Water Hardness

The water hardness is the amount of dissolved calcium and magnesium in the water. Water that contains salts of calcium and magnesium principally as bicarbonates, chlorides, and sulfates.

Sources of hardness:

Water hardness is determined by the concentration of multivalent cations in the water. Multivalent cations are positively charged metal complexes with a charge greater than 1^{+}Common cations found in hard water include Ca^{2+} and $Mg^{2+.}$ These ions enter a water supply by leaching from minerals within an originated from the sedimentary rocks, are most common in areas having extensive geological formation of limestone. Common calcium-containing minerals are calcite and gypsum (CaSO. $2H_2O$). A common magnesium mineral is dolomite ($CaMg\ (CO_3)_2$) which also contains calcium. Rainwater and distilled water are soft, because they contain few ions. Other factor that affects the values of total hardness was human activities such as factories and application of lime to the soil in agricultural areas.

Types of Hardness

1. Temporary hardness **2. Permanent hardness**

1. Temporary hardness

Temporary hardness is a type of water hardness caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate). When dissolved, these minerals yield calcium and magnesium cations (Ca^{2+}, Mg^{2+}) and carbonate and bicarbonate anions (CO_3^{2-}, HCO^{3-}). The presence of the metal cations makes the water hard. Temporary hardness can be reduced either by boiling the water, or by the addition of lime (calcium hydroxide) through the softening process of lime softening. Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.

2.Permanent hardness:

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. When this is the case, it is usually caused by the presence of calcium sulfate and/or magnesium sulfates in the water, which do not precipitate out as the temperature increases. Ions causing permanent hardness of water can be removed using a water softener, or ion exchange column.

Softening hard water

Methods for softening hard water involve the removal of calcium ions and magnesium ions from the water. There are two methods for softening hard water:

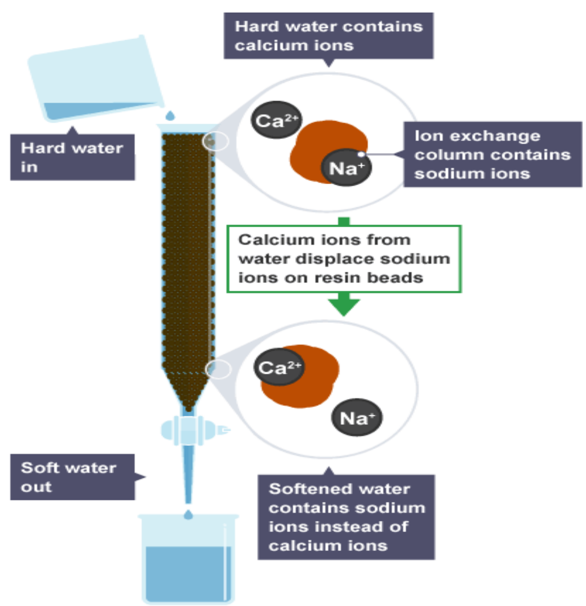
1. Adding sodium carbonate to the water. 2. Using ion exchange columns

1. Adding sodium carbonate:

Sodium carbonate, Na_2CO_3, is also known as washing soda can remove temporary and permanent hardness from water. Sodium carbonate is soluble but calcium carbonate and magnesium carbonate are insoluble. The carbonate ions from sodium carbonate react with the calcium and magnesium ions in the water to produce insoluble precipitates. For example: $\mathbf{Ca^{2+}(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2Na^{+}(aq)}$

2.Ion exchange columns:

The resin beads have sodium ions attached to them. As the hard water passes through the column, the calcium and magnesium ions displaces with the sodium ions. The calcium and magnesium ions are left attached to the beads, while the water leaving the column contains more sodium ions. Some ion exchange resins use hydrogen ions instead of sodium ions.



EDTA (Ethylene Diamine Tetra Acetic acid) method for hardness determination

The principle of this method:-

1- The original color of Eriochrome black T is blue when its added to hard water sample of PH (10) it combine with Ca^{+2}& Mg^{+2} in the water to form weak complex ion of a red wine color, during titration with EDTA its form a stable complex with Ca^{+2}&Mg^{+2} ion, the wine red change to blue color

2- When determining the amount of Ca in the water buffer solution (PH 12) is added. This strong base will precipitate Mg^{+2} ion as $Mg(OH)_2$what remain to react with indicator is Ca^{+2} ion.

Procedure:-

1. **Total hardness:**
   - **a.** Take 50 ml of sample and put into the conical flask.
   - **b.** Add 2 ml of buffer solution pH 10, and shake well.
   - **c.** Add few 0.2 grams of (Eriochrome black T indicator), shake well, and the solution will have a wine red color.
   - **d.** Titrate the sample against 0.01 M EDTA disodium (Ethylene Diamine Tetra Acetic cid) until the color of the sample color change from wine red to blue.
   - **e.** Calculation:

$$\textbf{Total hardness mg/L} = V_{EDTA} * N_{EDTA} * \frac{100}{1000} * \frac{10^6}{50}$$

2. **Calcium hardness:**
   - **a.** Take 50 ml of sample and put into the conical flask.
   - **b.** Add 2 ml of buffer solution pH 12, and shake well.
   - **c.** Add 0.2 gram of meroxide indicator, shake well, and the solution will have a pink color.
   - **d.** Titrate the sample against 0.01 M Na_2EDTA until the color of the sample color change from pink to purple.
   - **e.** Calculation

$$\textbf{Calcium hardness mg/L} = V_{EDTA} * N_{EDTA} * \frac{40}{1000} * \frac{10^6}{50}$$

Magnesium hardness mg/L =Total hardness - Calcium hardness

Why is pH 10 buffer used in EDTA titration?

pH 10 buffer is used in EDTA titration because in EDTA Y^{4-} is predominant, and we want Y^{4-} to react with the metal ions that are present in the titration solution. This can be achieved by using a pH 10 buffer.

Why EBT is used in EDTA titrations?

Eriochrome black T is used as an indicator for complexometric titrations because it forms a complex with calcium, magnesium and other metal ions in its protonated form. When titrated with EDTA, the metal ions complexed with eriochrome black T reacts with the EDTA forming a blue solution.

Determination of Water Hardness

In this experiment the indicator eriochrome black T (EBT) is used to signal the presence of ions in the water sample. EBT binds with free metal ions in the water to form a pink complex. EDTA has a stronger affinity for the metal ions than EBT so when EDTA is added it replaces the EBT and the EBT returns to its blue, uncomplexed color. The blue color is used as the end point in the titration. A sample of tap water is treated with EBT indicator. If the indicator turns from blue to pink, metal ions such as calcium and magnesium are present. To determine the concentration of ions present, the sample is titrated with a known molar concentration of EDTA.