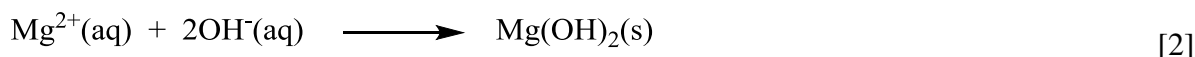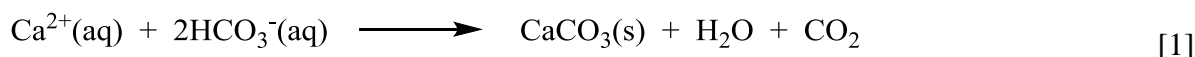Objective: To determine hardness of water in two differently sourced water samples in ppm by preparing a standard solution of $MgSO_4.7H_2O$ and using approx. 1/100 M EDTA solution as an intermediate solution. [Molecular weight of $MgSO_4.7H_2O$ = 246.47 gmol^{-1}, Molecular weight of $CaCO_3$ = 100 gmol^{-1}]

Reagents: $MgSO_4.7H_2O$ salt, approx. 1/100 M EDTA solution, EBT indicator, NH_3-NH_4Cl buffer solution, water samples from different sources.

Apparatus: Weighing balance, volumetric flask, pipette, burette, conical flask, beaker, measuring cylinder.

Theory: The operational definition of water hardness is the total concentration of cations in a sample capable of forming insoluble complexes with soap. Although most divalent and trivalent metal ions contribute to hardness, the most important are Ca^{2+} and Mg^{2+}. For example, when hard water is heated, Ca^{2+} ions react with bicarbonate (HCO_3^-) ions to form insoluble calcium carbonate ($CaCO_3$) (Eq. 1). This precipitate, known as scale, coats the vessels in which the water is heated, producing the mineral deposits. Eq. 2 presents magnesium hardness.

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \longrightarrow CaCO_3(s) + H_2O + CO_2 \qquad [1]$$

$$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s) \qquad [2]$$

Hardness is determined by titrating with EDTA (ethylenediaminetetraacetic acid) at a buffered pH of 10. EDTA in its fully deprotonated form, is a Lewis acid with six binding sites— four negatively charged carboxylate groups and two tertiary amino groups—that can donate six pairs of electrons to a metal ion. The resulting metal–ligand complex, in which EDTA forms a cage-like structure around the metal ion, is very stable, largely because of the entropic effect. The actual number of coordination sites depends on the size of the metal ion; however, all metal–EDTA complexes have a 1:1 stoichiometry. For simplicity, EDTA is assigned the formula H_4Y; the disodium salt is therefore Na_2H_2Y and the reaction with cations (M^{n+}) may be written as

$$M^{n+} + H_2Y^{2-} \rightleftharpoons MY^{(n-4)+} + 2H^+ \qquad [3]$$
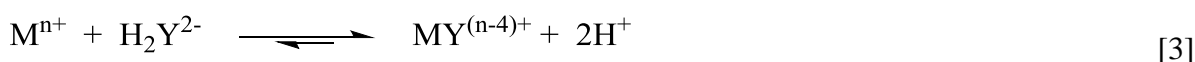
Although the reaction 1 is an equilibrium, it lies very far to right and shows that the dissociation of the complex will be governed by the pH of the solution. The stability of the complex is characterized by the stability constant K,
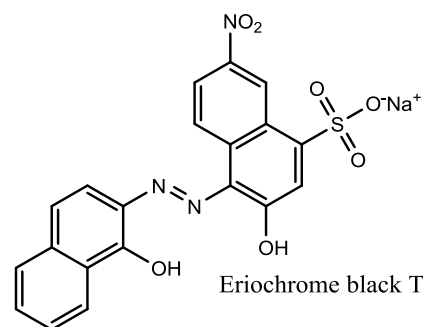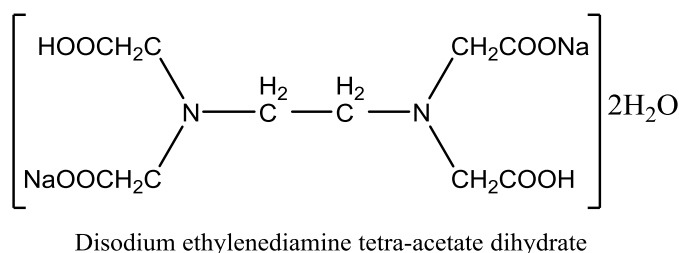
$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$$

$$K = [MY^{(n-4)+}] / [M^{n+}][Y^{4-}] \tag{4}$$

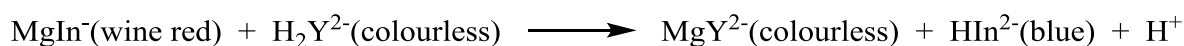The stability constant of metal-EDTA complexes for Ca^{2+} and Mg^{2+} as logK are 10.7 and 8.7 in a solution of ionic strength 0.1 at 20°C, respectively. In eq. 4 only the fully ionized form of EDTA has been considered, but at low pH values the species HY^{3-}, H_2Y^{2-}, H_3Y^-, H_4Y may well be present; in such cases conditional stability constant is used.

Ethylenediamine tetra-acetic acid
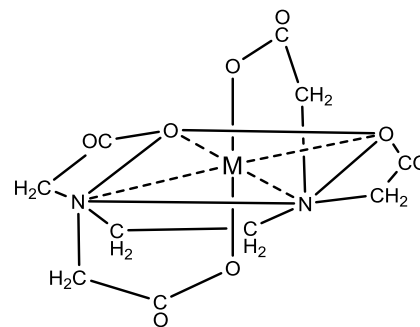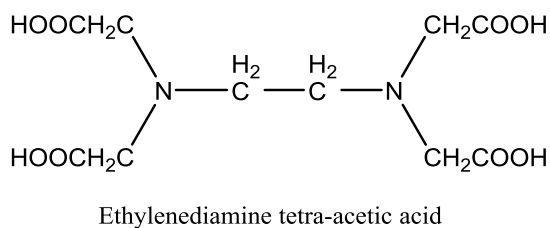
Steric configuration of a metal-EDTA complex
(Martell et. al. J.Chem.Educ. 29 (1952), 270)

Disodium ethylenediamine tetra-acetate dihydrate

Eriochrome black T

Although the metal-EDTA complexation reaction is stoichiometric, proceeds rapidly and goes to completion, it does not allow for easy endpoint detection. For the detection of endpoint, a metallochromic indicator such as Eriochrome Black T (EBT) is used. It being a triprotic organic acid contains three ionizable protons (H_3In) and is blue in colour in its free form i.e. not bound to any metal. When a small amount of indicator, H_3In, is added to the titrand's solution, it forms stable wine red complex with part of the Mg^{2+} ions present in solution. As soon as all the free metal ion (Ca^{2+} and Mg^{2+}) is titrated, the EDTA displaces the indicator form the Mg-EBT complex, causing a change in colour from red to blue.

$MgIn^-$(wine red) $+$ H_2Y^{2-}(colourless) $\longrightarrow$ MgY^{2-}(colourless) $+$ HIn^{2-}(blue) $+$ H^+

The metal-indicator complex must be less stable than the metal-EDTA complex, or else the EDTA will not displace it from the metal. On the other hand, it must not be too weak, or the EDTA will star replacing it at the beginning of the titration, and a diffuse endpoint will result.

Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate in parts per million (ppm). Once the concentration in ppm is determined, it can be related to the hardness scale.

Concentration (ppm)	Hardness Rating
< 61	Soft
$61 - 120$	Moderately hard
121-180	Hard
> 180	Very hard

Procedure:

1) 0.246 g of $MgSO_4.7H_2O$ needs to be weighted because the strength of the EDTA solution provided was approx. 1/100 M. The exact weight of the $MgSO_4.7H_2O$ was noted down and the strength of the standard solution of $MgSO_4.7H_2O$ was calculated.

2) Weighted $MgSO_4.7H_2O$ was transferred quantitatively into a 100 mL volumetric flask with the help of a funnel and was filled up to the mark with distilled water.

3) 10 mL of standard $MgSO_4.7H_2O$ solution was transferred in a conical flask with pipette followed by addition of 2 mL NH_3-NH_4Cl buffer solution and one 1 drop of EBT indicator. The colour of the solution turned wine red. The mixture was titrated against the supplied ~1/100 M EDTA solution (taken in the burette) until the wine red colour turned to blue. The titration was repeated as long as the two concordant readings were observed.

4) 50 mL tap water was taken in a conical flask with measuring cylinder followed by addition of 2 mL NH_3-NH_4Cl buffer solution and one drop of EBT indicator. The colour became wine red. The titrand was titrated against the standardized EDTA solution (taken in the burette) until the wine red colour turned to blue. The titration was repeated as long as the two concordant readings were observed.

5) Step 4 was repeated with water taken from other sources.

Note:

1) The colour change of Eriochrome black T at the endpoint was rather subtle. It was not an abrupt change from deep red to a dark blue; but rather it was from a light red (or pink) to a pale blue.

Observation and Calculation:

Laboratory temperature = AA.A °C

Preparation of stock solution (100 mL) of $MgSO_4.7H_2O$
Calculation for the gram of $MgSO_4.7H_2O$ required to make 100 mL of 1/100 M solution of $MgSO_4.7H_2O$,

$$\frac{1}{50}M = \frac{\frac{w\ g}{246.47\ g\ mol^{-1}}}{0.100\ mL} \times \frac{1000\ mL}{1L}\ , w = 0.246\ g$$

Actual weight of the $MgSO_4.7H_2O$ salt transferred = B.BBB g

So, strength of 100 mL stock solution of $MgSO_4$ (M_{Mg}) $= \frac{\frac{B.BBB\ g}{246.47\ g\ mol^{-1}}}{100\ mL} \times \frac{1000\ mL}{1L} = C.CCC\ M$

Table 1: Standardization of the supplied EDTA solution with 10 mL $MgSO_4.7H_2O$ solution.

No. of Observations	Initial burette readings of EDTA (mL)	Final burette readings of EDTA (mL)	Volume of EDTA consumed (mL)	Concordant volume of EDTA (mL)

At equivalence point, 1 mole EDTA = 1 mole Mg^{2+}

$M_{EDTA} \times V_{EDTA} = M_{Mg} \times V_{Mg}$

So, strength of the supplied EDTA solution $(M_{EDTA}) = \dfrac{M_{Mg} \, M \times V_{Mg} \, mL}{V_{EDTA} \, mL} = D.DDD \, M$

Table 2: Titration of the 50 mL tap water against standardized EDTA solution.

No. of Observations	Initial burette readings of EDTA (mL)	Final burette readings of EDTA (mL)	Volume of EDTA consumed (mL)	Concordant volume of EDTA (mL)

At equivalence point, 1 mole EDTA = 1 mole Metal ions

$M_{EDTA} \times V_{EDTA} = M_{tap \, water} \times V_{tap \, water}$

So, strength of the tap water $(M_{tap \, water}) = \dfrac{M_{EDTA} \, M \times V_{EDTA} \, mL}{V_{tap \, water} \, mL} = E.EEE \, M$

Therefore, the total hardness of tap water =

$\dfrac{M_{EDTA} \, mol \, L^{-1} \times V_{EDTA} \, mL}{V_{tap \, water} \, mL} \times$ molecular weight of $CaCO_3 \, g \, mol^{-1} \times \dfrac{1000 \, mg}{1 \, g} = F.F \, ppm$

NB. If we approximate the density of an aqueous solution as 1.00 g/mL then $ppm = \dfrac{mg}{L} = \dfrac{\mu g}{g}$

Table 3: Titration of the 50 mL water (from water purifier) against standardized EDTA solution.

No. of Observations	Initial burette readings of EDTA (mL)	Final burette readings of EDTA (mL)	Volume of EDTA consumed (mL)	Concordant volume of EDTA (mL)

At equivalence point, moles EDTA = moles Metal (Ca^{2+} and Mg^{2+})

$M_{EDTA} \times V_{EDTA} = M_{filtered \, water} \times V_{filtered \, water}$

So, strength of the filtered water ($M_{\text{filtered water}}$) $= \frac{M_{\text{EDTA}}\,M \times V_{\text{EDTA}}\,mL}{V_{\text{filtered water}}\,mL} = G.GGG\,M$

Therefore, the total hardness of filtered water $=$

$\frac{M_{\text{EDTA}}\,mol\,L^{-1} \times V_{\text{EDTA}}\,mL}{V_{\text{filtered water}}\,mL} \times$ molecular weight of $CaCO_3\,g\,mol^{-1} \times \frac{1000\,mg}{1\,g} = H.H\,ppm$

NB. If we approximate the density of an aqueous solution as 1.00 g/mL then ppm $= \frac{mg}{L} = \frac{\mu g}{g}$

Result: The total hardness of the tap water, and filtered water was found to be F.F, and G.G ppm, respectively.