Original Research Article

Study of estimation of hardness of water using pH −meter

Abstract

Hardness of water is one of the important parameters of water quality. Complexometric titration method is a very common technique to estimate concentrations of Ca^{2+} and Mg^{2+} ions individually, which are primarily responsible for 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 error during marking of end point of titration.

The present work reports that during titration of 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 end point 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 as well as eliminates any possible parallax error.

Key Words

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

Introduction

Hardness of water arises primarily due to the presence of profuse amount of Ca^{2+} and Mg^{2+} in natural water resources. However, extent of hardness depends on type of land, e.g., water is soft in hill area, but the same is sufficiently hard in industrial area, commercial area and coastal area. Melian et al.[1] made an attempt to estimate hardness of groundwater and rural drinking water using volumetric titration method. The latter is 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 end point of titration during determination of total hardness of water. Another researcher, P. Sengupta[6] documented the adverse impact of water hardness on health. Ramya et al.[7] studied estimation of hardness in ground water samples using volumetric titration method. Divya et al.[8] reported total hardness and iron content of freshwater resources. Volumetric method of determination of calcium and magnesium hardness of coastal water and sub-surface water is well documented in the literature[9-10].

The present work deals with 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.

Chemicals and hard water samples

Table 1 Details of chemicals used in this research work

Chemicals	Molecular Weight	Composition
Fused $CaCl_2$	111	Not Applicable (NA)
$MgSO_4, 7H_2O$	246	NA
Na_2EDTA	372	NA
Buffer solution (NH_4OH/NH_4Cl)	NA	1:1
EBT indicator	461	NA
Murexide indicator	284	NA

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.

Experimental 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 hard water sample, SC-20,is taken in a conical flask. 1 ml buffer solution along with a pinch of EBT indicator is added into the conical flask. The solution turns to 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. Initial and final readings are noted. Three such readings are recorded. 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 three readings are recorded. Total hardness, i.e., hardness due to Ca^{2+} and Mg^{2+} can be calculated using the mean burette reading.

(d) 10 ml of 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 formation of any Mg –complex during titration process. Add a pinch of Murexide indicator. The solution turns to pink colour due to formation of $[Ca - Murexide]$. It is then titrated against Na_2EDTA solution, running from the burette, till the pink colour changes to purple. Initial and final readings are noted. Three such 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 hard water sample, SC-20, is taken in a 250 mlbeaker. 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. Shake the mixture and immerse thepH electrode-set into it. Take the 1st reading. The beaker is taken out and 0.5 $mlNa_2EDTA$ solution is added into it from the burette. Shake the mixture and pH electrode-set is again immersed into it. Take the 2ndreading. The process is continued till the pH reads around 10.

(c) The pH readings are plotted against 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.

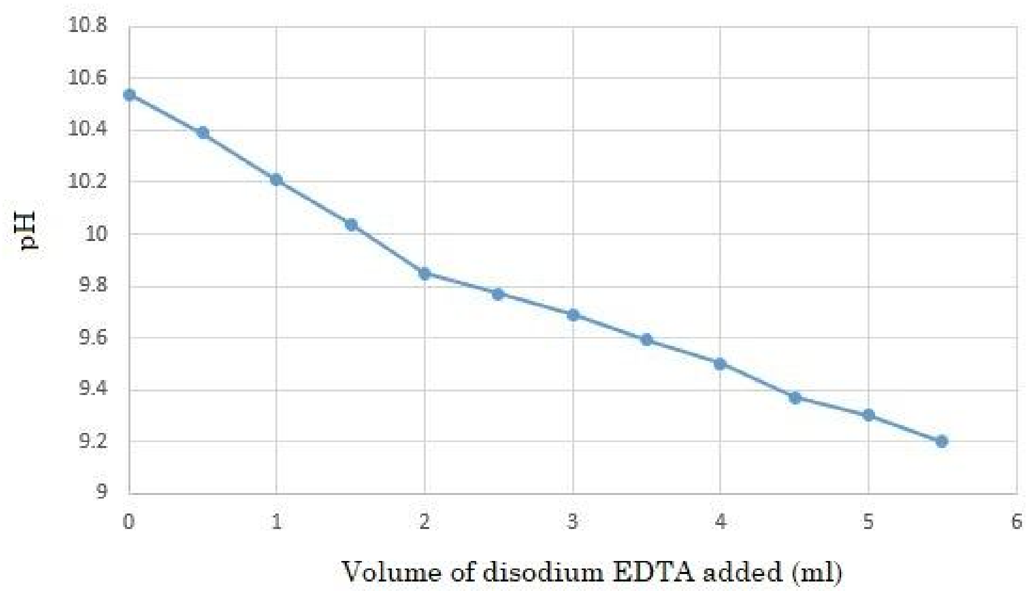

Figure 1 SC-20 sample: plot of pH –readins versus volume of titrant added.

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 formation of $[EDTA]^{4-}$ so that the latter is able to form stable complex,$[Ca - EDTA]$. As the reaction continues, concentration of $[OH]^-$ in 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).

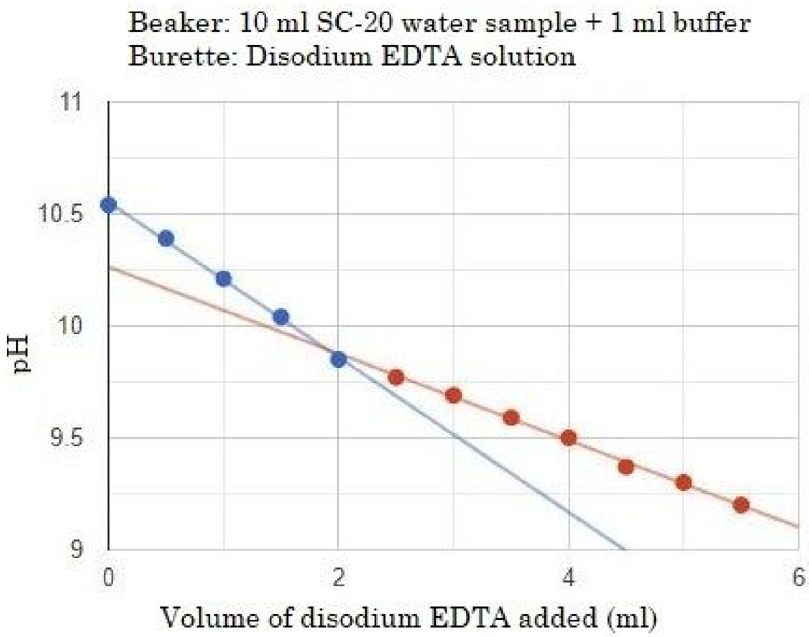

Figure 2 SC-20 sample: Linear plot of pH –readings versus volume of titrant added.

Intersection of the two straight lines occurs at 1.9 ml, which is assumed to be the end point of titration. So, the end point, obtained by pH –metric method, is almost same as that obtained by 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.

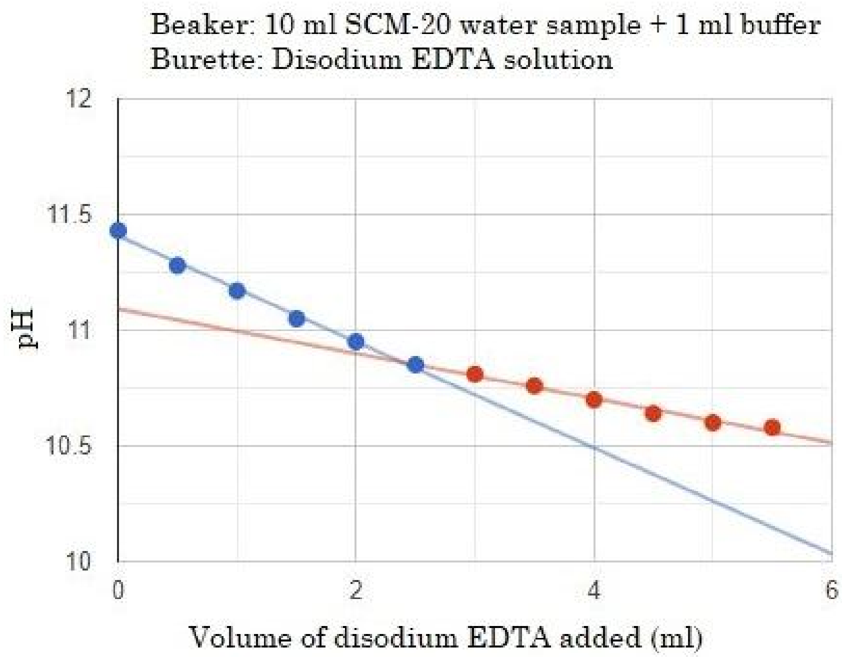

Figure 3 SCM-20 sample in presence of buffer: Linear plot of pH-readings versus volume of titrant added.

Intersection of the two straight lines occurs at 2.52 ml, which is believed to be the end point 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_2EDTAsolution added (ml)	Total volume of Na_2EDTAsolution 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

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

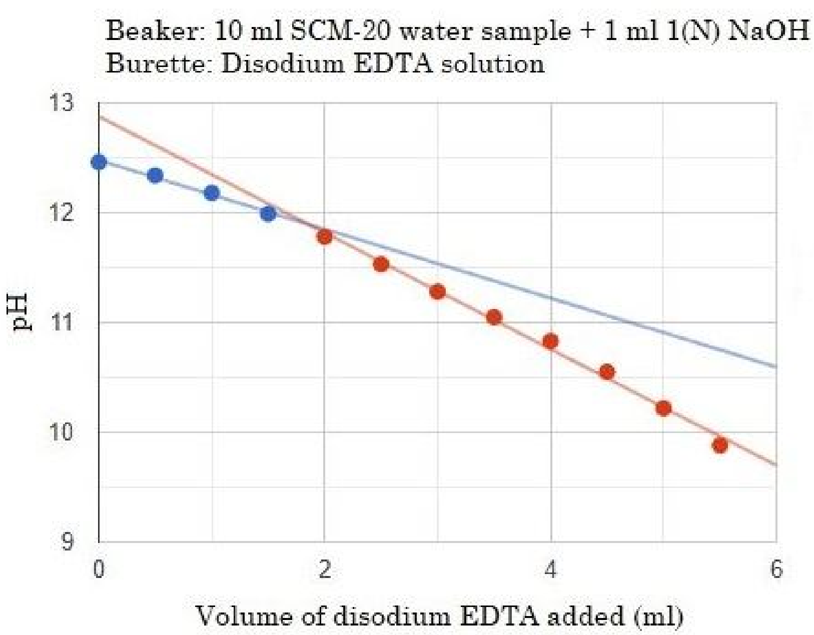

Figure 4 SCM-20 sample in presence of $NaOH$: Linear plot of pH-readings versus volume of titrant added.

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

$V_{Ca} + V_{Mg} = 2.4\ ml$ and $V_{Ca} = 1.6\ ml$. 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

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

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

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

Conclusions

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

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

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

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

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