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A Comparative Study on Estimation of Alkalinity in Water Using Natural Indicators - by Volumetric and Electro Analytical Methods

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Abstract: Alkalinity in water is a measure of ability of water to neutralize acids .Alkalinity in water causes nutritional imbalance to human health. Highly alkaline water may lead to caustic embrittlement . Bicarbonates of calcium and magnesium induce temporary hardness in water and hence it is essential to have an idea about the nature and extent of alkalinity present in water.

In the present study alkalinity of water was estimated volumetrically (using natural indicators) and also by electro analytical methods (potentiometry and pH metry) . An aliquot of the sample water was titrated using standard HCl.

An attempt was made to estimate the alkalinity of water using simple , easily available , homemade indicators and the results thus obtained were compared by conducting the studies pH metrically and potentiometrically. The results were reproducible and were found to be comparable and accurate.

Keywords: *Alkalinity , Natural Indicators , Potentiometry ,pH metry.*

I. INTRODUCTION

Alkalinity in water is a measure of buffering capacity of water. It is primarily due to the presence of hydroxide , bicarbonate, and carbonate ions (1). Salts of weak acids, such as borates, silicates and phosphates, may also make water alkaline.

The sources for natural alkalinity in water are rocks which contain carbonate, bicarbonate ,hydroxide compounds ,Borates, silicates, and phosphates through which it passes. Water flowing through lime stone regions will have high carbonate alkalinity Areas rich in granites , conglomerates and sandstones may have low alkalinity .(2-4)

Alkalinity is related to hardness in water because hardness is mostly due to metal carbonates and bicarbonates present in water. If $CaCO_3$ actually accounts for most of the alkalinity, hardness in $CaCO_3$ is equal to alkalinity (5).

Higher alkalinity levels or loss in buffering capacity in surface waters are harmful to aquatic life due to drop in pH levels. For the protection of aquatic life, alkalinity should be at least 20 mg/L. Alkalinity varies greatly due to differences in geology therefore there are no general standards for alkalinity .

Alkalinity 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 (CO_3^{2-}); below 8.3, alkalinity is present mostly as bicarbonate (HCO_3^-)[4].

II. METHODOLOGY

A. Materials

Natural indicators were extracted by purchasing fresh red cabbage , red radish and cherries from a local market , Banjara Hills , Hyderabad, Telangana ,India .15 ml of 50 % - 60 % ethyl alcohol was added to finely chopped cabbage, red radish , cherries and macerated. After 20 minutes macerated mixture was filtered using muslin cloth.

B. Instrumentation

Potentiometer, pH meter and conductivity meters were used for measuring difference in electrode potentials, pH and conductance values.

C. Determination of Alkalinity

The alkalinity in water can be determined by titrating the water sample with Standard HCl solution .The titration may be performed by various electro analytical 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 ie.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.(6)

1. $[OH^-] + [H^+] \square \square H_2O$
2. $[CO_3^{2-}] + [H^+] \square [HCO^{3-}]$
3. $[HCO^{3-}] + [H^+] \square H_2O + CO_2$

[H+] corresponds to standard HCl

D. Volumetric Analysis

20ml of the alkaline water (0.3gm/lit carbonate and 0.06gm/lit bicarbonate) was taken in a clean conical flask and two drops of phenolphthalein indicator was added and titrated against standard HCl (0.02N) until pink colour disappeared. Extracts of cabbage or red radish were added as indicators in place of phenolphthalein for comparative study . Colour change observed was from violet to red for red cabbage indicator and from pink to orange for red radish indicator. 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 , extracts of cherries was added as indicator in place of methyl orange for bicarbonate alkalinity. colour change observed was from orange to red .The titre value was taken as 'M'end point.(7)

The results are shown in Table-2 and calculations were done based on 'P' and 'M' values.

E. Instrumental Analysis

1. Potentiometry

Electrode potential differences of the cell were measured using potentiometer.The electrodes used were saturated calomel electrode and quinhydrone electrodes. Alkaline water (0.3gm/lit carbonate and 0.06gm/lit bicarbonate) was titrated against standard HCl taken in a burette .A differential graph was plotted

(ΔE/ΔV verses volume of HCl) (Figure-1) was plotted and equivalence point was noted from the graphical plot.

2. pH metry

pH values were noted using pH meter by titrating alkaline water as mentioned above against standard HCl using combined glass-calomel electrode . A differential graph was plotted (ΔpH/ΔV verses volume of HCl) (Figure-2) was plotted and equivalence point was noted from the graphical plot.

3. Conductometry

Conductance values were noted using conductivity meter by titrating standard alkaline water against standard HCl.

Table-1: Alkalinity of water (ppm)

Sno	Alkalinity	CO_3^{2-}	HCO^{3-}	OH^-
1	P=0	0	M	0
2	P=1/2M	2P	0	0
3	P>1/2	2(M-P)	0	(2P-M)
4	P<1/2M	2P	M -2P	0
5	P = M	0	0	P=M

Table 2**:** Estimation of carbonate and bicarbonate alkalinity volumetrically (Using phenolphthalein and methyl orange indicators or natural indicators)

SNo	Indicator	Carbonate End point (ml) (2P)	Bicarbonate End point (ml) (M-2P)
1	Phenolphthalein	11.0	--------
2	Methyl orange	--------	2.5
3	Red Cabbage	11.0	-------
4	Red Radish	11.0	--------
5	Cherries	---------	2.5

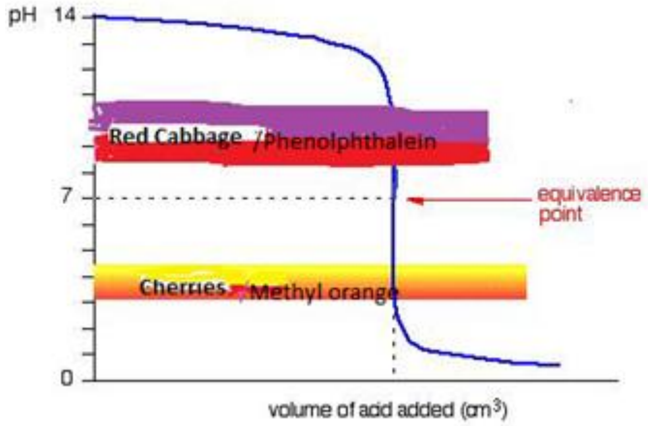

Figure 1: Plots showing the colour changes at different pH ranges for red cabbage / phenolphthalein and cherries / Methyl orange as indicators

Table -3: Potentiometry

S.N0	Volume of HCl (ml)	ΔE/ΔV
1	1	0.16
2	2	0.22
3	3	0.31
4	4	1.02
5	5	0.08
6	6	0.20
7	7	0.22
8	8	0.32
9	9	0.38
10	10	1.15

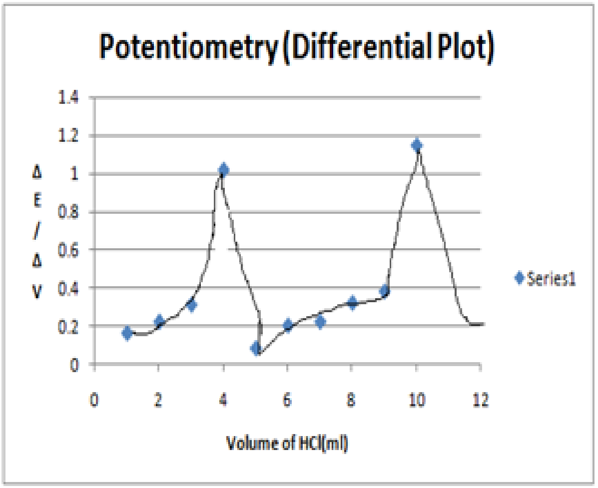

Figure 2: Graph of ΔE/ΔV Vs. volume of HCl

Table 4: Potentiometry

S.No	Volume of Alkaline water (ml)	Volume of 0.02N HCl run down through burette (ml)	
		Carbonates end point (2P)	Bicarbonates end point (M-2P)
1	20	8	2

Table: 5 pH metry

S.N0	Volume of HCl(ml)	ΔpH/ΔV
1	1	0.23
2	2	0.31
3	3	0.37
4	4	1.54
5	5	0.55
6	6	0.25
7	7	0.15
8	8	0.33
9	9	0.46
10	10	1.72
11	11	0.35
12	12	0.17

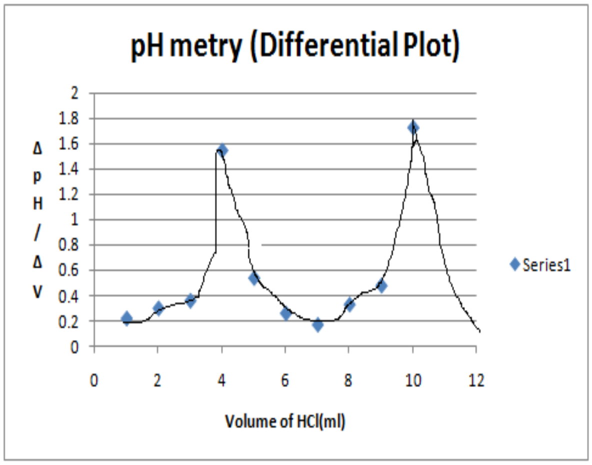

Figure 3: Graph of ΔpH /ΔV Vs. volume of HCl

Table – 6 pH metry

S.No	Volume of Alkaline water (ml)	Volume of 0.02N HCl run down through burette (ml)	
		Carbonates end point (2P)	Bicarbonates end point (M-2P)
1	20	8	2

III. RESULTS AND DISCUSSIONS

In volumetric analysis , the amount of acid used after phenolphthalein end point / red cabbage / red radish (P) corresponds to one half of carbonates , hence complete neutralization of carbonates is taken as 2P. M is considered as methyl orange /cherries end point .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. Alkalinity was expressed in parts per million of equivalent calcium carbonate (ppm $CaCO_3$). Figure shows the colour changes at different pH ranges for phenolphthalein / red cabbage /red radish and methyl orange/ cherries as indicators.(9)

A. Calculations- volumetric Analysis:

$CO_3{}^{2-}$:

Normality of CO_3^{2-}= Normality of HCl x Volume of HCl
Volume of CO_3^{2-}

= 0.02 x 11.0 = 0.011
20

Weight of CO_3^{2-} =
Normality of CO_3^{2-} x Equivalent weight x 1000 g/l
1000
= 0.33 gm/lit.

Weight of $CaCO_3$ equivalants = 550 ppm (mg/lit)

HCO_3^{2-}

Normality of $HCO_3{}^-$ = Normality of HCl x Volume of HCl
Volume of HCO_3^-

= 0.02 x 2.5 = 0.0025
20

Weight of HCO_3^- =
Normality of HCO_3^- x Equivalent weight x 1000 g/l
1000
= 0.0775gm/lit.

Weight of $CaCO_3$ equivalents = 65ppm(mg/lit)

B. Instrumental Analysis

Graphs of ΔE/ΔV Vs. Volume of HCl in potentiometry (Figure-2) , Graphs of ΔPH/ΔV Vs. Volume of HCl in PH metry (Figure-3) were plotted. For Conductance values conductometry was used , 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.

1 Calculations of Potentiometry and pH metry

$CO3^{2-}$:

Normality of $CO3^{\ 2-}$ = Normality of HCl x Volume of HCl
VolumeofCO3^{2-}

= 0.02 x 8.0 = 0.008
20

Weight of $CO3^{2-}$ =
Normality of $CO3^{2-}$ x Equivalent weight x 1000 g/l
1000
= 0.24gm/lit

Weight of CaCO3 = 400ppm (mg/lit)

$HCO3^-$

Normality of $HCO3^-$ = Normality of HCl x Volume of HCl
Volume of $HCO3^-$

= 0.02 x 2.5= 0.0025
20

Weight of $HCO3^-$ =
Normality of $HCO3^-$ x Equivalent weight x 1000 g/l
1000

= 0.0775gm/lit

Weight of CaCo3equivalants = 64ppm(mg/lit)

CONCLUSIONS

The results obtained for volumetric analysis using extracts of natural indicators in place of the conventionally used phenopthalein and methyl orange indicators and those obtained from potentiometric , pH metric analyses were comparable whilst those of conductometric analysis were erratic.

Anthocyanins, belonging to the group of flavonoids,are responsible for the orange, red colors in cherries ,red cabbage and red radish at different pH ranges. Anthocyanins can be used as pH indicators because their color changes with pH .(10)

Alkalinity in water induces hardness in water which if untreated causes scale formation ,caustic embrittlement in boilers(11) .Alkalinity in water may even cause nutritional or pH imbalance in humans(12).Therefore it is essential to have an idea about nature and extent of alkalinity present in water .

An attempt was made to determine the alkalinity of water using various methods. Estimation of alkalinity using natural indicators was found to be simple, easily available (homemade) and reproducible..The results were found to be more accurate showing a sharp colour change at the end points .

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