Objective: To determine amount of ZnO and Zn^{2+} in gL^{-1} in a supplied solution by preparing a standard solution of ZnO and using approx. 1/50 M EDTA solution as an intermediate solution. [Molecular mass of Zn^{2+} and ZnO are 65.38 and 81.38 $gmol^{-1}$, respectively]

Reagents: ZnO, approx.1/50 M EDTA solution, EBT indicator, NH_3-NH_4Cl buffer solution.
Apparatus: Volumetric flask (100 mL), pipette (10 mL), burette (25 mL), conical flask.

Theory: Many cations will form complexes in solution with a variety of ligands that have a pair of unshared electrons (e.g., N, O, S atoms in a molecule) capable of satisfying the coordination number of the metal e.g., heme molecule in blood holds the iron atom tightly because the nitrogen atoms of the heme form strong ligand. Such complexation reactions can serve as a means of determining ion concentration.

EDTA (ethylenediaminetetraacetic acid; Figure 1) is one such polydentate ligand 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 (Figure 2), 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

$$M^{n+} + H_2Y^{2-} \rightleftharpoons MY^{(n-4)+} + 2H^+ \qquad [1]$$

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,

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$$

$$K = [MY^{(n-4)+}] / [M^{n+}][Y^{4-}] \qquad [2]$$

The stability constant (logK) are of the order of 10^8 - 10^{25} depending on the metal and other conditions (LogK = 16.7 for Zn–EDTA complex in a solution of ionic strength 0.1 at 20°C). In eq. 2 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.

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, Figure 3) 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 (M^{2+}). 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 zinc ions present in solution. As soon as the entire free zinc is titrated, the EDTA displaces the indicator from the zinc-EBT complex, causing a change in colour from red to blue.

$$MIn^{-}(\text{wine red}) + H_2Y^{2-}(\text{colourless}) \longrightarrow MY^{2-}(\text{colourless}) + HIn^{2-}(\text{blue}) + H^{+} \quad [3]$$

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.

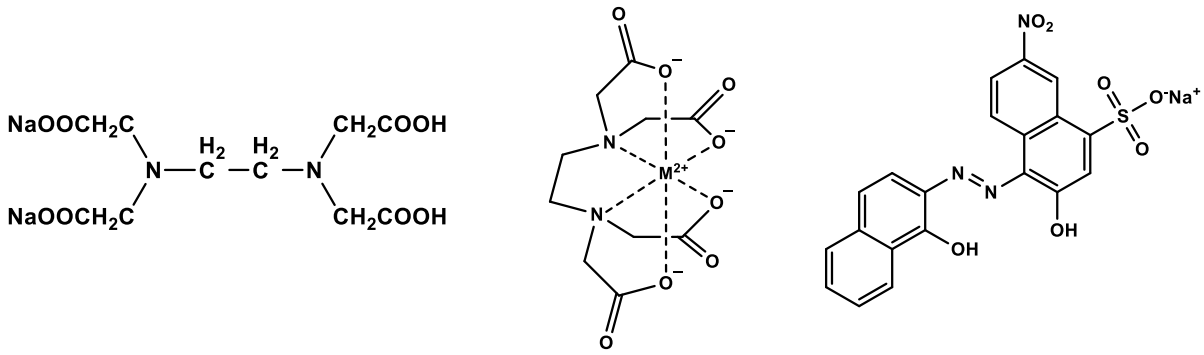

Figure 1. Structures of (a) disodium dihydrogen salt of ethylenediaminetetraacetic acid (EDTA), (b) in a six-coordinate metal–EDTA complex with a divalent metal ion, and (c) Eriochrome black T (EBT).

Procedure:

1) 0.163 g of ZnO was weighted because the strength of the EDTA solution provided was approx. 1/50 M.
2) Weighted ZnO was transferred quantitatively into a 100 mL volumetric flask with the help of a funnel. About 25 mL deionized water was added in the flask followed by dropwise addition of concentrated HCl solution with periodic stirring until the sample was completely dissolved. Finally, 2 drops in excess was added and the volumetric flask was filled up to the mark with distilled water.

   $$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

3) 10 mL of standard ZnO 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 ~1/50 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) 10 mL of the supplied solution was pipetted out in a conical flask followed by addition of 2 mL NH_3-NH_4Cl buffer solution and 1 drop of EBT indicator. The colour of the

solution became wine red. The mixture was titrated against the standardized EDTA solution (taken in the burette) until the wine red colour became blue. The titration was repeated as long as the two concordant readings were observed.

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

Calculation for the gram of ZnO required to make 100mL of 1/50 M solution of ZnO,

$$\frac{1}{50}\text{M} = \frac{\frac{\text{w g}}{81.38\ \text{g mol}^{-1}}}{0.100\ \text{L}}\ ,\text{w} = 0.163\ \text{g}$$

Weight of the ZnO transferred = B.BBB g

So, strength of 100 mL ZnO solution (M_{Zn}) = $\frac{\frac{\text{B.BBB}\ \cancel{g}}{81.38\ \cancel{g}\ \text{mol}^{-1}}}{0.100\ \text{L}}$ = C.CCC M

Table 1: Standardization of the supplied EDTA solution.

No. of observations	Volume of ZnO taken (mL)	Initial burette readings of EDTA (mL)	Final burette readings of EDTA (mL)	Volume of EDTA consumed (mL)	Concordant volume of EDTA (mL)
	10				
	10				
	10				

At equivalence point, moles EDTA = moles Zn^{2+}

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

So, strength of the supplied EDTA solution (M_{EDTA}) = $\frac{M_{Zn}\ \text{M} \times V_{Zn}\ \cancel{mL}}{V_{EDTA}\ \cancel{mL}}$ = D.DDD M

Table 2: Titration of the 10 mL of supplied solution of unknown concentration of zinc.

No. of Observations	Volume of ZnO solution taken (mL)	Initial burette readings of EDTA (mL)	Final burette readings of EDTA (mL)	Volume of EDTA consumed (mL)	Concordant volume of EDTA (mL)
	10				
	10				
	10				

At equivalence point, moles EDTA = moles Zn^{2+},

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

So, strength of the supplied solution ($M_{supplied}$) = $\frac{M_{EDTA}\ \text{M} \times V_{EDTA}\ \cancel{mL}}{V_{supplied}\ \cancel{mL}}$ = E.EEE M

Therefore, the amount of ZnO in the supplied solution =

$$\text{E. EE } \cancel{\text{mol}}\text{L}^{-1} \times \text{molar mass of ZnO g}\cancel{\text{mol}}^{-1} = \text{F. FFF gL}^{-1}$$

Therefore, the amount of Zn^{2+} in the supplied solution =

$$\text{E. EE } \cancel{\text{mol}}\text{L}^{-1} \times \text{molar mass of } Zn^{2+}\ \text{g}\cancel{\text{mol}}^{-1} = \text{G. GGG gL}^{-1}$$

Result: The amount of ZnO and Zn^{2+} in the supplied solution was found to be F.FFF and G.GGG gL^{-1}, respectively.