

**Objective:** To determine amount of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in  $\text{g L}^{-1}$  in a supplied solution by using 1/50 M EDTA solution. [Molar mass of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 246.47 \text{ g mol}^{-1}$ ]

**Reagents:** 1/50 M EDTA solution, EBT indicator,  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution.

**Apparatus:** 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  $\text{H}_4\text{Y}$ ; the disodium salt is therefore  $\text{Na}_2\text{H}_2\text{Y}$  and the reaction with cations ( $\text{M}^{n+}$ ) may be written as



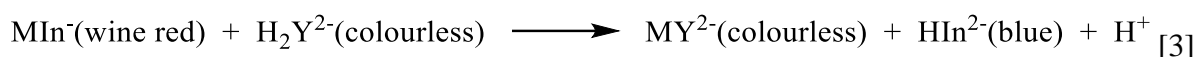
Although the reaction 1 is an equilibrium, it lies very far to right and shows that the dissociation of the complex will be governed by the pH of the solution. The stability of the complex is characterized by the stability constant K,



The stability constant ( $\log K$ ) are of the order of  $10^8 - 10^{25}$  depending on the metal and other conditions ( $\text{Log}K = 8.7$  for Mg–EDTA complex in a solution of ionic strength 0.1 at  $20^\circ\text{C}$ ). In eq. 2 only the fully ionized form of EDTA has been considered, but at low pH values the species  $\text{HY}^{3-}$ ,  $\text{H}_2\text{Y}^{2-}$ ,  $\text{H}_3\text{Y}^-$ ,  $\text{H}_4\text{Y}$  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  $Mg^{2+}$  ions present in solution. As soon as the entire free magnesium is titrated, the EDTA displaces the indicator from the  $Mg$ -EBT complex, causing a change in colour from red to blue.



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 start replacing it at the beginning of the titration, and a diffuse endpoint will result.

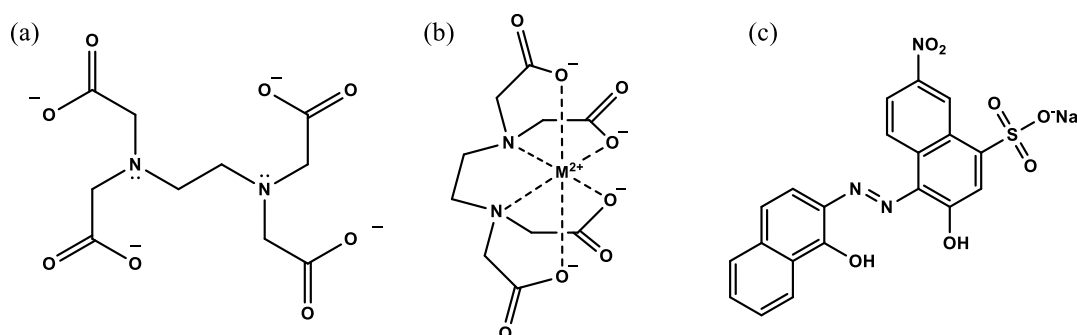


Figure 1. Structures of (a) EDTA, in its fully deprotonated form, (b) in a six-coordinate metal-EDTA complex with a divalent metal ion, and (c) Eriochrome black T.

### Procedure:

- 1) Take 10 mL of the supplied solution of unknown concentration of magnesium in a conical flask with pipette and add 2 mL  $NH_3-NH_4Cl$  buffer solution and one pinch (or 2-3 drops) of EBT indicator and mix thoroughly. The colour of the solution will be wine red.
- 2) Titrate the titrand with the supplied 1/50 M EDTA solution (taken in the burette) until the wine red colour turns to blue. Repeat the titration as long as the two concordant readings are observed.

### Note:

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

### Observation and Calculation:

Laboratory temperature = AA.A °C

**Table 1:** Titration of the 10 mL supplied solution of unknown concentration of magnesium.

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  $\text{Mg}^{2+}$ ,

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

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

Therefore, the amount of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in the supplied solution =

$$\text{B.BB molL}^{-1} \times \text{molar mass of } \text{MgSO}_4 \cdot 7\text{H}_2\text{O gmol}^{-1} = \text{C.CC gL}^{-1}$$

**Result:** The amount of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in the supplied solution was found to be C.CC  $\text{gL}^{-1}$ .

**Objective:** To determine amount of  $\text{Mg}^{2+}$  in  $\text{gL}^{-1}$  in a supplied solution by preparing a known strength solution of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and using approx. 1/50 M EDTA solution as an intermediate solution. [Molecular mass of  $\text{Mg}^{2+}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  are 24.305 and 246.47  $\text{gmol}^{-1}$ , respectively]

**Reagents:**  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , approx. 1/50 M EDTA solution, EBT indicator,  $\text{NH}_3\text{-NH}_4\text{Cl}$  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  $\text{H}_4\text{Y}$ ; the disodium salt is therefore  $\text{Na}_2\text{H}_2\text{Y}$  and the reaction with cations ( $\text{M}^{n+}$ ) may be written as



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The stability constant ( $\log K$ ) are of the order of  $10^8 - 10^{25}$  depending on the metal and other conditions  $\log K = 8.7$  for Mg–EDTA complex in a solution of ionic strength 0.1 at  $20^\circ\text{C}$ ). In eq. 2 only the fully ionized form of EDTA has been considered, but at low pH values the species  $\text{HY}^{3-}$ ,  $\text{H}_2\text{Y}^{2-}$ ,  $\text{H}_3\text{Y}^-$ ,  $\text{H}_4\text{Y}$  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. 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 the entire free magnesium ions is titrated, the EDTA displaces the indicator from the Mg-EBT complex, causing a change in colour from red to blue.



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 start replacing it at the beginning of the titration, and a diffuse endpoint will result.

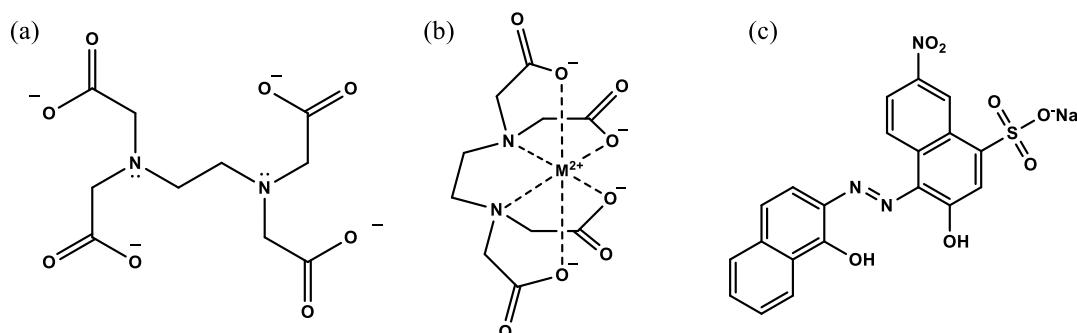


Figure 1. Structures of (a) EDTA, in its fully deprotonated form, (b) in a six-coordinate metal-EDTA complex with a divalent metal ion, and (c) Eriochrome black T.

### Procedure:

- 1) Weigh approx. 0.493 g of  $MgSO_4 \cdot 7H_2O$  salt (note down the exact weight).
- 2) Transfer  $MgSO_4 \cdot 7H_2O$  in 100 mL volumetric flask with the help of a funnel. Dissolve the  $MgSO_4 \cdot 7H_2O$  and then make up the volume of the volumetric flask with distilled water. Because this  $Mg^{2+}$  standard solution is used to standardize the EDTA titrant, it must be prepared very carefully so that you know its exact molarity. Therefore, an exactly known mass of  $MgSO_4 \cdot 7H_2O$  must be weighed out, dissolved completely, and transferred quantitatively into the 100 mL volumetric flask.
- 3) Take 10 mL of this standard  $MgSO_4 \cdot 7H_2O$  solution in a conical flask with pipette and add 2 mL  $NH_3-NH_4Cl$  buffer solution and one pinch (or 2-3 drops) of EBT indicator and mix thoroughly. The colour of the solution will be wine red. Titrate this mixture against the supplied  $\sim 1/50$  M EDTA solution (taken in the burette) until the wine red colour turns to blue. Repeat the titration as long as the two concordant readings are observed.
- 4) Take 10 mL of the supplied solution of unknown concentration of magnesium in a conical flask with pipette and add 2 mL  $NH_3-NH_4Cl$  buffer solution and one pinch (or 2-3 drops) of EBT indicator and mix thoroughly. The colour of the solution will be

wine red. Titrate this mixture against the standardized EDTA solution (taken in the burette) until the wine red colour turns to blue. Repeat the titration as long as the two concordant readings are observed.

**Note:**

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

**Observation and Calculation:**

Laboratory temperature = AA.A °C

Weight of the  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  salt transferred = B.BBB g

So, strength of 100 mL  $\text{MgSO}_4$  solution ( $M_{\text{Mg}}$ ) =  $\frac{\text{B.BBB g}}{0.100 \text{ L}} \times \frac{246.47 \text{ g mol}^{-1}}{1000} = \text{C.CC M}$

**Table 1:** Standardization of the supplied 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  $\text{Mg}^{2+}$

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

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

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

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  $\text{Mg}^{2+}$ ,

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

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

Therefore, the amount of  $\text{Mg}^{2+}$  in the supplied solution =

$$\text{E.EE mol L}^{-1} \times \text{molar mass of } \text{Mg}^{2+} \text{ g mol}^{-1} = \text{F.FF g L}^{-1}$$

**Result:** The amount of  $\text{Mg}^{2+}$  in the supplied solution was found to be  $\text{F.FF g L}^{-1}$ .