

An Approach towards the Determination of Alkalinity in Water, Its Experimental Consideration & Comparison with Traditional Method: An Overview

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ABSTRACT

Alkalinity is equal to the stoichiometric sum of the bases in solution therefore it includes all the acid neutralizing bases in water namely OH^- , CO_3^{2-} & HCO_3^- ions. In the natural environment carbonate alkalinity tends to make up most of the total alkalinity due to the common occurrence and dissolution of carbonate rocks and presence of CO_2 in the atmosphere. Alkalinity varies with the location Acid-base titration is performed for their estimation but the theoretical determination for the type and extent of these ions is tedious process through traditional formulas known to us, (Volume of acid used up till Phenolphthalein & Methyl orange end point). Here in this paper we are trying to simplify the method and reporting the direct determination of the extent of ions by simple calculation without using the formulas for specific ions under different conditions of alkalinity. Thus a comparative aspect of this approach with traditional method will be covered by us in this paper.

Key words: Alkalinity, acid-base titration, ions, phenolphthalein, methyl orange indicator.

Introduction

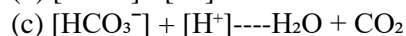
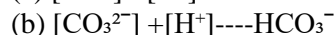
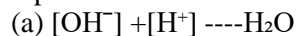
Alkalinity is primarily a way of measuring the acid neutralizing capacity of water. In other words, it is ability to maintain a relatively constant pH, the possibility to maintain constant pH is due to the hydroxyl, carbonate and bicarbonate ions present in water. The ability of natural water to act as a buffer is controlled in part by the amount of calcium and carbonate ion in solution. Both carbonate and calcium ion come from calcium carbonate or limestone so water that comes in contact with limestone will contain high levels of both Ca^{2+} and CO_3^{2-} ions and have elevated hardness and alkalinity. Alkalinity or “acid neutralizing capacity,” is measured by adding acid to the sample and figuring out the equivalent alkalinity in the water. The actual units for the alkalinity titration are moles or equivalents per volume (moles/L or eq/L), however converting alkalinity from equiv./L to “mg/L as CaCO_3 ” takes into account that one mole of carbonate (CO_3^{2-}) can neutralize 2 moles of acid H^+ .

The present piece of work highlights the simple method to determine the alkalinity of sample by simple calculation and it also covers the range which gives an idea about the type of ions which could be present.

Materials and Methods

The alkalinity of water is determined by titrating the water sample with Standard acid solution (HCl). Alkalinity of water is attributed to the presence of OH^- , CO_3^{2-} and HCO_3^- ions.

The titration is performed volumetrically using phenolphthalein and methyl orange indicators. In volumetric analysis phenolphthalein end point indicates alkalinity due to OH^- ions and one half of CO_3^{2-} ions i.e. completion of reactions (a) and (b) only whilst methyl orange end point marks the presence of carbonate and bicarbonate ions i.e. Completion of reactions (a), (b) and (c). Total amount of acid used represents the total alkalinity.



$[\text{H}^+]$ corresponds to standard HCl while hydroxide, carbonate and bicarbonate are the alkalinity causing ions present in water.

Five different samples of alkaline water (having 5 possible combination of ions in water) was prepared and titrated to obtain the volume of acid till P & M end point

TABLE-1

S.NO	Result of titrations	Alkalinity due to		
		Hydroxide (OH ⁻)	Carbonate (CO ₃ ²⁻)	Bicarbonate (HCO ₃ ⁻)
1.	P = 0	Nil	Nil	M
2.	P = M	Nil	Nil	Nil
3.	P=(1/2)M (or V ₁ =V ₂)	Nil	2 P	Nil
4.	P>(1/2)M (or V ₁ >V ₂)	(2 P - M)	2 (M - P)	Nil
5.	P<(1/2)M (or V ₁ <V ₂)	Nil	2 P	(M - 2 P)

This table has the formulas for calculating the extent of ions which is difficult to remember.

Results & Discussion

Alkalinity or “acid neutralizing capacity,” is measured by adding acid to the sample and figuring out the equivalent alkalinity in the water. The actual units for the alkalinity titration are moles or equivalents per volume (moles/L or eq/L), however converting alkalinity from equiv./L to “mg/L as CaCO₃” takes into account that one mole of carbonate (CO₃²⁻) can neutralize 2 moles of acid H⁺. Determining the extent of ions through the reported formulas for different conditions, mentioned in the Table-1 is difficult. Thus herein we report different conditions & method to determine the extent of ions directly from the values without using the formulas. Different cases with suitable examples are explained below.

The procedure described here is simple making it a preferred method for calculating alkalinity. The method is reliable as could be observed from the results obtained through the quoted examples.

Table: 2. FOR SEPARATE TITRATION

(Different aliquot of water sample for P & M end point determination)

	OH ⁻	CO ₃ ²⁻	HCO ₃ ⁻
1.	(V1 or V2) ml	Nil	Nil
2.	Nil	Nil	V2 ml
3.	Nil	(2V1 or V2) ml	Nil
4.	Nil	2V1 ml	(V2-2V1) ml
5	{ V1-(V2-V1) } ml	2(V2-V1) ml	Nil

Table: 3. FOR SINGLE/SAME TITRATION

(Same aliquot of watersample for P& M end point determination)

	OH ⁻	CO ₃ ²⁻	HCO ₃ ⁻
1.	Nil	(2V1 or 2V2) ml	Nil
2.	Nil	2V1	(V2-V1) ml
3.	(V1-V2) ml	2V2	Nil

Where, V₁ is the volume of acid required used with phenolphthalein indicator, while V₂ is the volume used with methyl orange indicator.

Table 2 & 3 summarize the volume of acid used for separate and single water sample titration till P and M end point. This simplifies our task of calculating the strength by identifying the volume of acid consumed instead of putting the traditional formulas.

CASE: 1

For HCO_3^- only:

When there is no change in color on adding phenolphthalein indicator it indicates the presence of only HCO_3^- in water sample. So the volume of acid required for complete neutralization of HCO_3^- will be equal to the volume of acid used for complete neutralization of HCO_3^- when methyl orange is taken for titration.

$$\text{Strength of } \text{HCO}_3^- = [V \cdot N(\text{acid}) \cdot 50 \cdot 1000] / \text{volume of water sample}$$

Where V is the volume of acid used for complete neutralization of HCO_3^- when methyl orange is taken for titration.

CASE: 2

For OH^- only:

When the volume of acid required for complete neutralization of ion by separate titration with methyl orange and phenolphthalein indicator is same, then it indicates the presence of only OH^- ion in water sample.

If V_1 is the volume of acid used for complete neutralization of OH^- using phenolphthalein as indicator and same volume V_2 of acid used for neutralization when titration is done separately by taking another lot of water sample using methyl orange as indicator.

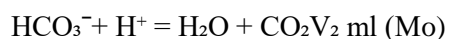
$$\text{OH}^- \text{ alkalinity} = [(V_1 \text{ or } V_2) \cdot N(\text{acid}) \cdot 50 \cdot 1000] / \text{volume of water sample}$$

Where V_1 or V_2 is equal to volume of acid used for neutralization of OH^- using either phenolphthalein or methyl orange indicator.

CASE: 3

For CO_3^{2-} only:

When the volume of acid required using methyl orange indicator is double, to the volume used using phenolphthalein indicator (in separate titration). However in single/same titration if (V_1) be the volume of acid required for half neutralization of CO_3^{2-} ions with phenolphthalein indicator and the further volume of acid (V_2) in same water sample with methyl orange indicator is utilized for neutralization of HCO_3^- generated by CO_3^{2-} and these two volumes of acid will be same (in same or single titration).



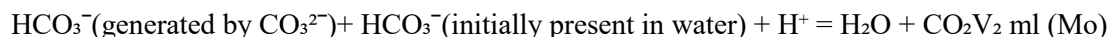
$$V_1 = V_2$$

$$\text{CO}_3^{2-} \text{ alkalinity} = [(\text{volume of acid used by } \text{CO}_3^{2-}) \text{ or } (V_1 \text{ or } V_2) \cdot N(\text{acid}) \cdot 50 \cdot 1000] / \text{Volume of water sample}$$

CASE: 4

For both CO_3^{2-} & HCO_3^- :

When the volume of acid required for neutralization of CO_3^{2-} is V_1 while V_2 represent the volume of acid that is required for neutralization of HCO_3^- generated by CO_3^{2-} as well as by those which are already there in water. Thus in this case $V_1 > V_2$



CO_3^{2-} alkalinity = [(Twice the volume of acid used for neutralization of CO_3^{2-}) or $(2V_1) * N(\text{acid}) * 50 * 1000$] / Volume of water sample

HCO_3^- alkalinity = [(volume of acid used by HCO_3^-) or $(V_2 - V_1) * N(\text{acid}) * 50 * 1000$] / volume of water sample

Let us consider this case through an example in which on titration of 100 ml of water sample with N/50 HCl 5ml of the acid was required uptill phenolphthalein end point. Which on adding a few drops of methyl orange to the same solution and titration was further continued, the yellow color of the solution just turned pink after the addition of another 12 ml of acid. The type and extent of alkalinity present in given water sample can be calculated by.

$$V_1 = 5 \text{ ml and } V_2 = 12 \text{ ml}$$

$$\text{Volume of } \text{CO}_3^{2-} = 2V_1 = 10 \text{ ml}$$

$$\text{Volume of } \text{HCO}_3^- = V_2 - V_1 = 7 \text{ ml}$$

$$\text{Volume of water sample} = 200 \text{ ml}$$

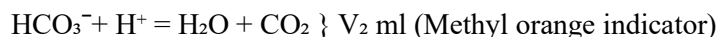
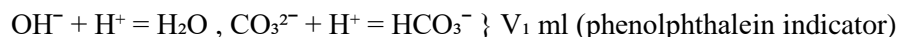
$$\begin{aligned} \text{CO}_3^{2-} \text{ alkalinity} &= [(\text{volume of acid used by } \text{CO}_3^{2-}) \text{ or } (2V_1) * N(\text{acid}) * 50 * 1000] / \text{volume of water sample} \\ &= [10 * 1/50 * 50 * 1000] / 100 \\ &= 100 \text{ ppm} \end{aligned}$$

$$\begin{aligned} \text{HCO}_3^- \text{ alkalinity} &= [(\text{volume of acid used by } \text{HCO}_3^-) \text{ or } (V_2 - V_1) * N(\text{acid}) * 50 * 1000] / \text{volume of water sample} \\ &= [7 * 1/50 * 50 * 1000] / 100 \\ &= 70 \text{ ppm} \end{aligned}$$

CASE: 5

For both OH^- and CO_3^{2-}

When V_1 is the volume of acid required for complete neutralization of OH^- & half neutralization of CO_3^{2-} , and V_2 is the volume of acid required to further neutralize the product of CO_3^{2-} i.e. HCO_3^- will be equal to the volume of acid require by half neutralization of CO_3^{2-} .



$$\text{Volume of } \text{CO}_3^{2-} = 2V_2 \text{ ml}$$

$$\text{Volume of OH}^- = V_1 - V_2 \text{ ml}$$

$$\text{OH}^- \text{ Alkalinity} = [(\text{volume of acid used by OH}^-) \text{ or } (V_1 - V_2) * N(\text{acid}) * 50 * 1000] / \text{volume of water sample}$$

$$\text{CO}_3^{2-} \text{ alkalinity} = [(\text{volume of acid used by CO}_3^{2-}) \text{ or } (2V_2) * N(\text{acid}) * 50 * 1000] / \text{volume of water sample.}$$

Let us consider this case through an example in which titration of 100 ml of water sample with 20ml of N/50 sulphuric acid was required up till phenolphthalein end point. After this on adding a few drops of methyl orange to the same solution and further acid required was 15ml. The type and extent of the alkalinity present in given the water sample can be calculated as follows.

$$\text{Volume of CO}_3^{2-} = 2V_2 \text{ ml} = 30\text{ml}$$

$$\text{Volume of OH}^- = V_1 - V_2 \text{ ml} = (20 - 15)\text{ml} = 5\text{ml}$$

$$\text{OH}^- \text{ alkalinity} = [(\text{volume of acid used by OH}^-) \text{ or } (V_1 - V_2) * N(\text{acid}) * 50 * 1000] / \text{volume of water sample}$$

$$= [5 * 1/50 * 50 * 1000] / 100$$

$$= 50 \text{ ppm}$$

$$\text{CO}_3^{2-} \text{ alkalinity} = [(\text{volume of acid used by CO}_3^{2-}) \text{ or } (2V_2) * N(\text{acid}) * 50 * 1000] / \text{volume of water sample}$$

$$= [30 * 1/50 * 50 * 1000] / 100$$

$$= 300 \text{ ppm}$$

Conclusion

On the basis of above observation it could be concluded that the type and extent of alkalinity in water sample could be determined by titrating an aliquot of the water sample with standard acid to phenolphthalein end point [P], and continuing the titration to methyl orange end point [M].

Determination of alkalinity is important as alkaline water may result in caustic embrittlement, it may also cause deposition of scale and sludge in boiler tubes and pipes due to which efficiency of boiler decreases.

The limitations of the traditional method (which utilizes the formulas for calculating the different possible combination of ions) and comparison of it with the direct methods of calculating ions in water has been reported in this paper. For the last two conditions having two ions (OH^- , CO_3^{2-}) & (CO_3^{2-} , HCO_3^-) a range is established which further helps in identification of these combination. Thus for OH^- & CO_3^{2-} combination (when separate water sample is taken for P & M end point) the minimum difference in the volume of acid consumed numerically is 1, while the maximum difference is less than or equal to (\leq) half of the volume of acid used till phenolphthalein end point. While for single water sample titration the volume of acid used till P end point is greater than the volume of acid till M.O. end point.

However for CO_3^{2-} and HCO_3^- combination, volume of acid used till M end point will be greater than twice the volume used till P end point, for separate titration while for single titration the volume of acid used till M end point will be greater than that used till P end point.

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