric flask. Make up to the mark with distilled water, stopper and mix.
2. Rinse and fill a second buret with the dilute HCl standard.

*Determination of Alkalinity of samples*

1. Obtain ~500 mL of at least one of the following available samples.
2. Pipet a 100.00 mL aliquot into a 250 mL beaker and record the initial pH prior to adding any **HCl**.
3. If the initial pH > 8.3, add a few drops of phenolphthalein and titrate with dilute **HCl** (~0.02 N) until the faint pink disappears and the solution is colourless. If you are using a pH meter, then titrate until pH=8.30.
4. Continue adding the dilute **HCl** titrant until the methyl orange (bromocresol-methyl red) end point or if you are using a pH meter, then titrate until pH=4.20.

*Determination of total alkalinity of Standard Reference Material (SRM)*

1. Obtain ~500 mL the standard reference material (SRM) and pipet 100.0 mL aliquots into Erlenmeyer flasks.
2. Titrate with dilute (~0.02N **HCl**) to the total alkalinity end-point by the same method used for the samples above (methyl orange, bromocresol-methyl red or pH=4.20).

As the end point is approached, proceed with dropwise addition of titrant. *You may wish to waste the first run to get an idea of your end-point volumes.*

**Data Tables**

Summarize all data with appropriate heading, units and uncertainties in tabular format.

**Result Tables**

Calculate the mean phenolphthalein and total alkalinity of your sample and the SRM. Report  $[\text{alk}]_P$  and  $[\text{alk}]_T$  in mol  $\text{H}^+$ /L and  $P_{\text{alk}}$  and  $T_{\text{alk}}$  in mg/L  $\text{CaCO}_3$ . Calculate and report the concentrations of  $\text{OH}^-$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in your sample. Report your precision as relative standard deviations (RSD's) and quote the 95% confidence intervals for your final values. Also, report the method accuracy as % bias based on the results of the SRM.

**References**

M.P. Roche, F.J. Millero, Measurement of total alkalinity of surface waters using a continuous flowing spectrophotometric technique, *Marine Chemistry*, 60 (1998), 85-94.