Measurement of hardness of water

- Hardness of water is measured in parts per millions (**ppm**) **as calcium carbonate equivalents.**
- Reasons for expressing hardness in $CaCO_3$ equivalents:
  - its molecular weight is 100; equivalent weight is 50.
  - it is the most common insoluble impurity in water.

$$\text{Hardness in terms of Equivalents of } CaCO_3 = \frac{\text{Mass of Hardness Producing Substance} \times \text{Equivalent Weight of } CaCO_3}{\text{Equivalent Weight of hardness-producing substance}}$$

Total Hardness= Temporary Water Hardness + Permanent Water Hardness

 # Calculate the temporary hardness and permanent hardness of a sample water containing $Mg(HCO_3)_2$ = 7.3 mg/L; $Ca(HCO_3)_2$ = 16.2 mg/L; $MgCl_2$ = 9.5 mg/L; $CaSO_4$ = 13.6 mg/L (atomic weight of Mg = 24, Ca = 40, Cl = 35.45 and S = 32). (Ans.: Temporary = 15 ppm, Permanent = 20 ppm)

Problem 1 for DA

 # Calculate the temporary hardness, permanent magnesium hardness, total permanent hardness & total hardness in terms of calcium carbonate equivalents in a water sample containing calcium bicarbonate (12.2 mg), magnesium bicarbonate (8.2 mg), magnesium sulphate (5.6 mg), magnesium chloride (6.2 mg), calcium sulphate (10.3 mg) & sodium sulphate (7.5 mg). Given that at. Wt. of Mg=24 amu, S=32 amu, Cl=35.5 amu, Ca=40 amu, O=16 amu, C=12 amu, H=1 amu.

Measurement of hardness of water

➢ **Units of hardness**

- ❖ **Parts Per million (ppm)**

Parts of $CaCO_3$ eq./10^6 parts of water

- ❖ **Milligrams per liter (mg/l)**

mg of $CaCO_3$ eq. present/ liter of water

- ❖ **Degree Clarke (^oCl)**

No. of geqv. of $CaCO_3$/70000 parts of water

- ❖ **Degree French (^oFr)**

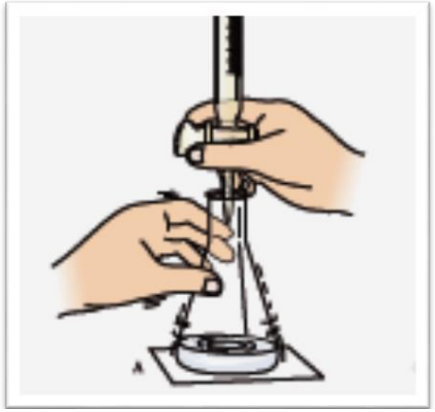
No. of geqv. of $CaCO_3$/10^5 parts of water

Relationship between units of water hardness

☐ 1 ppm = 1 mg/L = 0.1 °French = 0.07 °Clark

Estimation of hardness of water

➢ **O. Hehner's method:**



❖ ***Temporary Hardness:*** Acid-base titration is performed before and after boiling the hard water

Permanent Hardness: Chloride and sulphates of Ca and Mg are removed as insoluble $CaCO_3$ and $MgCO_3$ by boiling the hard water with excess Na_2CO_3. Acid-base titration is performed before and after removal

$$Ca(HCO_3)_2 \xrightarrow{\text{Boiling}} CaCO_3\downarrow + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Boiling}} Mg(OH)_2\downarrow + CO_2$$

$$CaCl_2 + Na_2CO_3 \xrightarrow{\text{Boiling}} CaCO_3\downarrow + 2\,NaCl$$

$$MgSO_4 + Na_2CO_3 \xrightarrow{\text{Boiling}} MgCO_3\downarrow + 2\,Na_2SO_4$$

➢ **Soap titration method:**

Hardness is estimated by adding a soap solution of known strength to a sample water solution until a permanent lather is formed after shaking

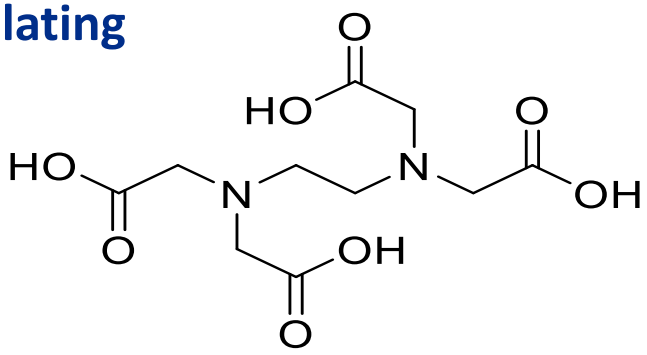
$$2\,C_{17}H_{35}COONa + Ca(HCO_3)_2 \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2\,NaHCO_3$$

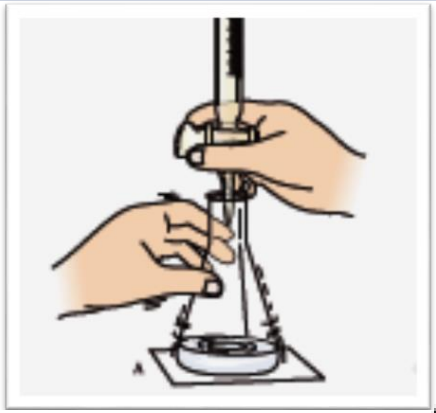
$$2\,C_{17}H_{35}COONa + MgCl_2 \longrightarrow (C_{17}H_{35}COO)_2Mg\downarrow + 2\,NaCl$$

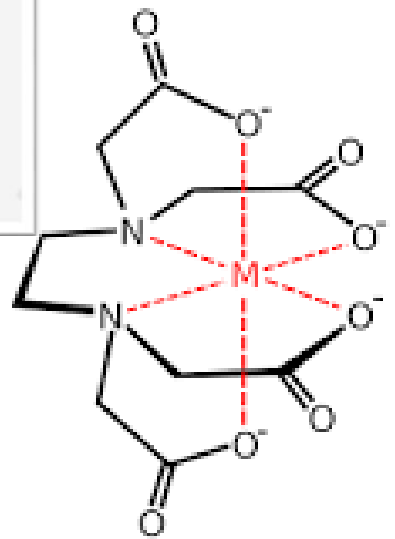
$$2\,C_{17}H_{35}COONa + CaSO_4 \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow + Na_2SO_4$$

Estimation of hardness of water: EDTA method

- Water hardness can be readily determined by complexometric titration with the chelating agent EDTA
- EDTA is *ethylene diamine tetraacetic acid*.
- EDTA solution is colorless

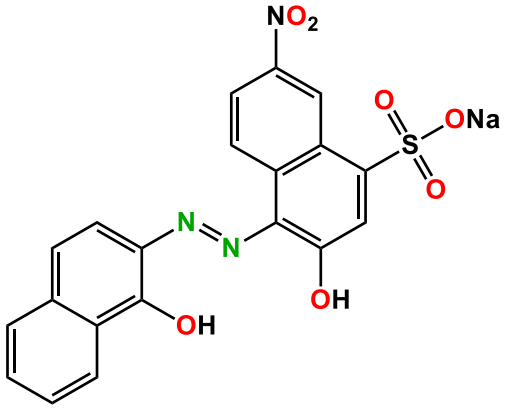






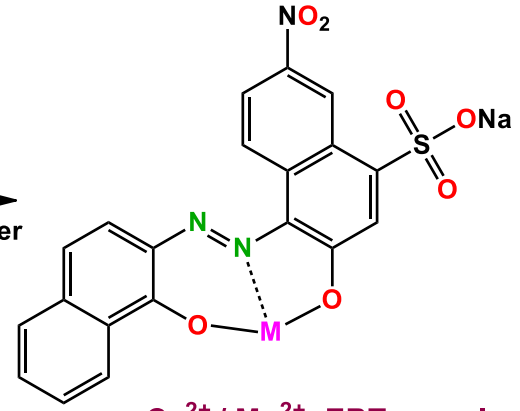
- Corresponding disodium salt is used for the hardness estimation, as this slat forms very strong and stable complex with Ca^{2+} and Mg^{2+}.

- Initially, Ca^{2+} and Mg^{2+} or the are treated with Eriochrome black T (EBT) indicator using ammonia buffer (to maintain pH between 9-10) to get an unstable Ca^{2+}/Mg^{2+} complex which imparts wine-red colour to the solution



EBT

M^{2+}
M = Ca, Mg
Ammonia buffer



Ca^{2+} / Mg^{2+}- EBT complex