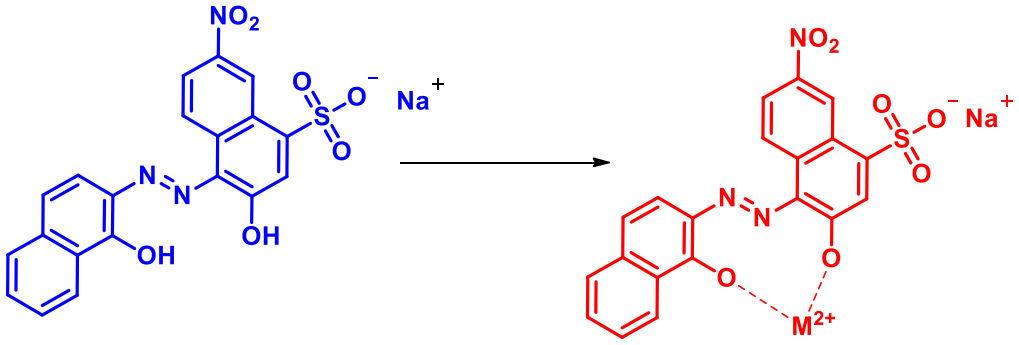
EXPERIMENT 3: Estimation of the hardness of water

Objective: To determine the total, permanent and temporary hardness of given water sample by complexometric titration using EDTA solution.

Principle: The presence of Ca^{2+} *and* Mg^{2+} ions (among many others e.g., iron, manganese, aluminium etc.) in water introduces hardness. Hard water consumes a lot of soap or detergent before it starts foaming. If hard water is used in a boiler, it results in excessive scaling and sludging which results in loss of efficiency and safety.

If Ca^{2+} *and* Mg^{2+} ions are present as bicarbonate salts, they can be easily removed by boiling as boiling decomposes bicarbonates to insoluble carbonate salts ($CaCO_3$ *and* $MgCO_3$). It is said to be temporary hardness. When Ca^{2+} *and* Mg^{2+} ions are present in any other form (e.g., chlorides, nitrates, sulphates etc.) it is called permanent hardness of water as this type of hardness cannot be removed easily.

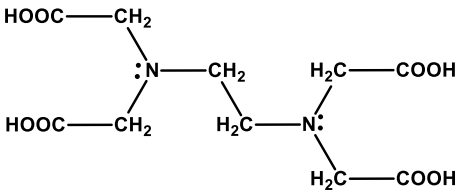
To determine the hardness of water, we perform a complexometric titration. Eriochrome Black-T (EBT) is used as an indicator and the titration is performed with ethylene diamine tetraacetic acid (EDTA) solution.



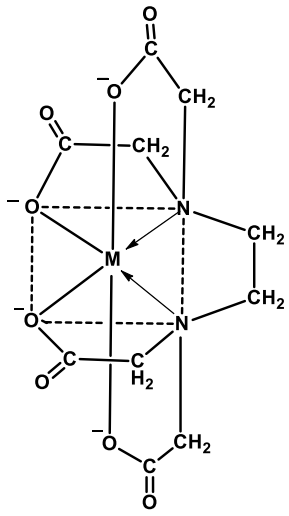
Free EBT (blue)

EBT-Metal complex (red)

When EBT is added to hard water, the indicator molecule forms a semi-stable complex with the hardness producing metal ions. The complex is wine-red in colour. When EDTA is added to this mixture, EDTA forms a colourless stable complex with the metal atoms and as a result, the indicator becomes free. Hence the end point of this titration identified by the colour change of wine red to blue.



Free EDTA (colourless)



Metal-EDTA complex (colourless)

EDTA is a chelating agent which behaves as a hexadentate ligand in the basic medium. In basic medium, the tetra-basic form of EDTA forms complexes with virtually all metal ions. Each of the acidic oxygen and each of the amine nitrogen can donate one pair of electrons to form a one-to-one complex with the metal ions.

The effectiveness of the complexing agent EDTA is strongly affected by pH. The electron pair of the carboxylic acid groups of EDTA are only available to the metal ion when the acid is dissociated. At low pH EDTA will be un-dissociated will not be an effective complexing agent. Additionally, many metal ions form complexes with hydroxide ions. Hydroxide ions compete with the chelating agent for coordination sites in the metal ion. Therefore, the effectiveness of the complexing agent will also be reduced at high pH.

Therefore, suitable buffer solution is added to keep pH of the solution nearly constant at pH = 10. A mixture of NH_4Cl *and* NH_4OH is used as a buffer solution.

Procedure:

Total Hardness:

1. Clean the burette and fill with standard EDTA solution and note the initial reading.
2. Pipette out 10 ml of hard water into a clean conical flask.
3. Add 5 ml of buffer solution (pH=10) and 2-3 drops of EBT indicator.
4. Titrate it against standard EDTA solution.
5. At the end point color changes from wine red to clear blue.
6. Note the burette reading and repeat it two more times to get the reading corresponding to the total hardness.

Permanent and temporary hardness:

7. Take 250 ml hard water in to 500 ml beaker and boil it gently for an hour, filter the solution in to a 250 ml measuring flask and make the solution up to 250 ml with distilled water and shake it thoroughly (if boiled and filtered water is supplied, skip this step).
8. Repeat steps 1-5 as mentioned above. Replace Step-3 with the boiled and filtered water sample to get the permanent hardness.
9. Temporary hardness can be obtained by subtracting the value of permanent hardness from the value of total hardness.

Observations:

Estimation of total hardness:

Sr. No.	Volume of hard water (ml)	Burette reading		Volume of EDTA consumed (ml)	Average burette reading (ml)
		Initial	Final		
1					
2					
3					

$$Total\ hardness = \frac{BR \times molarity\ of\ EDTA \times MW\ of\ CaCO_3(100) \times 1000}{Volume\ of\ hard\ water}$$

Estimation of permanent hardness:

Sr. No.	Volume of boiled hard water (ml)	Burette reading		Volume of EDTA consumed (ml)	Average burette reading (ml)
		Initial	Final		
1					
2					
3					

$$Total\ hardness = \frac{BR \times molarity\ of\ EDTA \times MW\ of\ CaCO_3(100) \times 1000}{Volume\ of\ hard\ water}$$

Result: The hardness of given water sample is

- Total hardness = _____ ppm
- Permanent hardness = _____ ppm
- Temporary hardness = _____ ppm