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 ofCa^{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 endpoints of titrations. Furthermore,themethod's accuracy is sacrificed due to inevitable parallax errors during themarking of theendpoint of thetitration.

This present work reports that during titration of ahard water sample with a complexing agent (here, Na_2EDTA solution), pH changes continuously. This change in pH is closely monitored and recorded graphically. Hence theend 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 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 aprofuse amount of Ca^{2+} and Mg^{2+}ionsin thenatural water resources. However,the extent of hardness depends onthe type of land, e.g., water is soft in hilly areas, but the same is sufficiently hard in industrialized areas, commercial areas, and coastal areas. Melian et al.[1]attempted to estimate thehardness of groundwater and rural drinking water using thevolumetric titration method. The latter isa very popular method to determine water hardness and iswell documented in the literature[2-4]. Diogo Ferreira et al.[5] reported the uncertainty of visual detection of theend point of titration during thedetermination of thetotal hardness of water. Another researcher, P. Sengupta[6]documented the adverse impact of water hardness on health.Ramya et al.[7] studied theestimation of hardness in groundwater samples using thevolumetric titration method. Divya et al.[8] reported thetotal hardness and iron content 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[9-10].

This present work employs a novel technique, the pH −metric method, to estimate the concentrations of Ca^{2+} and Mg^{2+} ionshardness of a given water sample.

Chemicals and hard water samples

Table 1 Details of chemicals used in this research work

Chemicals	Molecular Weight(g/mole)	Composition
Fused $CaCl_2$	111	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

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.

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 mlofthehard water sample, SC-20,is taken into a conical flask. 1 ml Buffersolution with a pinch of EBT indicator is added into the conical flask. The solution turns to a wine-redcolour. It is then titrated against Na_2EDTA solution, running from the burette. At the endpoint, thewine-redcolour changes to sky blue.The initial and final burettereadings are noted. Triplicate readings are recorded.The total hardnessof water can be calculated using the mean burette readings.

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

(d) 10 mlofthehard 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 theformation of any Mg –complex during thetitration process. A pinch of Murexide indicatoris added. The solution turns to apink colour due to theformation of $[Ca-Murexide]$. It is then titrated against Na_2EDTA solution, running from the burette, till the pink colour changes to purple.Theinitial and finalburette readings are noted. Triplicates readings are recorded.TheCa –hardness can be calculated using the mean burette readings.

(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 thehard water sample, SC-20, is taken into a 250 mlbeaker. 90 mldistilled water is added into it to immerse the electrodes safely into the solution. 1 ml buffer solution is added to the beaker. The mixture is shaken, and thepHelectrode setis immersed into it. The 1st reading is taken. The beaker is taken out and 0.5 $mlNa_2EDTA$ solution is addedto it from the burette. The mixture is shaken, and pH electrode-set is again immersed into it. The 2ndreading is taken. The process is continued till the pH reads around 10.

(c) The pH readings are plotted against thevolume 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	Total volume of Na_2EDTA solution added	pH reading

	(ml)	(ml)	
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.

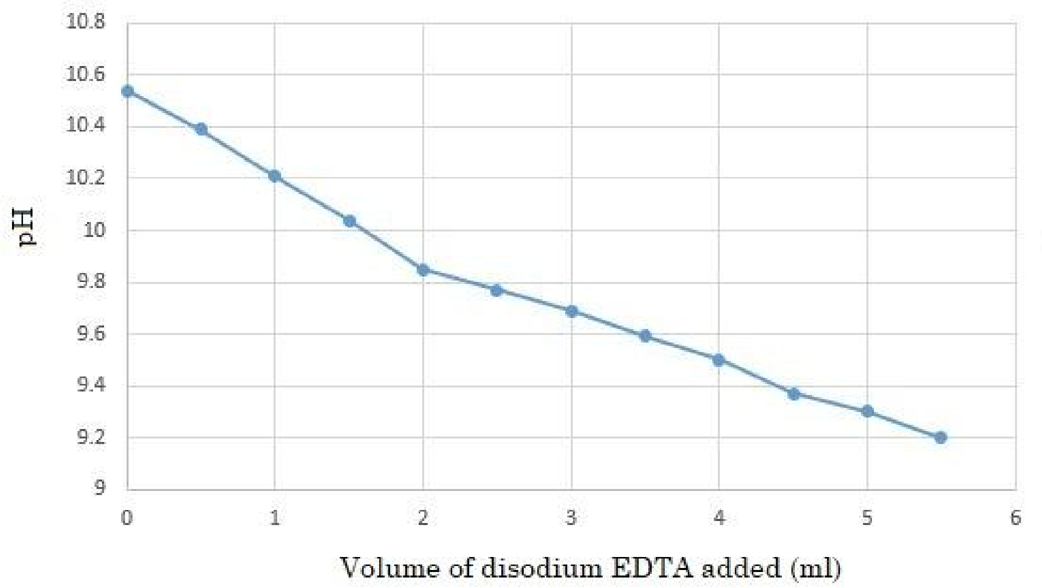

Figure 1 SC-20 sample: plot of pH −readings versus volume of titrant added.

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

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

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

The buffer consumes the H^+ ions, accelerating theformation of $[EDTA]^{4-}$ so that the latter can form astable complex,$[Ca - EDTA]$. As the reaction continues, theconcentration of $[OH]^-$ in thebuffer decreases, due to which, sharp drop of pH is observed (blue curve in the Fig.2) till the end point is reached. After the endpoint 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).

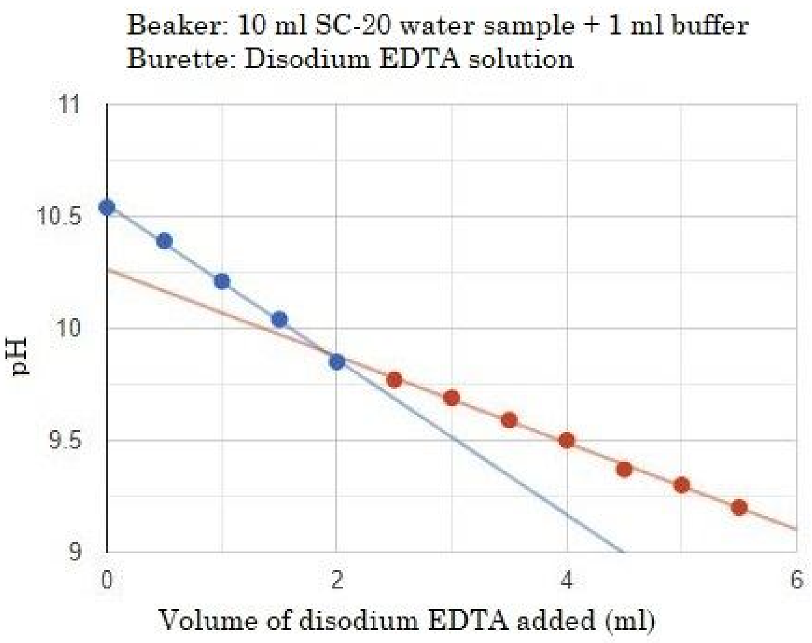

Figure 2 SC-20 sample: Linear plot of pH –readings versus volume of titrant added.

The intersection of the two straight lines occurs at 1.9 ml, which is assumed to be the endpoint of thetitration. So, the endpoint, obtained by the pH –metric method, is almost thesame as that obtained by thevolumetric 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	Volume of SCM-	Volume of Na_2EDTA consumed (ml)

observations	20 sample hard water taken (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.

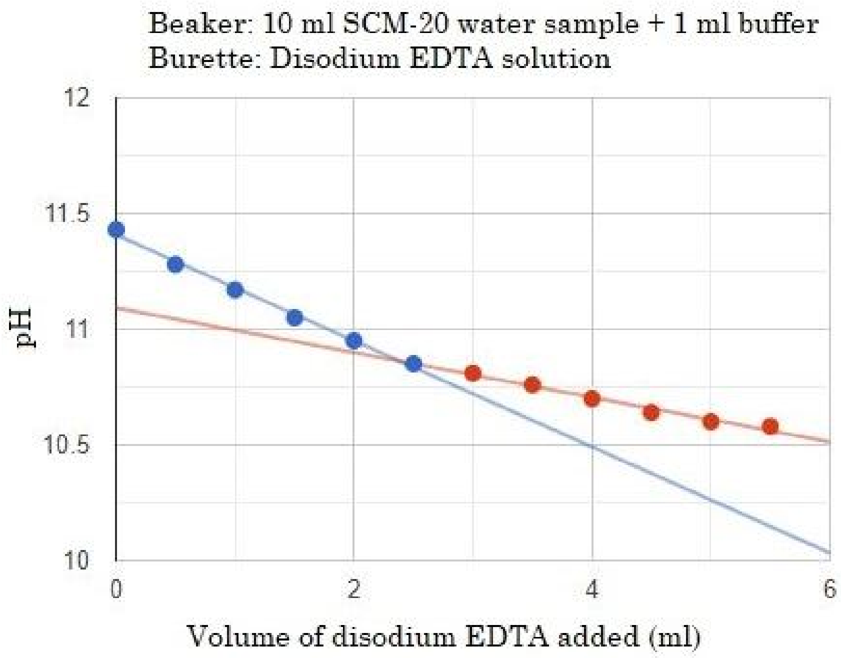

Figure 3 SCM-20 sample in thepresence of buffer: Linear plot of pH readings versus volume of titrant added.

The intersection of the two straight lines occurs at2.52 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 $\boldsymbol{ml}$ $\boldsymbol{1(N)MaOH}$ 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 Fig.4.

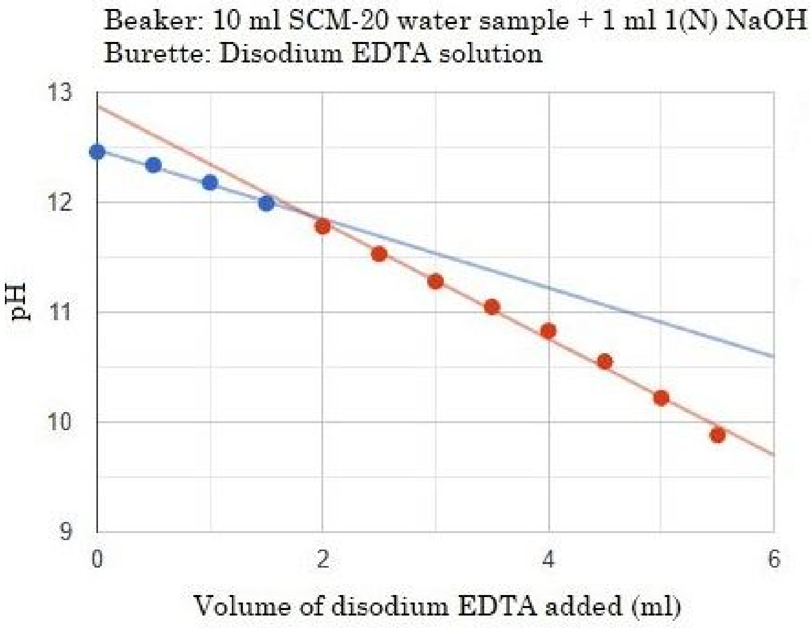

Figure 4 SCM-20 sample in presence of $NaOH$: Linear plot of pH-readings versus volume of titrant added.

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

$V_{Ca} + V_{Mg} = 2.4\ ml$ 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, thepH −metric titration result is very close to the theoretical value compared to the volumetric titration result. Thus, it is believed that thepH −metric titration method is more accurate than thevolumetric titration method.

Conclusions

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

2. The pH −metric determination of thehardness of water is more accurate than thevolumetric determination of the same as the end point of titration in thepH −metric method is obtained from the graph without any parallax errors.

3. No indicator is required inthepH −metric method of determination of hardness of water, which is considered a distinct advantage over thevolumetric method.

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

References

1. Melian, R., Myrlian, N., Gouriev, A., Moraru, C., and Radstake, F. (1999). "Groundwater quality and rural drinking-water supplies in the Republic of Moldova", *Hydrogeol. J.,* 1999, **vol.7**(2), pp.188–196.

2. Amelin, V.G. (2000). "Test method for the determination of overall quality characteristics of water using indicator papers", *J. Anal. Chem*., 2000, **Vol.55**(5), pp. 480–485.

3. Gudzenko, L.V. (2023). "Test Method for Determining the Total Hardness of Natural and Potable Water", *J. Water Chem*", *Technol.* 2023, **Vol.45**, 383–387.

4. Sawyer, C.N. and P.L. McCarty. (1978).“Chemistry for Environmental Engineering (3rd Ed)”, McGraw-Hill Book Company, New York, (1978).

5. Diogo Ferreira, Miguel Barros, Cristina M. Oliveira, Ricardo J. N. Bettencourt da Silva. (2019). “Quantification of the uncertainty of the visual detection of the end-point of a titration: Determination of total hardness in water”, *Microchemical Journal*, 2019, **Vol.146**, pp. 856-863.

6. Sengupta, P. (2013). “Potential health impacts of hard water”, *Int. J of Prev. Med.*, 2013, **Vol.4**, pp.866-875.

7. Ramya P., Babu, J. A., Reddy, T. E., and Rao, V. L.(2015).“A study on theestimation of hardness in groundwater samplesby EDTAtitrimetric method”, *International Journal of Recent Scientific Research*,2015, **Vol. 6**(6), pp.4505-4507.

8. Divya, T. and Rakhi, B. (2012). “Assessment of Water Quality in Terms of Total Hardness and Iron of Some Freshwater Resources of Kanpur and its Suburbs”, *Nature Environment and Pollution Technology*, 2012, **Vol.11** (2),pp.235-238.

9. Padmavati, T., Padhy, S.N., and Sahu, K.C. (2011). “Studies on thedistribution of calcium and magnesium incoastal waters of Gopalpur, Bay of Bengal”, Nat. *Env. Poll. Tech.*, 2011, **Vol.10** (3), pp.343-350.

10. Venkatasubramani, R., and Meenambal, T. (2007). “Study on subsurface water quality in Mettupalayam taluk of Coimbatore district, Tamilnadu”. Nat. Env. Poll. Tech., 2007, **Vol.6** (2), pp.307-310.