***Original Research Article***

# Study of Estimation of Hardness of Water Using pH-Meter

## ABSTRACT

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| 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 and 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, solution), changes continuously. This change in is closely monitored and recorded graphically. Hence the endpoint of titration is determined. The neutralization volume, thus obtained, is used to estimate and hardness of the water sample separately. This novel technique obviates the use of any external indicators and eliminates any possible parallax error. |

*Keywords: Hardness of water; complexometric titration; pH-metric titration; buffer solution; NaOH solution; disodium EDTA.*

## 1. INTRODUCTION

The hardness of water arises primarily due to the presence of profuse amount of and 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. (1999) 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 (Amelin, 2000, Gudzenko, 2023, Sawyer and McCarty (1978). Diogo Ferreira et al. (2019) reported the uncertainty of visual detection of the endpoint of titration during determination of total hardness of water. Another researcher, Sengupta (2013) documented the adverse impact of water hardness on health. Ramya et al. (2015) studied the estimation of hardness in ground water samples using the volumetric titration method. Divya et al. (2012) 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 (Padmavati et al., 2011, Venkatasubramani et al., 2007, Kumar, 2016, Joshi et al., 2023).

This present work proposes a novel technique, the metric method, to estimate the concentrations of and ions or in other words, calcium and magnesium hardness of a given water sample.

## 2. MATERIALS

**2.1 Chemicals and Hard Water Samples**

Details of chemicals used in the present work are documented in the Table 1.

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

## 3. METHODS

**3.1 Volumetric Titration**

1. standard solution of strength is prepared. of it is poured into a burette.
2. of the hard water sample, SC-20, is taken into a conical flask. 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 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.
3. For the hard water sample, SCM-20, the process (b) is followed. Here also triplicate readings are recorded. The total hardness, caused by and ions can be calculated using the mean burette reading.
4. of the hard water sample, SCM-20, is taken in a conical flask. Add solution. The function of is to block to avoid the formation of any complex during the titration process. A pinch of Murexide indicator is added. The solution turns to pink colour due to the formation of . It is then titrated against solution, running from the burette, till the pink colour changes to purple. The initial and final burette readings are noted. Triplicate readings are recorded. hardness can be calculated using the mean burette reading.
5. Using the results of the processes (c) and (d) hardness can be calculated by subtracting hardness from the total hardness.

**3.2 Metric Titration**

1. of prepared solution is poured into another burette.
2. of the hard water sample, SC-20, is taken into a beaker. distilled water is added into it in order to immerse the electrodes safely into the solution. buffer solution is added into the beaker. The mixture is shaken and the electrode-set is immersed into it. The 1st reading is taken. The beaker is taken out and solution is added to it from the burette. The mixture is shaken and electrode-set is again immersed into it. The 2nd reading is taken. The process is continued till the reads around .
3. The readings are plotted against the volume of solution added.
4. The step (b) is repeated for the other hard water sample, SCM-20. In this case, also, readings are plotted against volume of solution.
5. In case of SCM-20 hard water sample, the step (b) is repeated once more using solution instead of buffer solution. The readings are plotted against volume of solution added.

## 4. RESULTS AND DISCUSSION

**4.1 Sample SC-20**

This sample contains only ions. The results of volumetric titration of the sample are shown in the Table 3.

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

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

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 . In aqueous solution disodium salt of EDTA or dissociates to form . The latter reversibly dissociates to produce , which forms complexes with metal cations. In case of SC-20 hard water sample, only one type of complex, i.e., is formed. The reactions are given below

The buffer consumes the ions, accelerating the formation of so that the latter can form stable complex, . As the reaction continues, the concentration of in the buffer decreases, due to which, sharp drop of 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] ceases to occur and hence only a slow change in is observed due to buffer action (red curve in the Fig. 2.

The Intersection of the two straight lines occurs at , which is assumed to be the endpoint of titration. So, the endpoint, obtained by metric method, is almost same as that obtained by the volumetric method (Table 3).

**4.2. Sample SCM-20**

This sample contains both and ions. Two sets of volumetric titrations are performed to estimate the individual concentrations of and ions. Two sets of metric titrations are also performed.

**Table 1. Details of chemicals used in this research work**

|  |  |  |
| --- | --- | --- |
| **Chemicals** | **Molecular Weight (gm/mole)** | **Composition** |
| Fused  |  | NA |
|  |  | NA |
| Disodium salt of ethylene diamine tetraacetic acid () |  | NA |
| Buffer solution  | NA | 1:1 |
| Eriochrome Black T (EBT) indicator | 461 | NA |
| Murexide indicator | 284 | NA |

*NA = Not Applicable*

**Table 2. Composition of hard water samples**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Serial No.** | **Sample Code** |  **(Fused)** |  | **Weight ratio** | **Distilled water** |
|  | SC-20 |  |  | NA |  |
|  | SCM-20 |  |  |  |  |

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

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

|  |  |  |
| --- | --- | --- |
| **No. of observations** | **Volume of SC-20 sample hard water taken**  | **Volume of consumed**  |
| **Initial** | **Final** | **Difference** | **Mean volume** |
|  |  | 0 | 1.8 | 1.8 | 1.8 |
|  |  | 1.8 | 3.7 | 1.9 |
|  |  | 3.7 | 5.5 | 1.8 |

*The mean volume represents the volume of required to absorb all ions from the aliquotted sample solution (10 ml) to form stable complex*

**Table 4. Metric titration for the hard water sample SC-20**

|  |  |  |  |
| --- | --- | --- | --- |
| **No. of****observations** | **Volume of solution added (ml)** | **Total volume of solution added (ml)** |  **reading** |
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**Fig. 1. SC-20 sample: plot of readings versus volume of titrant added**



**Fig. 2. SC-20 sample: Linear plot of readings versus volume of titrant added**

**4.2.1 Set-1**

*4.2.1.1 Volumetric titration using buffer solution*

Volumetric titration of the sample SCM-20 has been performed using buffer solution and EBT indicator. The results are shown in the Table 5. Mean burette reading is 2.4 ml.

*4.2.1.2 metric titration using buffer solution*

*metric* titration results are given in the Table 6. The plot of readings versus volume of disodium EDTA gives rise to two straight lines of different slopes as shown in the Fig. 3.

The Intersection of the two straight lines occurs at , which is believed to be the endpoint of titration. So total hardness due to and ions can be calculated metrically.

**4.2.2 Set-2**

*4.2.2.1 Volumetric titration is performed using solution*

Volumetric titration of the sample SCM-20 has been performed using solution and Murexide indicator. The results are shown in the Table 7. Mean burette reading is 1.6 ml.

*4.2.2.2 metric titration using solution*

*metric* titration results are given in the Table 8. A similar plot of readings versus volume of disodium EDTA is shown in the Fig. 4.

The Intersection of the two straight lines occurs at , which is believed to be the end point of titration. So hardness, due to ions only, can also be calculated metrically. Using the results of Fig.3 and Fig.4, hardness due to ions can be calculated.

According to Table 2, in the hard water sample SCM-20 ratio of weights of and is . So the following relation holds good.

If and are the volumes (in ) of consumed due to ions and ions respectively, the following relation also holds good.

**Table 5. Volumetric titration for the hard water sample SCM-20 using buffer solution**

|  |  |  |
| --- | --- | --- |
| **No. of observations** | **Volume of SCM-20 sample hard water taken**  | **Volume of consumed**  |
| **Initial** | **Final** | **Difference** | **Mean volume** |
|  |  | 0 | 2.5 | 2.5 | 2.4 |
|  |  | 2.5 | 4.8 | 2.3 |
|  |  | 4.8 | 7.2 | 2.4 |

*The mean volume represents the volume of required to absorb all and ions from the aliquotted sample solution () to form stable and complexes*

**Table 6. pH-metric titration for the hard water sample SCM-20 using buffer solution**

|  |  |  |  |
| --- | --- | --- | --- |
| **No. of****observations** | **Volume of solution added (ml)** | **Total volume of solution added (ml)** |  **reading** |
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**Fig. 3. SCM-20 sample in the presence of buffer: Linear plot of readings versus volume of titrant added**



**Fig. 4. SCM-20 sample in presence of : Linear plot of readings versus volume of titrant added**

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

|  |  |  |
| --- | --- | --- |
| **No. of observations** | **Volume of SCM-20 sample hard water taken**  | **Volume of consumed**  |
| **Initial** | **Final** | **Difference** | **Mean volume** |
|  |  | 0 | 1.6 | 1.6 | 1.6 |
|  |  | 1.6 | 3.2 | 1.6 |
|  |  | 3.2 | 4.9 | 1.7 |

*The mean volume represents the volume of required to absorb all from the aliquotted sample solution () to form stable complexes*

**Table 8. pH-metric titration for the hard water sample SCM-20 using solution**

|  |  |  |  |
| --- | --- | --- | --- |
| **No. of****observations** | **Volume of solution added (ml)** | **Total volume of solution added (ml)** |  **reading** |
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(a) Considering volumetric titration results of sets 1 and 2 (Table 5 and Table 7), the following equations are true

 and . So,

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

 and . So,

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

## 5. CONCLUSIONS

1. The hardness of a given water sample can be estimated accurately using meter.
2. The metric determination of the hardness of water is more accurate than the volumetric determination of the same as the endpoint of titration in metric method is obtained from the graph without any parallax error.
3. No indicator is required in the 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 meter.

## DISCLAIMER (ARTIFICIAL INTELLIGENCE)

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

## COMPETING INTERESTS

Author has declared that no competing interests exist.

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