Original Research Article

Study of estimation of hardness of water using pH −meter

Abstract

The hardness of water is one of the important parameters of water quality. The complexometric titration method is a prevalent technique to estimate concentrations of Ca^{2+} and Mg^{2+} ions individually, which are primarily responsible for the hardness of water. However, the method needs two external indicators to mark the end points of titrations. Furthermore, accuracy of the method is sacrificed due to inevitable parallax errors during marking of the endpoint of titration.

This present work reports that during titration of a hard water sample with a complexing agent (here, Na_2EDTA solution), pH changes continuously. This change in pH is closely monitored and recorded graphically. Hence the endpoint of titration is determined. The neutralization volume, thus obtained, is used to estimate $Ca-$ and $Mg-$ hardness of the water sample separately. This novel technique obviates the use of any external indicators and eliminates any possible parallax error.

Key Words

Hardness of water, Complexometric titration, pH −metric titration, Buffer solution, $NaOH$ solution, Disodium EDTA.

Introduction

The hardness of water arises primarily due to the presence of profuse amount of Ca^{2+} and Mg^{2+} ions in the natural water resources. However, extent of hardness depends on the type of land, e.g., water is soft in hilly areas, but the same is sufficiently hard in industrialized areas, commercial areas and coastal area. Melian et al.[1] attempted to estimate the hardness of groundwater and rural drinking water using the volumetric titration method. The latter is a very popular method to determine water hardness and well documented in the literature[2-4]. Diogo Ferreira et al.[5] reported the uncertainty of visual detection of the endpoint of titration during determination of total hardness of water. Another researcher, Sengupta[6] documented the adverse impact of water hardness on health. Ramya et al.[7] studied the estimation of hardness in ground water samples using the volumetric titration method. Divya et al.[8] reported the total hardness of freshwater resources. The volumetric method of determination of calcium and magnesium hardness of coastal water and sub-surface water is well documented in the literature[9-12].

This present work proposes a novel technique, the pH −metric method, to estimate the concentrations of Ca^{2+} and Mg^{2+} ions or in other words, calcium and magnesium hardness of a given water sample.

Materials:

Chemicals and hard water samples

Table 1 Details of chemicals used in this research work

Chemicals	Molecular Weight (gm/mole)	Composition
Fused $CaCl_2$	111	NA
$MgSO_4, 7H_2O$	246	NA
Disodium salt of ethylene diamine tetraacetic acid (Na_2EDTA)	372	NA
Buffer solution (NH_4OH/NH_4Cl)	NA	1:1
Eriochrome Black T (EBT) indicator	461	NA
Murexide indicator	284	NA

NA = Not Applicable

Two different hard water samples are prepared as shown in the Table 2.

Table 2 Composition of hard water samples

Serial No.	Sample Code	$CaCl_2$ (Fused)	$MgSO_4, 7H_2O$	Weight ratio	Distilled water
1	SC-20	225 mg	0	NA	100 ml
2	SCM-20	150 mg	150 mg	1:1	100 ml

The sample SC-20 is responsible for Ca –hardness only, while the sample SCM-20 is responsible for both Ca – and Mg –hardness.

Methods

1. Volumetric titration

(a) 1 $litre$ standard Na_2EDTA solution of strength 0.601 $\left(\frac{M}{10}\right)$ is prepared. 40 ml of it is poured into a burette.

(b) 10 ml of the hard water sample, SC-20, is taken into a conical flask. 1 ml buffer solution with a pinch of EBT indicator is added into the conical flask. The solution turns to a wine-red colour. It is then titrated against Na_2EDTA solution, running from the burette. At the end point wine red colour changes to sky blue. The initial and final burette readings are noted. Triplicate readings are recorded. The total hardness can be calculated using the mean burette reading.

(c) For the hard water sample, SCM-20, the process (b) is followed. Here also triplicate readings are recorded. The total hardness, caused by Ca^{2+} and Mg^{2+} ions can be calculated using the mean burette reading.

(d) 10 ml of the hard water sample, SCM-20, is taken in a conical flask. Add 1 ml 1(N) $NaOH$ solution. The function of $NaOH$ is to block Mg^{2+} to avoid the formation of any Mg –complex during the titration process. A pinch of Murexide indicator is added. The solution turns to pink colour due to the formation of $[Ca-Murexide]$. It is then titrated against Na_2EDTA solution, running from the burette, till the pink colour changes to purple. The initial and final burette readings are noted. Triplicate readings are recorded. Ca –hardness can be calculated using the mean burette reading.

(e) Using the results of the processes (c) and (d) Mg –hardness can be calculated by subtracting Ca –hardness from the total hardness.

2. pH –metric titration

(a) 20 ml of prepared Na_2EDTA solution is poured into another burette.

(b) 10 ml of the hard water sample, SC-20, is taken into a 250 ml beaker. 90 ml distilled water is added into it in order to immerse the electrodes safely into the solution. 1 ml buffer solution is added into the beaker. The mixture is shaken and the pH electrode-set is immersed into it. The 1st reading is taken. The beaker is taken out and 0.5 ml Na_2EDTA solution is added to it from the burette. The mixture is shaken and pH electrode-set is again immersed into it. The 2nd reading is taken. The process is continued till the pH reads around 10.

(c) The pH readings are plotted against the volume of Na_2EDTA solution added.

(d) The step (b) is repeated for the other hard water sample, SCM-20. In this case, also, pH readings are plotted against volume of Na_2EDTA solution.

(e) In case of SCM-20 hard water sample, the step (b) is repeated once more using 1 ml $1(N)$ $NaOH$ solution instead of 1 ml buffer solution. The pH readings are plotted against volume of Na_2EDTA solution added.

Results and Discussion

1. Sample SC-20

This sample contains only Ca^{2+} ions. The results of volumetric titration of the sample are shown in the Table 3.

Table 3 Volumetric titration for the hard water sample SC-20

No. of observations	Volume of SC-20 sample hard water taken (ml)	Volume of Na_2EDTA consumed (ml)			
		Initial	Final	Difference	Mean volume
1	10	0	1.8	1.8	1.8
2	10	1.8	3.7	1.9	
3	10	3.7	5.5	1.8	

The mean volume $(1.8\,ml)$ represents the volume of Na_2EDTA required to absorb all Ca^{2+} ions from the aliquotted sample solution (10 ml) to form stable $[Ca - EDTA]$ complex.

The results of pH –metric titration of the sample SC-20 are shown in the Table 4.

Table 4 pH –metric titration for the hard water sample SC-20

No. of observations	Volume of Na_2EDTA solution added (ml)	Total volume of Na_2EDTA solution added (ml)	pH reading
1	0	0	10.54
2	0.5	0.5	10.39
3	0.5	1	10.21
4	0.5	1.5	10.04
5	0.5	2	9.88
6	0.5	2.5	9.77
7	0.5	3	9.69
8	0.5	3.5	9.59
9	0.5	4	9.5
10	0.5	4.5	9.37
11	0.5	5	9.3
12	0.5	5.5	9.2

pH –readings are plotted against volume of Na_2EDTA solution added. It is shown in the Fig.1.

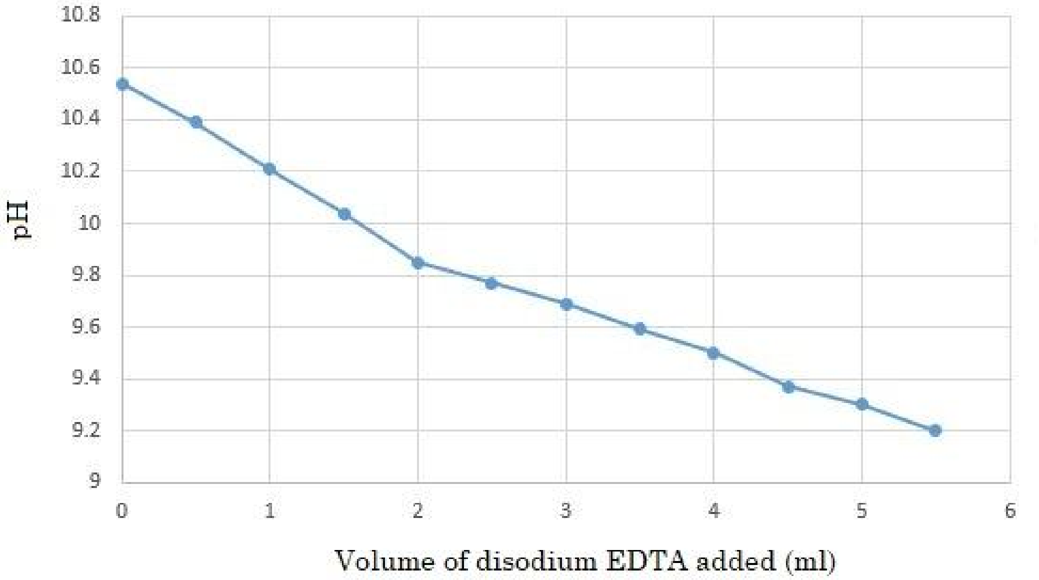

Figure 1 SC-20 sample: plot of pH –readings versus volume of titrant added.

Two straight lines with different slopes are quite distinguished from the Fig.1. These two straight lines are drawn separately in the Fig.2.

EDTA has four acidic H-atoms. So, it is best represented by H_4EDTA. In aqueous solution disodium salt of EDTA or Na_2H_2EDTA dissociates to form $[H_2EDTA]^{2-}$. The latter reversibly dissociates to produce $[EDTA]^{4-}$, which forms complexes with metal cations. In case of SC-20 hard water sample, only one type of complex, i.e., $[Ca-EDTA]$ is formed. The reactions are given below

$$[H_2EDTA]^{2-} \rightleftharpoons 2H^+ + [EDTA]^{4-} \quad \cdots\cdots (1)$$

$$[EDTA]^{4-} + Ca^{2+} \rightarrow [Ca-EDTA] \quad \cdots\cdots (2)$$

The buffer consumes the H^+ ions, accelerating the formation of $[EDTA]^{4-}$ so that the latter can form stable complex, $[Ca-EDTA]$. As the reaction continues, the concentration of $[OH]^-$ in the buffer decreases, due to which, sharp drop of pH is observed (blue curve in the Fig.2) till the end point is reached. After the end point the 2nd step of the above reaction [Equation(2)] ceases to occur and hence only a slow change in pH is observed due to buffer action (red curve in the Fig.2).

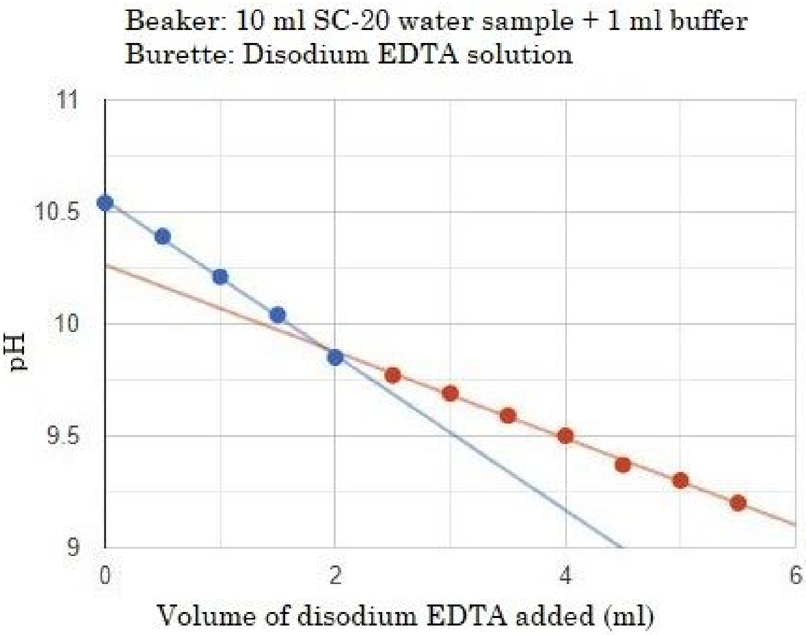

Figure 2 SC-20 sample: Linear plot of pH –readings versus volume of titrant added.

The Intersection of the two straight lines occurs at 1.9 ml, which is assumed to be the endpoint of titration. So, the endpoint, obtained by pH –metric method, is almost same as that obtained by the volumetric method (Table 2).

2. Sample SCM-20

This sample contains both Ca^{2+} and Mg^{2+} ions. Two sets of volumetric titrations are performed to estimate the individual concentrations of Ca^{2+} and Mg^{2+} ions. Two sets of pH –metric titrations are also performed.

Set-1

1. Volumetric titration using 1 ml buffer solution.

Table 5 Volumetric titration for the hard water sample SCM-20

No. of observations	Volume of SCM-20 sample hard water taken (ml)	Volume of Na_2EDTA consumed (ml)			
		Initial	Final	Difference	Mean volume

1	10	0	2.5	2.5	2.4
2	10	2.5	4.8	2.3	
3	10	4.8	7.2	2.4	

The mean volume (2.4 ml) represents the volume of Na_2EDTA required to absorb all Ca^{2+} and Mg^{2+} ions from the aliquotted sample solution (10 ml) to form stable $[Ca-EDTA]$ and $[Mg-EDTA]$ complexes.

2. pH –metric titration using 1 ml buffer solution.

Table 6 **pH-metric titration for the hard water sample SCM-20**

No. of observations	Volume of Na_2EDTA solution added (ml)	Total volume of Na_2EDTA solution added (ml)	pH reading
1	0	0	11.43
2	0.5	0.5	11.28
3	0.5	1	11.17
4	0.5	1.5	11.05
5	0.5	2	10.95
6	0.5	2.5	10.85
7	0.5	3	10.81
8	0.5	3.5	10.76
9	0.5	4	10.7
10	0.5	4.5	10.64
11	0.5	5	10.6
12	0.5	5.5	10.58

The plot of pH –readings versus volume of disodium EDTA gives rise to two straight lines of different slopes as shown in the Fig.3.

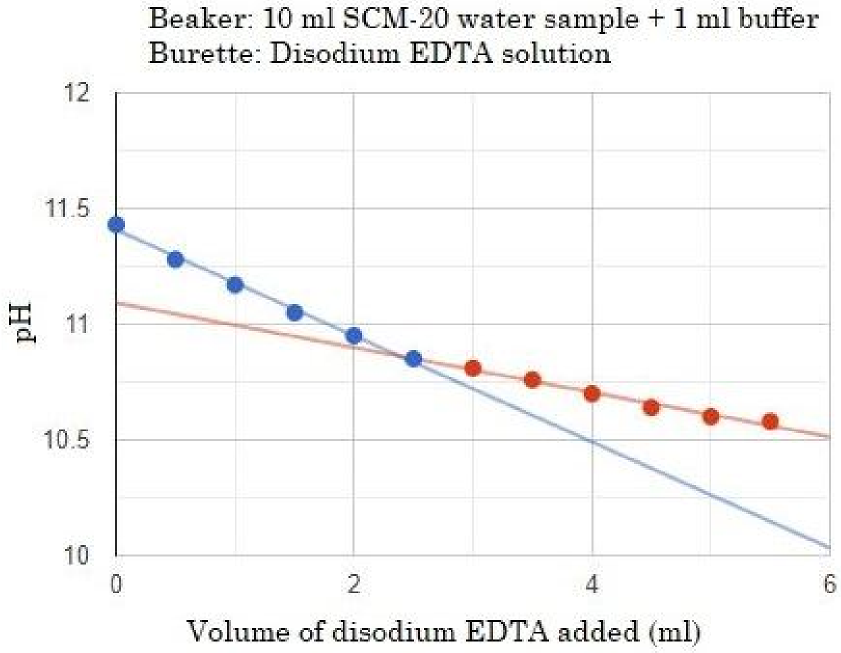

Figure 3 SCM-20 sample in the presence of buffer: Linear plot of pH –readings versus volume of titrant added.

The Intersection of the two straight lines occurs at 2.52 ml, which is believed to be the endpoint of titration. So total hardness due to Ca^{2+} and Mg^{2+} ions can be calculated pH –metrically.

Set-2

1. Volumetric titration is performed using 1 ml $1(N) MaOH$ solution.

Table 7 **Volumetric titration for the hard water sample SCM-20**

No. of observations	Volume of SCM-20 sample hard water taken (ml)	Volume of Na_2EDTA consumed (ml)			
		Initial	Final	Difference	Mean volume
1	10	0	1.6	1.6	1.6
2	10	1.6	3.2	1.6	
3	10	3.2	4.9	1.7	

The mean volume (1.6 ml) represents the volume of Na_2EDTA required to absorb all Ca^{2+} from the aliquotted sample solution (10 ml) to form stable $[Ca - EDTA]$ complexes.

2. pH –metric titration using 1 ml $1(N) NaOH$ solution.

Table 8 pH-metric titration for the hard water sample SCM-20

No. of observations	Volume of Na_2EDTA solution added (ml)	Total volume of Na_2EDTA solution added (ml)	pH reading
1	0	0	12.46
2	0.5	0.5	12.34
3	0.5	1	12.18
4	0.5	1.5	11.99
5	0.5	2	11.78
6	0.5	2.5	11.53
7	0.5	3	11.28
8	0.5	3.5	11.05
9	0.5	4	10.83
10	0.5	4.5	10.55
11	0.5	5	10.22
12	0.5	5.5	9.88

A similar plot of pH –readings versus volume of disodium EDTA is shown in the Fig.4.

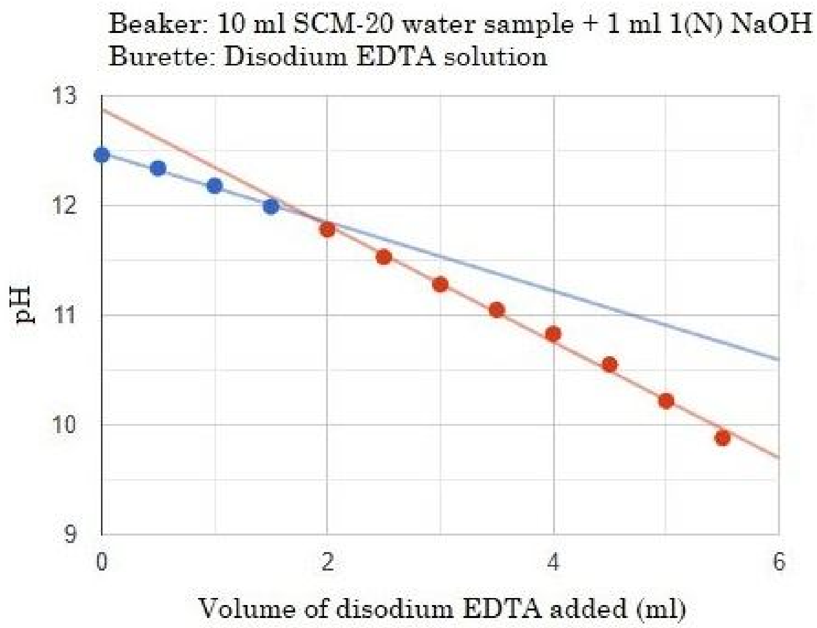

Figure 4 SCM-20 sample in presence of $NaOH$: Linear plot of pH –readings versus volume of titrant added.

The Intersection of the two straight lines occurs at 1.74 ml, which is believed to be the end point of titration. So hardness, due to Ca^{2+} ions only, can also be calculated pH –metrically. Using the results of Fig.3 and Fig.4, hardness due to Mg^{2+} ions can be calculated.

According to Table 1, in the hard water sample SCM-20 ratio of weights of $CaCl_2$ and $MgSO_4.7H_2O$ is $1:1$. So the following relation holds good

$$\frac{Ca - hardness}{Mg - hardness} = \frac{MW\ of\ MgSO_4.7H_2O}{MW\ of\ CaCl_2} = \frac{246}{111} = 2.216$$

If V_{Ca} and V_{Mg} are the volumes (in ml) of Na_2EDTA consumed due to Ca^{2+} ions and Mg^{2+}ions respectively, the following relation also holds good.

$$\frac{Ca - hardness}{Mg - hardness} = \frac{V_{Ca}}{V_{Mg}}.\ So, \quad \frac{V_{Ca}}{V_{Mg}} = 2.216 \text{ (Using theoretical approach)}$$

(a) Considering volumetric titration results of sets 1 and 2 (Table 4 and Table 6), the following equations are true

$$V_{Ca} + V_{Mg} = 2.4\,ml \text{ and } V_{Ca} = 1.6\,ml. \text{ So, } V_{Mg} = 0.8\,ml$$

$$So, \quad \frac{V_{Ca}}{V_{Mg}} = 2 \text{ (Using volumetric titration approach)}$$

(b) Considering pH –metric titration results of sets 1 and 2 (Fig.3 and Fig.4), the above equations become

$$V_{Ca} + V_{Mg} = 2.52\,ml \text{ and } V_{Ca} = 1.74\,ml. \text{ So, } V_{Mg} = 0.78\,ml$$

$$So, \quad \frac{V_{Ca}}{V_{Mg}} = 2.23 \text{ (Using } pH - \text{metric titration approach)}$$

So, the pH –metric titration result is very close to the theoretical value compared to the volumetric titration result. Thus, it is believed that the pH –metric titration method is more accurate than the volumetric titration method.

Conclusions

1. The hardness of a given water sample can be estimated accurately using pH –meter.

2. The pH –metric determination of the hardness of water is more accurate than the volumetric determination of the same as the endpoint of titration in pH –metric method is obtained from the graph without any parallax error.

3. No indicator is required in the pH –metric method of determination of hardness of water, which is considered a distinct advantage over the volumetric method.

4. This novel technique of determining the hardness of water is expected to explore future research works, based on pH –meter.

Disclaimer (Artificial intelligence)

Option 1:

The Author hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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