

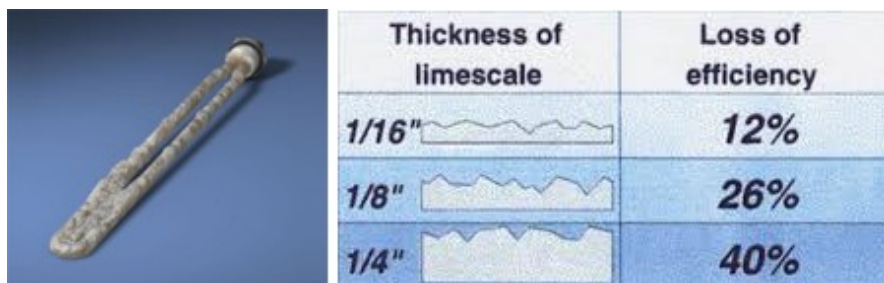
## CB101: Experiment 6: Determination of total hardness of water

### I- INTRODUCTION

Hardness of water is due to the presence of calcium  $\text{Ca}^{2+}$  and magnesium  $\text{Mg}^{2+}$  ions. The presence of these cations are essential for human health, but excessive hardness of water can pose several industrial and domestic problems. The Bureau of Indian Standards (BIS) prescribes the following limit for the hardness of water :

| Sl No. | Characteristic                        | Requirement<br>(Acceptable Limit) | Permissible<br>Limit in the<br>Absence of<br>Alternate<br>Source |
|--------|---------------------------------------|-----------------------------------|--|
| (1)    | (2)                                   | (3)                               | (4)  |
| vi)    | Calcium (as Ca), mg/l, <i>Max</i>     | 75                                | 200  |
| xiii)  | Magnesium (as Mg), mg/l, <i>Max</i>   | 30                                | 100  |
| xxiii) | Total hardness (as $\text{CaCO}_3$ ), | 200                               | 600  |

*Extract from Indian Standard DRINKING WATER – SPECIFICATION-2012*



*Extract from venushomappliances.com*

For domestic usage, the following classification is often used:

| Classification   | Soft | Moderately Hard | Hard    | Very Hard |
|------------------|------|-----------------|---------|-----------|
| Hardness in mg/l | <60  | 61-120          | 121-180 | >180      |

*Extract from USGS Water-Quality Information: Water Hardness and Alkalinity.*

### Different hardnesses of water

Different salts of calcium and magnesium are present in natural water.

- Bicarbonates of calcium and magnesium  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ . They transform into  $\text{CaCO}_3(\text{s})$  and  $\text{MgCO}_3(\text{s})$  as scale on boiling the water, and hence constitutes the temporary hardness of water.

- Other salts such as sulfates ( $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ) and chlorides ( $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ) produce permanent hardness since they cannot be removed by boiling the water.

- Total hardness of water is the sum of permanent hardness and temporary hardness.

- Calcium hardness and Magnesium hardness of water can also be distinguished.

## CB101: Experiment 6: Determination of total hardness of water

### Hardness of water – calculation

Hardness of water is expressed in mg/L as  $\text{CaCO}_3$ . It corresponds to the weight of calcium carbonate that 1L of water would contain, if its hardness was only due to the presence of  $\text{CaCO}_3$ .

Therefore, to calculate the hardness of water, one should multiply the molarity of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  by the molecular weight of  $\text{CaCO}_3$ .

### Complexometric titration:

Molarity of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions can be determined by titrating with EDTA (ethylenediamine tetraacetic acid) using EBT (Eriochrome Black T) as indicator.

In a pH range 7-11, when adding the indicator EBT to the analyte, a wine-red complex is immediately formed. It is less stable than the complex Mg-EDTA

Equations of reaction: (In = indicator EBT,  $\text{H}_2\text{Y}^{2-} = \text{EDTA}$ )

1- Before the end point :  $\text{M}^{2+} + \text{H}_2\text{Y}^{2-} \rightleftharpoons \text{MY}^{2-} + 2\text{H}^+$ , presence of **wine-red** complex  $\text{MIn}$

2- At the end point :  $\text{MIn} + \text{H}_2\text{Y}^{2-} \rightleftharpoons \text{MY}^{2-} + \text{HIn} + \text{H}^+$   
(wine-red) (blue)

**Objective: Determine the total hardness of sample water, the permanent hardness, the temporary hardness and the molarity of Magnesium and Calcium.**

### II- PRELIMINARY WORK

- 1) Read carefully the procedure, and make the necessarily preliminary calculations.
- 2) Why is it necessary to add buffer solution to the analyte for titrating?
- 3) Describe the change of color at the end point and explain it.

### III- PROCEDURE

#### Chemicals provided:

- Ethylene diamine tetra acetic acid (EDTA) MW = 336.2
- Standard solution of  $\text{Mg}(\text{NO}_3)_2$  of concentration 0.05M
- Indicator Eriochrome Black T (EBT)
- Ammonia buffer solution, pH=10.
- Sample water
- Ammonium oxalate



**Apparatus and laboratory glassware required:** See appended.

## CB101: Experiment 6: Determination of total hardness of water

**1)** Prepare 250.0 mL of 0.005M solution of EDTA (MW=336.2). Fill a burette.

*The EDTA provided is not pure, and cannot be considered as a primary standard. Standardisation using a known solution of  $Mg^{2+}$  is thus required*

**2)** Prepare 50.0 mL of 0.01M solution of  $Mg(NO_3)_2$  from the 0.05M solution provided.

**3)** Standardisation of EDTA solution

10.0 mL of 0.001M solution of  $Mg^{2+}$  is pipetted out and taken into a 100mL conical flask. 2mL of ammonia buffer is added as well as 2 drops of EBT indicator. The mixture is shaken well and titrated with the prepared 0.005M EDTA solution until the wine red colour changes to blue.

The titration is repeated to get concordant values. The standard molarity of EDTA solution is then calculated.

**4)** Determination of total hardness of water

The previous titration is repeated with 10.0 mL of tap water. The total hardness of water is calculated.

**5)** Determination of permanent hardness of water

Take 50 mL of sample water in a beaker, tap it with a watch glass, and boil it for 25 min. Allow the water to cool and filter with a

funnel, a filter paper and a conical flask. Repeat the same titration procedure than in 2) with 10.0 mL of boiled tap water.

The permanent and the temporary hardness of water is then calculated.

**6)** Determination of molarity of  $Mg^{2+}$  in total hardness of water

*$Ca^{2+}$  ions can be precipitated by oxalate ions  $C_2O_4^{2-}$  and be removed by filtration*

About 0.04g of ammonium oxalate is added to about 25 mL of tap water in a beaker (DO NOT add water for this step, you would dilute your analyte). The beaker is gently shaken by hand for 30s. The content is then filtered using funnel, filter paper type 41 or 42, and conical flask.

The filtrate is titrated as previously. The total magnesium hardness and the total calcium hardness is calculated.

**7)** Conclusion : Summarize the results for total hardness, permanent hardness, temporary hardness, molarity of  $Mg^{2+}$  and  $Ca^{2+}$ .

Does the provided water satisfy the limits precibes by the Bureau of Indian Standards? Specifiy if the water is Soft, Moderatly Hard, Hard or Very Hard.

## CB101: Experiment 6: Determination of total hardness of water

### **APPENDED: Apparatus and glassware required:**

- burette on stand
- volumetric flask 50 mL
- volumetric flask 250mL
- pipette pump
- 10 mL volumetric pipette
- spatula
- two watch glasses
- 2 funnel
- 100 mL conical flask
- dropper
- 250mL conical flask
- 500 ml beaker
- two 250mL beakers