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Research Article

ESTIMATION OF CARBONATE – BICARBONATE ALKALINITY IN WATER BY VOLUMETRIC AND ELECTRO ANALYTICAL METHODS – A COMPARATIVE STUDY

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Abstract

Alkalinity can be defined as the ability of water to neutralize acid or to absorb hydrogen ions. It is the sum of all acid neutralizing bases in the water. In municipal and industrial wastewater there are many factors which contribute to alkalinity like, the type of dissolved inorganic and organic compounds, the amount of suspended organic matter and also, the bicarbonate to dissolved CO₂ ratio. The bacteria and other biological entities which play an active role in wastewater treatment are most effective at a neutral to slightly alkaline pH of 7 to 8. In order to maintain these optimal pH conditions for biological activity there must be sufficient alkalinity present in the waste water to neutralize acids generated by the active biomass during waste treatment. This ability to maintain the proper pH in the wastewater as it undergoes treatment is the reason why alkalinity is so important to the wastewater industry. In our present work a comparative study was made to estimate the carbonate, bicarbonate alkalinity in water using volumetric and electro analytical techniques. An attempt was made to know the suitable and more accurate technique for the above analysis.

Keywords: Alkalinity, volumetric analysis, electro analytical techniques

Introduction

Alkali, when dissolved in water, creates a bitter taste and a slippery feel. Highly alkaline waters, above pH 7.0, can cause drying of the skin [1,2]. Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes and makes water less vulnerable to acid rain, protecting a major source of human consumption [3,4]. Alkalinity contributes to corrosiveness and influence chemical reaction rates, chemical speciation and biological processes [5]. Alkalinity not only helps regulate the pH of a water body, but also the metal content. Bicarbonate and carbonate ions in water can remove toxic metals (such as lead, arsenic, and cadmium) by precipitating the metals out of solution. Alkalinity varies greatly due to

differences in geology and so there are no general standards for alkalinity [6]. Levels of 20-200 mg/L are typical of fresh water. A total alkalinity level of 100-200 mg/L will stabilize the pH level in a stream. Levels below 10 mg/L indicate that the system is poorly buffered, and is very susceptible to changes in pH from natural and human-caused sources. Above pH 8.3, alkalinity is mostly in the form of carbonate (CO₃²⁻); below 8.3, alkalinity is present mostly as bicarbonate (HCO₃⁻) [4,6].

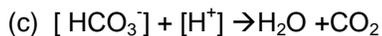
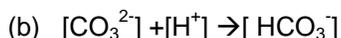
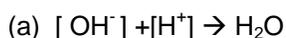
Materials and Methods

The alkalinity of water can be determined by titrating the water sample with Standard acid solution (HCl).

(i)

Stoichiometry of the reaction and number of moles of acid needed to reach the end point, the concentration of alkalinity in water is calculated by volumetric and electroanalytical methods. Alkalinity of water is attributed to the presence of OH^- , CO_3^{2-} and HCO_3^- ions [7].

The titration may be performed by various electroanalytical methods or 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 whilst hydroxide, carbonate and bicarbonate are the alkalinity causing ions present in water.

As shown in Table-1 (6)

P (Phenolphthalein alkalinity) = 0 that means the volume of acid used till the completion of reaction (a) and (b) is 0. This can only happen when both OH^- and CO_3^{2-} ions are not present in water. Alkalinity is present due to HCO_3^- ion only which can be determined using methyl orange indicator and called methyl orange alkalinity (M).

$P = \frac{1}{2} M$; indicates that only CO_3^{2-} ions are present. Using phenolphthalein indicator neutralization reaches up to HCO_3^- but using methyl orange indicator the complete neutralization of HCO_3^- takes place.

$P > \frac{1}{2} M$; implies OH^- ions are also present along with CO_3^{2-} ions. Up to phenolphthalein alkalinity, OH^- ions will be neutralized completely whereas CO_3^{2-} will be neutralized up to HCO_3^- ion. But using methyl orange indicator, HCO_3^- will be completely neutralized along with OH^- and CO_3^{2-} .

$P < \frac{1}{2} M$; indicates that beside CO_3^{2-} ions HCO_3^- ions are also present. The volume of acid required for the neutralization up to phenolphthalein end point corresponds half neutralization of CO_3^{2-} (equation b). Neutralization using methyl orange indicator corresponds to HCO_3^- obtained from CO_3^{2-} and HCO_3^- originally present in the water sample.

$P = M$; indicates only OH^- ions are present. (as shown in Table-1)

The possible combination of ions causing alkalinity are (1) OH^- only or (2) CO_3^{2-} only or (3) HCO_3^- only or (4) OH^- and CO_3^{2-} together or (5) CO_3^{2-} and HCO_3^- together. The possibility of OH^- and HCO_3^- ions together is ruled out because they combine instantaneously to form CO_3^{2-} ions.



Thus OH^- and HCO_3^- ions cannot exist together in water and hence can be concluded that all the three OH^- , HCO_3^- , CO_3^{2-} ions cannot exist together [7,8].

Standard HCl solution of concentration 0.02N and standard alkaline water containing known amounts (0.3gm/lit carbonate and 0.06gm/lit bicarbonate) of CO_3^{2-} and HCO_3^- were prepared.

Volumetric analysis

20ml of the above prepared alkaline water was taken in a clean conical flask and two drops of phenolphthalein indicator was added and titrated against standard HCl until pink colour disappeared. The titre value was taken as 'P' end point then 2 to 3 drops of methyl orange indicator was added and titrated until red colour was obtained. The titre value was taken as 'M' end point. The results are shown in Table-2 and calculations were done based on 'P' and 'M' values.

Instrumental analysis

Potentiometry

Phenomenon underlying the method was electrode potential differences of the cell and EMF was measured. The electrodes used were saturated calomel electrode and quinhydrone electrodes. Standard alkaline water was titrated against standard HCl taken in a burette. EMF values were noted and a graph of E/V versus volume of HCl (Figure-1) was plotted and equivalence point was noted from the graphical plot.

pH metry

The standard alkaline water was titrated against standard HCl. pH values were noted using combined glass-calomel electrode, which indicated the presence of alkalinity causing ions. A graph of pH/V Vs. Volume of HCl (Figure-2) was plotted and equivalence point was noted.

Table-1: alkalinity of water

S.No	Alkalinity	OH ⁻ (ppm)	CO ₃ ²⁻ (ppm)	HCO ₃ ⁻ (ppm)
i	P=0	0	0	M
ii	P = ½ M	0	2P	0
iii	P > ½ M	(2P-M)	2(M-P)	0
iv	P < ½ M	0	2P	(M-2P)
v	P = M	P = M	0	0

Table-2 Estimation of carbonate and bicarbonate alkalinity volumetrically

S.No	Volume of Alkaline water (ml)	Volume of 0.02N HCl run down through burette (ml)			
		Phenolphthalein end point [P]	2[P]	Methyl orange end point [M]	M-2[P]
1	20	5.1	10.2	11.2	01

Table -3 Potentiometry

S.No	Volume of HCl	E/ V
1	0	-
2	1	0.14
3	2	0.20
4	3	0.27
5	4	1.00
6	5	0.01
7	6	0.19
8	7	0.20
9	8	0.22
10	9	0.35
11	10	1.12
12	11	0.25
13	12	0.11
14	13	0.07
15	14	0.06
16	15	0.04

Table 4 potentiometry

S.No	Volume of Alkaline water (ml)	Volume of 0.02N HCl run down through burette (ml)			
		Phenolphthalein end point [P]	2[P]	Methyl orange end point [M]	M-2[P]
1	20	5.0	10.0	11.0	01

Figure-1 Graph of $\Delta E / \Delta V$ Vs. volume of HCl

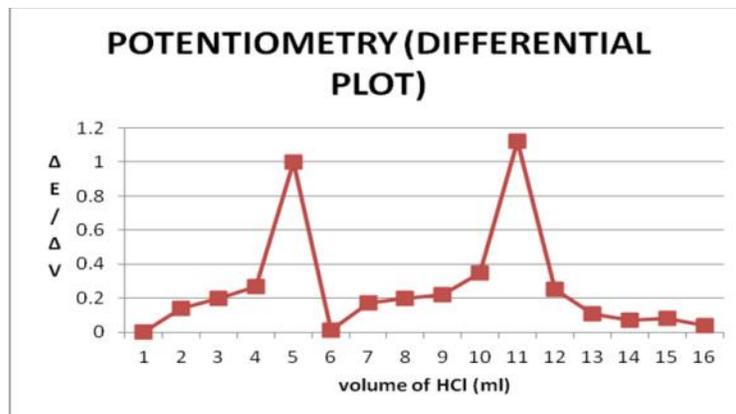


Table – 5 pH Metry

S.No	Volume of HCl	pH/ V
1	0	-
2	1	0.22
3	2	0.30
4	3	0.36
5	4	1.55
6	5	0.54
7	6	0.26
8	7	0.17
9	8	0.33
10	9	0.48
11	10	1.73
12	11	0.37
13	12	0.18
14	13	0.11
15	14	0.08
16	15	0.07

Figure-2. Graph of $\Delta pH / \Delta V$ Vs. volume of HCl

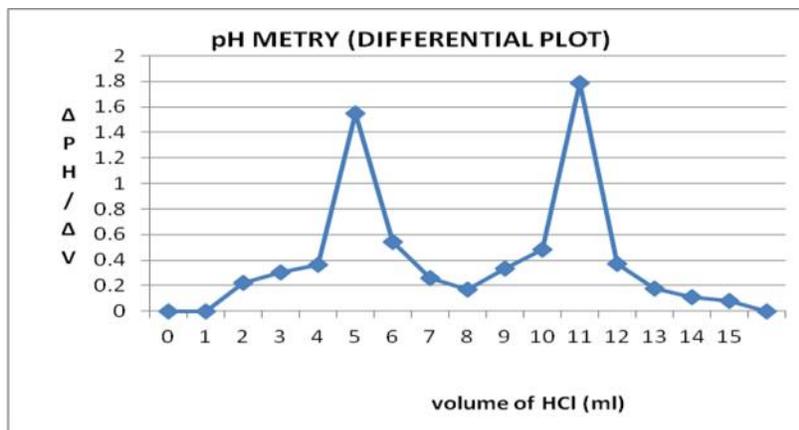


Table-6 pH Metry

S.No	Volume of Alkaline water (ml)	Volume of 0.02N HCl run down through burette (ml)			
		Phenolphthalein end point [P]	2[P]	Methyl orange end point [M]	M-2[P]
1	20	5.0	10.0	11.0	01

Conductometry

A conductivity cell, of cell constant one was dipped in the standard alkaline water and conductance values were noted while standard acid was added at 1 ml intervals.

Results and Discussion

Units of mg/L (ppm) are a “mass dissolved in a liquid.” Reporting alkalinity as “mg/L as CaCO₃” specifies that the sample has an alkalinity equal to that of a solution with a certain amount of calcium carbonate (CaCO₃) dissolved in water. The alkalinity test does not actually measure a mass per volume.

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). 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.

In volumetric analysis, the amount of acid used after phenolphthalein end point (P) corresponds to one half of carbonates, hence complete neutralization of carbonates is taken as 2P. As P is less than half of M end point (Table-1) alkalinity due to bicarbonates is taken as M-2P and the calculations were done accordingly (8). The data is tabulated in Table-2

Calculations:

CO₃²⁻ :

$$\begin{aligned} \text{Normality of CO}_3^{2-} &= \frac{\text{Normality of HCl} \times \text{Volume of HCl}}{\text{Volume of CO}_3^{2-}} \\ &= \frac{0.02 \times 10.2}{20} = 0.0102 \end{aligned}$$

$$\begin{aligned} \text{Weight of CO}_3^{2-} &= \frac{\text{Normality of CO}_3^{2-} \times \text{Equivalent weight} \times 1000 \text{ g/l}}{1000} \end{aligned}$$

$$= 0.306 \text{ gm/lit.}$$

$$\text{Weight of CaCO}_3 \text{ equivalent} = 510 \text{ ppm (mg/lit)}$$

HCO₃⁻

$$\text{Normality of HCO}_3^- = \frac{\text{Normality of HCl} \times \text{Volume of HCl}}{\text{Volume of HCO}_3^-}$$

$$\begin{aligned} &= \frac{0.02 \times 1.0}{20} = 0.001 \\ &= \frac{\text{Normality of HCO}_3^- \times \text{Equivalent weight} \times 1000 \text{ g/l}}{1000} \\ &= 0.061 \text{ gm/lit.} \end{aligned}$$

$$\text{Weight of CaCO}_3 \text{ equivalent} = 51 \text{ ppm (mg/lit)}$$

Instrumental Analysis

Graphs of E/ V Vs. Volume of HCl in potentiometry (Figure-1), Graphs of PH/ V Vs. Volume of HCl in PH metry (Figure-2), Conductance Vs volume of HCl in conductometry were plotted. In Conductometry with 0.02N HCl and prepared alkaline water it was observed that there was no change in conductance values even after addition of 15ml of standard acid and the conductance values thereafter were erratic. The data is shown in Tables 3 and 4 for potentiometry and Tables 5 and 6 for pH metry.

Calculations

CO₃²⁻ :

$$\begin{aligned} \text{Normality of CO}_3^{2-} &= \frac{\text{Normality of HCl} \times \text{Volume of HCl}}{\text{Volume of CO}_3^{2-}} \\ &= \frac{0.02 \times 10.0}{20} = 0.01 \end{aligned}$$

$$\begin{aligned} \text{Weight of CO}_3^{2-} &= \frac{\text{Normality of CO}_3^{2-} \times \text{Equivalent weight} \times 1000 \text{ g/l}}{1000} \\ &= 0.3 \text{ gm/lit} \end{aligned}$$

$$\text{Weight of CaCO}_3 = 500 \text{ ppm (mg/lit)}$$

HCO₃⁻

$$\text{Normality of HCO}_3^- = \frac{\text{Normality of HCl} \times \text{Volume of HCl}}{\text{Volume of HCO}_3^-}$$

$$= \frac{0.02 \times 1.0}{20} = 0.001$$

Weight of HCO₃⁻

$$= \frac{\text{Normality of HCO}_3^- \times \text{Equivalent weight} \times 1000 \text{ g/l}}{1000}$$

$$= 0.061 \text{ gm/lit}$$

$$\text{Weight of CaCO}_3 \text{ equivalentants} = 50 \text{ ppm (mg/lit)}$$

Calculations**CO₃²⁻ :**

$$\text{Normality of CO}_3^{2-} = \frac{\text{Normality of HCl} \times \text{Volume of HCl}}{\text{Volume of CO}_3^{2-}}$$

$$= \frac{0.02 \times 10.0}{20} = 0.01$$

Weight of CO₃²⁻

$$= \frac{\text{Normality of CO}_3^{2-} \times \text{Equivalent weight} \times 1000 \text{ g/l}}{1000}$$

$$= 0.3 \text{ gm/lit}$$

$$\text{Weight of CaCO}_3 \text{ equivalentants} = 500 \text{ ppm (mg/lit)}$$

HCO₃⁻Normality of HCO₃⁻

$$= \frac{\text{Normality of HCl} \times \text{Volume of HCl}}{\text{Volume of HCO}_3^-}$$

$$\frac{0.02 \times 1.0}{20} = 0.001$$

Weight of HCO₃⁻

$$= \frac{\text{Normality of HCO}_3^- \times \text{Equivalent weight} \times 1000 \text{ g/l}}{1000}$$

$$= 0.061 \text{ gm/lit}$$

$$\text{Weight of CaCO}_3 \text{ equivalentants} = 50 \text{ ppm (mg/lit)}$$

Conclusions

The results obtained for volumetric, potentiometric and pH metric analyses were found to be almost the same whilst those of conductometric analysis were erratic. Hence the analyses by potentiometric and pH metric titrations were considered in our present study and the results were found to be more accurate than volumetric analysis.

Potentiometric and pH metric titrations are based on standard electrode potential change and pH change observed through potentiometer and pH meter, respectively, whilst direct titrations are based on

physical observation on color change. The detection of the endpoint can be noted significantly by a drastic change in potential (in potentiometry) and pH values (in pH metry). So both precision and accuracy could be achieved. But in the case of direct titration using an indicator, change in the color is the criteria and the observation of color change can vary from one person to other and so both precision as well as accuracy cannot be achieved. For instance using methyl orange indicator, the color change observation may significantly vary from person to person. Electroanalytical analyses eliminate any indicator blank error and pinpoint accuracy over volumetric titration was obtained (9,10).

Hence it could be concluded that electroanalytical techniques are better methods for analysing alkalinity of water.

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BIOGRAPHIES

Dr. Shanthi Vunguturi was awarded M.Phil in the year 2008, PhD in the year 2013 by Osmania University, India, she has teaching and research experience of 10 years and published 8 research papers in national and international journals, her area of research is drug designing, chemoinformatics and bioassay studies.

Dr. P. Shobharani has completed her MSc. (with four gold medals – 1990), PhD (CSIR - 1995), Post Doctoral Research (CSIR - 2000), CSIR Research scientist, Pool Officer (2004) from Osmania University, India. She was a C.S.I.R fellow for a period of 14 years and has more than 18 years of research and teaching experience with 17 research papers published in national and international journals. Area of research is physico-organic chemistry.

Prof. Y. Arun Kumar was awarded PhD by Osmania University, India. He has about 35 years of teaching and research experience with more than 15 research papers in national and international journals, his area of research is physical chemistry.