UNIT 3

COMPLEXOMETRIC TITRATIONS

Structure

3.1 INTRODUCTION

In the previous experiments you have learnt about the qualitative inorganic analysis and also how to determine nickel and aluminium gravimetrically. In these experiments you will first determine complexometrically the amount of magnesium (or zinc) ions in a solution and then analyse a sample of water for hardness. In previous chemistry lab courses, you performed titrimetric estimations of only single cation present in any substance. In these experiments, you will perform complexometric titrations.

Expected Learning Outcomes

After performing the given experiments you should be able to:

- estimate the amount of magnesium (or zinc) ions complexometrically;
- describe the formation of a complex of metal ions with ethylenediamine tetraacetic acid (EDTA);
- discuss the role of the buffer and the indicator in complexometric titrations;
- define total, temporary and permanent hardness in water; and
- estimate total hardness in water by complexometric titration.

3.2 COMPLEXOMETRIC TITRATIONS

Numerous methods are available for titrimetric determination of various cations by titrations of their salts with certain organic reagents called complexing agents or complexones. Aminocarboxylic acids are tertiary amines that contain carboxylic acid groups form remarkably stable chelates with many metal ions. The most important member of this family of reagents is ethylenediaminetetraacetic acid, abbreviated as EDTA. The structure of EDTA is shown in Fig. 3.1.

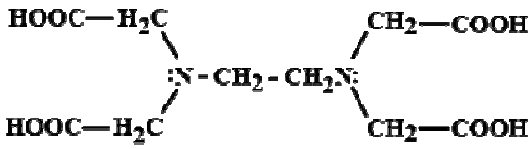

Fig. 3.1 The structure of EDTA

EDTA can form complexes with a number of cations like alkaline earth metals and many non-ferrous metal ions like Cu^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Mn^{2+}, Bi^{3+}, Zr^{4+} and Hf^{4+} etc. EDTA has very wide general application in analysis because of its powerful complexing action and commercial availability. Let us study complexation action of EDTA and the role of metal ion indicators in detail.

Complexation Reaction

A complexation reaction with a metal ion involes the replacement of the one or more of the coordinated solvent molecules by other nucleophilic groups. The groups bound to the central ion are called **ligands**. (Details about ligands you have already learnt in Units 4 and 5 of BCHCT 137). In aqueous solution, the reaction can be represented by the following equation:

$M(H_2O)_n + nL \rightarrow mL_n + nH_2O$

where, L= Ligand, e.g., NH_3, CN^-, EDTA

n = Coordination number of the metal ion and represents the maximum number of monodenate ligands that can be bound to it.

EDTA is only slightly soluble in water. However, its disodium salt is freely soluble in water. The disodium salt of EDTA, Na_2H_2Y, is generally used in EDTA titrations. Dihydrate of the disodium salt is available commercially in a state of high purity under the brand names 'Versen' or 'Trilon-B. It can be used as a primary standard. EDTA, generally, forms 1:1 complexes with metal ions. In reactions, EDTA and its disodium salt are represented as H_4Y and Na_2H_2Y, respectively. Reaction of the disodium salt with a bivalent cation can be written as follows:

$$Na_2H_2Y \rightarrow 2Na^+ + H_2Y^{2-}$$

$$H_2Y^{2-} + M^{2+} \rightarrow MY^{2-} + 2H^+$$

It is apparent from the above equation that there is always a competition in solution between the metal ions and the hydrogen ions in seeking the negative sites on EDTA. The equilibrium condition is determined by the strength of the

bond between the metal ion and the ligand, and the relative concentrations of metal ions versus hydrogen ions. In other words, we can say that the stability of the metal-EDTA complex will be governed by the hydrogen ion concentration or pH of the solution. Minimum pH values for the stability of EDTA complexes of some selected metal ions are listed in Table 3.1.

Table 3.1: Stability with respect to pH of some metal-EDTA complexes of complexes

Minimum pH at which complex is stable	Selected Metals
1 - 3	Zr^{4+}, Hf^{4+}, Th^{4+}, Bi^{3+},
4 - 6	Pb^{2+},Cu^{2+}, Zn^{2+}, Co^{2+}, Sb^{2+}, Mn^{2+}, Fe^{2+}
8 – 10	Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}

You can see from the Table that is general, EDTA complexes with alkaline earth metal ions are stable in alkaline solution, whilst complexes with tri-and tetra-valent metal ions are stable ions are stable in strongly acidic solutions.

EDTA is multidentate ligand as it can donate six pairs of electrons – two pairs from the two nitrogen atoms and four pairs from the four pairs from the four terminal oxygens of the COO^- groups. Such mutlidentate ligands prefer to form complexes having ring type structure. As you know, these complexes are called chelates and such ring forming ligands are called chelating agents.

The structure of a chelate of a divalent metal ions with EDTA is shown in Fig. 3.2.

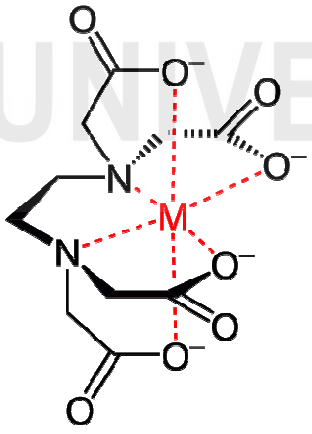

Fig. 3.2: The structure of a chelate of M^{2+} and EDTA

Eriochrome black T has acid-base properties, which are summarised as follows,

$H_2In^- \rightleftharpoons HIn^{2-} \rightleftharpoons In^{3-}$

(red) (blue) (orange)

Since it forms metal complexes with red form only, eriochrome black T is a useful metal-ion indicator only in the pH range 8.1-12.4.

Metal Ion Indicators

We can titrate a metal-ion solution directly with standard EDTA solution. At the end point, the concentration of metal ion decreases abruptly. This is generally determined by change in the colour of a metal ion indicator which responds to change in metal ion concentration.

The end point may also be determined by conductometric, colorimetric, or in some cases, by potentiometric methods. Since in this experiment, we would

be using metal ion indicators, we will briefly discuss them. A metal ion indicator forms a complex with a metal ion.

$$M^{2+} + HIn^{2-} \rightarrow Min^{-} + H^{+}$$

Where HIn^{2-} represents indicators form at a particular pH.

However, metal ion indicator complexes are generally less stable than the metal-EDTA complexes. The indicator releases the metal ions at the end point, and this shows a change in colour.

In the determination of the hardness of water, we use Eriochrome Black T or Solochrome Black as metal ion indicator. Eriochrome Black T is sodium 1-(1-hydroxy-2-napthylazo)-6-nitro-2-napthol-4-sulphonate. Its structure is given in Fig.3.3.

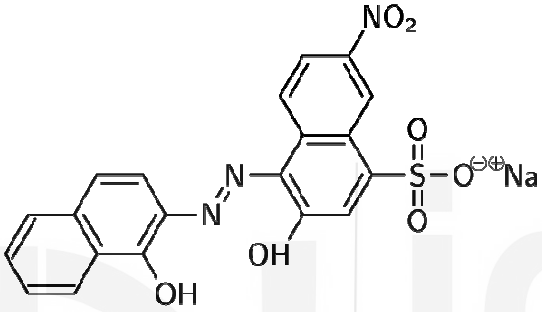

Fig. 3.3: Structure of Eriochrome Black-T

In the presence of metal ions, Eriochrome Black-T forms a wine red complex. The colour changes to blue of the free indicator when the metal ions are fully complexed with EDTA at the end point in a titration.

$$\underset{\text{(wine red)}}{Min^{-}} + H_2Y^{2-} \rightarrow \underset{\text{(colour less)}}{MY^{2-}} + \underset{\text{(blue)}}{HIn^{2-}} + H^{+}$$

Where H_2Y^{2-} represents disodium salt of EDTA and HIn^{2-} represents Erichrome Black-T in a buffer solution of pH 10.

As you know water is one of the most important substances used for life. It is indispensable to every form of life. Apart from being essential for agriculture, water has numerous industrial uses. Water containing salts of heavy metals, mainly calcium and magnesium is called ‘hard water’. Hard water is not desirable for use at home or in industry. Hardness of water precipitates soap, thus reducing its cleansing action. Dissolved solids precipitate on heating and thus clog boiler pipes and deposit on boiler plate when hard water is used for steam making. You many have noticed a similar hard white deposit called “scale” in the kettle used for boiling water for making tea.

It is important to find out the nature of the dissolved impurities present in water and also their concentration to judge whether a given sample of water is suitable for municipal or industrial use. For example, water with high magnesium content are not suitable for drinking.

Next, let us understand how to perform the experiments given in the title of the sections 3.3 and 3.4.

3.3 EXPERIMENT 3a: DETERMINATION OF MAGNESIUM OR ZINC IONS IN THE GIVEN SOLUTION BY COMPLEXOMETRY

In this experiment you would learn about and perform the determination of magnesium or zinc ions in the given solution by complexometry.

3.3.1 Principle

In complexometric determination of either magnesium or zinc ions in the solution, EDTA is used as titrant and Eriochrome Black-T(Solochrome Black) as an indicator. When indicator solution, which is blue is colour, is added to the solution containing magnesium ions, wine red coloured metal ion-indicator complexes of varying stability are formed. Since the magnesium-indicator (or zinc-indicator) complex is wine-red in colour and the free indicator is blue between pH 7 and 11, the colour of the solution changes from wine-red to blue at the end point.

During the complexometric determination of magnesium (or zinc) ions in the solution, the titration is carried out at pH 10 using NH_3-NH_4Cl buffer and the same sort of colour change as for magnesium (or zinc) ions is observed at the end point.

As EDTA is a primary standard, its molarity is known. Then using the molarity equation, $M_1V_1=M_2V_2$, the molarity of magnesium (or zinc) ions can be calculated.

3.3.2 Requirements

You will need the following apparatus, chemicals and solutions for this experiment.

Apparatus		**Chemical**
Beaker (250 cm^3)	1	Ammonia liquor
Burette (50 cm^3)	1	Hydrochloric acid(AR: 6 *M*)
Burette stand with clamp	1	Ammonium chloride
Conical flask (250 cm^3)	1	Disodium salt of EDTA
Funnel	1	Magnesium sulphate
Pipette (20/25 cm^3)	1	(or Zinc sulphate)
Pipette graduated (10 cm^3)	1	Sodium hydroxide
Volumetric flask (250 cm^3)	1	Eriochrome Black-T indicator
Wash bottle	1	Ethanol
Weighing bottle	1	
Analytical / Electronic balance	1	
Wire gauze		

Solutions provided:

1. **Test solution:** It can be prepared by dissolving 1 – 2 g of $MgSO_4$ (or $ZnSO_4$) into minimum quantity of dil. HCl and making up the volume to 250 cm^3 with distilled water.

Solution should be warmed to $50-60^\circ C$, but under no circumstances it should be boiled.

2. **NH_3 – NH_4Cl buffer solution of pH 10:** This can be prepared by dissolving 64 g of NH_4Cl in distilled water, adding 570 cm^3 of ammonia solution (sp.gr.088) and diluting to 1 dm^3 with disttled water.

3. **Eriochrome Black-T indicator (0.5% mass/volume):** 0.50 g indicator is weighted and dissolved in 100 cm^3 ethanol.

4. **0.1 *M* NaOH solution:** Dissolve 4 g of NaOH in 1 dm^3 of distilled water.

3.3.3 Procedures

The experiment procedure involves the following steps:

1) **Preparation of standard 0.1 *M* EDTA solution:** As said earlier, EDTA is available as a dehydrate of its disodium salt $(Na_2H_2Y.2H_2O)$. Take already dried disodium salt of EDTA from your counselor. Take rough mass of a glass weighing bottle, transfer about 9.5 g of the salt to the weighing bottle and weigh accurately. Transfer the salt to a clean and dry volumetric flask of 250 cm^3 capacity through a glass funnel. Find out the accurate mass of the weighing bottle after transferring the salt. The difference between the two masses gives the actual mass of the salt taken. Record these values in your observation note book for calculating the exact concentration of the solution. Now dissolve the salt in deionised or distilled water. Make up to the mark with distilled water and shake thoroughly to make a homogeneous solution.

2) **Titration of the test solution**

In this titration colour change develops a little late, hence, titration should be done slowly. If necessary, add 2-3 drops more of indicator at the final stage of titration. This will provide necessary contrast in colour.

i) Fix a clean burette in a burette stand.

ii) Fill the burette with the EDTA salt solution after rinsing it with this solution and mount the burette on a stand. Note the reading in the burette and record it in the Observation Table 1 under the column ‘Initital reading’.

iii) Pipette out 25 cm^3 of another portion of the test solution containing both magnesium (or zinc) ions, in a 250 cm^3 conical flask. Add 5 cm^3 of buffer solution (pH = 10) and dilute it to 50 cm^3 with distilled water. Ensure that the smell of ammonia persists. If necessary add 2-3 drops of liquor ammonia. Add Eriochrome Black-T indicator (3-4 drops) and warm up to $50-60^\circ C$. Now, titrate with EDTA solution till the wine red colour of the solution changes to bluish. Note the final reading in the burette and record it in the Observation Table I under the column ‘Final reading’’. Repeat the titration 3-4 times till concordant values are obtained. This gives the volume (V_1) of EDTA required for magnesium (or zinc) ions.

3.3.4 Observations

Approximate mass of the weighing bottle = m_1 = …….g

Mass of the weighing bottle + EDTA salt = m_2 = …… g

(before transferring the salt)

Mass of the weighing bottle = m_3 = …….g

(after transferring the salt)

Observation Table I

Titration of the test solution with EDTA using Eriochrome Black-T Indicator

Sl. No.	Volume of test solution in cm^3	Burette reading Initial Final	Volume of EDTA salt, V_1 in cm^3 (Final-Initial)
1.	25		
2.	25		
3.	25		
4	25		

3.3.5 Calculations

Molarity of EDTA salt solution

Mass of EDTA salt transferred $(m) = m_2 - m_3 = $ .....g

Molar mass (M_m) of sodium salt of EDTA $= 372.3$ $gmol^{-1}$

Volume of EDTA salt solution prepared $= 250$ cm^3

Molarity of EDTA salt solution $= M_1 = \frac{m \times 1000}{M_m \times 250} mol\,dm^{-3}$

$$= \frac{m \times 4}{372.31} mol\ dm^{-3}$$

Concentration of Magnesium (or Zinc) ions in solution

Volume of Magnesium (or Zinc) ion solution $= V_2 = 25$ cm^3

Molarity of Magnesium (or Zinc) ion solution $= M_2 = ?$

Volume of EDTA salt solution required for Magnesium (or Zinc) ions $= V_1\,cm^3$ (From Table I)

Molarity of EDTA salt solution $= M_1 = \frac{m \times 4}{372.31}$

Now, using the molarity equation, $M_1V_1 = M_2V_2$, we get,

$$M_2 = \frac{M_1V_1}{V_2}$$

$$= \frac{m \times 4 \times V_1}{372.31 \times 25}\ g\ dm^{-3}$$

Hence, concentration of Magnesium (or Zinc) ions = molarity × molar mass of Magnesium (or Zinc) ions

$$= \frac{m \times 4 \times V_1}{372.31 \times 25} \text{ mol dm}^{-3} \times \left(40.08 \text{ g mol}^{-1}\right)$$

$$= \frac{m \times 4 \times V_1 \times 40.08}{372.31 \times 25} \text{ g dm}^{-3}$$

3.3.6 Result

You can report result in the following form:

Magnesium content in the solution = …….. g dm^{-3}

or

Zinc content in the solution = …… g dm^{-3}

3.4 EXPERIMENT 3b: DETERMINATION OF TOTAL HARDNESS OF WATER BY COMPLEXOMETRY

Determination of the hardness of water is necessary for determining the quality of water for household and industrial uses. As we have stated earlier that hardness of water is due to the presence of salts of calcium and magnesium in it. When we add simple soap (not a synthetic detergent) to hard water, an insoluble substance commonly known as "soap scum" is produced. Therefore, we also sometimes define hardness as the soap consuming capacity of water. There are two types of hardness:

Hardness is expressed in ppm of $CaCO_3$ although in Experiment 9 the hardness may be due to magnesium or other cations.

It is usual to know $CaCO_3$ equivalent to some common salts causing hardness. 100 parts of $CaCO_3$ are equivalent to:

162 parts $Ca(HCO_3)_2$

111 parts $CaCl_2$

95 parts $HgCl_2$

136 parts $CaSO_4$

120 parts $MgSO_4$

i) **Temporary hardness:** This is due to bicarbonates of calcium and magnesium. Temporary hardness gets removed on boiling water, when soluble bicarbonates decompose to give insoluble carbonates, however, $MgCO_3$ is partially soluble.

$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$

$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2$

(partially soluble)

ii) **Permanent hardness:** It is so called because it does not get removed on boiling. Permanent hardness is due to chlorides and sulphates of calcium and magnesium. Total hardness is temporary and permanent hardness together.

Total hardness = Temporary hardness + Permanent hardness

It is necessary to know temporary and permanent hardness separately to devise a suitable treatment for water softening. Hardness of water is expressed in terms of mg of $CaCO_3$ per dm^3 of water or as ppm.

Hardness of a water sample can be determined by titration with soap solution or by complexometric titration with EDTA (Ethylenediamine

tetraacetic acid) or by conductometric methods. EDTA method is accurate, simple and fast. We shall first discuss the principle of complexometric titrations.

3.4.1 Principle

In complexometric titration we use, EDTA as complexing reagent, forms soluble complexes with metal ions like Ca^{++} and Mg^{++}. End point in this titration is detected by colour change of Eriochrome Black T indicator. As the stability of the complex and colour change of the indicator are sensitive to pH changes, the solution to be titrated must be well buffered by ammonium hydroxide-ammonium chloride buffer solution of pH 10.

In the determination of the total hardness by EDTA titration, since Ca/Mg-EDTA complexes are stabled at pH 8 -10, the pH of the solution during the titration must be maintained at pH 10 by adding a suitable buffer like NH_4Cl/OH solution. In this titration, calcium ions do not form a sufficiently strong complex with Eriochrome Black-T, Mg-EDTA complex is added to the titration flask, if the sample either does not contain sufficient magnesium ions or does not contain these ions at all to provide a sharp colour change at the end point.

A white crystalline precipitate of calcium carbonate may appear after the buffer is added, if the water is very hard. This should dissolve during the course of the titration. The precipitate may dissolve slowly, however, it must dissolve before the end point is reached.

In some cases, where the alkalinity of the water sample is very high, it is recommended to boil a known volume of the water sample with a few drops of HCl to remove CO_2. Cool, add a few drops of methyl red and neutralise with NaOH solution till the red colour is discharged.

Chemical changes during titration may be written as:

$$Ca^{2+} + H_2Y^{2-} \longrightarrow CaY^{2-} + 2H^+ \quad \ldots(3.1)$$

$$Mg^{2+} + H_2Y^{2-} \longrightarrow MgY^{2-} + 2H^+ \quad \ldots(3.2)$$

$$Mg^{2+} + HIn^{2-} \longrightarrow MgIn^- + H^+$$

$$MgIn^- + H_2Y^{2--} \longrightarrow MgY^{2-} + HIn^{2-} + H^+ \text{ (at the end point)}$$

Wine Colourless Colourless Blue red

From the Eq. 3.1 and 3.2, it is clear that one mole of the disodium salt of EDTA reacts with one mole of Ca^{2+}/Mg^{2+} ions. Therefore, the molarities are related as per the following equation.

$$\frac{M_1V_1}{M_2V_2} = \frac{1}{1} \quad \ldots(3.3)$$

$$M_1V_1 = M_2V_2$$

Where M_1 and M_2 are the molarities of EDTA salt and metal-ion solutions, respectively. V_1 and V_2 are the volumes of EDTA salt and metal-ion solutions, respectively.

In the next section we are going to give you experimental details for determination of the total hardness of water and the method of calculation. Before that try the following SAQs.

SAQ 1

Why is water sample buffered at pH 10 before titration with EDTA?

SAQ 2

Explain why Mg^{2+} ion may be added when water sample is titrated with EDTA using Eriochrome Black-T as indicator.

3.4.2 Requirements

You will need the following apparatus, chemicals and solutions for this experiment.

Apparatus		**Chemical**
Beaker (250 cm^3)	1	Ammonia liquor
Burette (50 cm^3)	1	Ammonium chloride
Burette stand with clamp	1	Disodium salt of EDTA
Conical flask (250 cm^3)	2	Eriochrome Black-T indicator
Funnel	1	Ethanol
Pipette (20/25 cm^3)	1	Magnesium chloride
Pipette graduated (10 cm^3)	1	
Volumetric flask (250 cm^3)	1	
Wash bottle	1	
Weighing bottle	1	
Analytical / Electronic balance	1	
Wire gauze		

Solutions Provided

Water sample

NH_4OH-NH_4Cl Buffer solution, pH 10

It is prepared by dissolving 64 g of NH_4Cl in distilled water, adding 570 cm^3 of ammonia solution (sp.gr. 0.88) and diluting to 1 dm^3 with distilled water.

Eriochrome black T (0.5% mass/volume)

0.50 g indicator is weighed and dissolved in 100 cm^3 ethanol.

Mg-EDTA complex (0.005 *M*) solution

It is prepared by adding stoichiometric amounts of 0.01 *M* disodium salt of EDTA and 0.01 *M* $MgCl_2$. A portion of Mg-EDTA solution, when treated with a few drops of Eriochrome Black-T at pH 10 should change to a wine red colour, which should change to pure blue on the addition of one drop of 0.01 *M* EDTA solution and wine red on addition of a single drop of 0.01 *M* $MgCl_2$ solution.

3.4.3 Procedure

The experimental procedure involves the following steps:

1) Preparation of standard 0.01 *M* EDTA solution: As said earlier, EDTA is available as its disodium dihydrate salt ($Na_2H_2Y.2H_2O$). First take already dried disodium salt of EDTA from the counsellor. Then take rough mass of a glass weighing bottle and transfer about 0.95 g of the salt to the weighing bottle and weigh accurately. Transfer the salt to a clean and dry volumetric flask of 250 cm^3 capacity through a glass funnel. Find out the accurate mass of the weighing bottle after transferring the salt. The difference between two masses gives the actual amount of EDTA salt taken. Record these values in your observation note book to calculate exact concentration according of the mass of the EDTA salt taken. Now dissolve the salt in deionised or distilled water. Make up to the mark with distilled water and shake thoroughly to make a homogeneous solution.

2) Titration of water sample

   i) Fill the burette with the EDTA salt solution after rinsing it with this solution and mount the burette on a stand, also insert a parallex card. Note the reading in the burette and record it in the observation Table I under the 'Initial reading' column.

   ii) Pipette out 60 cm^3 or the water sample using a 20 cm^3 pipette in a 250 cm^3 conical flask, add 2 cm^3 of the buffer solution, 0.5 cm^3 of Mg-EDTA complex solution-mandatory, and five drops of Eriochrome black T indicator. Colour of the mixture at this stage must be wine red.

   iii) Titrate with 0.01 *M* EDTA from the burette with constant swirling. End point is detected by the colour change form wine red through purple to a clear blue. The solution be stirred thoroughly and the titrant added slowly near the end point.

   iv) Note the burette reading and record in the observation Table I under the 'Final reading 'column. The difference of the two readings gives the volume of EDTA salt solution used in the titration. Repeat the titration to get at least two concordant readings.

   The volume of EDTA salt solution used for the titration should not be less than 10 cm^3. Adjust the volume of the water sample accordingly.

3.4.4 Observations

Approximate mass of the weighing bottle	= m_1 =…….g
Mass of the weighing bottle + EDTA (before transferring the salt)	= m_2 =…….g
Mass of the weighing bottle (after transferring the salt)	= m_3 =…….g

Amount of EDTA salt transferred	$=m_2 - m_3 = m$ =…….g
Molar mass (M_m) of sodium salt of EDTA	= 372.3 g mol^{-1}
Volume of EDTA salt solution prepared	= 250 cm^3
Molarity of EDTA salt solution	$M_1 = \frac{m \times 1000}{M_m \times 250} \text{mol dm}^{-3}$
	$= \frac{m \times 4}{372.31} \text{mol dm}^{-3}$

Observation Table I

Water sample vs EDTA salt solution

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of EDTA salt in cm^3 (Final – Initial)
		Initial	Final	
1	60			
2	60			
3	60			

3.4.5 Calculations

Estimation of total hardness of water sample

Molarity of EDTA salt solution	= M_1 = m×4/372.3=…….mol dm^{-3}
Volume of EDTA salt solution used (From Table I)	= V_1 =…….cm^3
Volume of water sample	= V_2 = 60 cm^3…….g
Molarity of Ca^{2+}/Mg^{2+} in the water sample	= M_2 = ?
Using Eq. 3.3,	
$M_1V_1 = M_2V_2$	
Molarity of Ca^{2+}/Mg^{2+} in water sample	
$M_2 = \frac{M_1V_1 \times 1000}{V_2} \text{mol dm}^{-3}$ =…..mol dm^{-3}	

Total hardness of water sample in mg of $CaCO_3$ in one dm^3 of water

= M_2×Molar mass of $CaCO_3$×1000

Molar mass of $CaCO_3$= 100.09

For all the practical purposes this may be taken as 100.00 for the sake of convenience in calculations. Now, we have,

Total hardness of water sample = M_2×100×1000 =……..ppm of $CaCO_3$.

3.4.6 Result

Total hardness of water sample =……..ppm of $CaCO_3$.

Hardness of more than 300-500 mg dm^{-3} of $CaCO_3$ is considered excessive for public water supply and result in high soap consumption as well as objectionable scale in heating vessels and pipes. Keeping these points in view, discuss the suitability of water sample given to you.

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