Water Purification: Hardness Estimation by EDTA method and its Removal using Ion-exchange Resin

1. Introduction to Hard Water and its Classification:

Water described as "hard" contains high levels of dissolved $Ca^{2+}$and Mg^{2+}ions. Ground and surface water dissolve the Ca^{2+}/Mg^{2+} containing ores/minerals from surrounding soil and rock and are enriched with these cations. Hardness is most commonly expressed as milligrams of $CaCO_3$ eq. per liter. Water containing hardness causing species at concentrations below 60 mg/l are generally considered as soft; 60–120 mg/l as moderately hard; 120–180 mg/l, as hard; and more than 180 mg/l as very hard water. Based on the type of anions (Cl^-, SO_4^{2-}, HCO^{3-}) associated with Ca^{2+}/Mg^{2+} ions, the hardness is categorized into temporary (carbonate, HCO^{3-}) hardness & permanent (non-carbonate, Cl^-, SO_4^{2-}) hardness.

2. Problems caused by Hard Water:

Hard water can cause costly breakdowns in boilers, cooling towers and plumbing. When hard water is heated, the hardness causing salts tend to precipitate out of solution, forming a hard scale or soft sludges in pipes and surfaces, thereby completely plugging pipes and restricting flows. In boilers, scale formation prevents efficient heat transfer, thereby resulting in energy loss and overheating which could lead to serious accidents. At the domestic level, hard water lessens the effectiveness of soap by forming scums/precipitates, which adhere to human skin. Human consumption of water containing excess of Ca and Mg are associated with increased risks of osteoporosis, nephrolithiasis, colorectal cancer, hypertension, stroke, coronary artery disease, insulin resistance, diarrhea and obesity.

3. Estimation of Hard Water:

Traditionally, hardness in water is estimated by complexometric titration using sodium salt of EDTA and EBT as indicator at pH = 9-10. EBT forms an unstable wine-red colored complex with Ca^{2+}/Mg^{2+}ions, which upon titrating with EDTA, results in the breaking of EBT-Ca^{2+}/Mg^{2+} unstable bond and formation of stable EDTA-Ca^{2+}/Mg^{2+} bond. The endpoint changes from wine-red (EBT-Ca^{2+}/Mg^{2+}) to steel blue (free EBT).

4. Modern Treatment of Hard Water:

Hard water is made soft by the use of a water softener i.e., ion-exchange resins (IER) which are very small porous spherical polymeric beads, with specific functional groups (sulphonic/carboxylic acid) attached to the polymeric backbone. Therefore, the IERs carrying a negatively charged exchange site can hold a positively charged ion. When the hard water is passed through the resin beads, Ca^{2+}/Mg^{2+}ions in hard water are exchanged from the solution for hydrogen/sodium ions, which are much more soluble and does not precipitate out to form scale or sludges. Eventually, the resin beads get saturated with hardness causing ions and the exhausted beads are regenerated by using a mild acid or brine solution to flush out the Ca^{2+}/Mg^{2+}ionsretained in the resin beads.

Expt. No.: 1 **Date:** 2021/01/21

Experiment	**Water Purification Hardness Estimation by EDTA method and its Removal using Ion-exchange Resin**
Problem definition	Hardness of water is due to the presence of dissolved calcium and magnesium salts in water. EDTA forms stable complex with hardness causing salts and is used in the removal of scale and sludge forming impurities in industrial boilers.
Methodology	EBT indicator-Metal ion complex is weaker compared to EDTA-metal ion complex. The end point is the color change from wine red (EBT-Metal ion complex) to steel blue (free EBT indicator).
Solution	Estimation of Calcium hardness (in ppm) in the given unknown sample. Understanding the water softening using ion-exchange resins.
Student learning outcomes	Students will learn to a) perform complexometric titration b) understand the efficiency of ion-exchange resins using in water purifiers

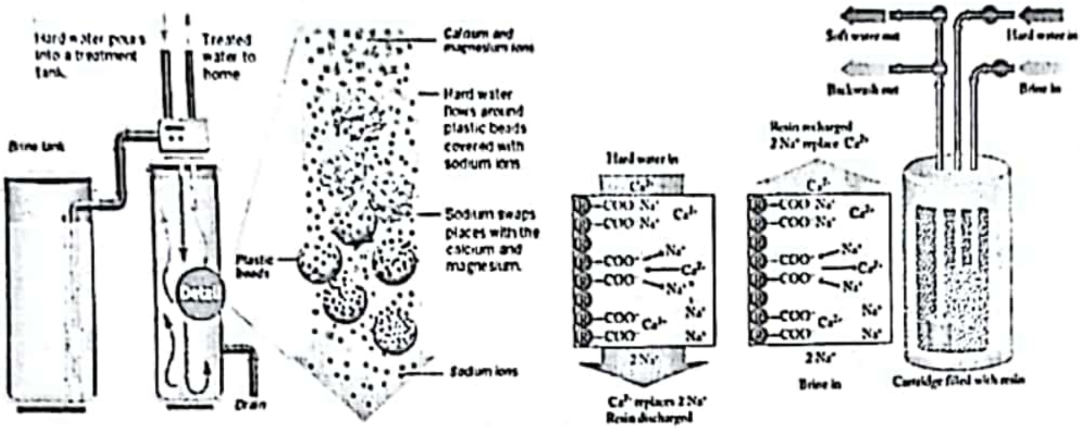
Principle:

Ehtylenediaminetetraacetic acid (EDTA) forms complexes with a large number of cations including Ca^{2+} and Mg^{2+} depending upon pH of solution. Hence, it is possible to determine the total hardness of water using EDTA solution. EDTA in the form of its sodium salt (H_2Y^{2-}) is commonly used in complexometric titration for estimation of metal ion because pure EDTA (H_4Y) is sparingly soluble in water. EDTA has six binding sites (the four carboxylate groups and the two amino groups) providing six pairs of electrons. The resulting metal-ligand complex, in which EDTA forms a cage-like structure around the metal ion, is very stable at specific pH. All metal-EDTA complexes have a 1:1 stoichiometry. The H_2Y^{2-} form complexes with metal ions as follows.

$$M + H_2Y^{2-} \rightarrow MY^{2-} + 2H^+ \quad \text{-----------} \ (1)$$

Where, M is Ca^{2+} and Mg^{2+} present in water. Reaction (1) can be carried out quantitatively at pH 10 using Eriochrome Black T (EBT) as indicator. EBT forms a wine-red complex with M^{2+} ions which is relatively less stable than the M^{2+}-EDTA complex. On titration, EDTA first reacts with free M^{2+} ions and then with the metal-EBT indicator complex. The latter gives a colour change from wine-red to steel blue at the equivalence point.

Removal of hardness using ion exchange resins (IER): Ion exchange is a reversible process. When hard water is passed through cation ion-exchange resins packed in a narrow column, Ca^{2+} and Mg+ cations in hard water are exchanged with Na+ or H+ ions in the resins. The exhausted resins are regenerated by passing 10% dil. HCl through the column. A typical example of application is preparation of high-purity water for power engineering, electronic and nuclear industries and in household water purifiers.



Requirements

Reagents and solutions: Standard hard water (1mg/mL of $CaCO_3$ equivalents), 0.01 N EDTA solution, EBT indicator, hard water sample, NH_3-NH_4Cl buffer solution and ion exchange resin.

Apparatus: Burette, pipette, conical flask, standard flask burette stand and IER column.

Procedure

Titration-I: Standardization of EDTA

Pipette out 20 mL of the standard hard water containing 1mg/mL of $CaCO_3$ (1000 ppm) into a clean conical flask. Add one test tube full of ammonia buffer (NH_4OH – NH_4Cl) solution to maintain the pH around 10. Add three drops of Eriochrome Black – T (EBT) indicator and titrate it against the given EDTA solution taken in the burette. The end point is change of colour from wine red to steel blue. Repeat the titration for concordant titer values. Let 'V_1' be the volume of EDTA consumed.

S. No.	Volume of standard hard water (mL)	Burette reading (mL)		Volume of EDTA (V_1, mL)
		Initial	Final	
1	20	0	25.3	
2	20	0	24.5	24.5
3	20	0	24.5	
		Concordant titer value		

Calculation:

20 mL of given hard water consumes V_1 mL of EDTA

20 mg of $CaCO_3$ requires V_1 mL of EDTA for complexation

$\therefore$ **1 mL of EDTA requires = 20/V_1 mg $CaCO_3$ for complexation**

This relation will be used in other two titrations

Titration-II: Estimation of total hardness of hard water sample

Pipette out 20 mL of the given sample of hard water into a clean conical flask. Add one test tube full of ammonia buffer (NH_4OH – NH_4Cl) solution and three drops of Eriochrome Black–T (EBT) indicator. Titrate this mixture against standardized EDTA solution taken in the burette. The end point is the change of color from wine red to steel blue. Repeat the titration for concordant titer value. Let 'V_2' be the volume of EDTA consumed.

S. No.	Volume of sample hard water (mL)	Burette reading (mL)		Volume of EDTA (V_2, mL)
		Initial	Final	
1	20	0	25.3	
2	20	0	25.4	25.4
3	20	0	25.4	
		Concordant titer value		

Calculation:

From Titration 1, we have the following relation:

$\therefore$ 1 mL of EDTA requires = 20/V_1 mg $CaCO_3$ for complexation

From Titration 2,

20 mL of sample hard water consumes = V_2 mL of EDTA.

= V_2 x 20/V_1 mg of $CaCO_3$ eq.

$\therefore$ 1000 mL of hard water sample consumes = $V_2 \times \cancel{20}/V_1 \times 1000/\cancel{20}$

= $V_2/V_1 \times 1000$ ppm

$\therefore$ Total hardness of the water sample = "X" ppm

Titration-3: Removal of hardness using ion exchange method

Arrange the ion exchange column on to a burette stand and place a clean funnel on top of the column. Pour the hard water sample (around 40 to 50 mL) remaining after the completion of Titration – 2 through the funnel and into the ion exchange column. Place a clean beaker under the column and collect the waterpassing through the column over a period of 10minutes. Adjust the valve of the column to match the duration of outflow.

From the water collected through the column, pipette out 20 mL into a clean conical flask and repeat the EDTA titration as carried out above. Note down the volume of EDTA consumed as 'V_3'.

Calculation:

From Titration 1, we have the following relation:

$\therefore$ 1 mL of EDTA requires = $20/V_1$ mg $CaCO_3$ for complexation

From this relation, it can be seen that

20 mL of water sample after softening through the column consumes = V_3 mL of EDTA.

$$= V_3 \times 20/V_1 \text{ mg of } CaCO_3 \text{ eq.}$$

$\therefore$ 1000 mL of water sample after softening through the column consumes =

$$= V_3 \times \cancel{20}/V_1 \times 1000/\cancel{20}$$

$$= V_3/V_1 \times 1000 \text{ ppm}$$

$\therefore$ Residual hardness of the water sample = "Y" ppm

S. No.	Volume of sample hard water (mL)	Burette reading (mL)		Volume of EDTA (V_3, mL)
		Initial	Final	
1	20	0	6.7	
2	20	0	6.7	6.7
3	—	—	—	
		Concordant titer value		

Result:

Total hardness of the water sample= 1036.73 (X) ppm

Residual hardness in the water sample= 273.4 (Y) ppm

Hardness removed through the column = 763.27 (X–Y) ppm